VOLUME II

TEXT

CHAPTER 4

(CONTINUED)

4.3 ORGANIC GEOCHEMISTRY

Unless otherwise stated, the reflectance data of the samples discussed in the following sections do not exceed $\%R_o\text{av}\approx 0.70$. Most samples have reflectances in the range $\%R_o\text{av}\approx 0.55\text{-}0.65$, thus any variation in the geochemistry of the kerogens or soluble extracts is likely to reflect principally differences in organic-matter type rather than rank.

4.3.1 Elemental Analysis

Kerogen isolations and analyses were performed on thirteen samples from Fife containing various types of organic matter. These results, along with the calculated H/C and O/C ratios of the kerogens analysed are shown in Table 4.1. All the samples have been discussed previously, with illustrations included in Section 4.2. To summarise, the first two samples are typical lamosites, and the third and fourth samples in the Table are torbanitic shales. Samples SM1 to Q were collected from the coastal sections (mainly Calciferous Sandstone Measures) east of St.Monance whilst BSOS is a carbargilite collected from the Middle Coal Measures sequence at West Wemyss.

A van Krevelen plot of data is shown in Fig.4.6, from which it is evident that there is a marked variation in the elemental composition of different types of organic assemblages found in Carboniferous sediments of the Midland Valley.

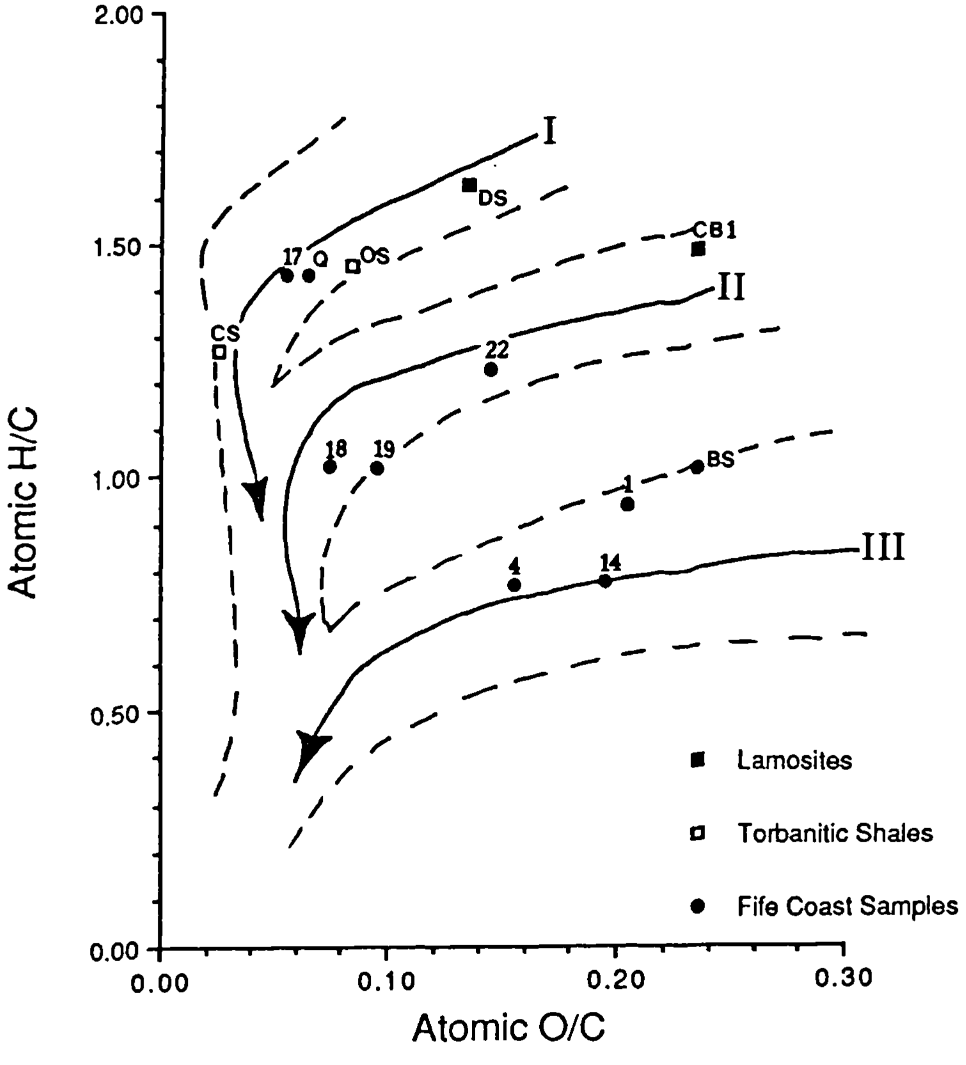


Fig.4.6 van Krevelen diagram for kerogens from Fife (assignations are abbreviations of the sample notations in Table 4.1).

Table 4.1 Elementary analyses of kerogens from Fife.

Sample	%C	%H	%N	%S	%O*	H/C (Atomic)	O/C (Atomic)
Dunnet Shale (DS)	72.9	9.8	2.8	2.1	12.4	1.61	0.13
Carron Harbour Shale (CB 1)	67.9	8.3	3.0	-	20.8	1.47	0.23
Westfield Oil Shale(WDOS)	79.9	9.5	2.1	-	8.5	1.43	0.08
Westfield Canneloid Shale (WDCS)	79.6	8.3	8.4	2.1	1.6	1.25	0.02
SM 1	66.5	5.1	9.8	0.9	17.7	0.92	0.20
SM 4	73.8	4.6	5.1	1.9	14.6	0.75	0.15
SM 14	72.4	4.6	2.3	2.3	18.4	0.76	0.19
SM 17	79.2	9.3	4.9	1.4	5.2	1.41	0.05
SM 18	77.9	6.5	4.3	1.8	9.5	1.00	0.09
SM 19	72.4	6.0	2.8	2.3	16.5	1.00	0.17
SM 22	74.4	7.5	2.6	1.5	14.0	1.21	0.14
Q	79.1	9.3	3.4	1.6	6.6	1.41	0.06
BSOS	69.6	5.8	2.5	1.2	20.9	1.00	0.23

* By difference

The high H/C ratios of the kerogens from the torbanitic Westfield shales agree with those cited for other *Botryococcus* telalginites (Millais and Murchison 1969) and confirm the highly aliphatic nature of the kerogens. The H/C ratios of the Carron Harbour shale (CB1) and Dunnet Shale (DS) agree with those determined for lamosites in other localities worldwide (Hutton *et al.* 1980; Cook *et al.* 1981). Both the Midland Valley lamosites plot within the broad range of elemental compositions cited by Cook *et al.* (1981) for lamosites *viz.* within the area encompassing the type I and type II kerogen fields. There is clearly a marked disparity between the O/C ratios of the Dunnet and Carron Harbour lamosites. This discrepancy may reflect differences in the types of lamalginite contributing to the sediments (solely discrete lamalginite in the Carron Harbour shale and a mixture of discrete and layered lamalginite in the Dunnet Shale) or it could indicate that the contribution of naphthenic and aromatic matter from vascular-plant debris is greater in the Carron Harbour shale than the results of light microscopy suggest. The data of Cook *et al.* (1981) and Sherwood *et al.* (1984) lend support to the former suggestion since the van Krevelen plots of numerous lamositic kerogens indicate that the O/C ratios of lamosites containing predominantly discrete lamalginite (Rundle and Condor-type lamosites) are considerably higher than those for lamosites containing mainly layered lamalginite (Green River-type lamosites). As kerogen isolation was only performed on two Midland Valley lamosites, more samples need to be examined to gain a more detailed insight of variations in elementary composition of different types of lamalginite present in the Carboniferous of this province.

Sample SM17, rich in wispy liptodetrinite Plate (4.105), plots in the type I field, corroborating the inference, made from fluorescence analysis, that this material is of algal origin. The highly aliphatic nature of the kerogen assemblage in sample Q, suspected from optical examinations, is also confirmed by its position in the type I field. Notwithstanding the fact that SM18,19 and 22 together contain discrete lamalginite, *Botryococcus* remains and liptodetrinite thought to be of algal affinity, the dilution of these hydrogen-rich components by more oxygen-rich humic materials results in the samples plotting within the type II field. Although sample SM14 has a high sporinite content, which might be expected to place it in the type II field, its sporinite content (and that of the liptodetrinite) is obviously not sufficiently high to offset the contribution of vitrinite and inertinite in the sample, thus placing it within the type III field. The remaining samples (SM1,4 and BSOS) all have maceral assemblages dominated by humic components and accordingly plot in the type III field.

4.3.2 Rock-Eval Analysis

4.3.2.1 Miscellaneous Samples from Fife

To assess the source potential of the various types of organic assemblages occurring in the Carboniferous succession, Rock-Eval analyses were initially performed on twenty-nine samples from Fife, the majority of which were collected from coastal sections. The results of the analyses are presented in Table 4.2 and are interpreted within the guidelines set out on p.140 and p.141.

The total organic carbon (TOC) contents of all the samples are high (1.3-46.0%) and lie within the good-rich categories of organic richness defined on p.67. These values are in agreement with the high organic contents determined by optical methods, and are all well above the 0.5% TOC level often cited as the minimum required for a sediment to be a viable source rock (Ronov 1958). As anticipated, the TOCs are highest in carbargilites and algal-rich shales. Of the latter, the torbanitic shales have higher TOC contents than the lamosites, the former shales averaging *c*.38%TOC and the latter possessing TOCs in the range *c*.9-29%. The TOC values of samples SM17 to T in Table 4.2 (*c*.11-46%) show that the upper part of the Anstruther Beds and part of the Pittenweem Beds constitute a particularly organic-rich part of the Calciferous Sandstone Measures succession, at least in east Fife. Although no Rock-Eval data were available for samples from the Anstruther Borehole, the sediments in the lower part of the Anstruther Beds are, overall, less organic-rich than those in the upper part of the unit, as indicated by the reduced (*c*.1-24%) TOC values obtained from sediments in the Randerston field section, which is thought to lie within the lower part of the Anstruther Beds sequence (Forsyth and Chisholm 1968, 1977).

Apart from the two samples in the central Fife sections (BUSH SH and AB3), the maturity of all samples is $\leq\%R_o av=0.70$ (most, in fact, are ≤ 0.60). The Tmax values (420-447) are consistent with the low maturity of the samples as established by optical examination. The highest values are recorded in the most algal-rich sediments rather than in the sediments of highest rank.

The genetic potentials (GP) of the sediments analysed indicate that most of them would be moderate to good source rocks on the scale of Tissot and Welte (see p.140). The sediments possess good to excellent source-rock potential based on S_2 yield. Sediments with poor or at most a fair potential for sourcing hydrocarbons have S_2 yields of $\leq$*c*.5mgHC/g rock ($<$*c*.5Kgt^{-1}) and correspond to sediments in which the organic assemblages are dominated by humic macerals with relatively little or no liptinite, the latter represented by sporinite. Sediments with significant contents of algal matter and/or with liptodetrinite which is thought to be of algal origin have excellent source-rock potential, based on

Table 4.2 Rock-Eval data for Fife samples (parameters defined in Section 3.3.8).

LAMOSITES

Sample	S1	S2	PI	T_{max}	TOC	HI	GP
Dunnet (DS)	5.61	232.19	0.02	443	28.9	803	237.80
Carron Harbour (CB 1)	1.80	72.79	0.02	442	10.9	666	74.59
St. Monance (east) (SM 7)	1.21	60.74	0.02	439	8.9	680	61.95
Claremont Burn (OS 1)	2.32	97.40	0.02	439	14.3	679	99.72
TORBANITIC SHALES							
Westfield Oil Shale (WDOS)	3.02	298.15	0.01	445	42.9	694	301.17
Westfield Canneloid Shale (WDCS)	1.07	246.66	0.00	445	31.8	775	247.73
FIFE COAST							
ST. MONANCE-ANSTRUTHER AND WORMISTONE SECTIONS							
SM 1	0.08	2.35	0.03	437	3.5	66	2.43
SM 4	0.12	3.24	0.04	433	3.7	87	3.36
SM 5	0.18	1.80	0.09	420	1.7	109	1.98
SM 12	0.60	2.07	0.22	436	3.0	68	2.67
SM 14	1.04	6.91	0.13	432	19.5	35	7.95
SM 15	0.07	5.10	0.01	441	2.6	193	5.17
SM 17	1.23	60.9	0.02	447	10.9	557	62.13
SM 18	2.19	107.70	0.02	438	23.4	461	109.89
SM 19	0.72	35.32	0.02	429	21.7	162	36.40
SM 22	1.53	183.27	0.01	439	46.0	398	184.80
P sh	2.21	142.30	0.02	439	20.6	689	144.51
Q	1.41	94.72	0.01	442	18.0	525	96.13
T	1.79	98.84	0.02	439	28.8	343	100.63
SM 29	0.07	2.15	0.03	433	1.5	142	2.22
RANDERSTON SECTION							
SM 24	0.28	26.7	0.01	439	7.6	353	26.98
SM 25	0.08	2.75	0.03	420	1.3	209	2.83
SM 26	1.42	20.04	0.07	428	24.2	82	21.46
SM 27	0.07	1.69	0.04	432	1.7	96	1.76
KINGHORN-KIRKALDY SECTION							
MK 2	0.35	4.77	0.07	432	3.5	135	5.12
AB 3	0.14	0.57	0.20	370	5.4	10	0.71
AB 2	0.12	0.69	0.15	431	3.7	185	0.81
WEST WEMYSS							
BSOS	1.55	53.17	0.03	425	20.9	254	54.72
BUSH SH	0.13	0.88	0.13	432	1.7	51	1.01

S_2 yields of over 20mgHC/g rock (Table 3.5). The lamosites and torbanites have the greatest potential with S_2 yields of over 60mgHC/g rock in the former and well over 200mgHC/g rock in the latter. The high values of S_2 yield (c.35-142mgHC/g rock) for several samples in the Pittenweem Beds and Anstruther Beds in the sections shown in Fig.4.3 clearly indicate that the high organic richness of this stratigraphic interval is paralleled by a significant hydrocarbon potential. The hydrocarbon potential of sediments within the lower parts of the Anstruther Beds is significantly lower than in those above, as indicated by the reduced S_2 yields (c.2-27mgHC/g rock) in samples from the Randerston section.

Whether the hydrocarbon potential is realised by oil or gas generation can be assessed by the hydrogen index (HI) which measures the "quality" of the organic matter present. Type (and rank) variation based on this parameter can be readily established by constructing a cross plot of Tmax *vs.* hydrogen index. (Fig.4.7). Evolution lines for the different kerogens are superimposed on the diagram. The sample AB3 has been omitted as the Tmax value is thought to be erroneously low. The torbanitic shales and lamosites are all highly oil-prone, possessing hydrogen indices well above 600. An exceptionally high value (803) was recorded for a sample of the Dunnet Shale (sample DS). The high hydrogen contents of some lamosites (particularly those rich in layered lamalginite) have been attributed to the presence of dispersed bitumens in the samples (Cook 1988). Although some bituminous matter was seen infilling fusinite cavities (e.g. Plate 4.16), it is not thought to be a significant contributor to the source potential of the sediments because the production index is not abnormally high and, in fact, is lower than that for many sediments containing virtually no algal matter. The high hydrogen index of the Dunnet Shale may therefore reflect the larger amounts of layered lamalginite present in the sample, this possibly being of a more aliphatic nature than discrete lamalginite, as suggested from elementary analyses.

The increased amount of humic detritus has led to the algal-rich samples SM18, SM22, SM24 plotting in the upper part of the type II field. The HIs of the samples (343-461) are still sufficiently high for them to be classed as oil-prone. The organic assemblages of samples plotting within the lower half of type II field are dominated by vitrinite and inertinite with liptinite (mainly sporinite) comprising c.20-30% of the total organic matter present. Although SM19 has a high organic content, like those of other sediments analysed from the Pittenweem and Anstruther Beds (top half), the high hydrocarbon potential of this sediment (as indicated by S_2 yield and genetic potential) is likely to be achieved through gas generation, so contrasting with the oil-prone nature of the kerogens in the other sediments analysed from the sections mentioned above. The low

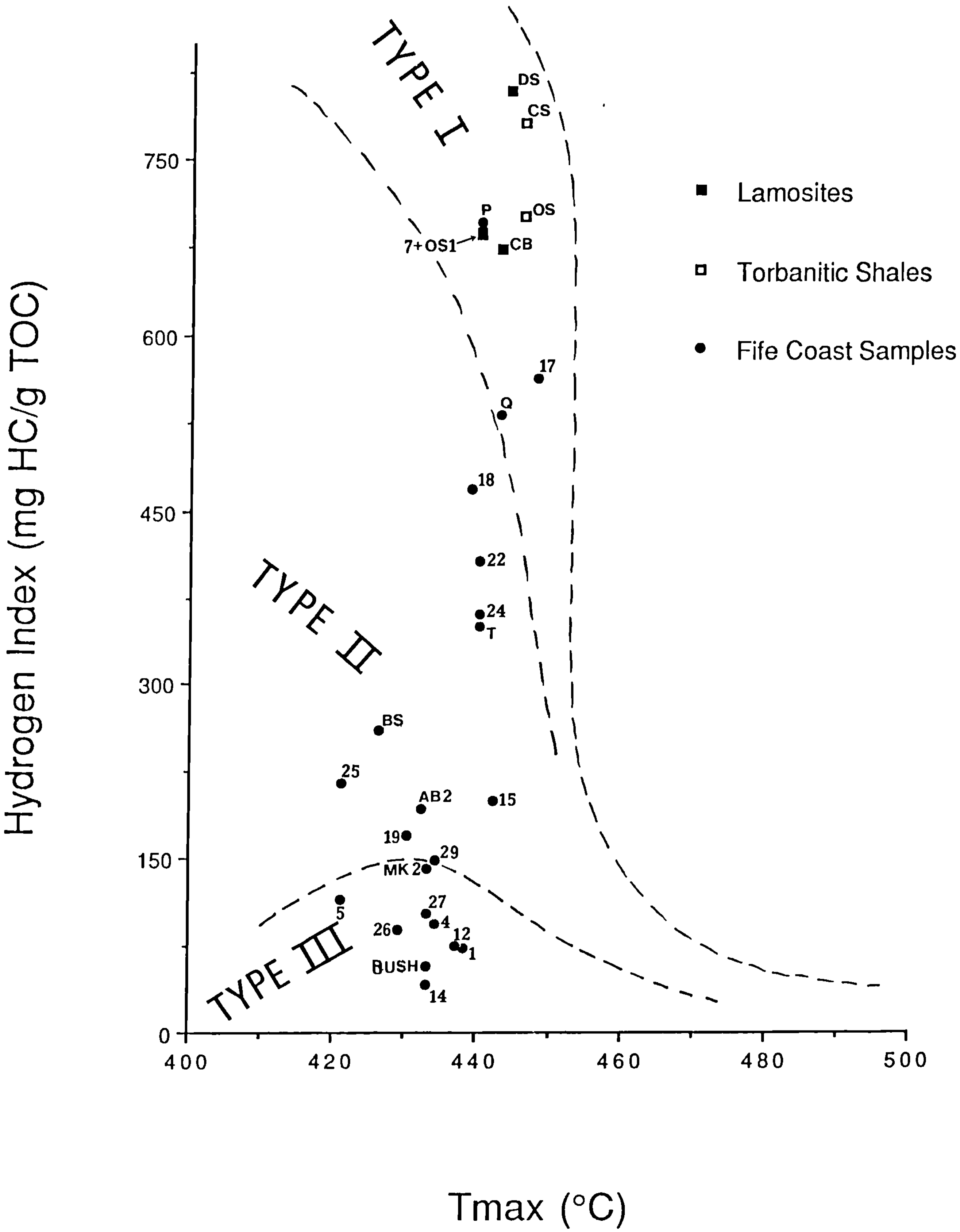


Fig.4.7 Hydrogen Index *vs.* Tmax plot for Fife samples (assignations are abbreviations of the sample notations in Table 4.2).

HI (162) of sample SM19 is consistent with the liptinitic matter comprising mainly spores and spore-derived liptodetrinite rather than algal matter, although the trace amounts of hydrogen-prone *Botryococcus* are probably sufficient to enable the sample to plot within the type II field rather than the type III field as other samples with similar amounts of sporinite do (e.g. SM26, SM14). Some source potential has been conferred on the marine shale AB2 by the presence of algal-derived liptodetrinite wisps in kerogen otherwise dominated by vascular-plant debris (mainly humic components). The HIs of BSOS(254), SM15(193) and SM25(209), indicating mixed oil and gas proneness of the kerogens, are abnormally high given that the liptinite (sporinite) represents only 30%, 20% and trace amounts, respectively, of the total organic matter present in the samples. These samples contain abundant vitrinite (≥30%) from which exudes brown, bituminous-like matter that completely saturates the matrix in the carbargilite BSOS. The brown exudate and the enhanced oil proneness of the samples in which it occurs provide further evidence in the Midland Valley of the occurrence of vitrinites into which hydrocarbon matter has been incorporated. Unlike the vitrinites from the Westfield Basin (Section 4.2.2.1), those from the above samples did not display markedly "scruffy" surfaces or show the Newton Ring phenomenon. The hydrocarbon potential of SM15 may have been enhanced to some degree by the presence of trace quantities of algal cysts.

Most of the samples plotting in the type III field of Fig.4.7 had kerogens comprising mainly humic vascular-plant debris. The low HIs of the samples are generally consistent with their petrographic composition although the value for MK2 seems anomalously low in view of its high liptinite content (c.70% of the kerogen) which includes algal-derived liptodetrinite and *Botryococcus*. The HIs (<150) indicate that the aforementioned samples have little (gas) or no hydrocarbon potential.

4.3.2.2 Kelty Blackband

Since the Kelty Blackband proved to be an exceptionally organic-rich horizon on the basis of optical examination, with very high liptinite contents occurring in many samples (often >50% of the kerogen), it is feasible that many parts of this horizon could be potential source rocks despite the organic matter comprising mainly vascular-plant debris (see Section 4.2.3.4). The organic content and source potential of this horizon were evaluated more precisely by submitting eighteen samples, from an area stretching from the Fife-Midlothian Basin to west Fife, for Rock-Eval analysis. All but three of the samples analysed (KBBI 12,10 and 16) had liptinite contents ≥40% of the total organic matter present, based on microscopical evaluation. The results of Rock-Eval analysis are shown in Table 4.3.

Table 4.3 Rock-Eval data for Kelty Blackband samples.

EXTRACTED SAMPLES

Sample	S1	S2	PI	T_{max}	TOC	HI	GP
KBBI 185	1.13	30.31	0.04	428	19.6	155	31.44
KBBI 547/2	0.39	21.83	0.02	427	10.4	209	22.22
KBBI 535/9	0.72	24.40	0.03	423	21.0	116	25.12
KBBI 140	3.88	134.67	0.03	436	35.2	382	138.55
KBBI 174	2.65	69.08	0.04	433	38.1	181	71.73
KBBI 382	0.94	19.45	0.05	439	6.8	287	20.39
KBBI 385	0.51	21.78	0.02	445	5.3	408	22.29
SAMPLES NOT EXTRACTED							
KBBI 1	0.19	2.36	0.07	440	1.5	162	2.55
KBBI 44	0.17	0.94	0.15	437	1.1	88	1.11
KBBI 16	0.12	0.39	0.24	429	0.9	43	0.51
KBBI 10	0.37	2.84	0.12	446	2.0	139	3.21
KBBI 35	0.14	2.06	0.06	439	2.3	88	2.20
KBBI 195	0.31	4.70	0.06	443	2.7	171	5.01
KBBI 383	0.09	0.76	0.11	434	0.9	86	0.85
KBBI 537	0.20	14.00	0.01	428	6.4	220	14.20
KBBI 535/3	0.18	6.10	0.03	427	4.7	130	6.28
KBBI 549	0.18	5.97	0.03	429	7.3	429	6.15
KBBI 12	0.51	24.12	0.02	435	6.7	359	24.63

The TOC data conform with the petrographic assessments of organic content and indicate that the samples are good-rich (Table 2.2). The results lie in the range 0.9-38.1% TOC, and therefore all satisfy the minimum TOC value of 0.5% required for a sediment to be an effective source rock (Ronov 1958). The richest samples (TOC >10%) all lie in a relatively restricted area around the Cowdenbeath-Lochore Syncline, west of the Burntisland Arch (see Fig.1.4 for structural map).

The source potential of the sediments varies from poor (<2mgHC/g rock) to excellent (>20mgHC/g rock) based on S_2 yield. The samples with the greatest potential correspond to those with the very high TOCs mentioned above (S_2values =21.83-134.67), but also include the three samples analysed from west Fife (KBBI Nos.382,385 and 12; S_2=19.45-24.12; TOCs=5.3-6.8%). The kerogens of these samples nearly all comprise $\geq$50% liptinite, which mainly consists of sporinite, but which is usually supplemented by liptodetrinite and *Botryococcus* telalginite. All but one (KBBI 383) of the samples with poor or at most fair source potential lie east of the Burntisland Arch in the Markinch-Leven district (KKBI 383 lies almost on the axis of the Arch). These sediments all contain liptinite which constitutes $\leq$50% of their kerogen, mainly represented by sporinite. Inertinite comprises most of the remaining maceral assemblage.

Although the organic matter in the Kelty Blackband samples analysed is composed mainly of vascular-plant matter, a cross plot of HIs *vs.* Tmax (Fig.4.8) shows that some samples are clearly oil-prone (HIs>350) while others have mixed oil- and gas-prone potential (HIs 200-350). Apart from sample KBBI 12, the other oil-prone kerogens have high (*c.*70%) liptinite contents of which *c.*10% comprises *Botryococcus*. Remaining liptinite comprises liptodetrinite and spores. Although only 40% of the organic matter in KBBI 12 is liptinite, half of this is represented by *Botryococcus* telalginite which probably accounts for the oil-prone nature of the sample. The mixed oil- and gas-prone samples (HIs 200-350) all contain $\geq$50% liptinite which, in samples KBBI 547/2 and KBBI 537, is sporinite (50%) supplemented by lamalginite (10%) in the latter. The organic matter in KBBI 382 comprises *c.*50% liptodetrinite which probably represents comminuted sporinite rather than alginite since the sample plots in the type II field, unlike sample SM17 in which the liptinite was inferred to have an algal affinity and which plotted in the type I field (Fig.4.7). The enhanced hydrocarbon potential of KBBI 382 is probably due to the abundance of liptodetrinite and the contribution of *Botryococcus* telalginite.

That many of the remaining samples plot in the type II field reflects the abundance of sporinite in the samples, which renders these samples gas-prone. Although samples KBBI 1 and KBBI 10 have liptinite contents which are lower than

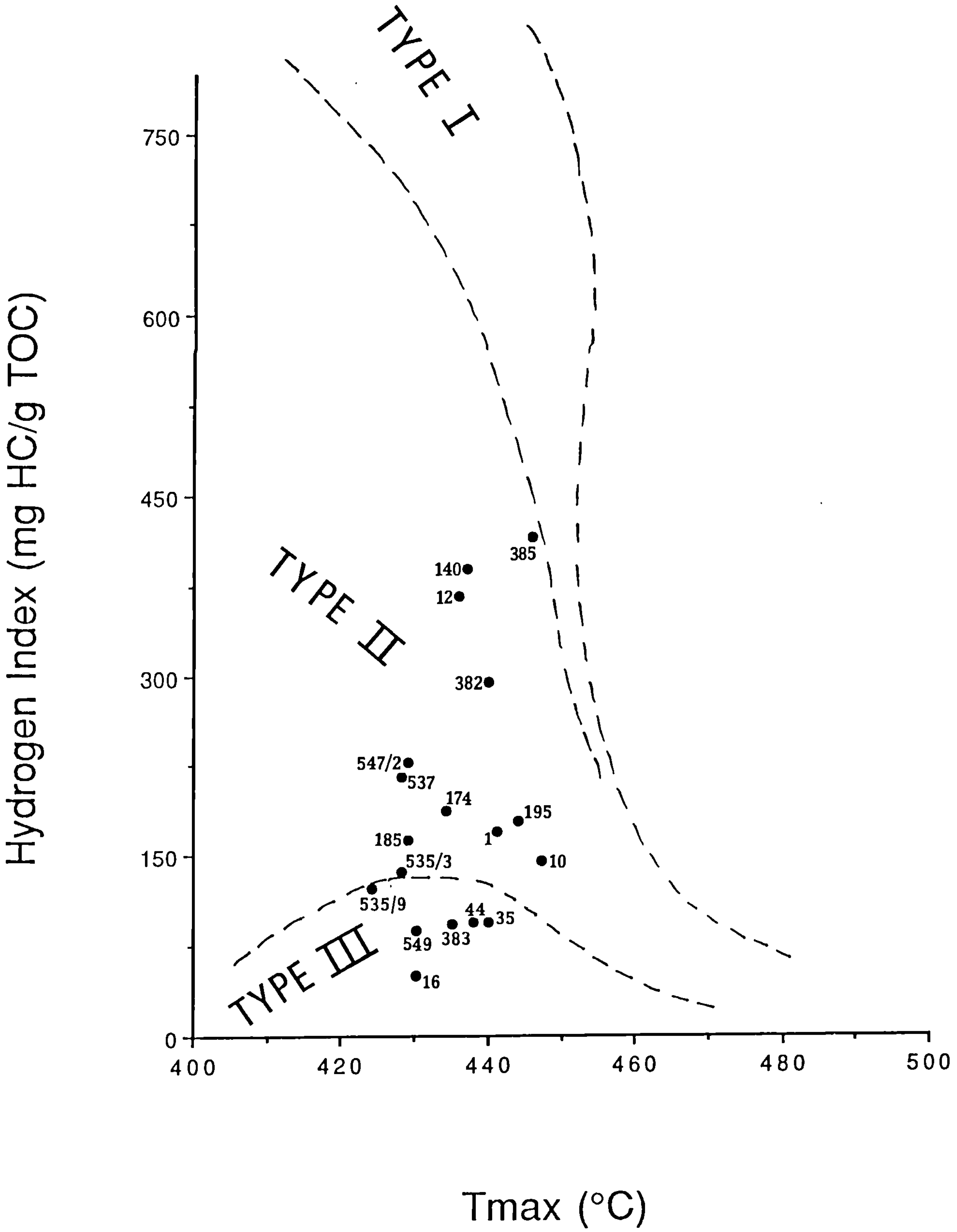


Fig.4.8 Hydrogen Index *vs.* Tmax plot for Kelty Blackband samples (numbers correspond to samples prefixed KBBI listed in Table 4.3).

for many other samples plotting in the type III and type II fields, their presence in the latter is probably accounted for by the incorporation of bituminous matter in vitrinites which is seen to exude from them in the same manner as shown in Plate 4.99. A point of further interest in relation to KBBI samples 1 and 10 is that their maturity as indicated by Tmax (440 and 446°C respectively) is higher than that indicated by vitrinite reflectance data ($\%R_o$av=0.45 and 0.34 respectively). Studies of reflectance profiles in boreholes from which the above samples were taken and reflectance data from closely associated coaly samples indicate that the reflectances of the above two samples have been suppressed by the impregnation of the vitrinite. The estimated "true" maturities of the Kelty Blackband horizon in the localities where the samples were taken are $\%R_o$av=0.71 and 0.80 respectively, values which are more in keeping with the Tmax results. In view of the occurrence of other samples containing abundant vascular-plant matter which have relatively high Tmax values (c.440 and above) and low reflectance values ($\%R_o$av <0.50), it is suspected that the latter may also be suppressed, although this could not be firmly proved due to a lack of samples from which to calculate "true" reflectance values. Vitrinite-reflectance suppression is thought to be widespread within the Kelty Blackband and is discussed in more detail in Chapter 5.

4.3.3 Extractable Organic Matter (EOM)

The results and discussion of the geochemical investigation of the variation of organic-matter type within the Midland Valley are presented under the headings broadly paralleling those in Section 4.2. For ease of reference, the petrographic descriptions, reflectance data and results of the geochemical analyses of the EOM for all samples extracted in the current study are presented together in Appendix II. The data tables in the Appendix are prefixed "A". It should be borne in mind that the measured reflectance data for many liptinite-rich samples may not necessarily be indicative of their true maturity due to the suppression phenomenon mentioned on p.60 . This topic is dealt with at greater length in Chapter 5. "True" reflectance levels were estimated by examining sediments or coals closely associated with the anomalously low-reflecting samples whose petrographic composition suggests that impregnation of vitrinite by bituminous matter is unlikely.

Total organic carbon data, to which extract yields should be normalised for effective comparisons, were only available for the samples referred to in the foregoing section.

4.3.3.1 Algal-Rich Sediments

4.3.3.1.1 Extract Yields and Gross Compositions

The localities of the lamosites extracted are shown in Fig.4.9 whilst their petrographic characteristics, along with those for the other algal-rich sediments analysed, are included in Table A.1. The data for the higher-rank samples are included for completion, although a detailed discussion of these is deferred until Chapter 5. Yields of extractable organic matter (EOM) and their gross compositions are included in Table A.2. The low-rank lamositic samples analysed are rich in terms of EOM yield (0.3-1.6%) which is consistent with their high organic carbon contents. Carbon-normalised yields are relatively low (*c.*40-55mg/gTOC) and correspond with average yields ($\leq$45mg/gTOC) cited for many other oil shales analysed from different parts of the world (Hutton *et al.* 1980). The low concentration of EOM in the Midland Valley lamosites analysed reflects their low maturities.

Differences in the compound-class constitution of the EOM for the lamosites (and other sediments) may be readily visualised by plotting the data from Table A.2 on a ternary diagram (Fig.4.10). It is apparent that the aliphatic fractions of most of the lamosites analysed comprise *c.*20-60% of the total EOM and that the aromatic fractions comprise <40% of the EOM. The marked compositional variability of the EOM of the low-rank lamosites is particularly pronounced considering that the lamosites taken from the east (SM7) and west (O/SBLA) of St.Monance are from the same bed which has attained the same maturity level, corresponding to $\%R_o av \approx 0.55$, at both localities.

The EOM yields of the torbanite and torbanitic shales lie in the range 0.3-1.4% and are of the same order of magnitude as those for the lamosites. When normalised to TOC, however, the yields of the Westfield shales prove to be nearly five times less than the average carbon-normalised yields of the low-rank lamosites for which TOC data are available. The carbon-normalised yield of the Lillies shale may be higher due to the slightly higher rank of the sample as inferred by biomarker data. From the ternary plot in Fig.4.10 it is evident that there exists a bipartite division of the samples in terms of aliphatic hydrocarbon content. This segregation does not appear to be related to rank since the Lillies and Eskmouth shales are more mature than the Westfield shales, based on petrographic observations and biomarker data.

Petrographic and EOM data for other sediments whose organic assemblages are dominated by algal matter (excluding marine bands) which were discussed in Section 4.2.4 are included in the Fife coast sample suite. The relevant samples are SM17,18,Psh and Q, all of which have high bitumen yields (0.5-1.3%

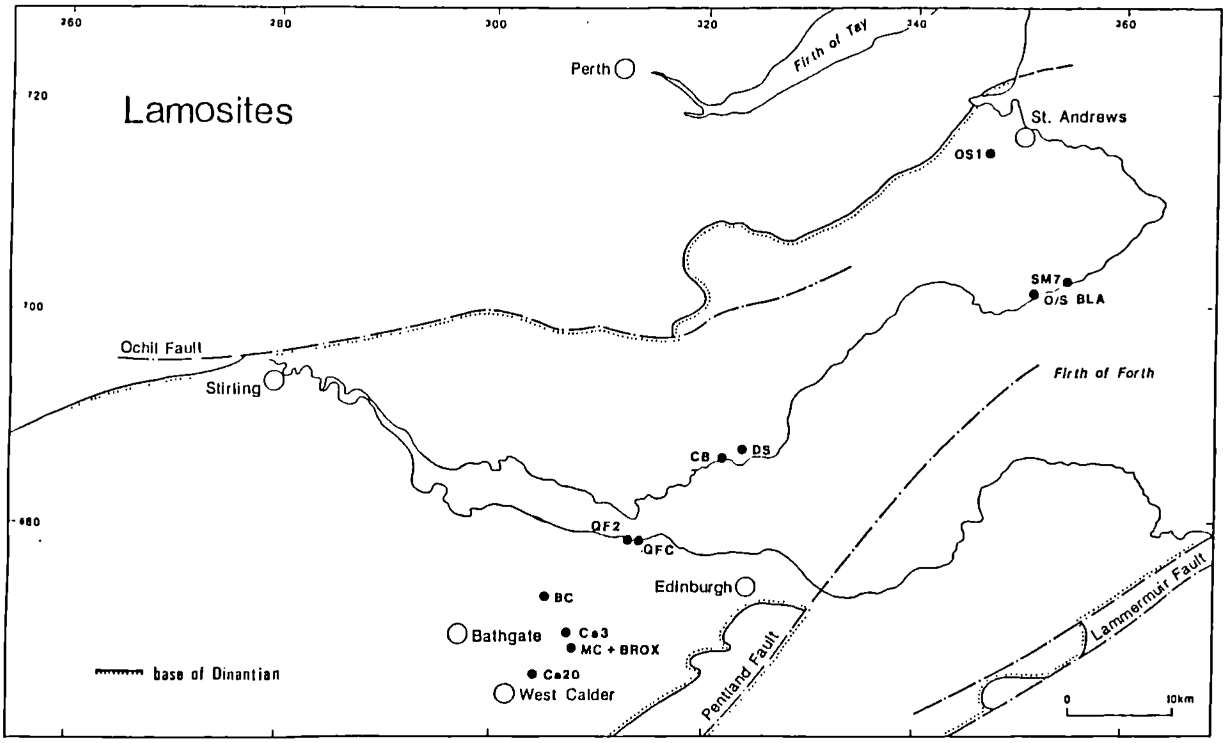


Fig.4.9 Location map for the lamosites extracted.

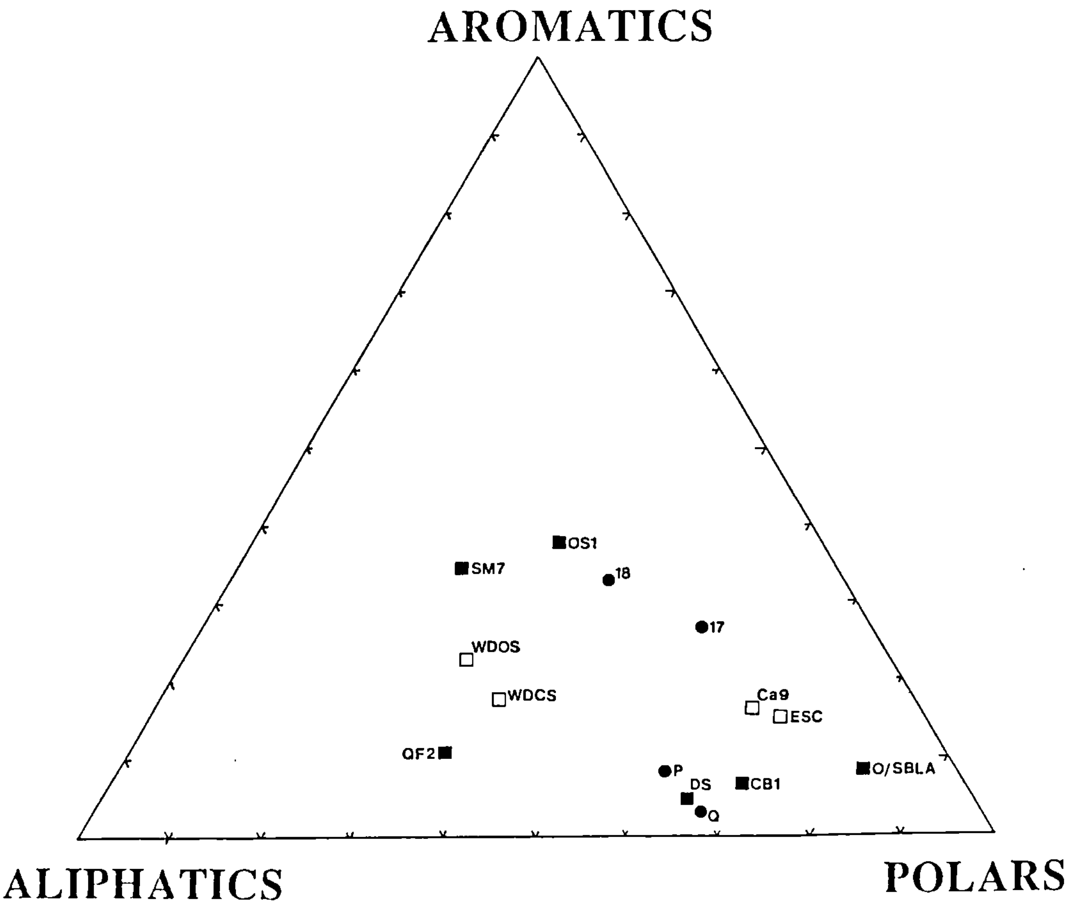


Fig.4.10 Ternary plot showing gross composition of EOM in low-rank algal-rich shales. "Aliphatics" and "Aromatics" refer to hydrocarbon fractions. ■ lamosites; □ torbanites or torbanitic shales; ● other algal-rich shales.

extractibility) reflecting their high organic contents. The carbon-normalised yields are poor/fair (30.5-58.7mg/gTOC). The samples all have aliphatic hydrocarbon fractions comprising >c.20% of the EOM with aromatics accounting for <40%, in keeping with those of most of the other algal-rich sediments investigated.

4.3.3.1.2 Lamosites

4.3.3.1.2.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Representative gas chromatograms of the saturated hydrocarbon fractions of lamosites from various localities are shown in Fig.4.11. Apart from the Fells Shale, the maturity of the sediments indicated in Fig.4.11 is not thought to exceed $\%R_oav{=}0.55$. The basic geochemical parameters calculated from the gas chromatograms of these lamosites (and those of higher rank, discussed in Chapter 5) are shown in Table A.3.

The gas chromatograms of the lamosites studied show distributions of *n*-alkanes ranging from about *n*-C_{10}-C_{36}, these predominating over the regular acyclic isoprenoid alkanes in all but one sample (St.Monance, west). Peak assignments for the isoprenoids are given in Table 4.4.

Table 4.4 Peak assignments for regular acyclic isoprenoid alkanes

Peak	Identity	Common Name
A	C_{13} acyclic isoprenoid	
B	C_{14} acyclic isoprenoid	
C	C_{15} acyclic isoprenoid	farnesane
D	C_{16} acyclic isoprenoid	
E	C_{18} acyclic isoprenoid	norpristane
Pr	C_{19} acyclic isoprenoid	pristane
Ph	C_{20} acyclic isoprenoid	phytane

Hopanoid biomarkers are present in sufficiently large concentrations in some samples (e.g. Figs 4.11a,b) for them to be readily discernible in the gas chromatograms.

Some samples display bimodal *n*-alkane distributions defined by peak maxima at *n*-C_{15} or *n*-C_{17} and *n*-C_{25} or *n*-C_{27}. The bimodality is particularly pronounced in the low-rank Dunnet Shale (Fig.4.11a) and is readily apparent in other lamosites developed within the Lothians Oil-Shale Group on the south side of the Firth of Forth e.g. the Fells Shale (Fig.4.11b). Although the dominance of *n*-C_{15} and *n*-C_{17} is rather less in the Fells Shale than in the Dunnet Shale, probably because of the higher maturity of the former sample (determined through optical examination and

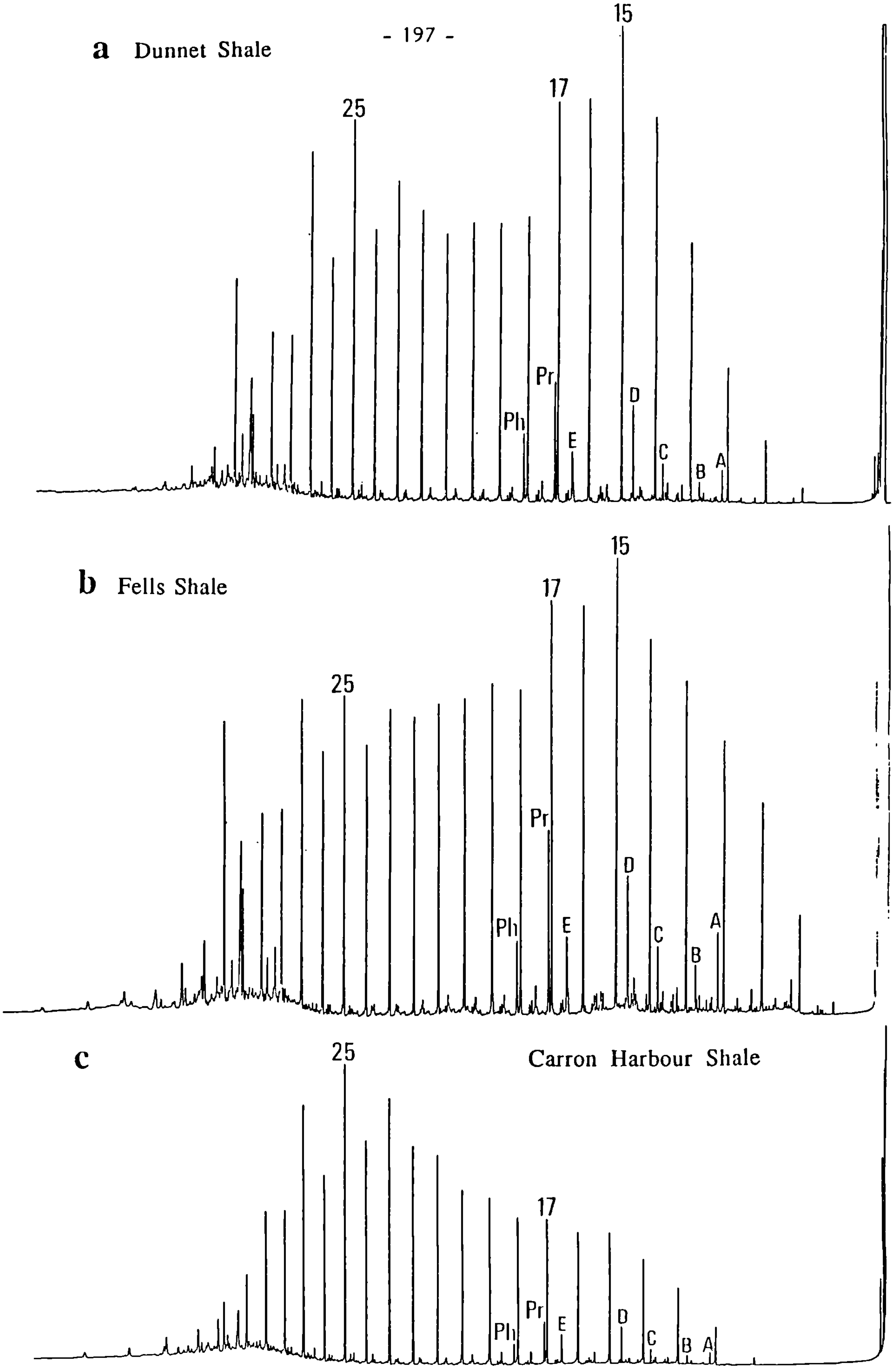


Fig.4.11 Gas chromatograms of the saturated hydrocarbon fractions of lamosites (isoprenoid assignments in Table 4.4; numbers indicate *n*-alkane chain length).

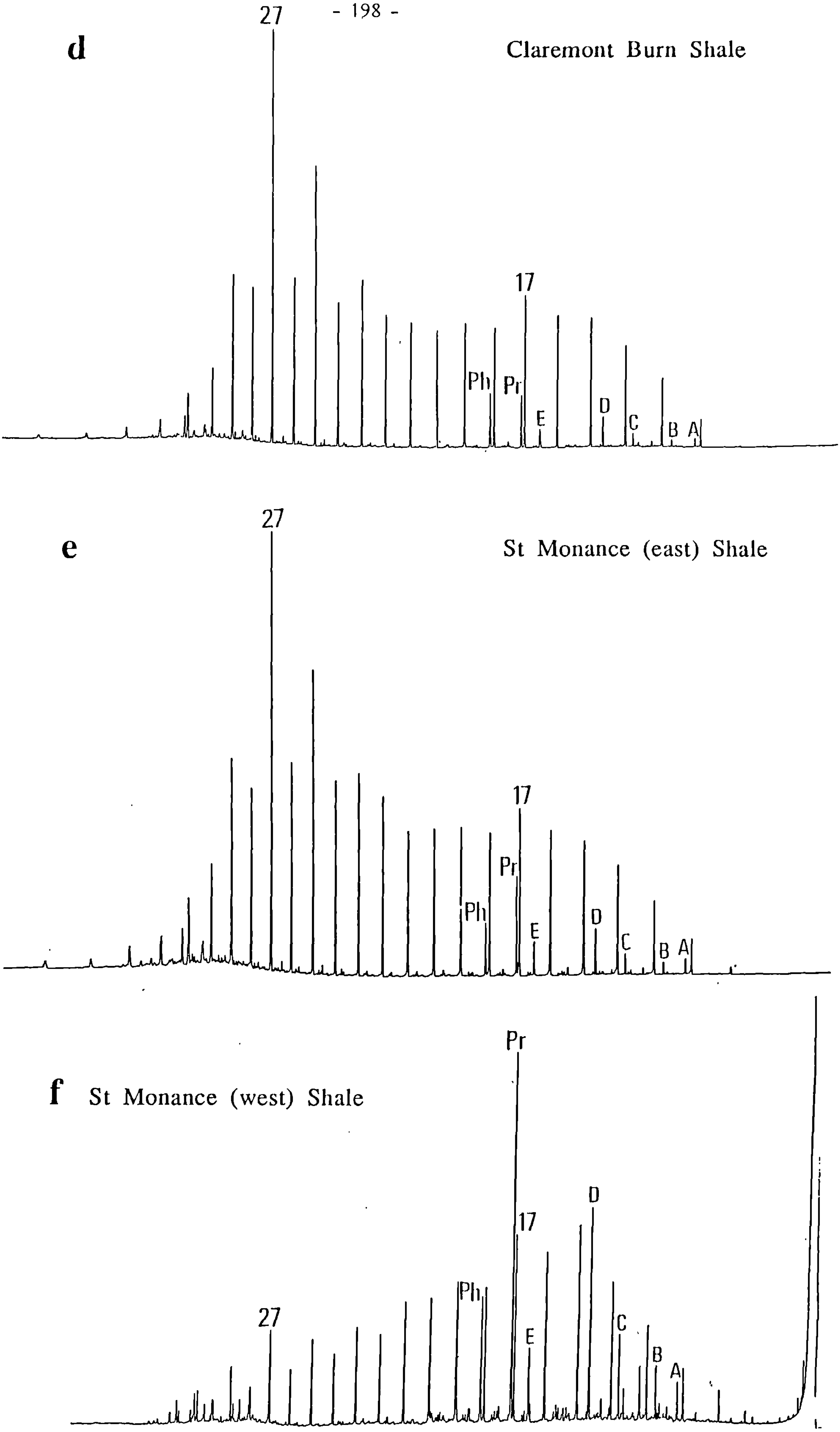

d
Claremont Burn Shale
27
17
Ph
Pr
E
D
C
B
A
e
St Monance (east) Shale
27
17
Pr
Ph
E
D
C
B
A
f
St Monance (west) Shale
Pr
D
17
Ph
27
E
C
B
A

Fig.4.11 (cont.).

biomarker data), enhancement of these medium molecular-weight peaks still reflects a type imprint inherited from biological precursors. When present, bimodality of the *n*-alkane envelope is much less pronounced in lamosites from east Fife (e.g. Figs 4.11d,e). Further differences exist between the east Fife lamosites (lying in the Pathhead Beds) and those within the Lothians Oil-Shale Group (i.e. the shales from Burntisland and the Lothians): although relatively abundant in all the low-rank lamosites, the C_{27}*n*-alkane is in very high abundance in the Claremont Burn (Fig.4.11d) and St.Monance (east) lamosites (Fig.4.11e) whereas it is much less prominent in the shales of the Lothians Oil-Shale Group (Figs 4.11a-c) in which *n*-C_{25} is the most prominent high molecular-weight *n*-alkane.

The low-maturity lamosites display an odd-over-even carbon-number preference covering part or all of the range *n*-C_{21}-C_{29}. Since all the samples have odd carbon-number preferences from *n*-C_{23}-C_{27}, carbon preference indices (CPIs) have been calculated over this range to provide effective comparisons. The marked dominance of *n*-C_{27} in the Claremont Burn and St.Monance (east) lamosites causes high CPIs (1.83 and 1.55 respectively), whilst the CPIs for the Carron Harbour and Dunnet lamosites are lower (1.36 and 1.38 respectively). An intermediate CPI value (1.43) is recorded for the St.Monance (west) lamosite (Fig.4.11f) notwithstanding its lateral equivalence with SM7.

The enhanced concentrations of *n*-C_{15} and *n*-C_{17} in the lamosites is indicative of algal input (Clark and Blumer 1967; Han *et al.* 1968a) which accords with the presence of lamalginite in the samples as determined by fluorescence microscopy.

The prominence of high molecular-weight *n*-alkanes in aliphatic fractions is often ascribed to higher-plant input (Eglinton and Hamilton 1963). The concentrations of microscopically discernible higher-plant matter in the lamosites investigated are low, indeed only trace amounts of vitrinite are present in most of the samples analysed and sporinite never exceeds 5% of the total organic assemblage. Point counting of some Lothians oil shales by Hall (1981) indicated that less than 5% of the sediment comprised vascular-plant debris. The concentrations of high molecular-weight *n*-alkanes in the lamosites therefore seem anomalously high in view of the paucity of terrestrial components. Similar discrepancies were noticed by Hutton *et al.* (1980) following gas chromatographic analyses of the Rundle lamosite. The gas chromatograms of this shale show markedly bimodal *n*-alkane envelopes with *n*-C_{27} present in very high concentrations. The Rundle lamosite is noted for its low terrestrial content leading Hutton *et al.* (1980) to remark that "the significance of bimodal *n*-alkane distributions needs further examination".

Differences in *n*-alkane distributions within the Midland Valley lamosites examined do not appear to be related to differences in the types of lamalginite in the samples. The Dunnet Shale contains large amounts of layered and amorphous algal matter of the types shown in Plates 4.11-4.14, and yet its *n*-alkane envelope is similar to that of the Fells Shale in which the lamalginite is entirely of the discrete form (Plates 4.11, 4.18). The Carron Harbour and Claremont Burn lamosites contain abundant layered lamalginite, albeit less than in the Dunnet Shale, but their *n*-alkane distributions are skewed towards the high molecular-weight end, contrasting with the bimodal envelope of the latter (*cf.* Fig.4.11a and Figs 4.11c,d).

It has now been established that pristane and phytane have sources other than phytol (principally archaebacteria), which limits their utility as redox indicators (see p.*75*). Because no archaebacterial lipid signatures were detected in the lamosites, or indeed in any of the samples analysed in this project, the traditional use of the pristane to phytane ratio as a palaeoenvironmental indicator has been maintained in the current work.

Apart from the St.Monance (west) lamosite, the Pr/Ph ratios of the low-rank lamosites are all in the range of *c.*1-2 which is consistent with their lacustrine origin (Powell 1986). The relatively high value (2.97) for the St.Monance (west) lamosite reflects a more oxic depositional environment than that in which the laterally-equivalent St.Monance (east) lamosite accumulated. The Pr/Ph ratio of 0.96 for the Claremont Burn shale suggests alternating oxic/anoxic conditions during sediment accumulation rather than the development of highly reducing conditions which might be marked by a Pr/Ph ratio significantly lower than 1 (Didyk *et al* 1978). Pr/n-C_{17} ratios of <0.5 for the Dunnet, Carron Harbour and Claremont Burn lamosites all suggest open-water conditions of sedimentation (Lijmbach 1975). The slightly higher value (0.59) for the St.Monance (east) lamosite indicates a more restricted, but not highly oxic depositional environment while the significantly higher value of 1.98 for the sample from the same horizon further to the west (O/SBLA) corroborates the high Pr/Ph ratio and strongly suggests sediment accumulation in a restricted inland environment, possibly in association with peat swamps.

Gas Chromatography-Mass Spectrometry (GC-MS)

The typical distribution of terpanes in the low-maturity lamosites investigated is shown in Fig.4.12a from which it is apparent that tricyclic and tetracyclic terpanes are of minor abundance relative to the pentacyclics. An enlargement of the region in which the tricyclics and tetracyclics elute is shown in Fig.4.12b, and the pentacyclics are presented more clearly in Fig.4.12c. Peak assignments

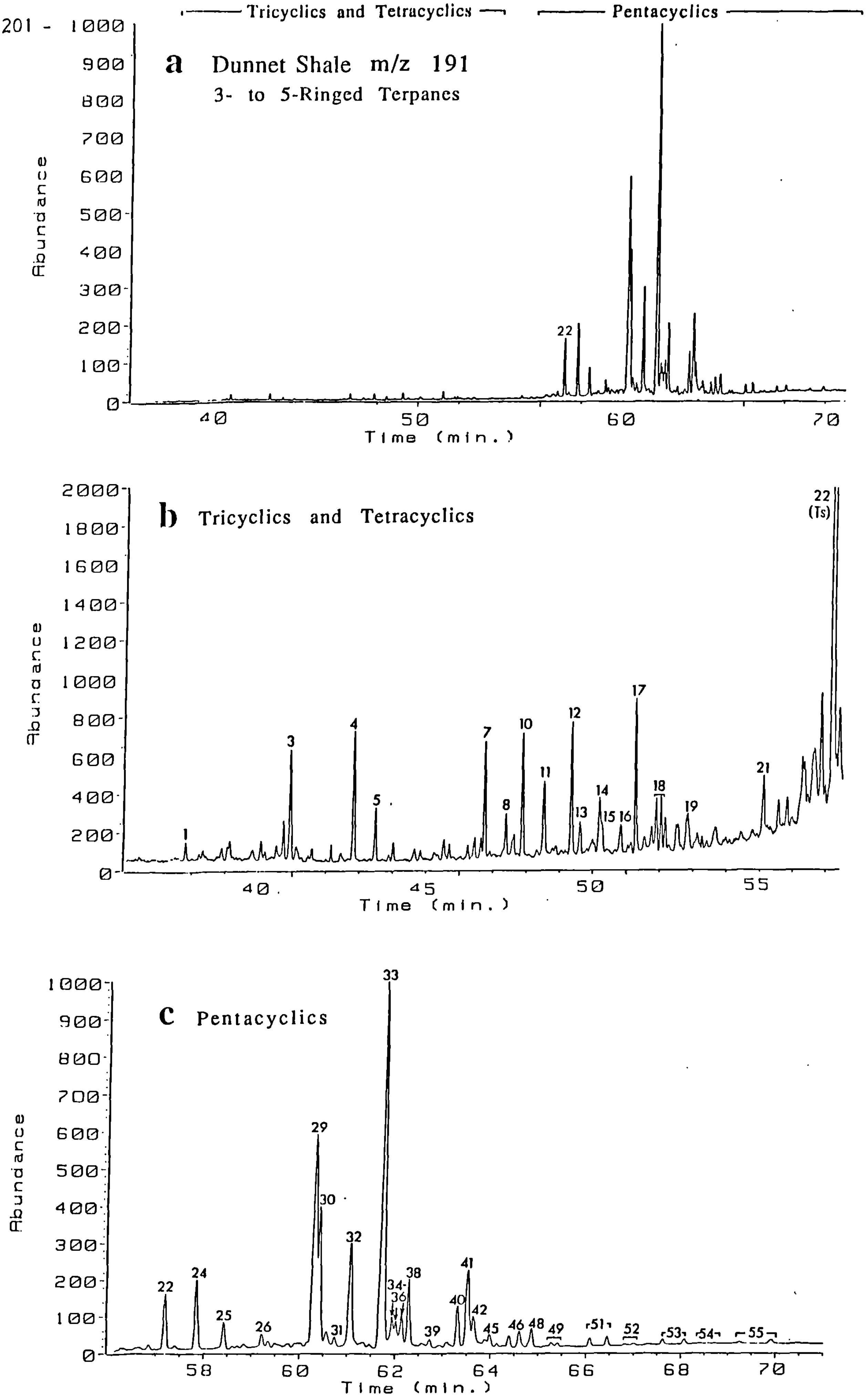


Fig.4.12 Mass fragmentograms (m/z 191) illustrating typical distributions of 3- to 5-ringed terpanes in low-rank lamosites (peak assignments in Table 4.5).

Table 4.5 Peak assignments for terpanes (m/z 191 mass fragmentograms).

1	C_{19} tricyclic
2	C_{20} tricyclic
3	C_{20} tricyclic
4	C_{21} tricyclic
5	C_{21} tricyclic
6	C_{21} tricyclic
7	C_{23} tricyclic
8	C_{23} tricyclic
9	C_{23} tetracyclic
10	C_{24} tricyclic
11	C_{23} tetracyclic
12	C_{24} tetracyclic
13	C_{24} tetracyclic
14	C_{25} tricyclic
15	C_{24} tetracyclic
16	C_{24} tetracyclic
17	C_{24} tetracyclic (17,21-secohopane)
18	C_{26} tricyclic (isomeric pair)
19	C_{25} tetracyclic (17,21-secohopane)
20	C_{26} tetracyclic (17,21-secohopane)
21	C_{27} tetracyclic (17,21-secohopane)
22	18α(H),22,29,30-trisnorneohopane (Ts)
23	C_{29} tetracyclic
24	17α(H),22,29,30-trisnorhopane (Tm)
25	17β(H),22,29,30-trisnorhopane
26	C_{29} pentacyclic terpane
27	28,30-bisnorhopane
28	C_{29} tetracyclic terpane
29	17α(H),21β(H),30-norhopane
30	Unknown C_{29} triterpane
31	Unknown C_{30} triterpane
32	17β(H),21α(H),30-norhopane
33	17α(H),21β(H)-hopane

34	Unknown C_{29} triterpane
35	Unknown C_{30} triterpane
36	Unknown C_{30} triterpane
37	17β(H),21β(H),30-norhopane
38	17β(H),21α(H)-hopane
39	Unknown C_{31} triterpane
40	17α(H),21β(H)-homohopane (22S)
41	17α(H),21β(H)-homohopane (22R)
42	Unknown C_{31} triterpane
43	C_{31} triterpane (methylhopane)
44	17β(H),21β(H)-hopane
45	17α(H),21β(H)-homohopane (22S+22R)
46	17α(H),21β(H)-bishomohopane (22S)
47	Unknown C_{32} triterpane
48	17α(H),21β(H)-bishomohopane (22R)
49	17β(H),21α(H)-bishomohopane (22S+22R)
50	17β(H),21β(H)-homohopane
51	17α(H),21β(H)-trishomohopane (22S+22R)
52	17β(H),21α(H)-trishomohopane (22S+22R)
53	17α(H),21β(H)-tetrakishomohopane (22S+22R)
54	17β(H),21α(H)-tetrakishomohopane (22S+22R)
55	17α(H),21β(H)-pentakishomohopane (22S+22R)

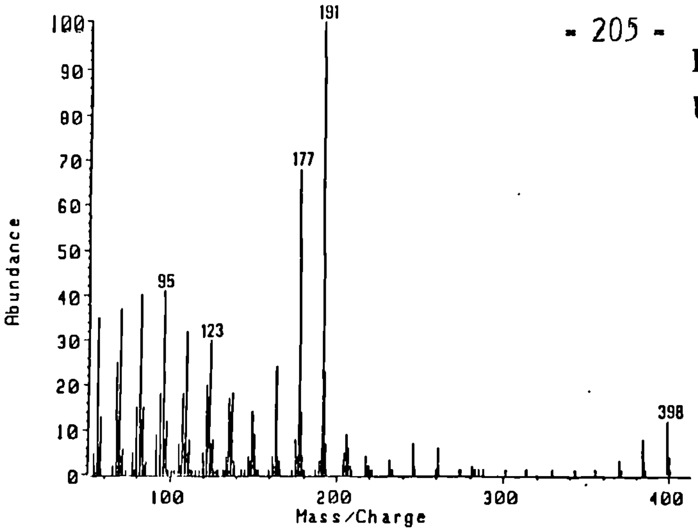
Table 4.5 (cont.).

are shown in Table 4.5 and various molecular parameters based on the hopanes are given in Table A.4.

Tricyclic terpanes encompassing the range C_{19}-C_{26} occur in the m/z 191 fragmentograms of all the lamosites analysed and correspond to those identified by Aquino Neto *et al.* (1983, 1986). The C_{19} member of the series is not always readily discernible. The C_{24}-C_{27} series of tetracyclic terpanes (17,21-secohopanes) recognised by Aquino Neto *et al.* (1983) is also present (peaks 17,19,20 and 21). Although only one C_{24} tetracyclic component is documented by the above authors, up to five peaks with spectra consistent with the structure of C_{24} tetracyclic terpanes are identified in the Midland Valley lamosites. A C_{23} tetracyclic terpane is also evident (peak 11). Tricyclics and tetracyclics are present in roughly equal proportions in the lamosites.

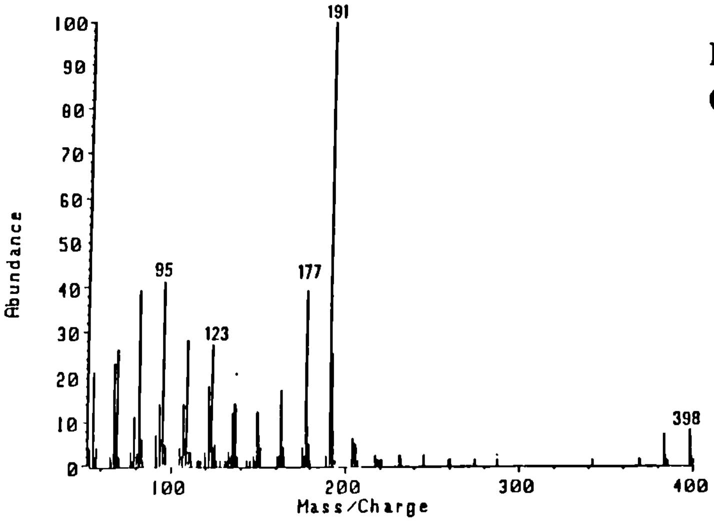
The $C_{29}\alpha\beta$ and $C_{30}\alpha\beta$ hopanes dominate the pentacyclic terpane distribution (Fig.4.12c) so that the intensities of the 22S and 22R epimers of the $\alpha\beta$ hopanes $\geq C_{31}$ are relatively low in abundance. In addition to the commonly-occurring hopanes, there are several peaks in the m/z 191 trace which are not well documented in the literature, if at all. The most prominent of these is peak 30 which occurs as a shoulder on the $C_{29}\alpha\beta$ hopane (peak 29). The compound eluting as peak 30 is found in all the lamositic shales investigated, in which it is usually in very high abundance relative to the C_{29} and $C_{30}\alpha\beta$ hopanes. An empirical measurement of its abundance was determined using ratio h in Table A.4. The mass spectrum of peak 30 (Fig.4.13a) is consistent with a compound possessing a C_{29} triterpane skeleton. Structural similarities to both the $C_{29}\alpha\beta$ and $C_{29}\beta\alpha$ hopanes are inferred on the basis of spectral comparison (Figs 4.13b,c), although it is possible that there is a contribution from the $C_{29}\alpha\beta$ hopane from which it has not been completely resolved. Attempts to separate completely peaks 29 and 30 using 50m OV-1 and 5% phenylmethyl silicone columns with various gas-flow rates failed. Peak 30 is invariably associated with enhanced concentrations of peak 31, an unidentified C_{30} pentacyclic terpane whose mass spectrum is shown in Fig.4.13d. The carbon numbers and basic skeletal configurations of other compounds commonly occurring in Midland Valley lamosites were deduced from the spectra in Fig.4.14.

Although the terpane distribution in the Dunnet Shale is fairly typical of those found in other low-maturity lamosites, additional components may appear in the m/z 191 fragmentograms as shown in Figs 4.15a and b. Peak 23 occurs in the St.Monance (east) and Claremont Burn lamosites only, and its spectrum (Fig.4.16a) suggests the compound is a C_{29} tetracyclic terpane. A C_{29} pentacyclic terpane can be detected in some lamosites (peak 26; Fig.4.16b) where it elutes a



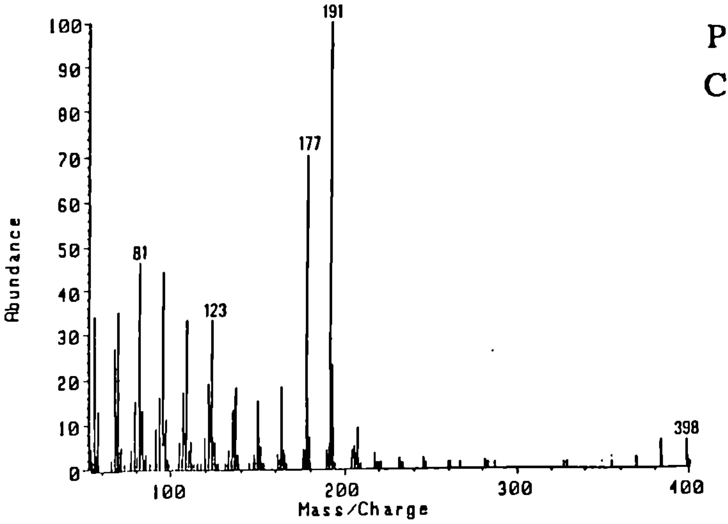
Peak 30
Unknown C_{29} Triterpane

b



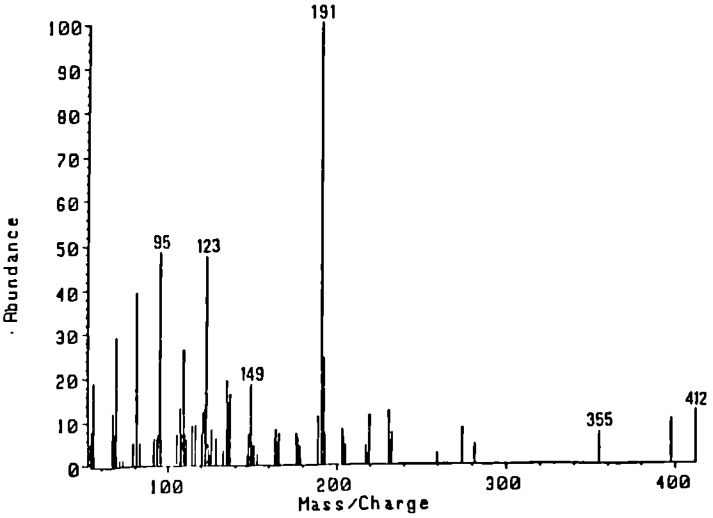
Peak 29
$C_{29}\alpha\beta$ Hopane

c



Peak 32
$C_{29}\beta\alpha$ Hopane

d



Peak 31
Unknown C_{30} Triterpane

Fig.4.13 Mass spectra of some pentacyclic terpanes occurring in lamosites.

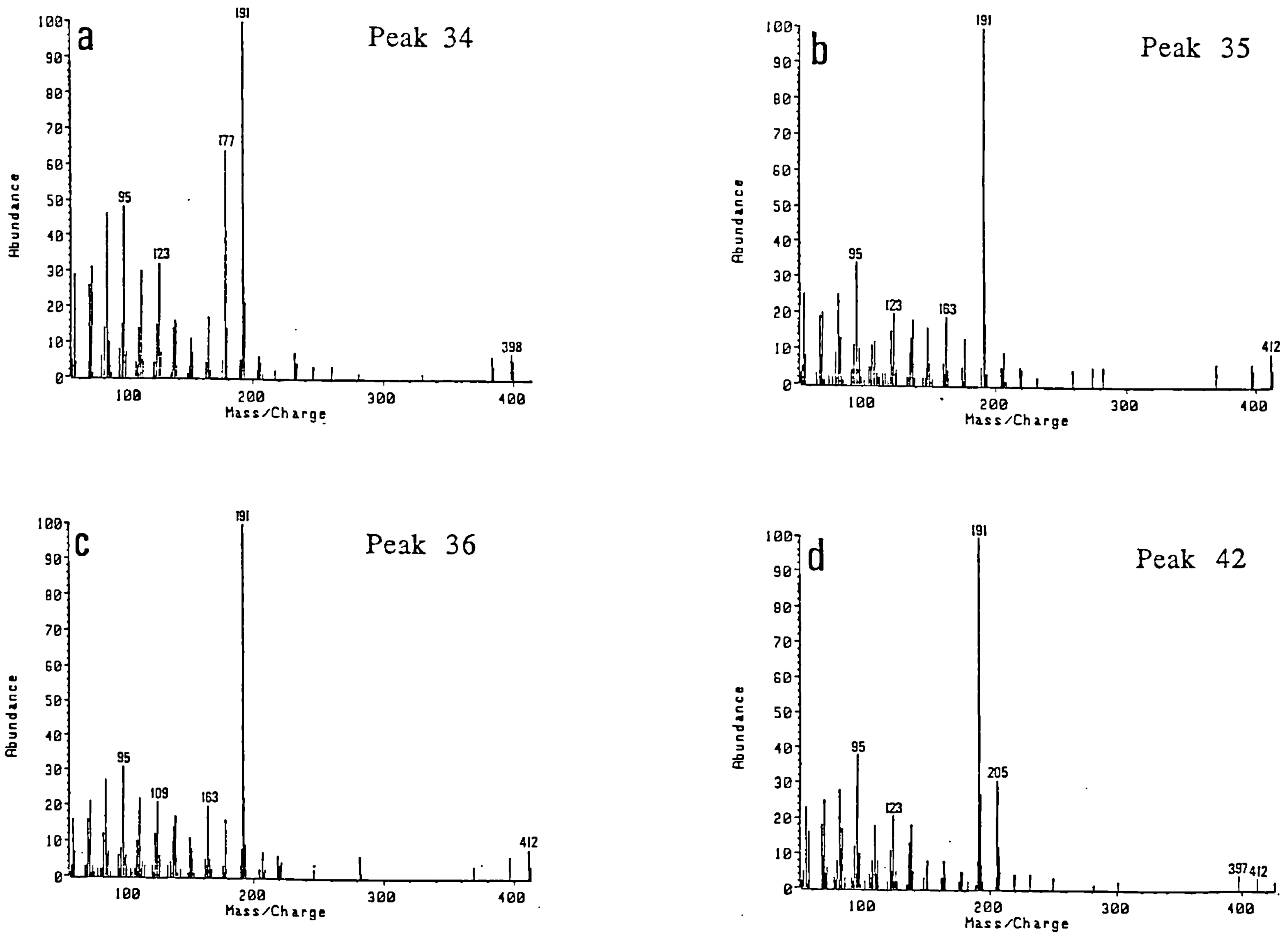


Fig.4.14 Mass spectra of unknown triterpanes commonly occurring in lamosites.

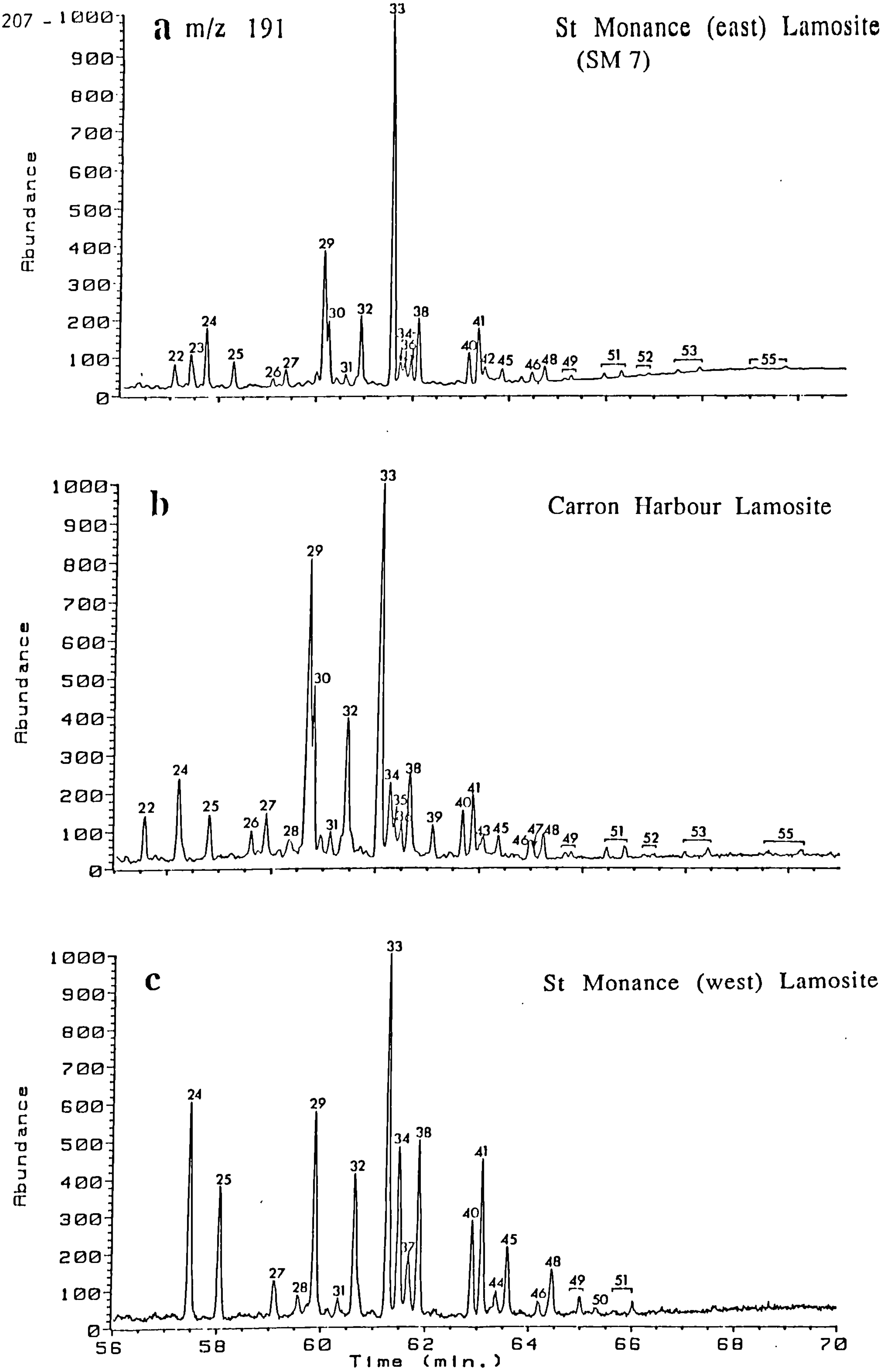


Fig.4.15 Mass fragmentograms (m/z 191) showing the distribution of tetracyclic and pentacyclic terpanes in lamosites from Fife (peak assignments in Table 4.5).

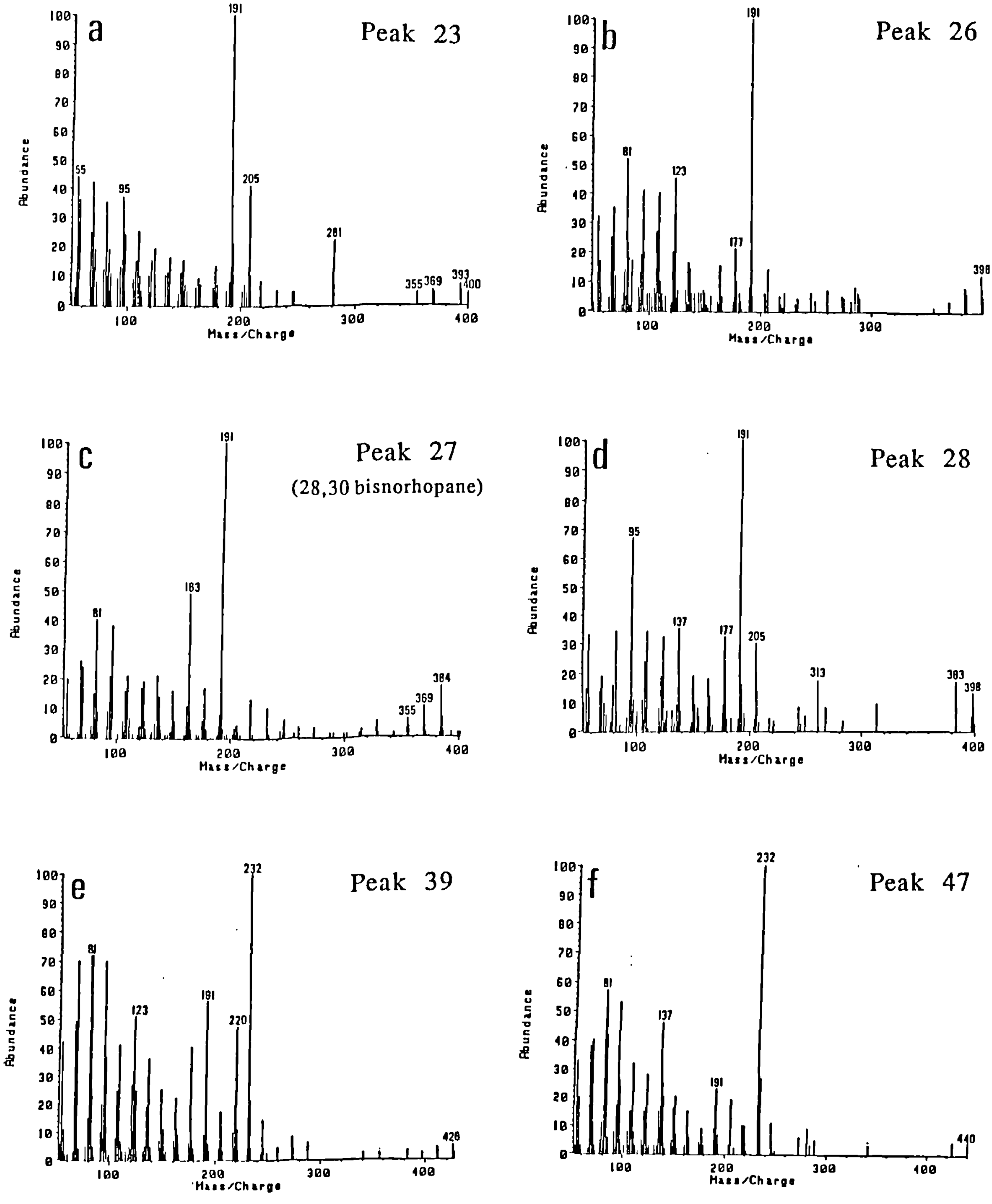


Fig.4.16 Mass spectra of polycyclic terpanes occurring in lamosites.

before the 28,30-bisnorhopane (peak 27; Fig.4.16c). The latter compound is not ubiquitous in the lamosites, and its abundance varies greatly as indicated by ratio g in Table A.4. Peaks 39 and 47 correspond to unusual C_{31} and C_{32} pentacyclic terpanes which show major fragment ions at m/z 232 (Figs 4.16e,f). Of the lamosites extracted, both of these compounds were only detected together in the sample from Carron Harbour. Trace amounts of the compound eluting as peak 39 are evident in the Dunnet Shale (Fig.4.12c).

A feature of particular interest in the hydrocarbon distribution of the lamosites described above (and also the Claremont Burn lamosite) is that whilst the prominence of the 17β(H) trisnorhopane (peak 25), the dominance of the biologically-inherited 22R epimer in the hopane doublets $\geq C_{31}$ and vitrinite reflectance data are all clear indicators of a mild thermal history for the samples, their hopane/moretane ratios (parameter d in Table A.4) are all high and near to the equilibrium value of *c*.0.90. The widespread use of the hopane/moretane ratio as a maturity parameter in petroleum geochemistry is based on the assumption that any variation in this index occurs independently of organic-matter type variation. The observation of anomalously low concentrations of moretanes in immature lamositic shales clearly points to a type influence on the hopane/moretane ratio.

Optical and geochemical data suggest that the St.Monance (west) lamosite (sample O/SBLA) is of similar maturity to the lamosites discussed above, yet its hopane/moretane ratio is significantly lower and its hopane fingerprint (Fig.4.15c) differs markedly from that of its lateral equivalent, SM7 (Fig.4.15a) and from those of the other lamosites extracted. In contrast to the majority of other lamosites, which show relatively high concentrations of peak 30, in O/SBLA this compound is present in such low amounts that it can only just be detected in the m/z 177 trace. Furthermore, the abundance of αβ homologues $\geq C_{31}$ is higher, relative to the $C_{30}\alpha\beta$ hopane, in O/SBLA than in other lamosites, and the $C_{29}\beta\beta$ and $C_{30}\beta\beta$ hopanes are also present. The relatively simple pentacyclic biomarker distribution in the St.Monance (west) lamosite is atypical amongst those of other Midland Valley lamosites.

Typical sterane distributions occurring in low-rank lamosites rich in layered and discrete lamalginite are shown in Fig.4.17a and b respectively. The corresponding peak assignments are given in Table 4.6. Molecular parameters based on sterane distributions are given in Table A.5.

Ethyl cholestanes (C_{29}) dominate the sterane distributions in all the immature lamosites studied except in the sample from Carron Harbour where C_{29} and C_{28} steranes are present in roughly equal amounts. The carbon-number distributions

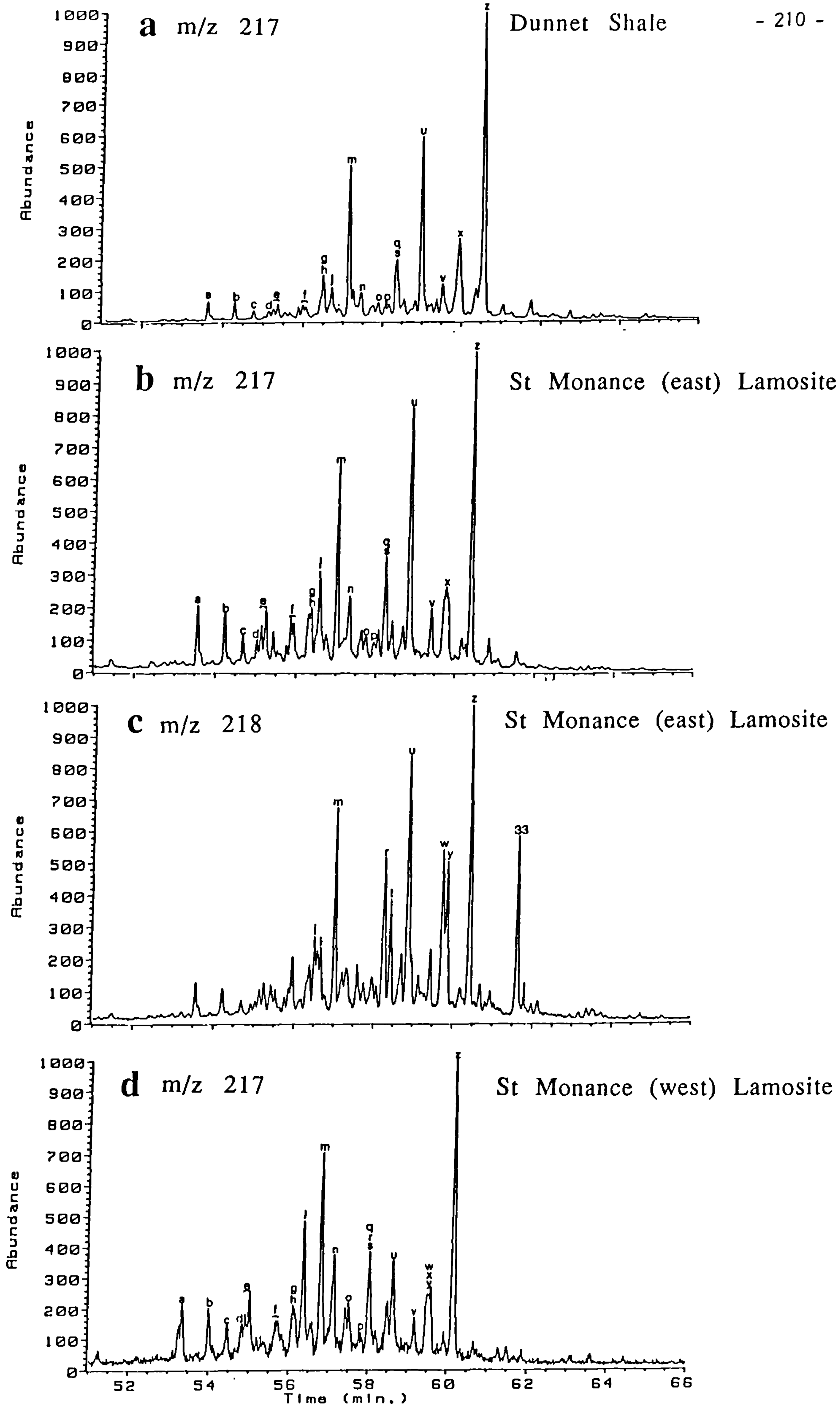


Fig.4.17 Mass fragmentograms illustrating sterane distributions in lamosites (peak assignments in Table 4.6).

Table 4.6 Peak assignments for steranes (m/z 217 mass fragmentograms).

a	13β(H),17α(H)-diacholestane (20S)
b	13β(H),17α(H)-diacholestane (20R)
c	13α(H),17β(H)-diacholestane (20S)
d	13α(H),17β(H)-diacholestane (20R)
e	24-methyl-13β(H),17α(H)-diacholestane (20S)*
f	24-methyl-13β(H),17α(H)-diacholestane (20R)*
g	24-methyl-13α(H),17β(H)-diacholestane (20S)* +5α(H),14α(H),17α(H)-cholestane (20S)
h	5β(H),14α(H),17α(H)-cholestane (20R)
i	5α(H),14β(H),17β(H)-cholestane (20R)
j	24-ethyl-13β(H),17α(H)-diacholestane (20S)
k	24-methyl-13α(H),17β(H)-diacholestane (20R)
l	5α(H),14β(H),17β(H)-cholestane (20S)
m	5α(H),14α(H),17α(H)-cholestane (20R)
n	24-ethyl-13β(H),17α(H)-diacholestane (20R)
o	24-ethyl-13α(H),17β(H)-diacholestane (20S)
p	24-methyl-5α(H),14α(H),17α(H)-cholestane (20S)
q	24-ethyl-13α(H),17β(H)-diacholestane (20R)
r	24-methyl-5α(H),14β(H),17β(H)-cholestane (20R)
s	24-methyl-5β(H),14α(H),17α(H)-cholestane (20R)
t	24-methyl-5α(H),14β(H),17β(H)-cholestane (20S)
u	24-methyl-5α(H),14α(H),17α(H)-cholestane (20R)
v	24-ethyl-5α(H),14α(H),17α(H)-cholestane (20S)
w	24-ethyl-5α(H),14β(H),17β(H)-cholestane (20R)
x	24-ethyl-5β(H),14α(H),17α(H)-cholestane (20R)
y	24-ethyl-5α(H),14β(H),17β(H)-cholestane (20S)
z	24-ethyl-5α(H),14α(H),17α(H)-cholestane (20R)

* possibly isomeric at C-24

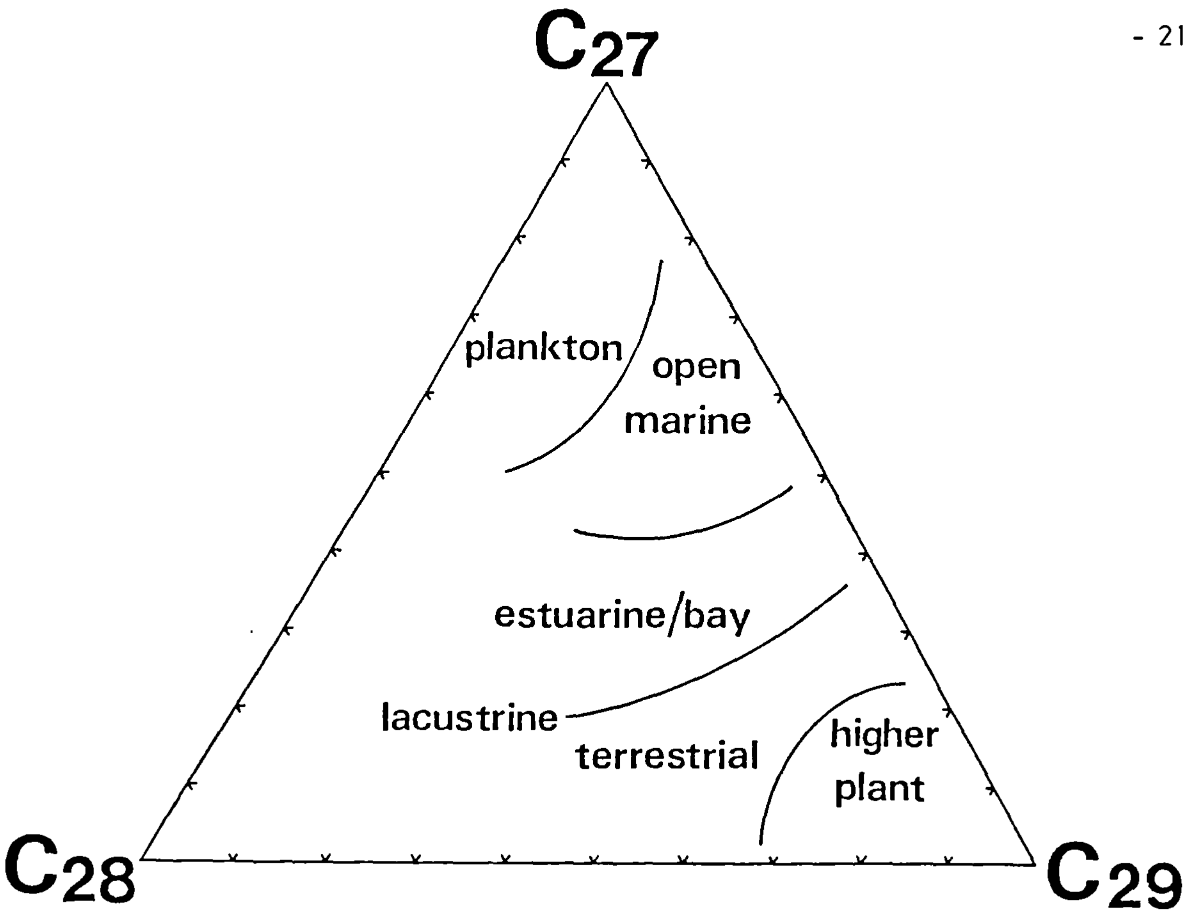


Fig.4.18 Carbon-number distributions of sterols in biological materials and sediments (from Huang and Meinschein 1979).

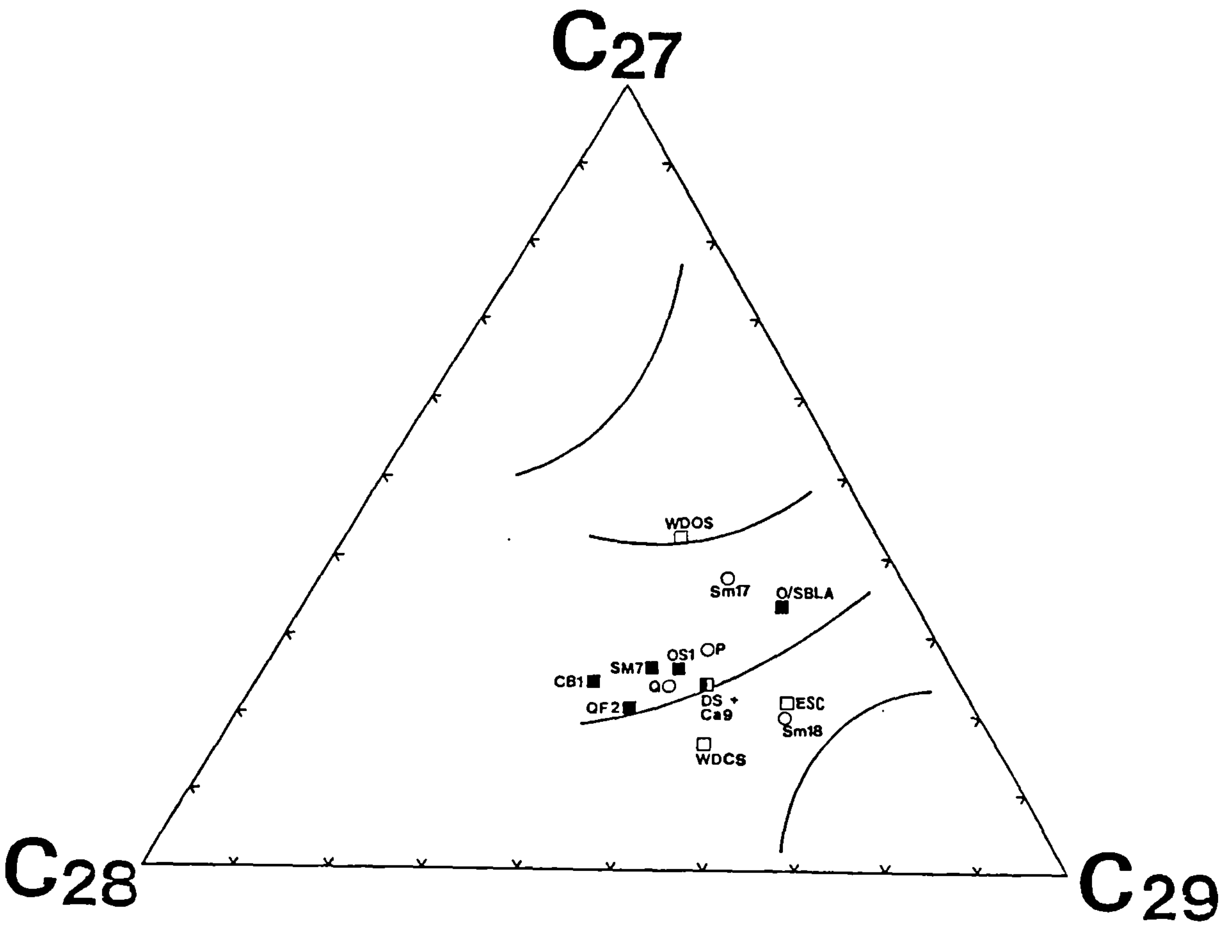


Fig.4.19 Carbon-number distribution of steranes in algal-rich sediments (see Fig.4.10 for symbol definitions).

generally decrease in the order $C_{29}>C_{28}>C_{27}$. Samples containing abundant layered lamalginite and ooze-like matter (DS, OS1) have slightly higher concentrations of C_{29} steranes (relative to the C_{27} steranes) than lamosites rich in discrete lamalginite (CB1, SM7, O/SBLA). Diasteranes are present in relatively low abundance in all lamosites, but enhanced concentrations generally correlate with samples whose lamalginite is predominantly discrete in form. Akin to its hopane distribution, the sterane distribution of sample O/SBLA (Fig.4.17d) does not conform to that seen in other low-rank lamosites: the C_{28} steranes are in relatively low abundance and the diasterane/sterane ratio is the highest measured for any lamosite in this study, including those of high rank.

Variations in the relative proportions of C_{27}, C_{28} and C_{29} steranes are best visualised using ternary plots of the type introduced by Huang and Meinschein (1976, 1979) to discriminate between different sources and depositional environments of organic matter based on the sterol distributions found in living organisms (Fig.4.18). The apices in Fig.4.19 refer to concentrations of the biologically-derived $\alpha\alpha\alpha$20R steranes. Apart from the anomalous sample O/SBLA, all the low-maturity lamosites plot towards the lacustrine end of the "estuarine/bay" field.

Within the suite of lamosites studied, steranes are much less abundant than hopanes. Hopane to sterane ratios (parameter i in Table A.4) lie in the range 5-13 in those samples whose biomarker distributions are thought mainly to reflect the influence of organic-matter type (i.e. the first six samples in Table A.4).

4.3.3.1.2.2 Aromatic Hydrocarbons

All low-rank lamositic shales (apart from the sample O/SBLA) have aromatic hydrocarbon distributions typified by the total ion current (TIC) chromatogram shown in Fig.4.20. Peak assignments are shown in Table 4.7. Low molecular-weight alkylbenzenes are not found in all samples probably because of either weathering loss at the outcrops or evaporative loss during laboratory work-up.

The TIC up to 58 minutes is dominated by several components which represent partially or wholly aromatised compounds based on naphthalene or phenanthrene skeletons. The widely occurring series of alkylated naphthalenes and phenanthrenes are in relatively low abundance, and a pronounced high molecular-weight unresolved complex mixture (UCM) or "hump" is present in the samples investigated.

Peak 5 is a prominent component in all the lamosites studied, and its mass spectrum (Fig.4.21a) is identical to that of a compound identified as 1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene (C_3 tetralin) in the bitumen of the Green River Shale (Anders *et al.* 1973). An earlier eluting compound (peak 4) with a similar mass spectrum (Fig.4.21b) is thought to be ionene (Achari *et al.* 1973).

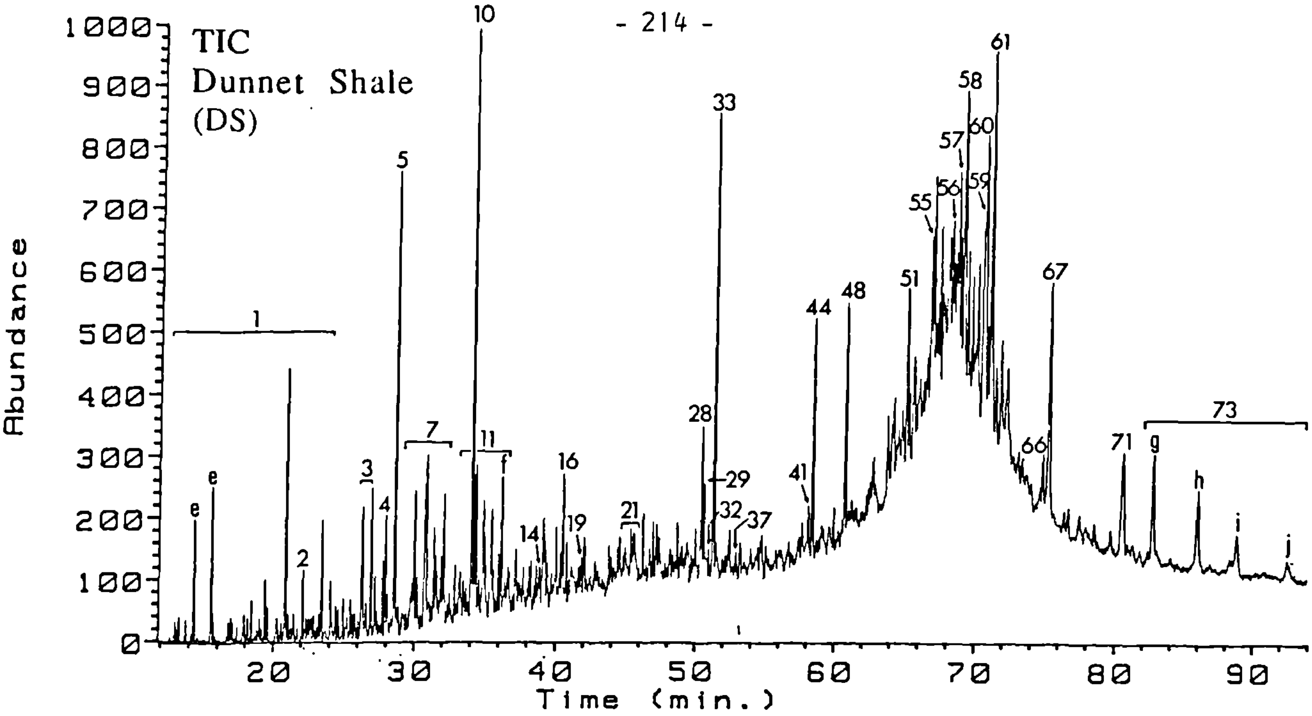


Fig.4.20 TIC trace showing typical distribution of aromatic compounds in lamosites (peak assignments in Table 4.7).

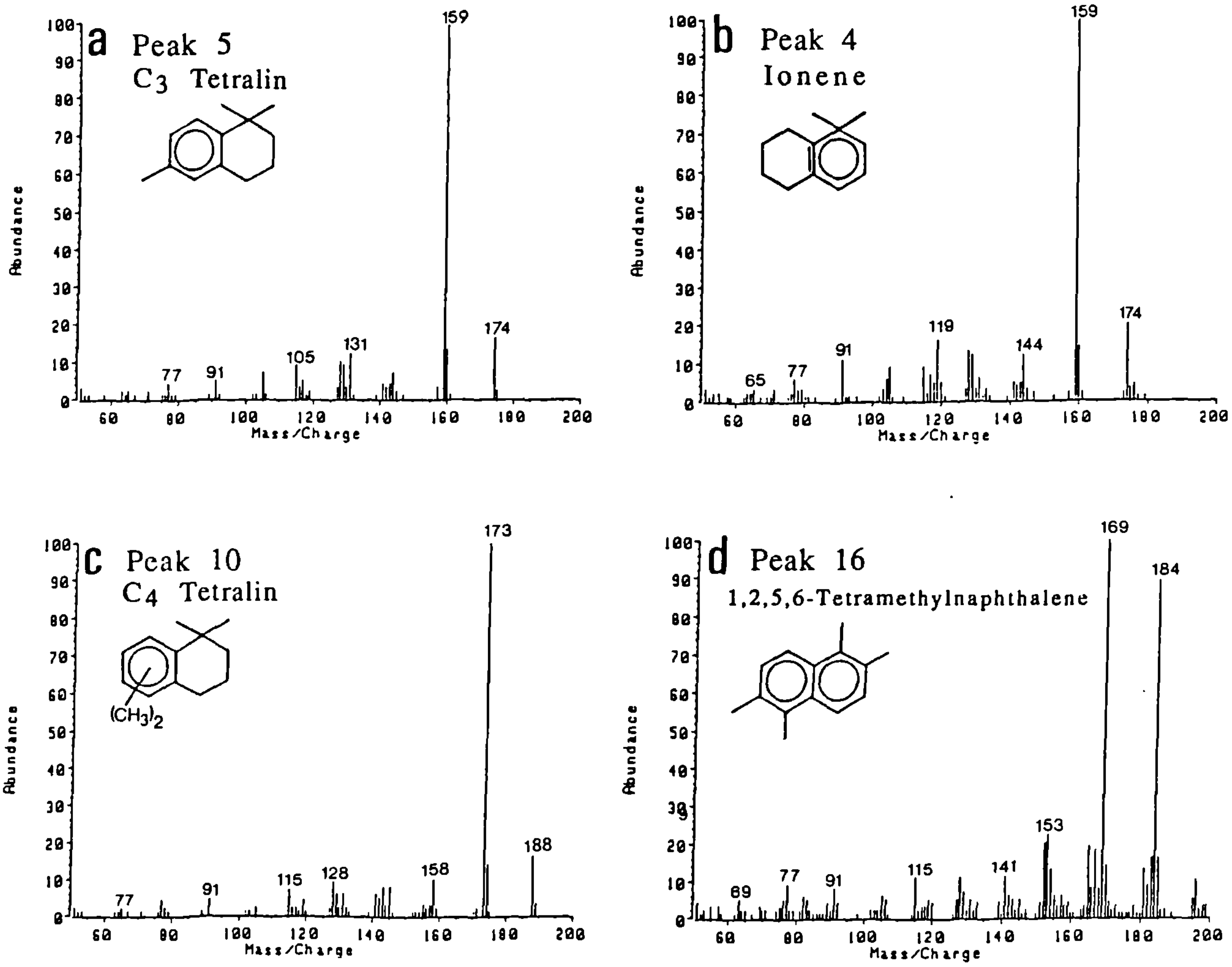


Fig.4.21 Mass spectra of bicyclic aromatic hydrocarbons in Midland Valley lamosites.

Table 4.7 Peak assignments for aromatic compounds.

Peak No	Assignment	Major Ions (m/z)	Mol. Wt.
1	Alkylbenzenes	91,105,119	C_nH_{2n-6}
	a Toluene	91,92	92
	b Ethylbenzene	91,106	106
	c m+p-Xylene	91,106	106
	d o-Xylene	91,106	106
	e C_3-Benzenes	105,120	120
2	Naphthalene	128	128
3	Methylnaphthalenes	142,127	142
4	Ionene	159,174	174
5	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene (C_3 Tetralin)	159,174	174
6	Biphenyl	154,139	154
7	C_2-Naphthalenes	156,141,127	156
8	Methylbiphenyls	168,153	168
9	Dibenzofuran	168,139	168
10	1,1,5,6-Tetramethyl-1,2,3,4-tetrahydronaphthalene(C_4 tetralin)	173,188	188
11	C_3 Naphthalenes	170	170
	f 1,2,5-Trimethylnaphthalene	155,170	170
12	C_2-Biphenyls	182,152,169	182
13	?C_5-Tetralin	187,202	202
14	Cadalene	183,198	198
15	Methylflourene(s)	165,180	180
16	1,2,5,6-Tetramethylnaphthalene	169,184	184
17	?C_3-Biphenyls	196	196
18	Dibenzothiophene	169,184	184
19	Phenanthrene	178	178
20	?C_4-Biphenyl	195,210	210
21	Methylphenanthrenes	192	192
22	4*H*-Cyclopenta[*def*]phenanthrene	190	190
23	?C_5-Biphenyl	224	224
24	Methyl-4*H*-cyclopenta[*def*]phenanthrene	204	204
25	?C_6-Biphenyl	238	238

26	C_2-Phenanthrenes	206	206
27	Fluoranthene	202	202
28	Unknown	141,254,115	254
29	Unknown	183,254,165	254
30	Pyrene	202	202
31	Dimethyl-4*H*-cyclopenta[*def*]phenanthrene[a]	218	218
32	Simonellite	237,252,195	252
33	1,2,3,4-Tetrahydroretene	223,238,193	238
34	Benzo[*a*]fluorene	216	216
35	Benzo[*b*]fluorene	216	216
36	Methylfluoranthenes/pyrenes	216	216
37	Retene	219,234,204	234
38	C_3-Phenanthrene	205,220	220
39	Dimethyfluoranthenes/pyrenes[a]	230	230
40	Benzo[*ghi*]fluoranthene	226	226
41	Unknown	229,241,311	326
42	Benz[*a*]anthracene	228	228
43	Chrysene(+?Triphenylene)	228	228
44	Unknown	213,295,225	310
45	Trimethylfluoranthenes/pyrenes[b]	244	244
46	Methylchrysenes/methylbenz[*a*]anthracenes	242	242
47	Dimethylchrysenes/benz[a]anthracenes[a]	256	256
48	C_{24} monoaromatic tetracyclic terpenoid	309,171,157	324
49	3,4,7-Trimethyl-1,2,3,4-tetrahydrochrysene	259,274,229	274
50	Benzo[*j*]fluoranthene and Benzo[*k*]fluoranthene	252	252
51	Unknown	225,350	350
52	Benzo[*e*]pyrene	252	252
53	Benzo[*a*]pyrene	252	252
54	Perylene	252	252
55	C_{29} D-ring monoaromatic 8,14-secohopane(s)	365,159,187	394
56	C30 D-ring monoaromatic 8,14-secohopanes(s)	365,159	408
57	Unknown	345,360,275	360
58	Unknown	225,263,213	378
59	Unknown	359,374	374
60	Unknown	187,157,363	392
61	Unknown	225,239,377	392
62	Indeno(1,2,3-c,d)pyrene	276,139	276

Table 4.7 (cont.).

63	C_{28}Dimethyl nuclear-substituted triaromatic steroid[a]	259,229	372
64	Unknown	299,313,328,	328
65	1,12-Benzoperylene	276,138	276
66	Unknown	209,375,221	390
67	Unknown	207,221,374	374
68	C_{29}Dimethyl nuclear-substituted triaromatic steroid[a]	259,229	386
69	7-Methyl-3`-ethyl-1,2-cyclopentenochrysene	281,310	310
70	C_{30}Dimethyl nuclear-substituted triaromatic steroid[a]	259,229	400
71	Unknown	388,221,235	388
72	2,9-Dimethylpicene	306,289	306
73	Benzohopanes	191	C_nH2_{n-16}
	g C_{32}-Benzohopane	191,211,226	432
	h C_{33}-Benzohopane	191,158,170	446
	i C34-Benzohopane	191,172,184	460
	j C_{35}-Benzohopane	191,186,198	474
74	Coronene	300,150	300

[a] could be ethyl

b could be ethylmethyl or propyl

Table 4.7 (cont.).

The mass spectra of other bicyclic aromatic compounds commonly found in the lamosites are shown in Figs 4.21c and d. Peak 10 dominates the distribution of aromatics in all the lamosites studied. Its mass spectrum (Fig.4.21c) suggests that it is of the same structural type as that of peak 5, with the intense $(M-15)^+$ ion indicating a gem dimethyl function on the saturated ring (Anders *et al.* 1973; Gallegos 1973). Two C_4 tetralins have been identified as prominent components in several coals and shales (Püttmann and Villar 1987; Villar *et al.* 1988) and the retention time of one of these (1,1,5,6-Tetramethyl-1,2,3,4-tetrahydronaphthalene) corresponds closely to that of peak 10. The mass spectral characteristics and retention time of peak 16 (Fig.4.21d) closely correlate with those cited by Püttmann and Villar (1987) for 1,2,5,6-Tetramethylnaphthalene (1,2,5,6-TeMN), which these authors have also shown to be a major constituent in the aromatic fractions of many coals and shales.

Other prominent components in the Midland Valley lamosites elute at *c.*50 minutes in the TIC traces and are phenanthrene derivatives. The most prominent of these is peak 33 whose mass spectrum (Fig.4.22a) closely resembles that of 1,2,3,4-Tetrahydroretene (Wakeham *et al.* 1980b; Simoneit and Mazurek 1982). Other components seen in Midland Valley lamosites (albeit not in great abundance in the Dunnet Shale) are simonellite (peak 32; Fig.4.22b) and retene (peak 37; Fig.4.22c). Two unknown components (peaks 28 and 29) are also common. The molecular ions of their mass spectra (Figs 4.22d and e) suggest that they belong to the C_nH_{2n-12} compound series and could therefore be monoaromatised compounds based on the steroid skeleton or alkylated naphthalenes.

Although only a few compounds eluting after 58 minutes could be positively identified, spectral characteristics of prominent components suggest that they probably derive from the aromatisation of steroid and terpenoid precursors. Compounds corresponding to peaks 41, 44 and 48 are common in lamositic shales. The mass spectra of peaks 41 and 44 (Figs 4.22f and g respectively) do not correspond with any of those presented in the literature, but that of peak 48 (Fig.4.22h) closely resembles the mass spectrum of a C_{24} monoaromatic tetracyclic terpenoid with a des-A-fernane skeleton recently published by Loureiro and Cardoso (1990). These authors identified this compound in the lacustrine Paraiba Valley oil shale, whose petrological characteristics suggest a close resemblance to Scottish lamosites. A possible formation pathway envisages the ring-A degradation of a triterpenoid precursor. Akin to its occurrence in the Messel Shale, the presence of the fernane-related compound in the Paraiba shale is thought to be due to a significant bacterial contribution to the sedimentary biomass.

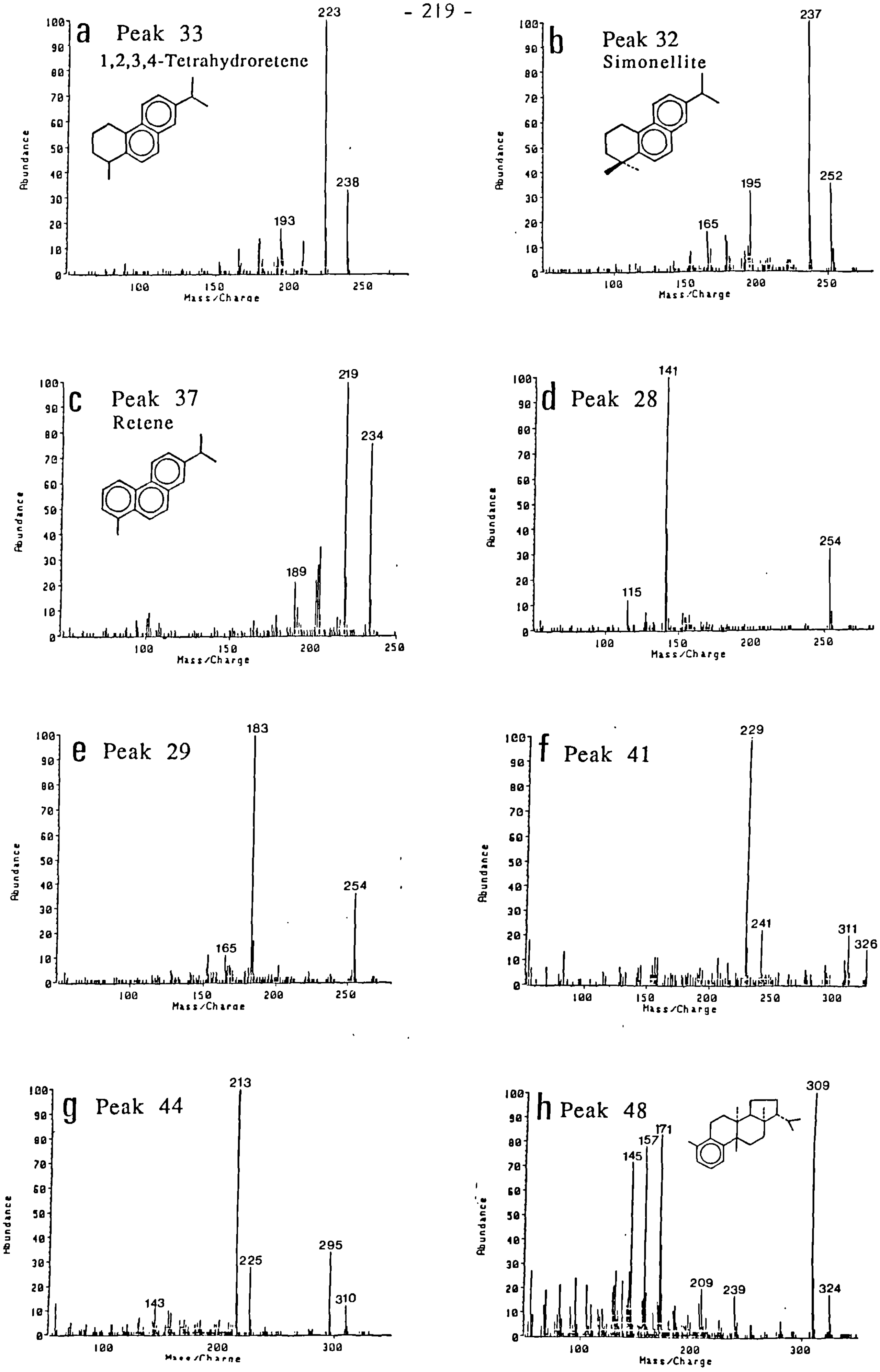


Fig.4.22 Mass spectra of aromatic compounds occurring in Midland Valley lamosites.

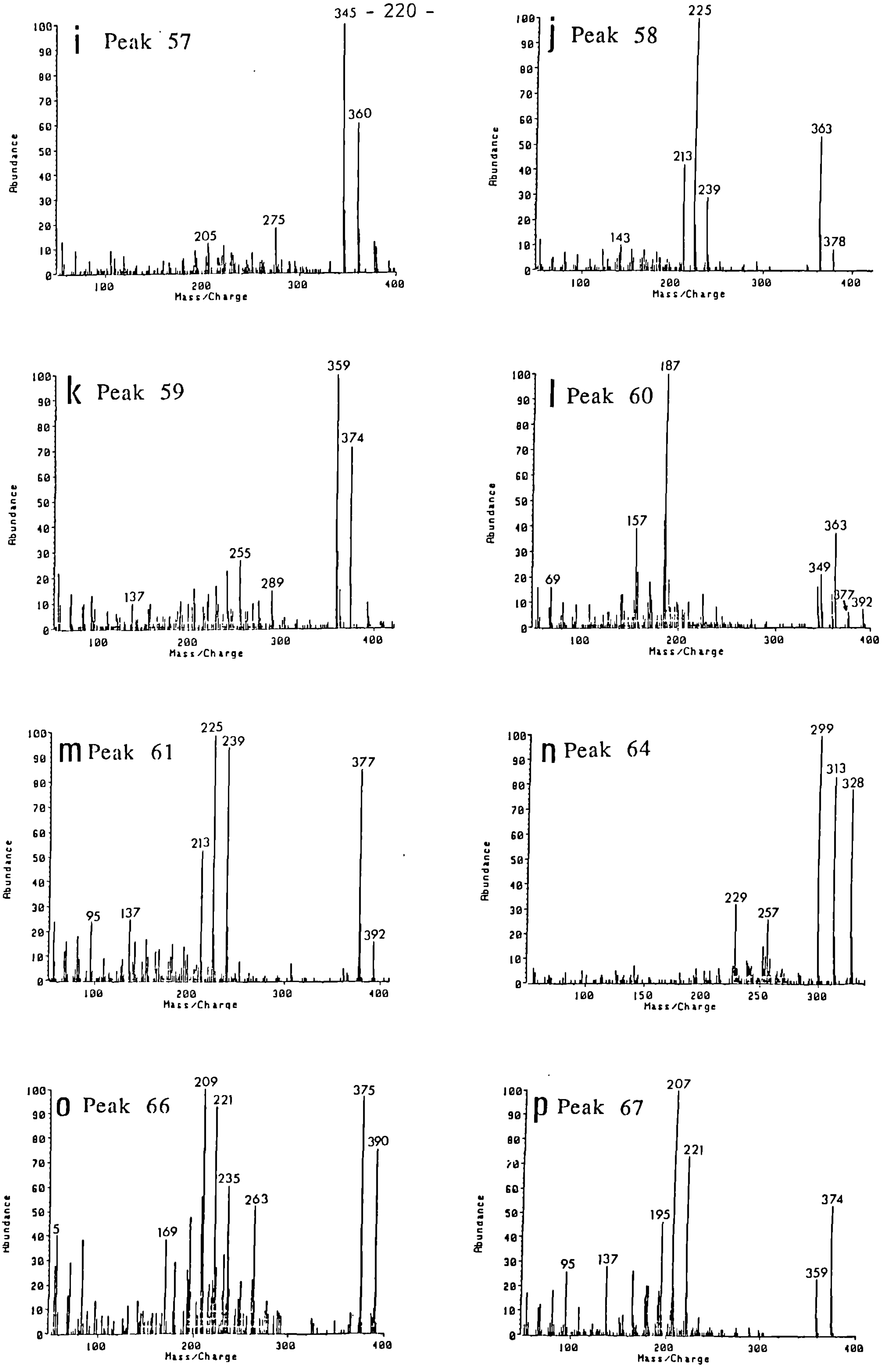

i Peak 57
345
360
275
205
j Peak 58
225
363
213
239
143
378
k Peak 59
359
374
255
289
137
l Peak 60
187
157
363
349
69
377
392
m Peak 61
225
239
377
213
95
137
392
n Peak 64
299
313
328
229
257
o Peak 66
209
221
375
390
235
263
5
169
p Peak 67
207
221
195
374
95
137
359
Abundance
Mass/Charge
0
10
20
30
40
50
60
70
80
90
100
100
150
200
250
300
400

Fig.4.22 (cont.).

In addition to several other unidentified prominent aromatic components (spectra shown in Figs 4.22i-p), the high molecular-weight "hump" contains the widely-occurring C-ring monoaromatic and triaromatic steroids along with the less commonly reported methyltriaromatic compounds. Typical distributions of these components occurring in lamositic shales of the Midland Valley are shown in Fig.4.23, and peak annotations are given in Tables 4.8 and 4.9. Assignments were made by comparing the aromatic distributions in the lamosites with those shown in Mackenzie (1984), Wardroper *et al*, (1984) and Riolo *et al.* (1986). Structures of the aromatic steroids are shown in Fig.4.24. Assignments of the methyltriaromatics are tentative and were made by comparing the retention times of components in the m/z 245 fragmentograms with those of Hoffmann (1984) and Riolo *et al.* (1986).

The carbon-number distribution of aromatic steroids in the m/z 231 and 253 traces mirrors that seen in the saturate fractions, i.e. $C_{29}>C_{28}>C_{27}$, but the reverse appears to be the case for the methyltriaromatic compounds. The dominance of 5α over 5β non-rearranged monoaromatics confirms the immaturity of the samples as indicated by the distributions of saturated biomarker compounds and petrological observations. Rearranged monoaromatics (non co-eluting compounds are shaded red) are of relatively minor abundance. An assessment of the proportion of triaromatic to methyltriaromatic compounds was made by dividing the areas of peaks 3-7 in the m/z 231 fragmentogram by those of peaks 3-11 in the m/z 245 trace. All lamosites except O/SBLA (even those of high rank) showed a predominance of the non-methylated triaromatic species (ratios are included in Table A.6).

Interference in the 65-68 minute range of the m/z 253 fragmentograms is often recorded in samples from the Midland Valley and arises because of the strong contribution of $(M+1)^+$ ions which is associated with the intense molecular ions of benzofluoranthenes, benzopyrenes and perylene ($M^+=252$). A m/z 252 mass chromatogram failed to record the presence of any of the above PAH in the Dunnet Shale. Thus, none of the peaks beyond 64 minutes in Fig.4.23a represent artefacts of interference with parent PAH. In the other lamositic shales studied, contributions from the above non-alkylated PAH were negligible or absent. The arrowed peaks beyond 66 minutes in Fig.4.23a all show a major fragment ion with m/z 253; they could not be identified, but may represent an additional series of rearranged monoaromatic steroidal compounds.

Other components discernible in the high molecular-weight "hump" were identified as members of the D-ring monoaromatic 8,14-secohopane series described by Hussler *et al.* (1984). Homologues $\geq C_{29}$ have an intense ion with

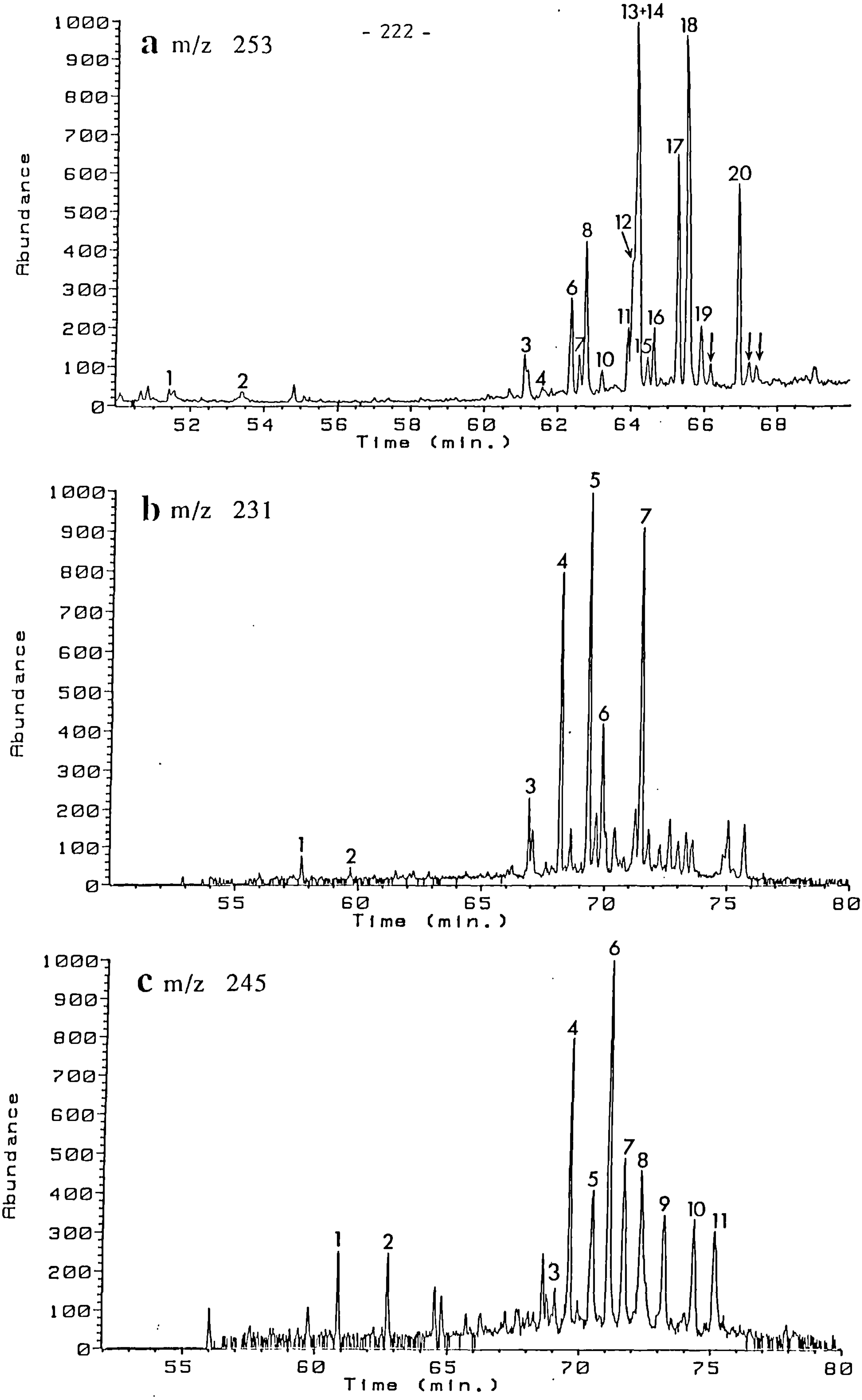


Fig.4.23 Distribution of aromatic steroid hydrocarbons in the Dunnet Shale (see Tables 4.8 and 4.9 for peak assignments).

Table 4.8 Peak assignments for monoaromatic steroids (m/z 253 mass fragmentograms).

Peak	Carbon Number	Structure	Stereochemistry
1	21	Ia	5β(H)
2	22	Ib	5β(H)
3	27	IIa	5β(H),20S
4	27	IIIa	5β(Me),20S
5	27	IVa	5α(Me),20S
6	27	IIa	5β(H),20R
	27	IIIa	5β(Me),20R
7	27	Va	5α(H),20S
8	28	IIb	5β(H),20S
9	27	IVa	5α(Me),20R
	28	IIIb	5β(Me),20S
10	28	IVb	5α(Me),20S
11	27	Va	5α(H),20R
12	28	Vb	5α(H),20S
13	28	IIb	5β(H),20R
	28	IIIb	5β(Me),20R
14	29	IIc	5β(H),20S
	29	IIIc	5β(Me),20S
15	28	IVb	5α(Me),20R
16	29	IVc	5α(Me),20S
17	29	Vc	5α(H),20S
18	28	Vb	5α(H),20R
	29	IIc	5β(H),20R
	29	IIIc	5β(Me),20R
19	29	IVc	5α(Me),20R
20	29	Vc	5α(H),20R

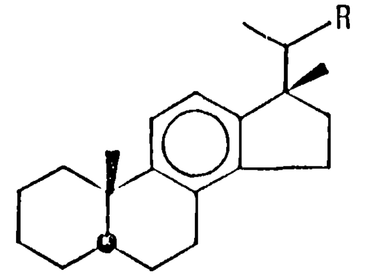
Table 4.9 Peak assignments for triaromatic steroids.

a m/z 231

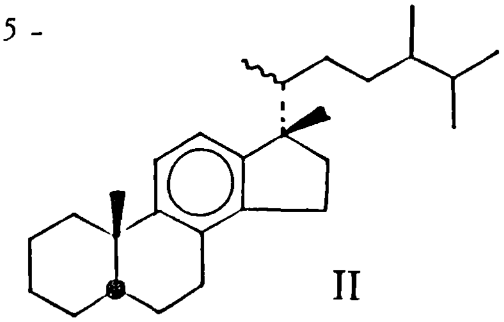
Peak	Carbon Number	Structure	Stereochemistry
1	20	VIa	-
2	21	VIb	-
3	26	VIIa	20S
4	26	VIIa	20R
	27	VIIb	20S
5	28	VIIc	20S
6	27	VIIb	20R
7	28	VIIc	20R

b m/z 245

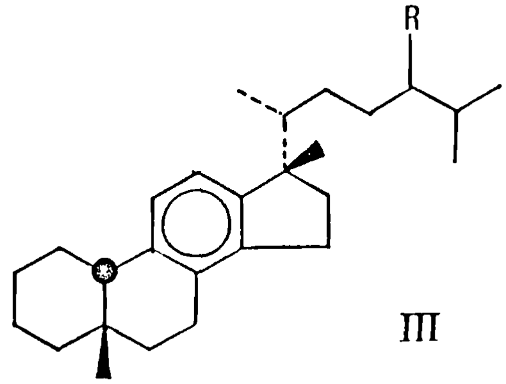
1	21	VIIIa	4-Me
2	22	VIIIb	4-Me
3	27	?IXa	?1-Me
4	27	Xa	4-Me
5	27	?IXa	?1-Me
6	27	Xa	4-Me
7	28	?IXb	?1Me
8	28	Xb+?IXb	4Me+?1Me
9	29	Xc+?IXc	4Me+?1Me
10	29	?IXc	?1Me
11	29	Xc	4Me



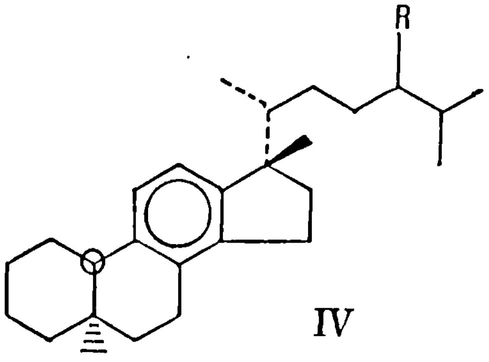
I



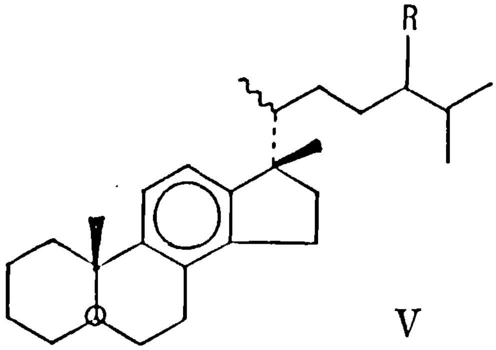
II



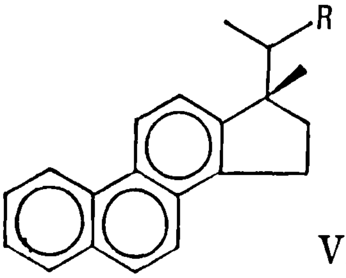
III



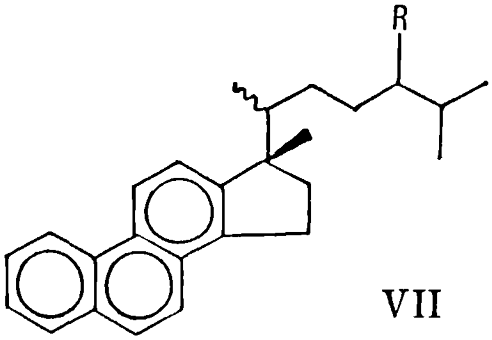
IV



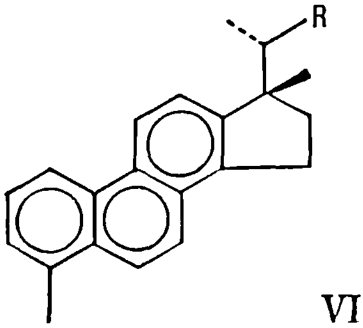
V



VI



VII



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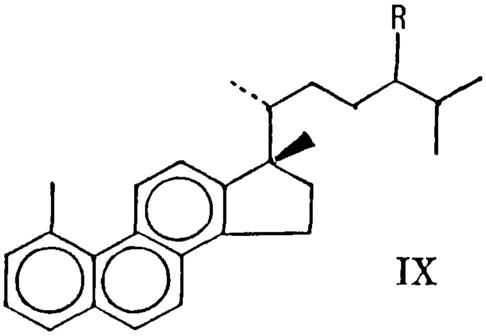
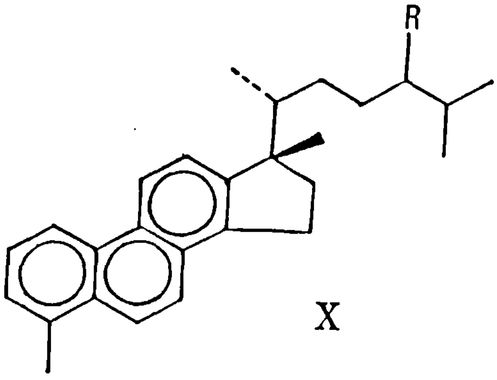


IX



X

a R=H

b R=CH_3

c R=C_2H_5

Fig.4.24 Structures of aromatic steroidal hydrocarbons listed in Tables 4.8 and 4.9.

m/z=365, thus the distribution of these secohopanes can be delimited in m/z 365 fragmentograms. A fragmentogram typifying the aromatic secohopane distribution in the lamositic shales is shown in Fig.4.25. Unlike the distributions described by Hussler *et al* (1984), in which one of each of the C_{29} and C_{30} components is present, mass spectra of peaks a-d in Fig.4.25 (Figs4.26a-d) show the presence of two C_{29} and two C_{30} compounds. Compounds B and D are probably isomers of A and C respectively. The unknown aromatic secohopane in Fig.4.25 has the same retention behaviour as the C_{27} 8,14-monoaromatic secohopane elucidated by Hussler *et al.* (1984), but shows a base peak with m/z 365 instead of 159: the latter would be expected if the unknown compound was the C_{27} homologue. A weak molecular ion of 394 indicates that it is a C_{29} compound. Carbon-number assignments are tentative and are based on similar distribution patterns recorded in the mass chromatograms of Hussler *et al.* (*op.cit.*).

The C_{32}-C_{35} members of the benzohopane series described by Hussler *et al* (1984) are readily discernible in all the low-rank lamosites investigated. Mass spectra of the C_{32}-C_{34} members are shown in Fig.4.27, along with the spectrum of another unknown component (peak 71) which is present in all the lamositic shales investigated.

The aromatic hydrocarbon distribution of the lamosite sampled from the section west of St.Monance differs from the others (Fig.4.28a). The salient differences are the greatly reduced high molecular-weight "hump" and the relatively lower contribution from the benzohopanes and peaks 66, 67 and 71. The alkyltetralins are still prominent as is 1,2,5,6-TeMN. Naphthalene and phenanthrene and their alkylated homologues are more abundant relative to other components than in the other lamosites as are the aromatised diterpenoids simonellite (peak 32) and retene (peak 37). The monoaromatic steroid distribution differs significantly from those of other lamosites due to the greatly enhanced concentrations of the rearranged components (Fig.4.28b). The qualitative distribution of triaromatics is similar, but, unlike the other lamosites, the methyltriaromatic compounds are subordinate to the non-methylated components.

4.3.3.1.3 Torbanite and Torbanitic Shales

4.3.3.1.3.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the hydrocarbon fractions of the *Botryococcus*-rich shales extracted are shown in Figs 4.29a-d. Figs 4.29a,b and d represent saturated hydrocarbon fractions whilst 4.29c is a total aliphatic fraction.

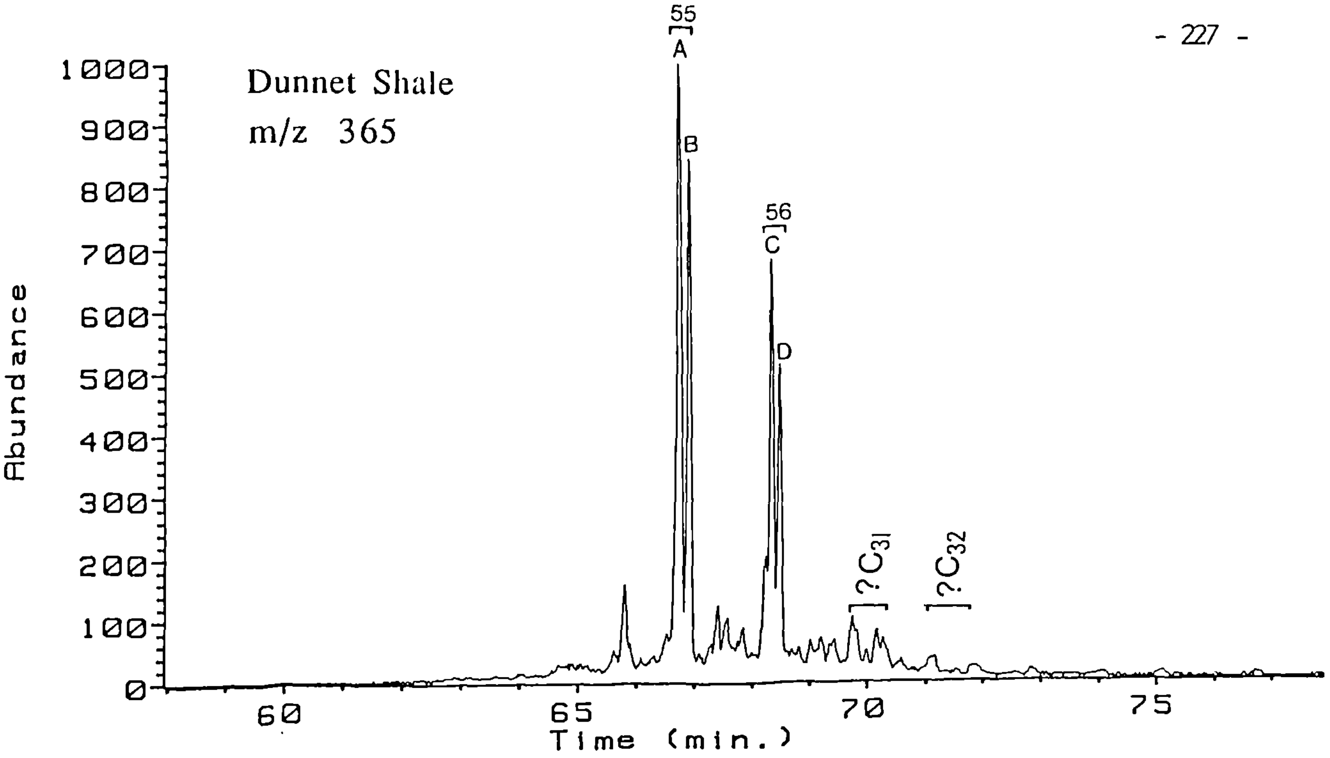


Fig.4.25 Typical distribution of 8,14-secohopanes in lamositic shales. (Peak assignments shown in Table 4.7).

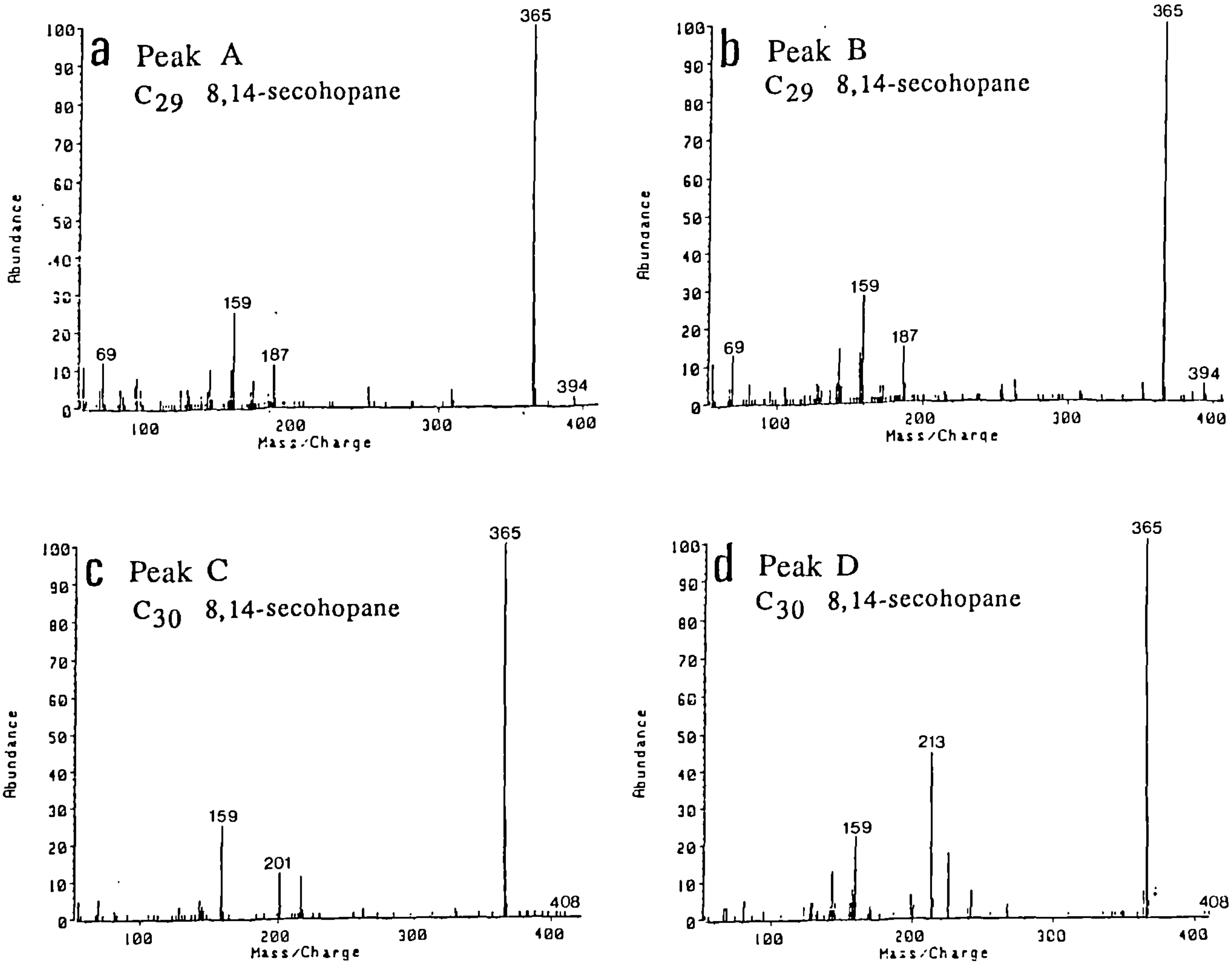
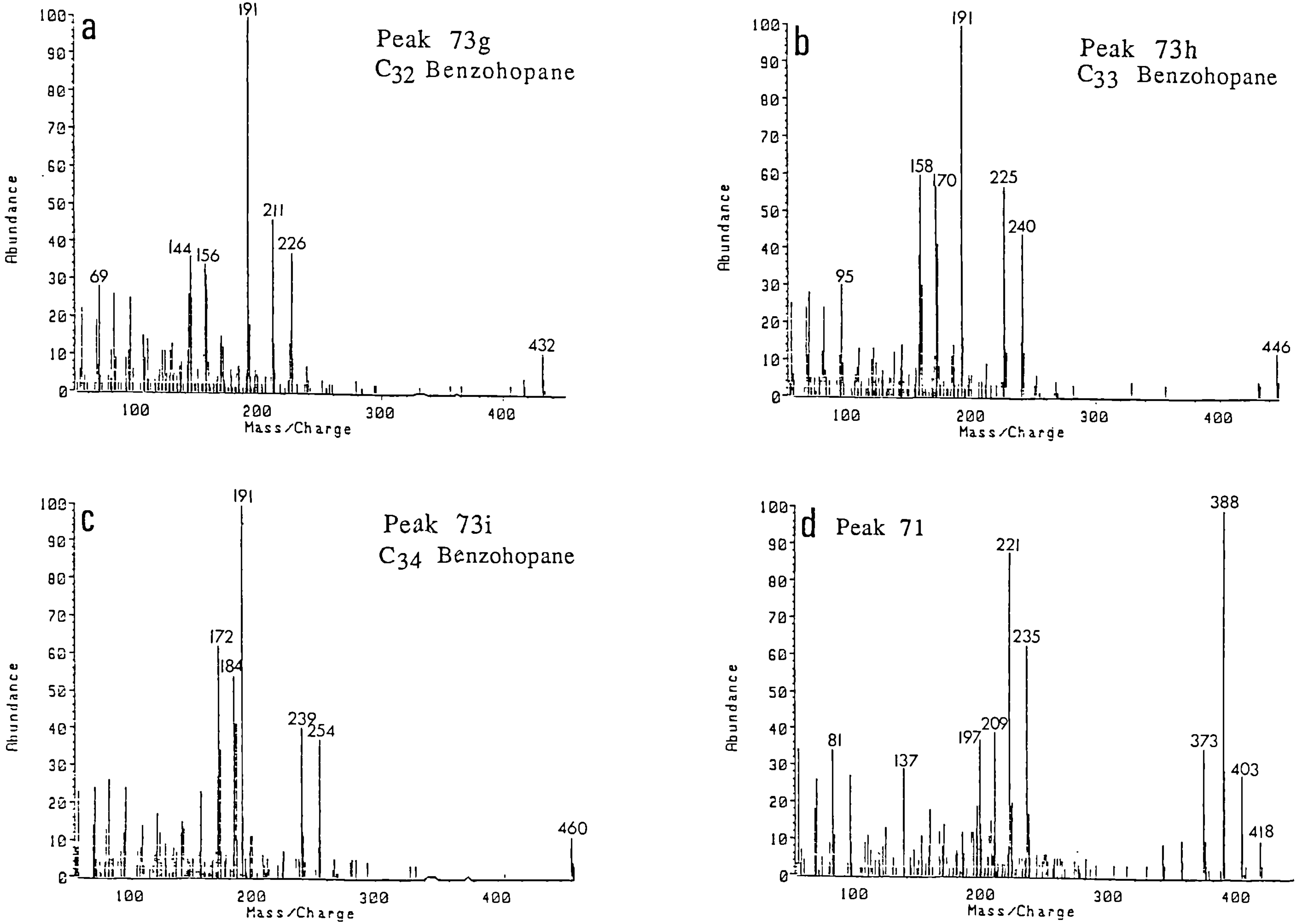


Fig.4.26 Mass spectra of peaks 55 and 56 in Fig.4.25.

Fig.4.27 Mass spectra of benzohopanes and peak 71.



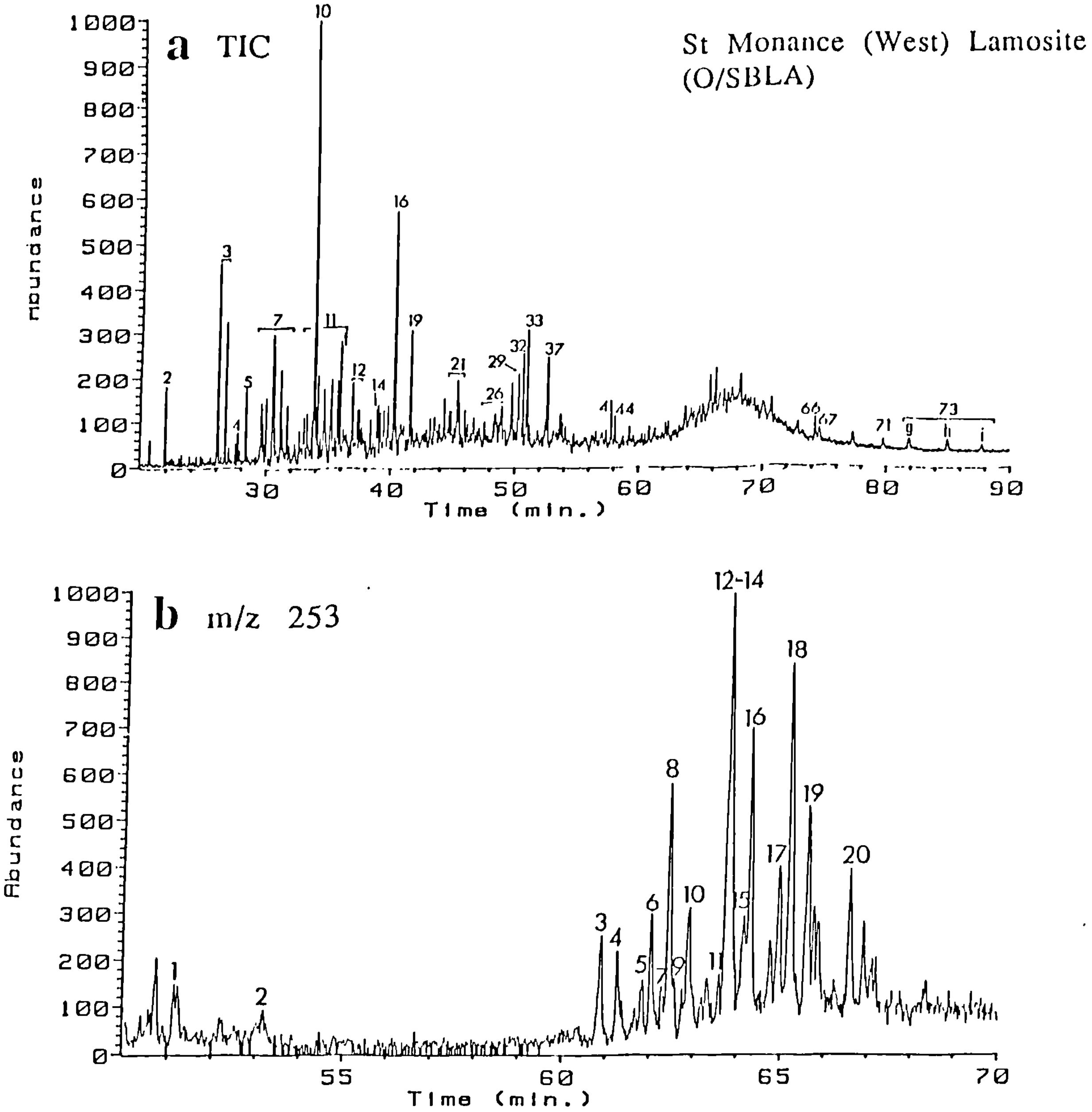


Fig.4.28 Distribution of aromatic hydrocarbons (a) and C-ring mono-aromatic steroids (b) in the St.Monance (west) lamosite (peak assignments in Tables 4.7 and 4.8 respectively.

The *n*-alkanes display a saurian-type distribution which encompasses the range C_9-C_{38} with peak maxima occurring at *n*-C_{21} or *n*-C_{23}. *N*-alkanes were not discernible in the gas chromatograms of the aliphatic fractions of the Westfield or Lillies shales, and when further separation of the aliphatics was attempted using argentation TLC, no bands corresponding to unsaturated components were recognised on the plate. In contrast, gas chromatographic analysis of the Eskmouth torbanite revealed the presence of a homologous series of *n*-alkenes which has also been identified in aliphatic fractions in the Torbanehill torbanite (Allan 1975; Hall 1981).

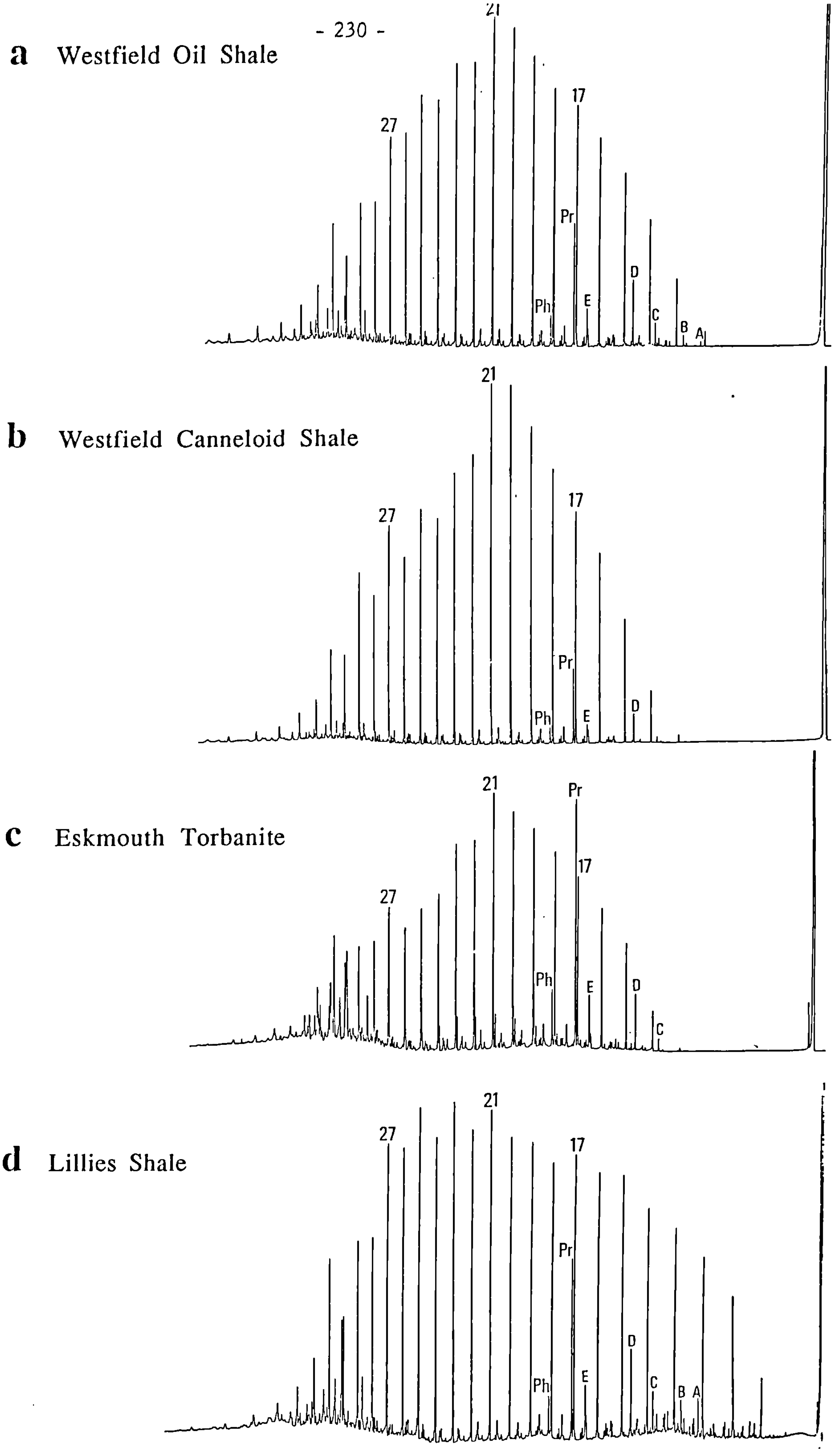


Fig.4.29 Gas chromatograms of aliphatic hydrocarbon fractions of torbanite and torbanitic shales (isoprenoid assignments in Table 4.4).

The enhanced concentrations of long-chain *n*-alkanes in the Lillies Shale, giving rise to a slight skew towards the high molecular-weight end of the envelope, may be a reflection of the higher amounts of vascular-plant matter in the sample compared with the amounts observed in the other sediments analysed, which has long been thought to be the reason why oils retorted from the Lillies Shale were significantly waxier than oils retorted from other *Botryococcus*-rich shales (Skilling 1938).

Odd-over-even *n*-alkane carbon-number preferences are less pronounced in the torbanitic shales than in the lamosites, resulting in lower values of CPIs over the same carbon-number range (1.08-1.17). Pr/Ph ratios are higher in the torbanitic shales (3.90-4.28), presumably reflecting the closer association of these deposits with oxidising, peat-swamp environments where algae accumulated in shallow lakes of relatively restricted areal extent (MacGregor 1938; Moore 1938). The restricted nature of the depositional environment of the Eskmouth torbanite is indicated by its relatively high Pr/*n*-C_{17} ratio (1.44). More open-water conditions of sedimentation for the other shales are inferred by their lower Pr/*n*-C_{17} ratios (0.32-0.64). As stated earlier, values less than *c*.0.50 have been cited as indicating the accumulation of organic matter in environments not associated with inland, oxidising peat swamps (Lijmbach 1975; Didyk *et al.* 1978); thus,the low values for the Westfield shales appear anomalous in view of the known association of torbanites and torbanitic shales with restricted, oxidising environments. Consideration of the geological background of the Westfield Basin may offer some explanation. The basin was a relatively large, rapidly subsiding, synsedimentary structure. It is possible that the Westfield shales bear the imprint of open-water conditions due to the growth of algae in the central, deep-water part of this basin which was probably more laterally extensive than other basins in which torbanites and torbanitic shales accumulated. Dissociation from oxidising, peat-swamp environments is not likely since the Westfield Basin is renowned for its exceptionally thick development of coals. This example illustrates the importance of integrating geochemical data with the geological history, thus reducing the likelihood of erroneous interpretations.

Gas Chromatography-Mass Spectrometry (GC-MS)

Tricylic and tetracyclic terpanes are present in much lower abundance than pentacyclic terpanes in the torbanite and torbanitic shales studied. The relative concentration of 3- and 4-ring terpanes to 5-ring terpanes in the Westfield Oil Shale (Fig.4.30a) is very similar to that in the Lillies Shale, whilst the greatest relative concentration of tricyclics and tetracyclics is found in the Westfield

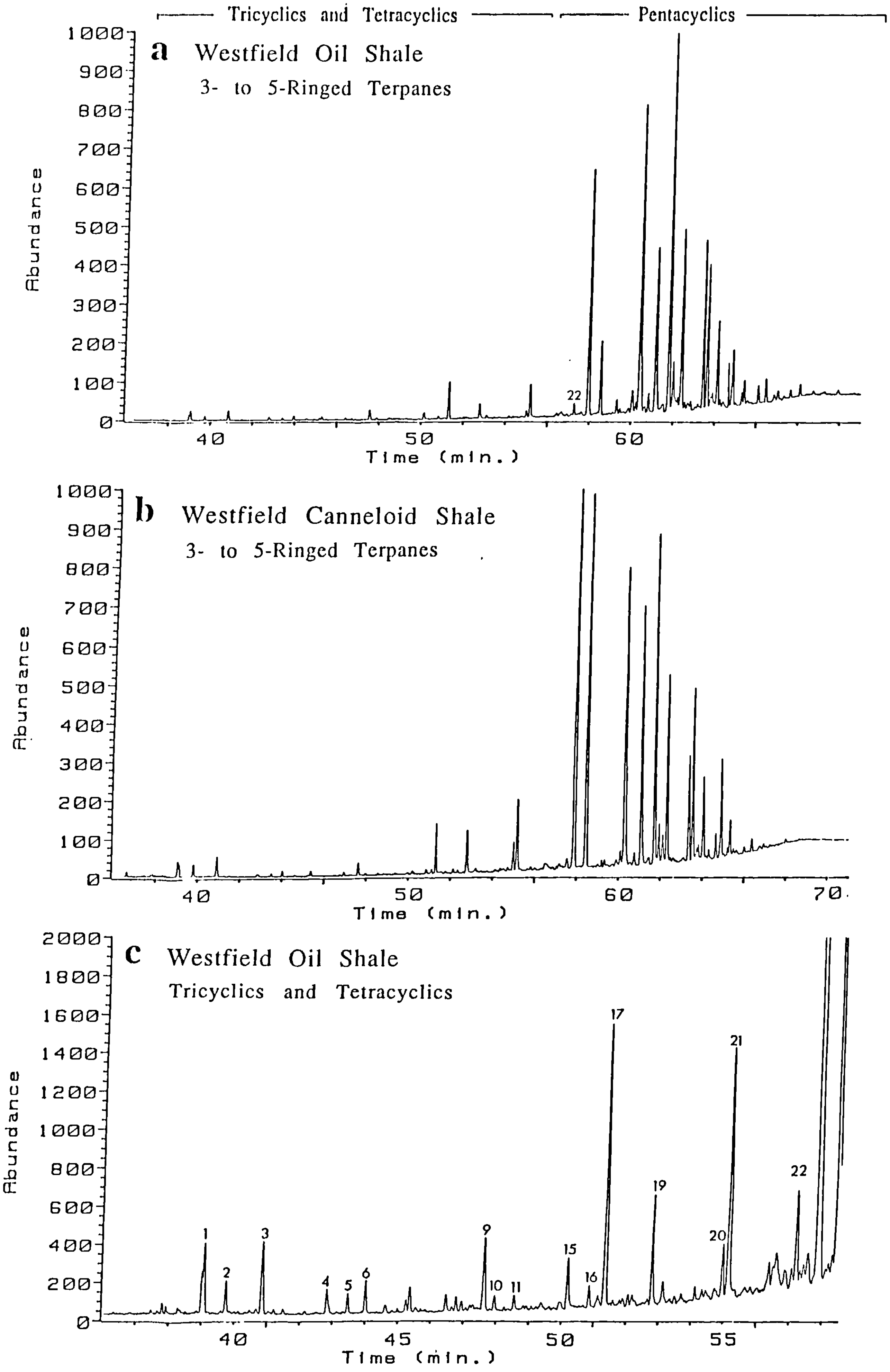


Fig.4.30 M/z 191 fragmentograms illustrating the distributions of 3- to 5-ringed terpanes in the Westfield shales (peak assignments in Table 4.5).

Canneloid Shale (Fig.4.30b). Tricyclic and tetracyclic terpanes are barely detectable in the Eskmouth torbanite. Tetracyclic components are present in greater abundance than the tricyclics in all the above samples, but no tricyclics could be detected $>C_{21}$.

The most complex tri- and tetracyclic terpane distribution is found in the Westfield Oil Shale (Fig.4.30c). Slightly simpler distributions of tricyclics and tetracyclics are seen in the other torbanitic shales and in the torbanite, as the two C_{24} tetracyclics represented by peaks 15 and 16 and the C_{23} tetracyclic (peak 9) were not identified.

Fragmentograms illustrating the difference in the pentacyclic triterpane distributions are shown in Fig.4.31. The m/z 191 trace for the Lillies Shale closely resembles that of the Eskmouth torbanite.

The overall distribution of hopanes is similar in all samples. The salient difference is the dominance of Tm and 17β(H) trisnorhopane (peaks 24 and 25 over the $C_{30}\alpha\beta$ hopane in the Canneloid Shale which, along with the marked prevalence of the 22R epimers in the extended αβ hopanes and the relatively high moretane concentrations, suggests this is the most immature of the four samples, a judgement that could not be made on the basis of vitrinite reflectance alone.

The unknown C_{29} pentacyclic compound (peak 30) that shoulders the $C_{29}\alpha\beta$ hopane is present in the Eskmouth and Lillies shales in amounts comparable with those found in most lamosites. Of relatively minor importance in the Westfield Oil Shale, the peak could not be detected at all in the Canneloid Shale. 28,30 bisnorhopane was not detected in the Westfield shales, but was identified as a minor constituent in the Lillies and Eskmouth shales.

Variations in the sterane distributions of the torbanite and torbanitic shales are exemplified by the m/z 217 fragmentograms of the Westfield shales (Figs 4.32a,c) and the Eskmouth torbanite (Fig.4.32d). The fragmentograms of the Westfield shales may be regarded as end-member distributions, with those of the Eskmouth and Lillies shales being intermediate.

In the Westfield Oil Shale, Lillies Shale and Eskmouth torbanite, hopanes predominate over steranes to such a degree that the minor m/z 217 ion which arises during hopane fragmentation assumes a much greater importance so that the hopane-sourced m/z 217 rivals the intensity of the m/z 217 fragments from steranes, thus accounting for the hopane interference on the "sterane" m/z 217 mass fragmentograms. This phenomenon is particularly pronounceed in the m/z 217 traces of the Westfield Oil Shale and Lillies Shale, where the hopane to sterane ratios are 37:1 and 35:1 respectively.

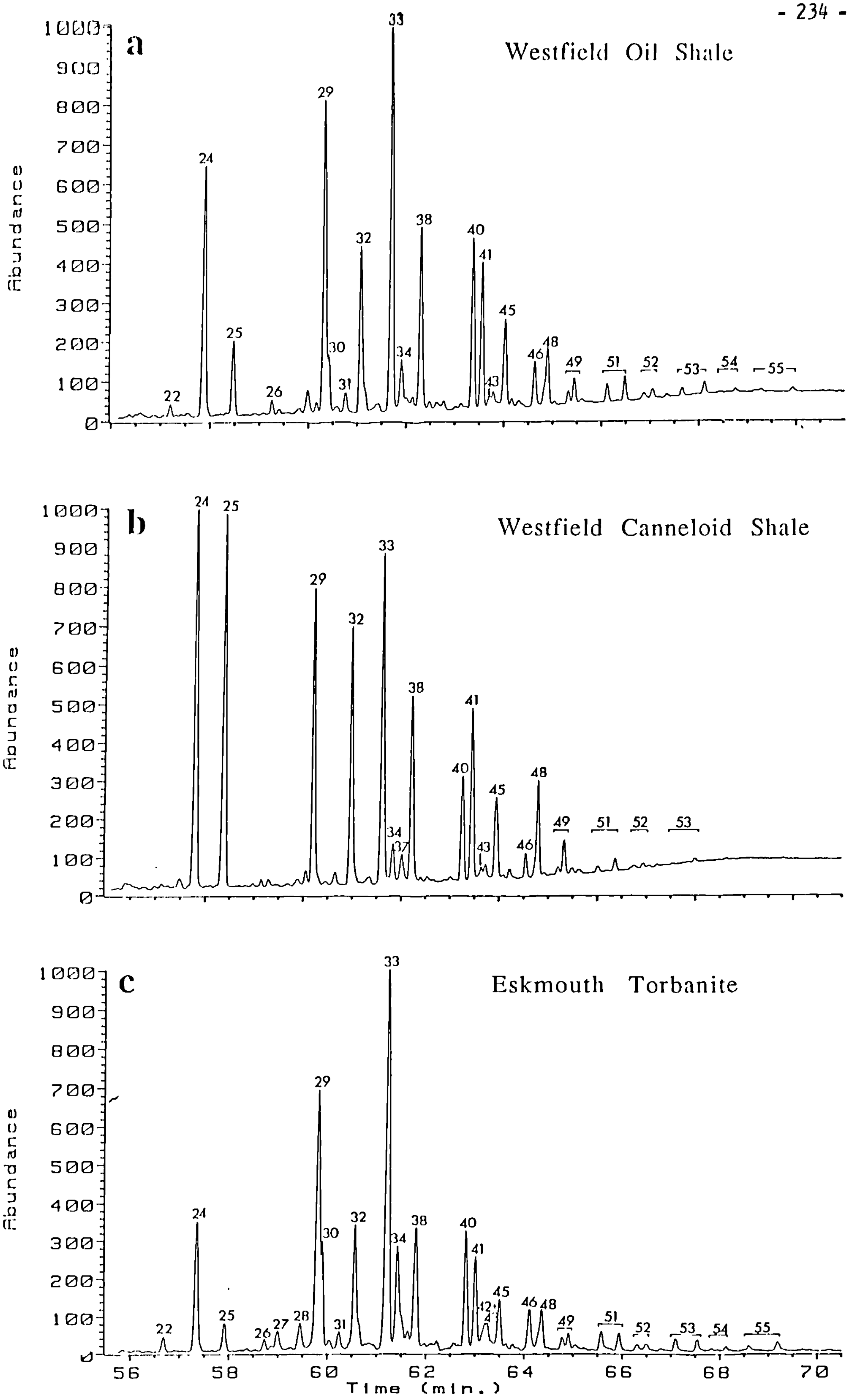


Fig.4.31 Distribution of triterpanes in the Westfield shales and Eskmouth torbanite (peak assignments are shown in Table 4.5).

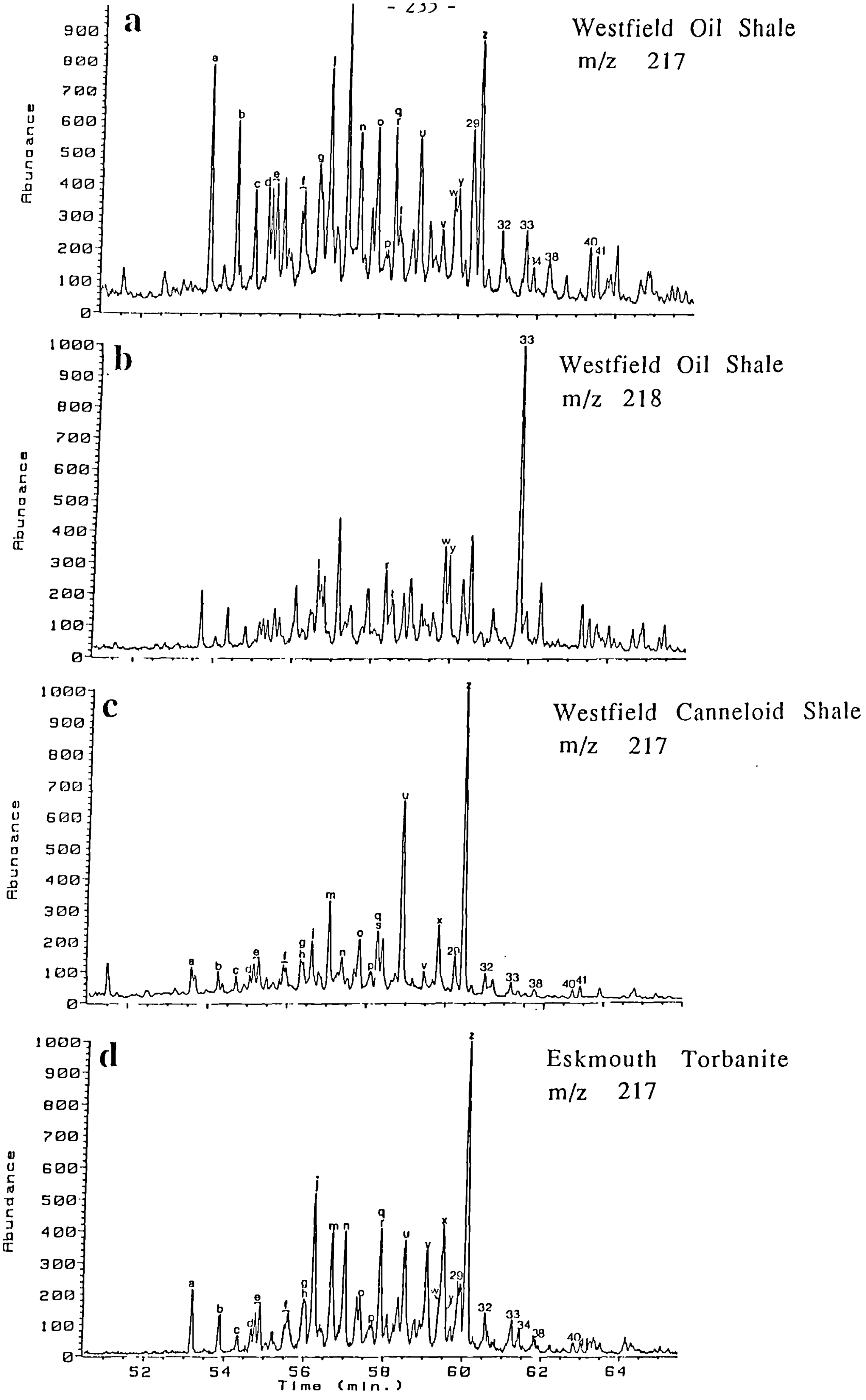


Fig.4.32 Distribution of steranes in the Westfield shales and Eskmouth torbanite (numbered peaks are hopanes; see Tables 4.5 and 4.6 for assignments).

The dominance of $C_{29}\alpha\alpha\alpha20R$ (peak z) in the Canneloid, Lillies and Eskmouth samples has also been recorded in torbanites from different localities worldwide (Derenne *et al* 1988). The prevalence of the $C_{27}\alpha\alpha\alpha20R$ sterane in the Westfield Oil Shale would therefore appear to be anomalous. The concentration of the C_{27} sterane in the latter sample is sufficiently high to enable it to plot in the "open marine" field in Fig.4.19, contrasting markedly with the location of the other samples which plot in the "terrestrial" field. In view of their petrographic similarities, low rank and occurrence in the same restricted depositional basin, it is perhaps surprising that that there is such a marked disparity between the $\alpha\alpha\alpha20R$ sterane distributions in the Westfield shales. The higher concentrations of the $C_{29}\alpha\alpha\alpha20R$ in the Canneloid Shale are unlikely to be the result of the slightly higher concentrations of *Botryococcus* telalginite in the sample since, although C_{29} components are major sterols in this alga, sterols are very minor constituents in extant strains and so are unlikely to modify significantly the total sterane content or distribution in sediments in which *Botryococcus* remains are preserved. Furthermore, the sterol distribution reported in a living colony of *Botryococcus braunii* (C_{27}:C_{28}:C_{29}=8:50:42; cited in McKirdy *et al.* 1986) bears little resemblance to the carbon-number distribution of the steranes in the Westfield and Lillies shales or in the Eskmouth torbanite, suggesting that it is the co-existing liptodetrinite and/or terrestrial components which have most strongly influenced the sterane fingerprints in these deposits. The marked difference in the $C_{29}\alpha\alpha\alpha20R$ content of the Westfield shales is not likely to be related to differences in the amount or type of terrestrial components since, from microscopical analysis, these are present in roughly equal proportions in both samples.

C_{27} sterols are often cited as the principal sterols in zooplankton and higher animals (e.g. Huang and Meinschein 1976; Nishimura and Koyama 1977; Nes and Nes 1980). It is therefore possible that the enhanced concentration of C_{27} steranes in the Westfield Oil Shale reflects an input of freshwater zooplanktonic organisms. Since no liptinite other than *Botryococcus* telalginite or sporinite could be discerned in the Westfield Oil Shale, it is possible that at least some of the liptodetrinite may comprise the remains of the zooplanktonic matter. Alternatively, the enhanced concentration of $C_{27}\alpha\alpha\alpha20R$ may derive from algae, as a few species of some algal families such as Prymnesiophyceae, Xanthophyceae and Euglenophyceae contain high concentrations of C_{27} sterols (Volkman 1986). An additional possibility is that the relatively high C_{27} sterane content might result from higher-animal input (? fish/invertebrates/primitive tetrapods), the macroscopic remains of which have not been preserved in the shale sample studied here. That many of the best preserved amphibian and fish faunas occur in oil shales of the Midland Valley (Smithson 1985) lends further support to this suggestion.

In addition to the raised concentration of the $C_{27}\alpha\alpha\alpha20R$ component, discussed above, the sterane distribution in the Westfield Oil Shale is unusual in two other respects. First, the proportion of αββ steranes present is high given the relatively low rank of the sample (estimated unsuppressed reflectance is $\%R_o av \approx 0.55$). Assuming that it is thermal maturation which results in the conversion of ααα steranes to αββ steranes (Mackenzie *et al.* 1980), then the concentration of αββ steranes in the Westfield Oil Shale is more representative of a sample that has attained a much higher level of organic maturation (Mackenzie *et al.* 1980; Mackenzie and Maxwell 1981; Mackenzie *et al.* 1988; compare also the biomarker ratios of high-rank samples in this thesis). Although high concentrations of αββ steranes have been reported in extracts of immature organic matter that has accumulated under hypersaline regimes (Ten Haven *et al.* 1985, 1986), the development of such extreme environmental conditions at the time of deposition in the Westfield Oil Shale does not accord with the known sedimentological history of the cyclothemic, coal-bearing sequence in the Westfield Basin. Second, the diasterane content of the Westfield Oil Shale is exceptionally high: the diasterane/sterane ratio is not only significantly higher than the ratios determined for other *Botryococcus*-rich shales, it is higher than the ratios obtained for the majority of samples investigated during the course of the entire project. It seems that the environmental factors that operated during and shortly after the deposition of the Westfield Shale, but perhaps more important the clay composition of the inorganic matrix,have been particularly conducive to the formation of diasteranes (see Rubinstein *et al.*1975 for clay-catalysed steroidal transformations) and αββ steranes from their steroidal precursors.

4.3.3.1.3.2 Aromatic Hydrocarbons

The distribution of aromatic compounds in the torbanitic shales studied is exemplified by the TIC trace of the Westfield Oil Shale (Fig.4.33). Naphthalene, phenanthrene and their alkylated homologues are prominent components, as is the C_4 tetralin (peak 10) and 1,2,5,6-TeMN (peak 16). The last two components are not as abundant, relative to other components, as they were in the lamosites, nor is tetrahydroretene (peak 33). The mass spectra of compounds eluting on the high molecular-weight "hump" were generally very complex, probably a consequence of coelution. Two of the peaks whose mass spectra could be matched to compounds identified by Wakeham *et al.* (1980a,b) were peak 49 (3,4,7-Trimethyl-1,2,3,4-tetrahydrochrysene) and peak 69 (7-Methyl-3'-ethyl-1,2-cyclopentenochrysene); their

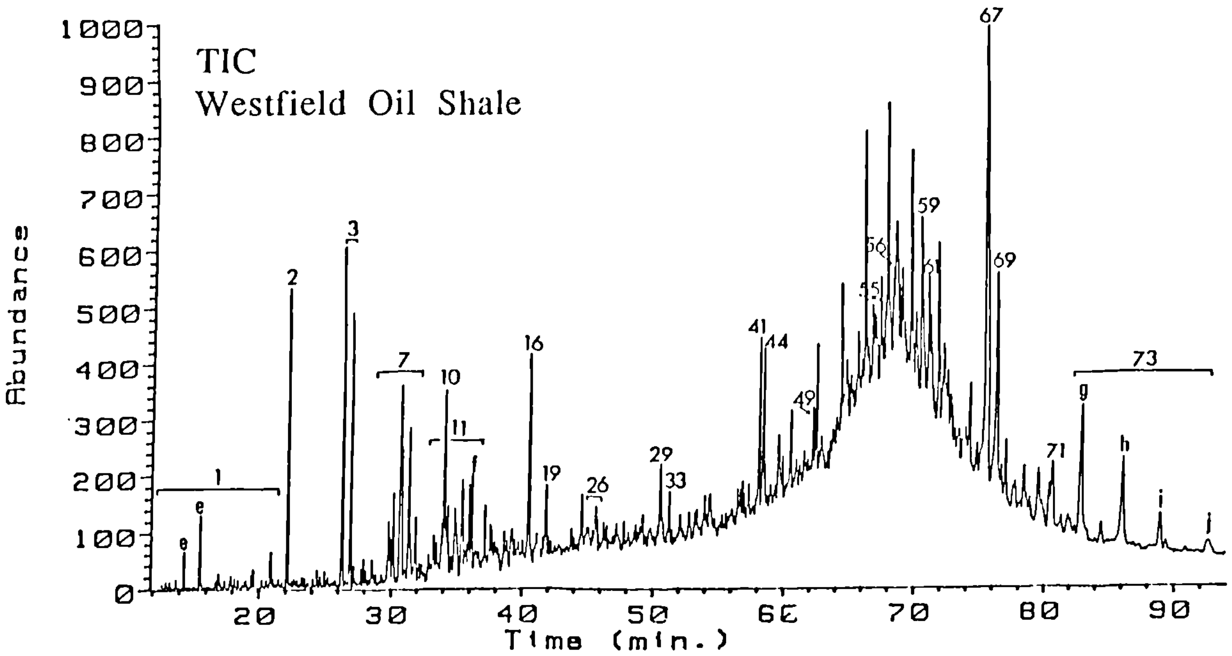


Fig.4.33 Typical distribution of aromatics in the torbanitic shales studied (assignments given in Table 4.7).

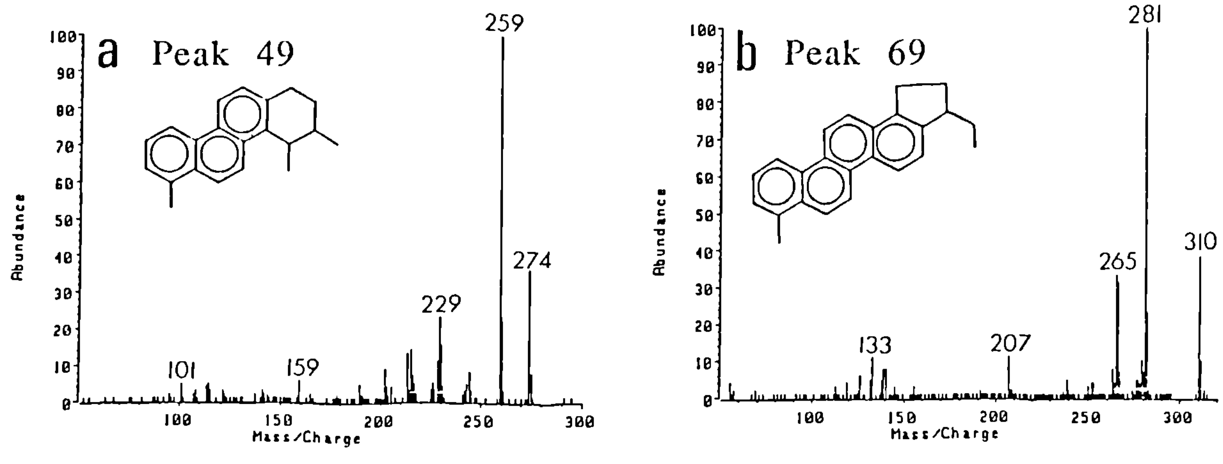


Fig.4.34 Mass spectra of peaks 49 and 69.

mass spectra are shown in Figs 4.34a and b. The compound represented by peak 67 (see Fig.4.22p for its mass spectrum) is prominent in all the torbanitic shales, but only dominates the aromatic distribution in the Westfield Oil Shale. Benzohopanes are conspicuous in all the torbanitic samples analysed as are the 8,14-secohopanes, whose distributions are virtually identical to that given in Fig.4.25.

The distribution of monoaromatic steroidal hydrocarbons in the Westfield Oil Shale typifies that of the Lillies and Canneloid shales (Fig.4.35a). Rearranged structures are prominent, and coelution of some of the high molecular-weight components with benzofluoranthenes and benzopyrenes (M^+=252; Fig.4.35b) is evident. It should be noted that the retention times of the parent PAH relative to the monoaromatics varies depending on the type and age of the gas chromatographic column. The distributions of triaromatic steroids in the Westfield shales

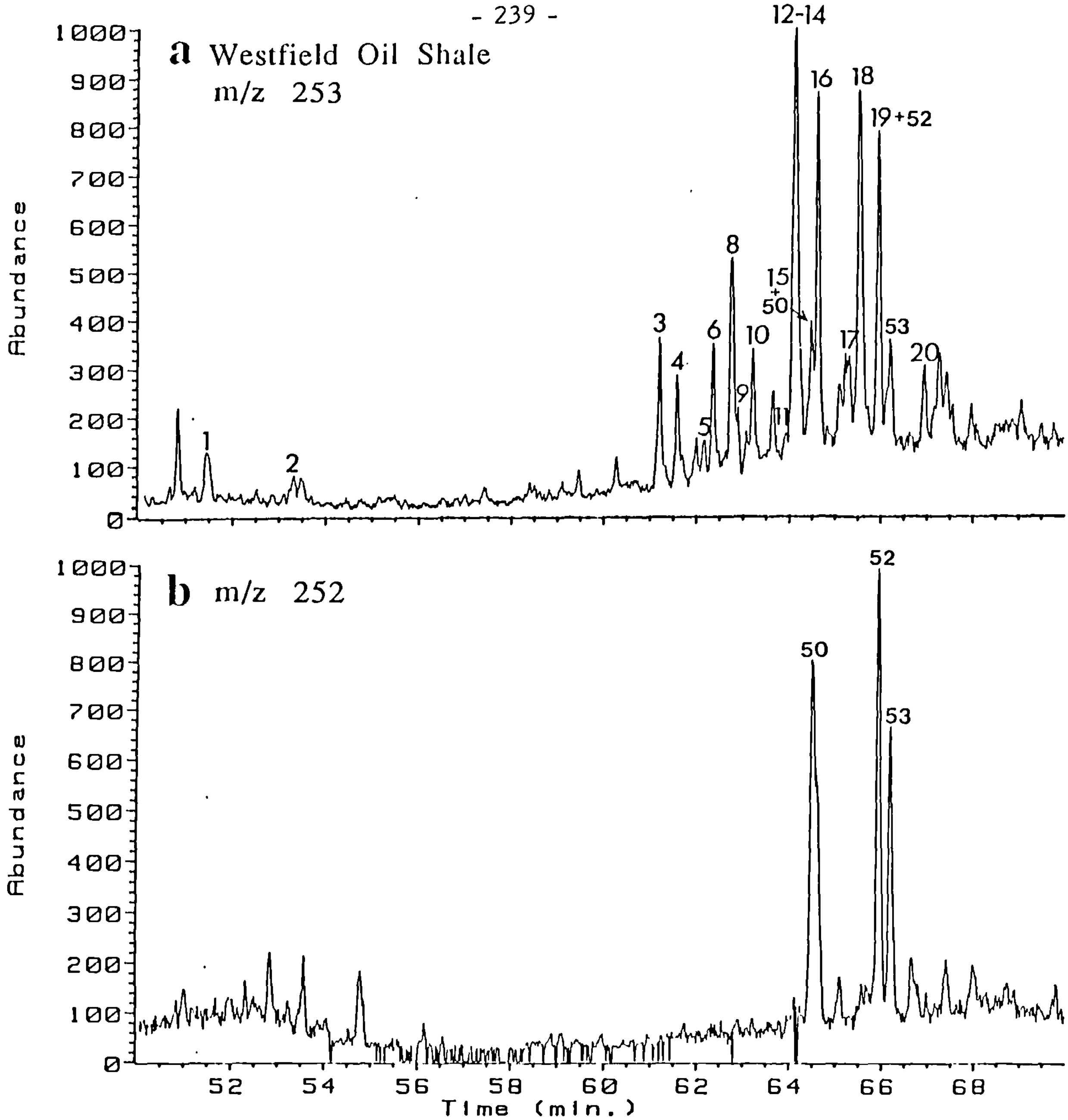


Fig.4.35 Typical distribution of C-ring monoaromatic steroids (a) in torbanitic shales and their interference with parent PAH (b) (peak assignments given in Tables 4.7 and 4.8).

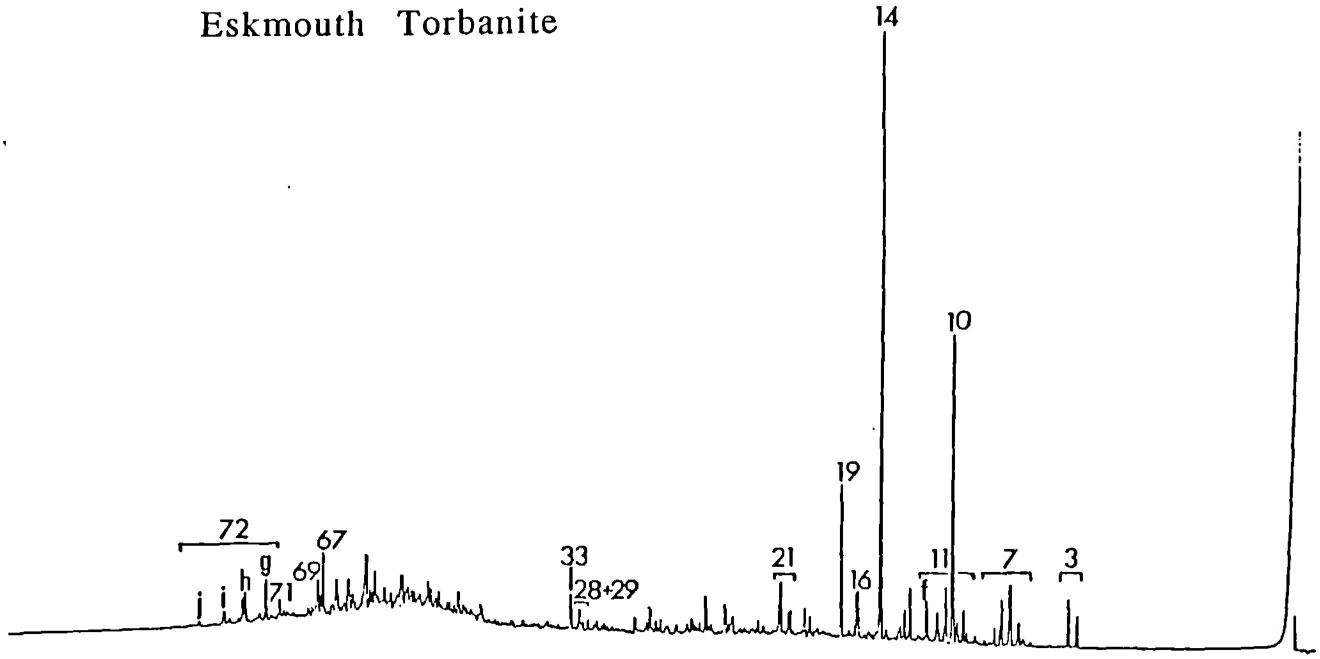


Fig.4.36 Gas chromatogram of the aromatic hydrocarbon fraction of the Eskmouth torbanite (peak assignments in Table 4.7).

are qualitatively similar to that of the Dunnet Shale (Fig.4.23b), but the Lillies Shale revealed almost equal concentrations of C_{26} and C_{28} triaromatics, with a reduced contribution from the C_{27} components. Methyltriaromatic steroid distributions were all of the type shown for the Dunnet Shale (Fig.4.23c). In the torbanitic shales studied, the methyltriaromatic steroids all exceed the non-methyl-substituted triaromatics in abundance.

Gc-ms was not performed on the aromatic fraction of the Eskmouth torbanite, but a gas chromatogram of this fraction (Fig.4.36) reveals a compound distribution that is markedly different from those of the other torbanitic shales. The major peak has a relative retention time that is identical to that of a compound identified as cadalene in other samples (see later). The other prominent peak (10) was ascribed to the C_4 tetralin. Benzohopanes and peaks 67 and 69 lie at the high molecular-weight end of the chromatogram.

4.3.3.1.4 Miscellaneous Algal-Rich Sediments

4.3.3.1.4.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of other low-rank sediments in which the kerogens are dominated by algal matter (SM17,18, Psh and Q from east Fife) are shown in Fig.4.37.

N-alkane distributions cover the range *n*-C_{10}-C_{36} and are accompanied by high concentrations of polycyclic biomarkers, discernible beyond *n*-C_{28} in the chromatograms. Other branched/cyclic components are visible within the gas chromatogram of the unusual Q shale (Fig.4.37d) which, along with the other high molecular-weight biomarkers, were investigated further by gc-ms analysis (see next section).

Akin to the other lamalginite-rich shales from east Fife, the sediments in Figs 4.37a,b and d show enhanced concentrations of *n*-C_{17}, consistent with an algal input. Relatively high concentrations of *n*-C_{15}, also indicative of an algal contribution, are only observed in the Q shale which, together with *n*-C_{17}, imparts a slight bimodality to its *n*-alkane envelope. Bimodal *n*-alkane distributions are not evident in the remaining samples of this suite: the distributions are unimodal and are skewed towards the high molecular-weight end of the chromatogram.

Unlike the lamosites and torbanitic shales, in which the *n*-alkane odd-over-even predominance occurs discontinuously over the *n*-alkane range (i.e. between, say, *n*-C_{15}-C_{19} and then *n*-C_{21}-C_{29}), samples SM17 and SM18 show odd predominances extending over the entire medium to high molecular-weight range, possibly

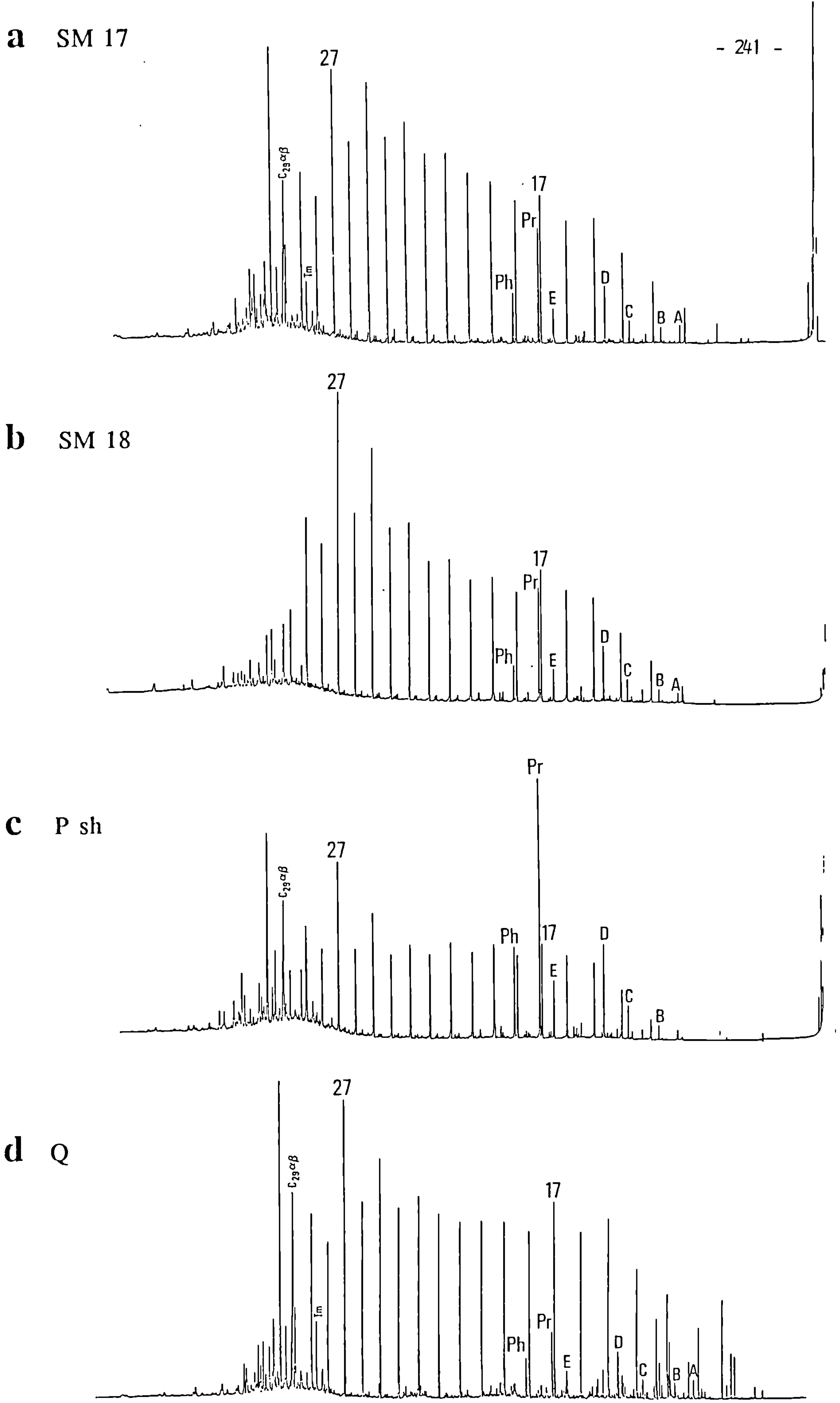


Fig.4.37 Gas chromatograms of the saturated fractions of algal-rich samples from the east Fife coast (isoprenoid assignments in Table 4.4).

indicating a contribution from algal precursors different from those contributing to the Fife lamosites.

Apart from SM17, CPI values lie in the range 1.24-1.37 and are lower than the values obtained from the east Fife lamosites and are surprisingly low in view of the higher overall contributions of vascular-plant debris in samples SM18, Psh and Q. The CPI value of 1.50 for SM17 is more akin to the values measured from chromatograms of east Fife lamosites, additional evidence corroborating the suggestion made in Section 4.2.4.1 and 4.3.1 that the liptodetrinite wisps are derived from lamalginite.

Other than sample Q, Pr/Ph values lie in the range 2.24-3.20, indicating oxic depositional environments, more oxic than those in which lamosites accumulated. The relatively low value for Q (1.65) indicates greater environmental anoxicity than for the other algal-rich samples in the east Fife suite at the time of sediment deposition.

Pr/n-C_{17} ratios in the range 0.34-2.74 suggest that the sediment accumulation occurred in a variety of aquatic environments. Ratios <0.50(Q) indicate open-water conditions of sedimentation whilst sample SM17 with a ratio >1 may have accumulated in a more restricted inland aquatic regime, possibly associated with peat swamps (Lijmbach 1975; Didyk *et al.* 1978). The intermediate values for SM18 and Psh suggest their deposition in a transition zone.

Gas Chromatography-Mass Spectrometry (GC-MS)

Terpane distributions in the samples SM17, 18 and Psh, whose kerogens comprise mainly algal remains (discrete lamalginite and *Botryococcus* telalginite), are similar to those of the lamosites and *Botryococcus*-rich shales in that tricyclics and tetracyclics are minor constituents relative to the pentacyclic terpanes. The tricyclic and tetracyclic distributions closely resemble that shown for the Dunnet Shale (Fig.4.12b), although the C_{24}, C_{25} and C_{27} secohopanes in SM18 are slightly enhanced relative to the other 3- and 4-ringed components. The m/z 191 fragmentogram of the petrographically unique sample Q (Fig.4.38a) differs from those of the other algal-rich deposits as it not only shows a greater abundance of tricyclics and tetracyclics, relative to pentacyclics, but reveals a prevalence of C_{20} and C_{21} tricyclics over all other 3- and 4-ringed components, apart from the C_{24} secohopane (peak 17). The overall qualitative distribution of pentacyclics in sample Q (Fig.4.38c) is similar to those observed in the algal-rich samples from east Fife as well as in the lamosites and torbanites. Samples Q, Psh (Fig.4.39b) and SM18 all contain the two components found in the Carron Harbour lamosite which show a major fragment ion with m/z 232

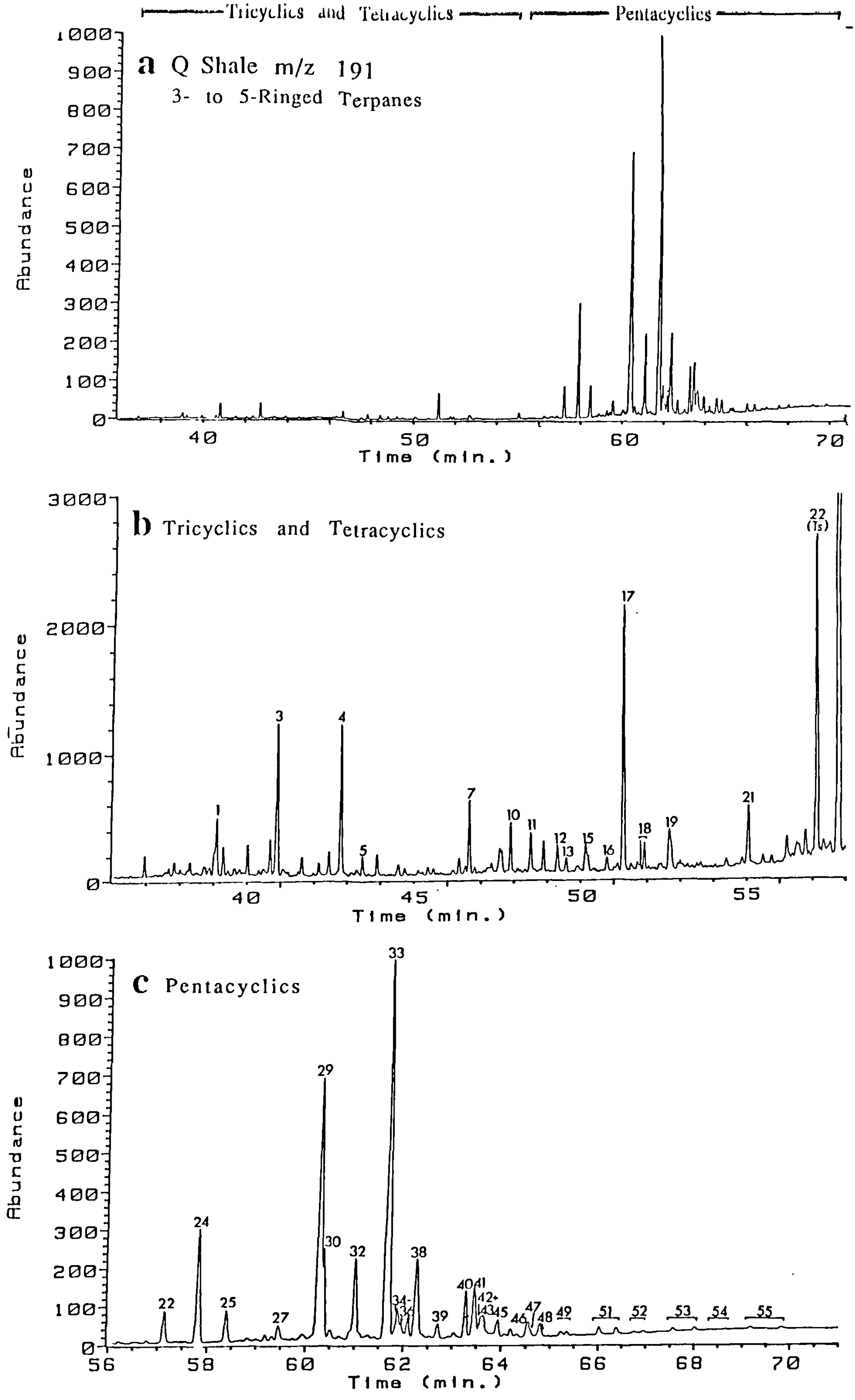


Fig.4.38 M/z 191 mass fragmentograms showing the distribution of 3- to 5-ringed terpanes in the unusual sample Q (peak assignments in Table 4.5).

(peaks 39 and 47) and sample Psh contains the unknown C_{29} tetracyclic (peak 23) which elutes between Ts and Tm. The hopane distributions of SM17 (Fig.4.39a) and SM18 (virtually identical to SM17) are additionally complicated by the presence of ββ hopanes. The 28,30-bisnorhopane and unknown C_{29} pentacyclic (peak 30) both occur in Q, but are not seen to exist in samples SM17, SM18 and Psh.

In quantitative terms, the intensity of the 22R and 22S epimers in the extended hopanes, relative to the $C_{30}\alpha\beta$ hopane, is relatively lower in the lamalginite-rich shales Q and Psh than in samples SM17 and SM18, which contain greater proportions of *Botryococcus* telalginite and vascular-plant matter. In this respect, the pentacyclic hopane "envelopes" of the samples Psh and Q bear a greater resemblance to those of the lamositic shales than do those of SM17 and SM18.

Peak 43 can be discerned in the m/z 191 fragmentograms of virtually all the low-rank lamosites and *Botryococcus*-rich shales so far investigated and can always be detected in their m/z 205 fragmentograms in which it is a prominent component. The mass spectrum of peak 43 (Fig.4.40f) is consistent with the compound being a C_{31} hopane which is methylated in the A or B rings. Coelution with a C_{30} triterpenoid (Fig.4.14d) is sometimes observed. Inspection of the m/z 205 traces shows that peak 43 of the m/z 191 fragmentograms (=peak 12 in the m/z 205 traces) does not occur in isolation, but as part of a homologous series. The carbon-number assignments and stereochemistry of these components could not be elucidated over the entire range of methylhopanes present in the lamosites and torbanites, since some members of the series were not always present in sufficient quantity to permit the acquisition of satisfactory mass spectra. In the algal-rich shales from east Fife, however, the contribution from methylhopanes was sufficiently strong (albeit still markedly subordinate to that of the regular hopanes) to allow spectral characterisation of most of the methylated components (Fig.4.40). The distribution of methylhopanes found in Midland Valley samples is illustrated in Fig.4.39c. Methylhopanes have been shown to be major contributors to the soluble organic fraction of the Serpiano Oil Shale (McEvoy and Giger 1986), and a sample of this deposit was extracted to aid compound identification. Through the synthesis of methylhopane standards, Summons and Jahnke (1990) have recently shown that the prominent series of "3-methylhopanes" recognised by McEvoy and Giger (1986) was erroneously assigned and corresponds to a suite of 2α-methylhopanes. Although compounds belonging to the latter series, which elute close to the corresponding hopanes, have been reported as the most abundant methylhopane series in sediments and oils (Seifert and Moldowan 1978; Summons and Powell 1987; Hoffmann *et al.* 1987), this series was not dominant in Midland

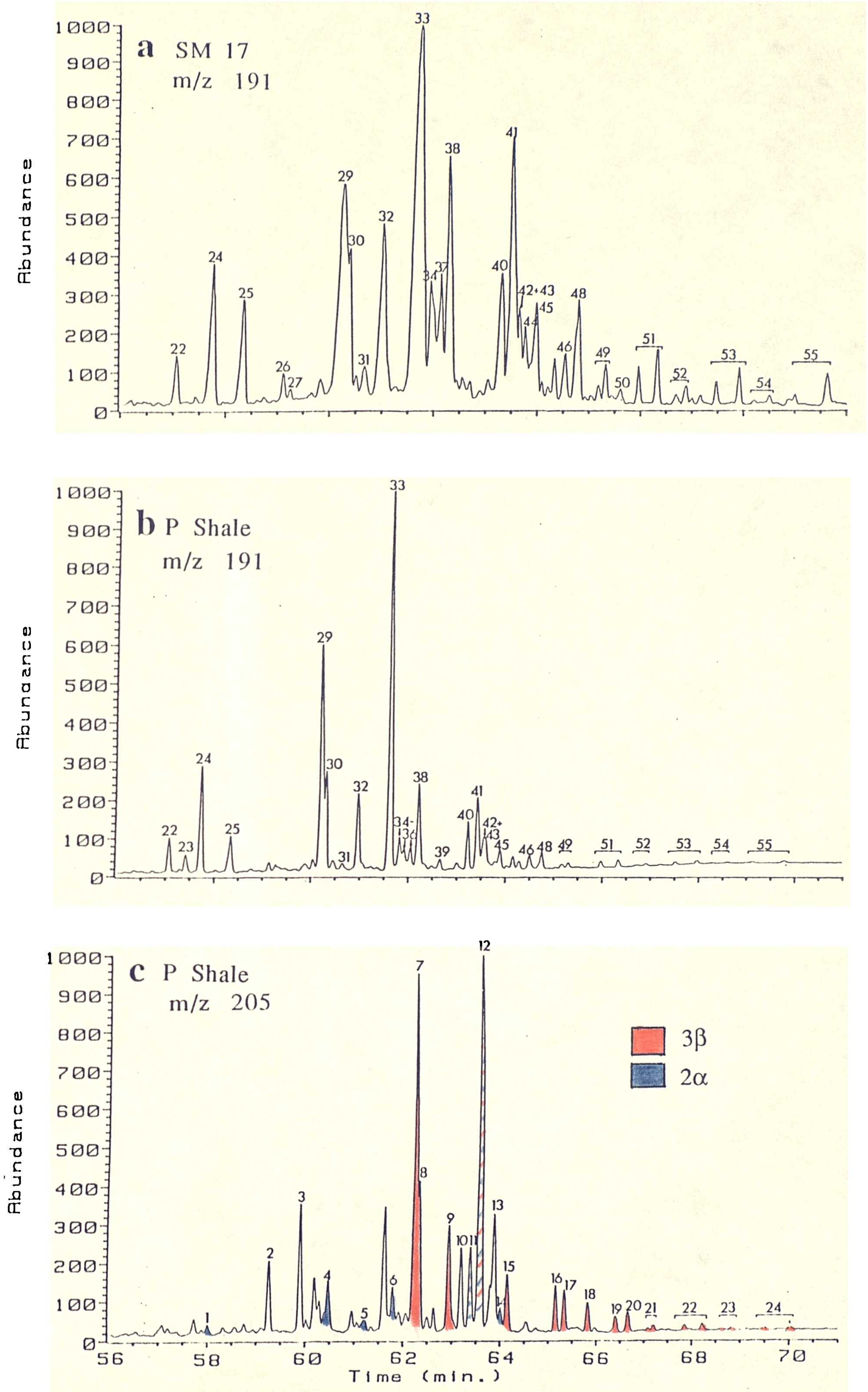


Fig.4.39 Mass fragmentograms showing the distribution of terpanes in algal-rich shales from east Fife (peak assignments for m/z 191 and m/z 205 fragmentograms are given in Tables 4.5 and 4.10 respectively).

Table 4.10 Peak assignments for m/z 205 mass fragmentograms.

1	2α-methyl-17α(H)-22,29,30-trisnorhopane	(C_{28})
2	?3α-methyl-17α(H),22,29,30-trisnorhopane	(C_{28})
3	?3α-methyl-17β(H),22,29,30-trisnorhopane	(C_{28})
4	2α-methyl-17α(H),21β(H)-30-norhopane	(C_{30})
5	2α-methyl-17β(H),21α(H)-30-norhopane	(C_{30})
6	2α-methyl-17α(H),21β(H)-hopane	(C_{31})
7	3β-methyl-17α(H),21β(H)-30-norhopane	(C_{30})
8	?3β-methyl-norhopane	(C_{30})
9	3β-methyl-17β(H),21α(H)-30-norhopane	(C_{30})
10	17α(H),21β(H)-homohopane (22S)	(C_{31})
11	17α(H),21β(H)-homohopane (22R)	(C_{31})
	+2α-methyl-17α(H),21β(H)-homohopane (22S)	(C_{32})
12	2α-methyl-17α(H),21β(H)-homohopane (22R)	(C_{32})
	?3β-methyl-17α(H),21β(H)-30-norhopane	(C_{31})
13	17β(H),21α(H)-homohopanes (22S+22R)	(C_{31})
14	2α-methyl-17β(H),21α(H)-homohopanes (22S+22R)	(C_{32})
15	3β-methyl-17β(H),21α(H)-30-homohopane	(C_{31})
16	3β-methyl-17α(H),21β(H)-bishomohopane (22S)	(C_{32})
17	3β-methyl-17α(H),21β(H)-bishomohopane (22R)	(C_{32})
18	3β-methyl-17β(H),21α(H)-bishomohopane (22S+22R)	(C_{32})
19	3β-methyl-17α(H),21β(H)-trishomohopane (22S)	(C_{33})
20	3β-methyl-17α(H),21β(H)-trishomohopane (22R)	(C_{33})
21	3β-methyl-17β(H),21β(H)-trishomohopane (22S+22R)	(C_{33})

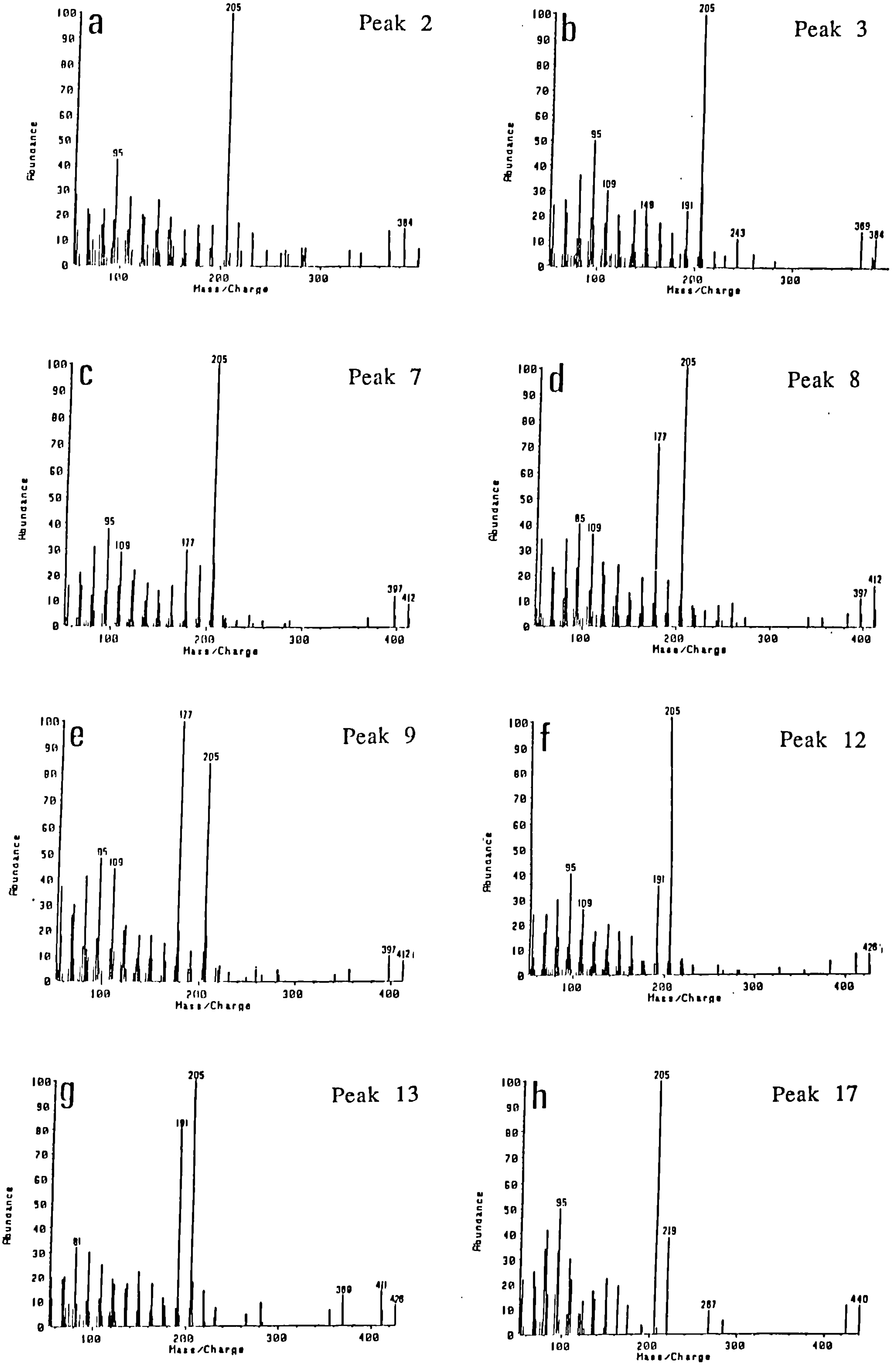


Fig.4.40 Mass spectra of methylhopanes in Midland Valley samples (see Fig.4.39).

Valley samples: a later-eluting suite thought to correspond to the 3β-methylhopanes of Summons and Jahnke (*op.cit.*) is more abundant. Tentative peak assignments for the methylhopanes in Midland Valley samples are given in Table 4.10. That the distribution of the 3β-methylhopanes parallels that of the hopanes (even the unknown C_{29} pentacyclic compound [peak30] that shoulders the $C_{29}\alpha\beta$ hopane has a methylated counterpart [peak 8]) suggests that the former series derive from precursors by the same diagenetic route that leads to the production of the latter.

The rarity of sample Q, as established from petrographic examination, is also expressed by a unique geochemical signature which can be discerned in its gas chromatogram (Fig.4.37d). The multiplet of peaks eluting around *n*-C_{23} is exclusive to the sample, as are several components in the series of peaks eluting between the C_{13} and C_{20} *n*-alkanes.

Gc-ms analysis revealed that most of the compounds unique to Q gave major fragment ions of m/z 97. Other compounds restricted to the sample showed relatively strong m/z 123 ions. A composite mass fragmentogram of m/z 97+123 is shown in Fig.4.41a whilst the individual ion scans are shown in Figs 4.41b and c. Peak assignments are in Tables 4.11 and 4.12. Molecular ion identification of the components showing strong contributions of m/z 97 ions enabled them to be assigned to four compound classes discussed below.

(i) The molecular ions of peaks 1, 3, 4, 5, 8, 12 and 19 (Fig.4.42) all indicate that the compounds constitute a series of monocyclic alkanes ranging from C_{15}-C_{21}, but with no C_{20} member. The spectra of peaks 1, 8 and 12 closely resemble those published for compounds belonging to the methyl-*n*-alkylcyclohexane series (Rubinstein and Strausz 1979; Fowler *et al.* 1986; Hoffmann *et al.* 1987). The m/z 97 ion is due to the $C_7H_{13}^+$ methylcyclohexyl ion which forms following the cleavage of an alkyl side chain from a methylcyclohexane ring. The other compounds with prominent ions of m/z 97 could be isomers of compounds 1, 8 and 12 and/or monocyclic methyl-substituted cyclohexanes possessing branched side chains. The latter configuration seems likely for the compounds corresponding to peaks 3, 4 and 5 whose spectra show enhanced concentrations of ions with m/z 153 or m/z 167.

The occurrence of methyl-*n*-alkylcyclohexanes is not confined to sample Q: they are readily detectable in the urea non-adduct fractions of all algal-rich sediments investigated from the Midland Valley and are particularly abundant in torbanitic and lamositic shales where they form well-developed homologous multiplets. The methyl-*n*-alkylcyclohexanes co-exist with a homology of *n*-alkylcyclohexanes, characterised by a base peak of m/z 83. Both these series of

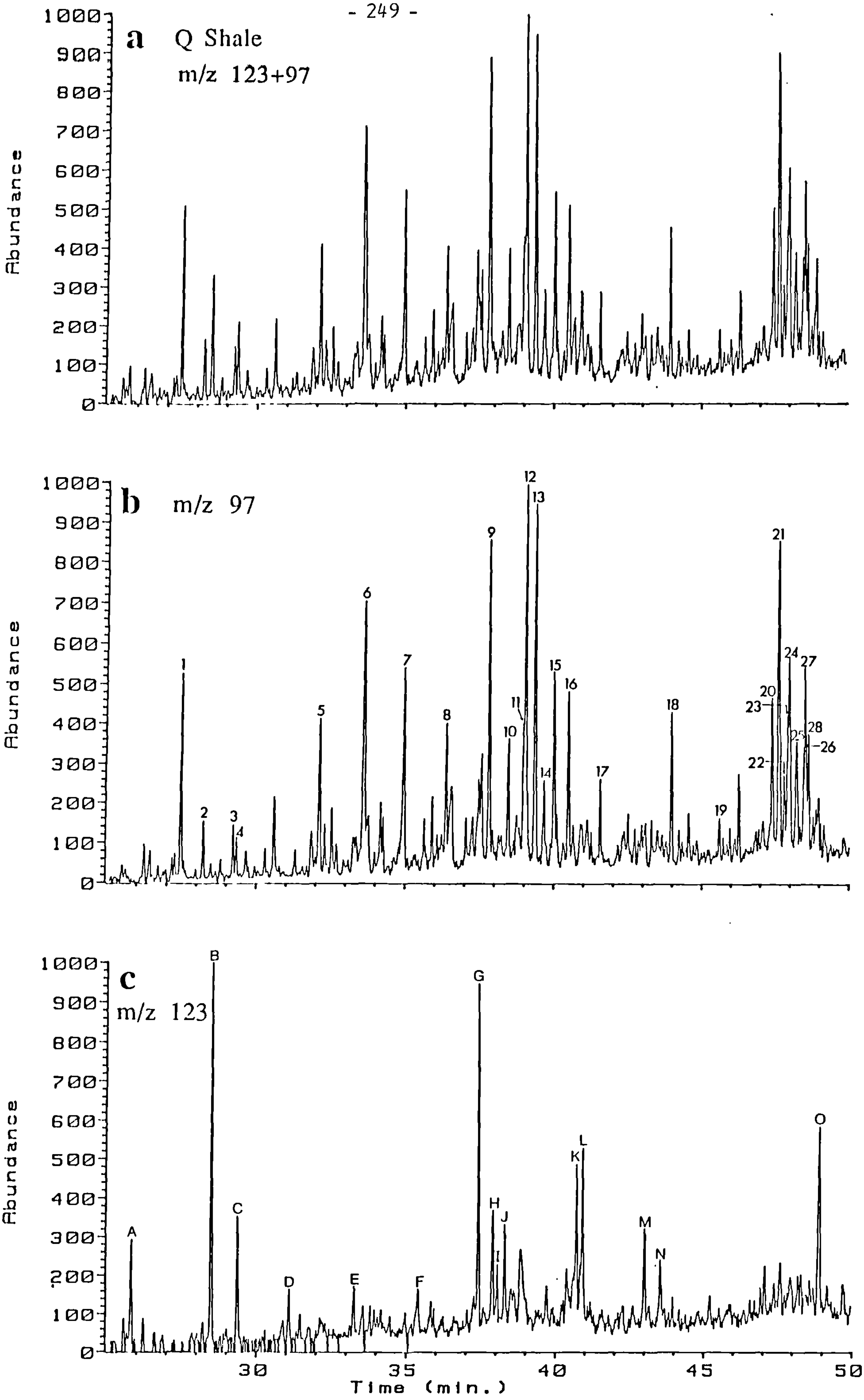


Fig.4.41 Fragmentograms showing the distribution of compounds giving major ions with m/z 97 and m/z 123 in the Q shale (see Tables 4.11 and 4.12 for identifications).

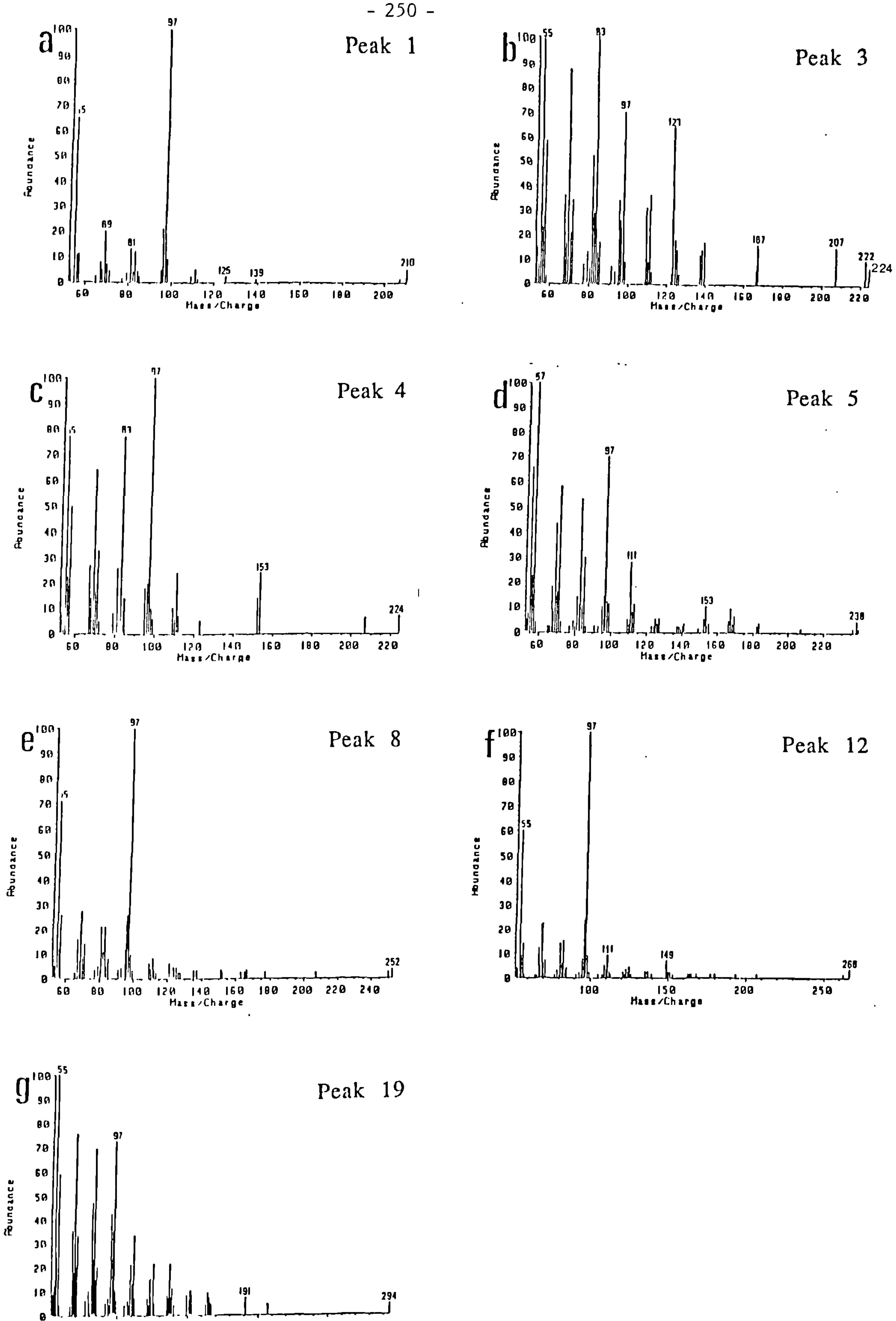


Fig.4.42 Mass spectra of peaks in Fig.4.41 thought to correspond to monocyclic alkanes (peak assignments in Table 4.11).

Table 4.11 Peak assignments for m/z 97 mass fragmentograms.

1	C_{15} methyl-*n*-alkylcyclohexane
2	C_{15} bicyclic alkane
3	C_{16} methyl-*n*-alkylcyclohexane (+8α(H)-homodrimane)
4	C_{16} bicyclic alkane + C16 methyl-*n*-alkylcyclohexane
5	C_{17} methyl-*n*-alkylcyclohexane
6	C_{17} bicyclic alkane
7	C_{17} bicyclic alkane
8	C_{18} methyl-*n*-alkylcyclohexane
9	C_{18} bicyclic alkane
10	C_{19} tricyclic alkane
11	C_{19} bicyclic alkane
12	C_{19} methyl-*n*-alkylcyclohexane
13	C_{19} bicyclic alkane
14	C_{20} tricyclic alkane
15	C_{19} bicyclic alkane
16	C_{19} bicyclic alkane
17	C_{20} tricyclic alkane
18	C_{21} bicyclic alkane
19	C_{21} methyl-*n*-alkylcyclohexane
20	C_{23} bicyclic alkane
21	C_{23} bicyclic alkane
22	C_{23} tricyclic alkane
23	C_{23} bicyclic alkane
24	C_{23} bicyclic alkane
25	C_{23} bicyclic alkane
26	C_{23} bicyclic alkane
27	C_{23} tetracyclic alkane
28	C_{23} bicyclic alkane

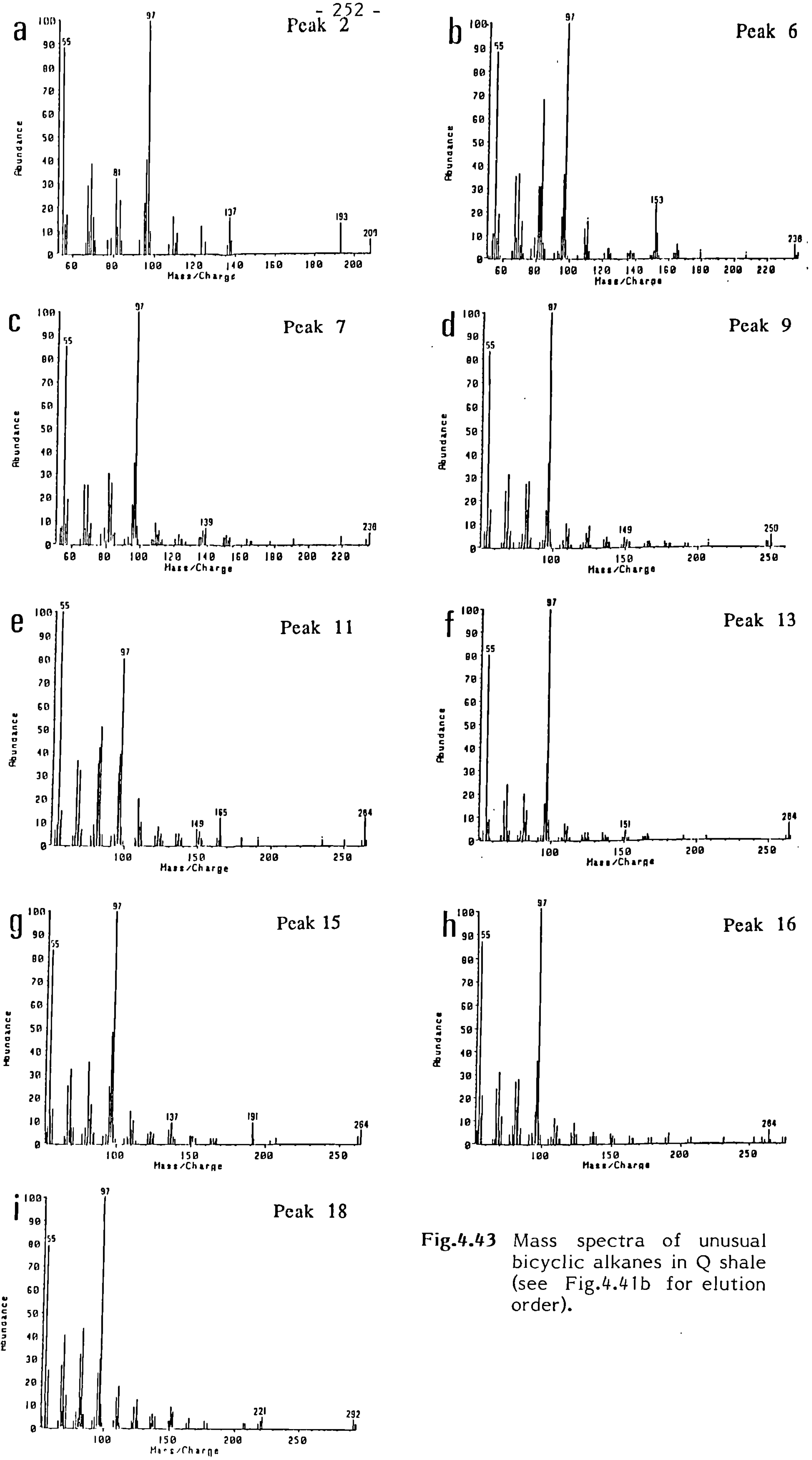


Fig.4.43 Mass spectra of unusual bicyclic alkanes in Q shale (see Fig.4.41b for elution order).

monocyclic alkanes are thought to form from the cyclisation of fatty acids (see Hoffmann *et al.* 1987 for a review).

(ii) The mass spectra of peaks 2, 6, 7, 9, 11, 13, 15, 16, 18 (Fig.4.43) and peaks 20, 21, 23-26 and 28 (Fig.4.44) all show molecular ions consistent with those of bicyclic alkanes. These compounds show major fragment ions of m/z 97, which is invariably the base peak, in contrast to the m/z 123 ion which is usually dominant in the mass spectra of bicyclanes Philp *et al.* 1981; Alexander *et al.* 1984b).

The series of bicyclic compounds present in Q encompasses the range C_{15}-C_{23} although no C_{20} and C_{22} members were detected. The multiplet of peaks eluting at around *n*-C_{23} comprises almost entirely of a group of bicyclic compounds with 23 carbon atoms (peaks 20, 21, 23-26 and 28; Fig.4.44). None of the bicyclic components identified was recognised in any other sample studied during this project.

Weston *et al.* (1989) have reported the presence of a monocyclic sesquiterpenoid with a major m/z 97 ion in terrestrially-sourced oils from New Zealand, whilst Richardson and Miller (1983) have presented the spectrum of a tetracyclic terpane showing a base peak of m/z 97. The formation of this ion in the latter compound was explained by assuming the presence of an alkyl chain on a methyl-substituted terminal ring of the tetracyclic terpane skeleton.

A series of C_{15}-C_{24} bicyclic compounds with isoprenoid side chains has been reported in the Athabasca oil-sand bitumens, but the mass spectra of these compounds show base peaks at m/z 123 (Dimmler *et al.* 1984). As far as is known, there are no reports in the literature of any bicyclic alkanes whose spectra contain major ions with m/z 97. From the spectra presented in Figs 4.43 and 4.44, it seems feasible that the parent compounds are bicyclic alkanes in which a side chain is attached to a methyl-substituted ring. Ring cleavage and loss of the side chain gives rise to the formation of the methylcyclohexyl ion (m/z 97). That the side chain in some of the novel bicyclics in sample Q may be branched is inferred from the increased concentrations of ions with m/z 139, 153 and 167, relative to other ions, which occur in the spectra of peaks 2, 6, 11, 21, 23, 24, 26 and 28. Enhanced concentrations of m/z 139 and 153 have been observed in the mass spectra of unusual saturated monocyclic compounds in which an isoprenoid side chain is attached to the cyclohexane ring (Barbe *et al.* 1988). The remaining bicyclic compounds, showing progressive decrease in fragment-ion intensity with increasing ion mass, probably have unbranched side chains.

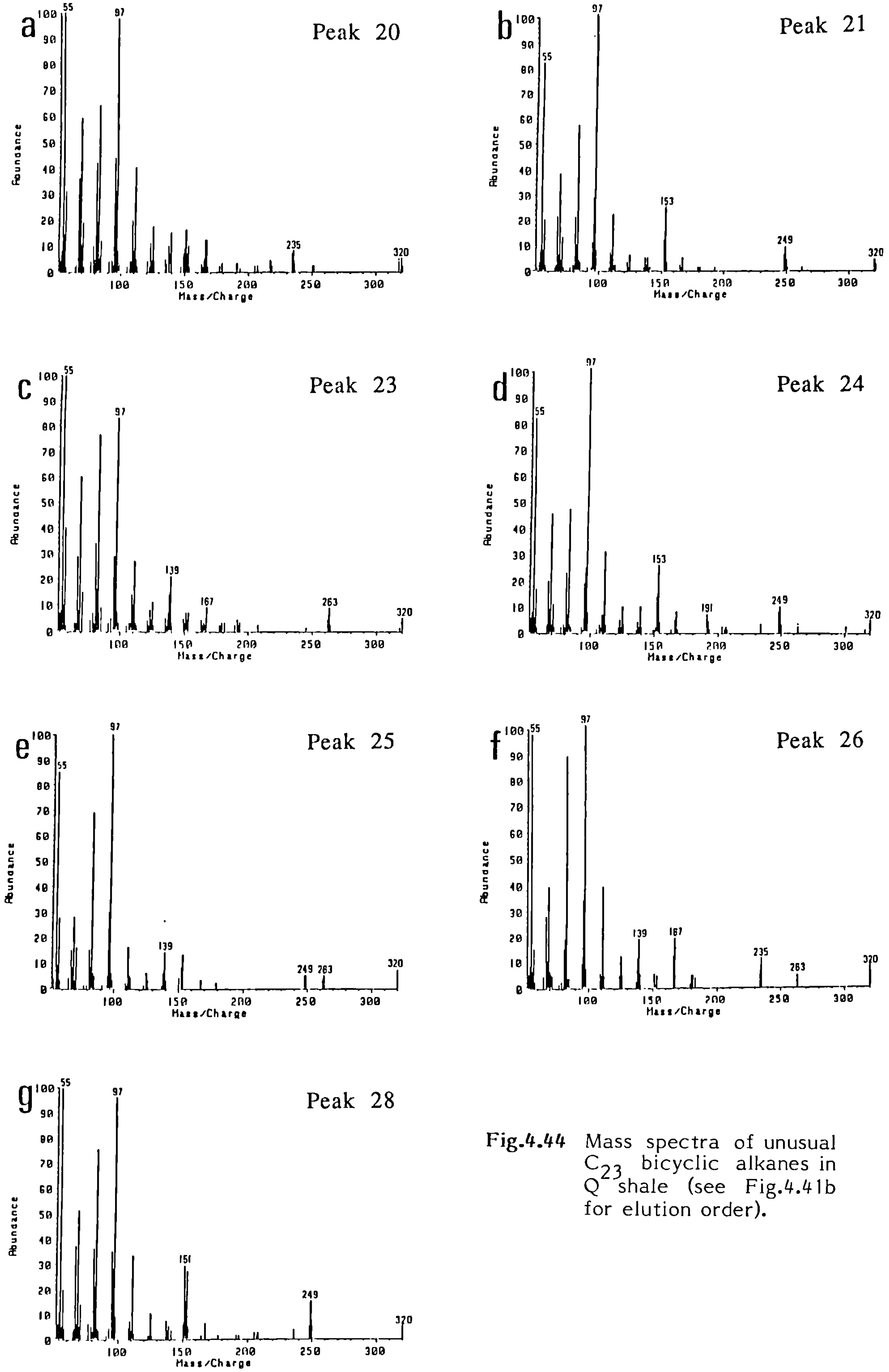


Fig.4.44 Mass spectra of unusual C_{23} bicyclic alkanes in Q shale (see Fig.4.41b for elution order).

(iii) On the basis of spectral evidence (Figs 4.45a-d), peaks 10, 14, 17 and 22 are inferred to belong to a tricyclic terpane series which is structurally related to the bicyclic components referred to above. Enhanced concentrations of ions with m/z 137 (Fig.4.45b), m/z 139 and 167 (Fig.4.45d) suggest side-chain branching. No saturated tricyclic compounds with major fragment ions of m/z 97 have been documented in the literature.

(iv) One tetracyclic compound (C_{23}) which is structurally analogous to the bicyclic and tricyclic components in (ii) and (iii) was detected (peak 27; Fig.4.45e). A C_{27} tetracyclic with a base peak at m/z 97 was described by Richardson and Miller (1983), but apart from the dominance of the m/z 97 ion, its spectrum does not resemble that of peak 27. The "smoothness" of the ion distribution beyond m/z 97 in the spectrum of peak 27 suggests that a linear side chain is attached to the methylcyclohexyl ring.

In addition to the bicyclic components possessing major fragment ions of m/z 97, Q shale contains bicyclanes which were detected in the m/z 123 ion fragmentogram (Fig.4.41c). Compounds corresponding to peaks A and B

Table 4.12 Peak assignments for m/z 123 mass fragmentograms.

A	8β(H)-drimane (C_{15})
B	8β(H)-homodrimane (C_{16})
C	8α(H)-homodrimane (+ coeluting C_{16} methyl-*n*-alkylcyclohexane)
D	C16 bicyclic
E	C_{17} bicyclic
F	C_{18} bicyclic
G	C_{19} bicyclic
H	C_{19} tricyclic
I	C_{19} norditerpane (?based on pimarane skeleton)
J	C_{19} bicyclic
K	C_{20} diterpane (?based on pimarane skeleton)
L	C_{20} tricyclic
M	C_{21} tricyclic
N	C_{21} bicyclic
O	C_{23} tetracyclic (peak 27 in Table 4.11)

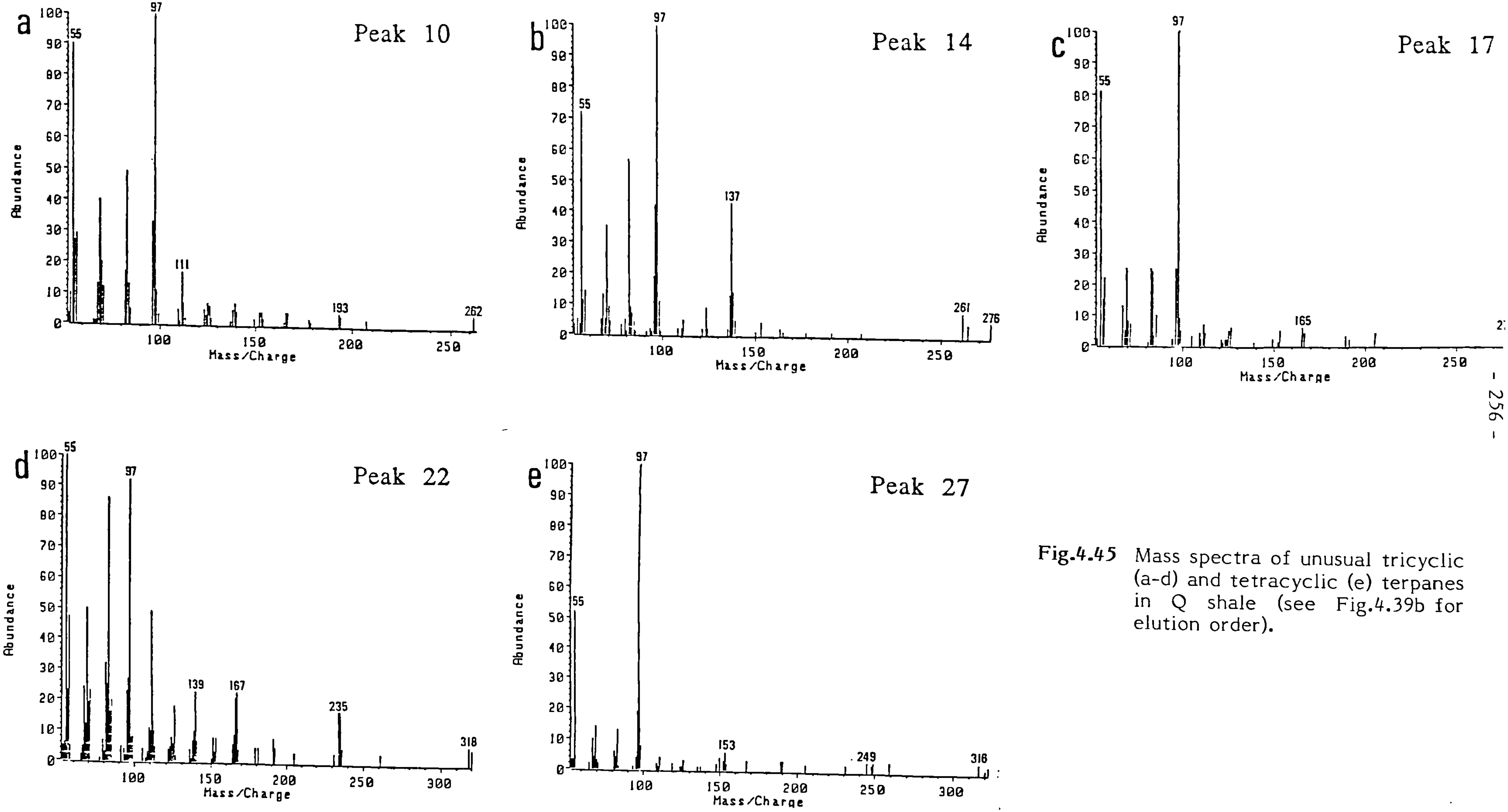


Fig.4.45 Mass spectra of unusual tricyclic (a-d) and tetracyclic (e) terpanes in Q shale (see Fig.4.39b for elution order).

were identified as 8β(H)-drimane and 8β(H)-homodrimane by comparison of their mass spectra (Figs 4.46a and b) with those of authentic standards (Alexander *et al.* 1983, 1984b). The retention time of peak C corresponds with that of 8α(H)-homodrimane. The mass spectrum of the authentic compound is identical with that of its 8β(H) epimer (Noble 1986), but a "pure" spectrum could not be obtained for 8α(H)-homodrimane in the Q shale due to coelution with a C_{16} methyl-*n*-alkylcyclohexane (Fig.4.42b).

The mass spectra of other bicyclic compounds identified in Q (peaks D, E, F, J and N) are shown in Figs 4.46c-g. The base peak of m/z 123 in compound J suggests that its structure is based on the drimane skeleton (Alexander *et al.* 1983, 1984b). A series of drimane-based bicyclanes with members higher than C_{16} has been documented in the Athabasca oil sand bitumens (Dimmler *et al.* 1984), and it is possible that compound J belongs to this suite. The mass spectra of the other bicyclics in sample Q do not correspond with those of the bicyclics $>C_{16}$ discussed by Dimmler *et al.* (1984), and the lack of base peaks at m/z 123 suggests that the compounds are probably not based on drimane skeletons. Compounds with the same relative retention time as peak J in the m/z 123 fragmentograms occur in other Midland Valley samples containing different types of organic matter, but none of the other bicyclics in Fig.4.46 occurs in any samples other than Q.

The mass spectra of other components in the m/z 123 fragmentogram in Fig.4.41 are shown in Fig.4.47. These compounds are not restricted to sample Q, but are widespread constituents in the organic extracts of Midland Valley coals and sediments. The spectra shown in Figs 4.47 a-d correspond to compounds belonging to the near-ubiquitous tricyclic terpane series described by Aquino Neto *et al.* (1983), Ekweozor and Strausz (1983) and Chicarelli *et al.* (1988).

The mass spectra of peaks I and K (Figs 4.47e and g respectively) indicate C_{19} and C_{20} compounds, respectively, with structures based on the diterpenoid skeleton. A similar spectrum to that of the C_{19} tricyclic was presented by Richardson and Miller (1982), from a terrestrially-sourced crude oil, but the compound was not specifically identified. The spectrum of I bears some resemblance to a spectrum of a compound thought to be norisopimarane published by Livesey *et al* (1984 ; Fig.4.47f). Compound I is therefore inferred to be a nor-diterpane based on the pimarane skeleton.

The mass spectrum of peak K shows similarities with that recently published for an authentic sample of isopimarane (Blunt *et al.* 1989; Fig.4.47h), although peak K shows no m/z 247 ion in its spectrum. The overall fragmentation pattern does, however, suggest that compound K is based on the pimarane skeleton (*cf.* Figs 4.47g and h).

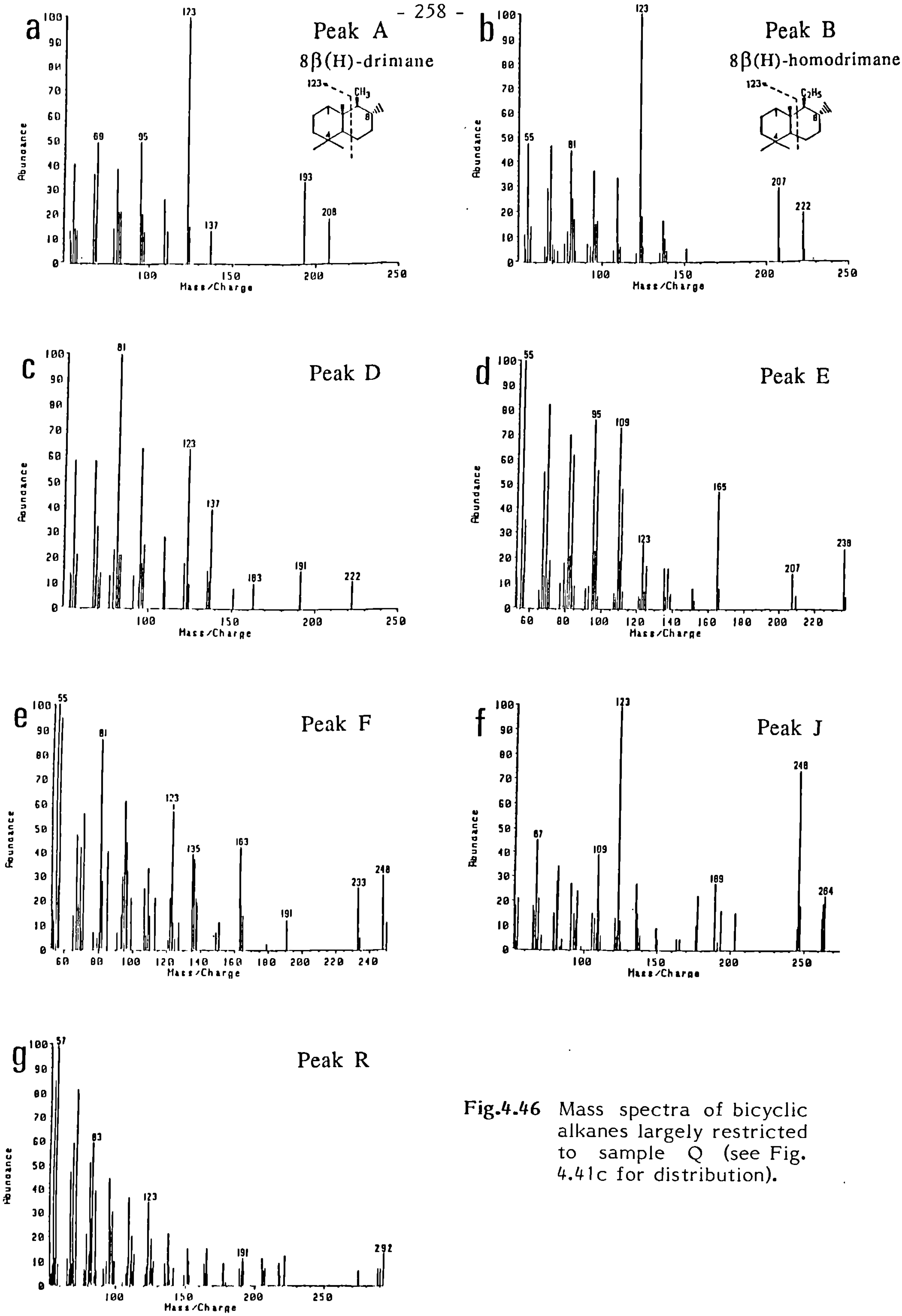


Fig.4.46 Mass spectra of bicyclic alkanes largely restricted to sample Q (see Fig. 4.41c for distribution).

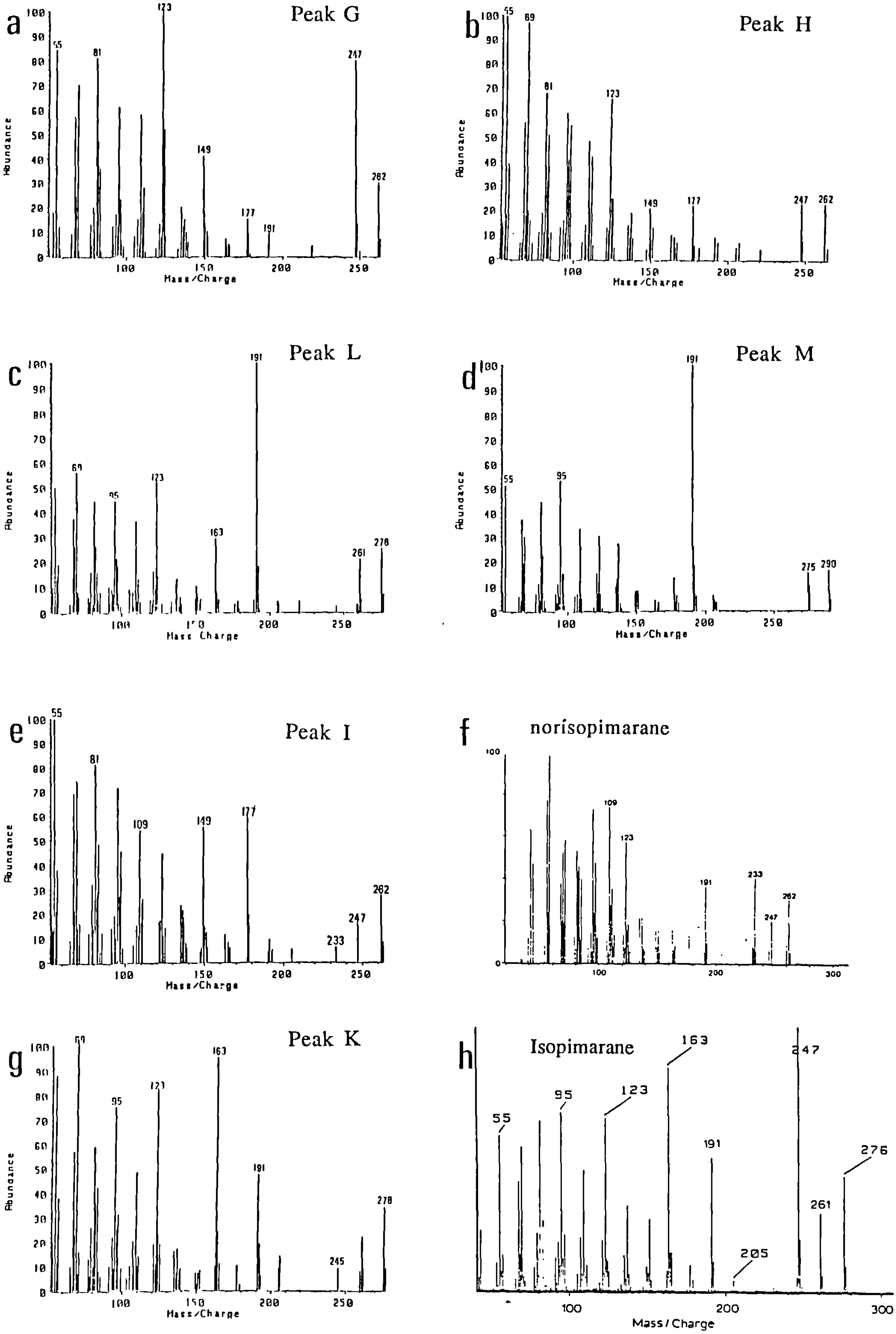


Fig.4.47 Mass spectra of tricyclic compounds occurring in Fig.4.41c. Figs b and h are of authentic standards (see text).

Diterpenoids are important constituents of plant resins, particularly those of conifers (Thomas 1969; Hanson 1972). The occurrence of pimarane-related compounds in sample Q is therefore an indication of a terrigenous contribution to the sediment. The input of resinous material is considered to be minor, relative to the contribution of organic matter from other sources, since the diterpenoids in Q were only detectable by gc-ms analysis.

The source of the organic matter from which the oils containing the C_{27} tetracyclic terpane of Richardson and Miller (1983) and the C_{15} monocyclic sesquiterpenoid of Weston *et al.* (1989) (both giving major m/z 97 ions) were derived is reported to be of Tertiary age and derived from an angiosperm flora. Such a source for the structurally analogous bicyclic, tricyclic and tetracyclic components giving major m/z 97 ions in the Q shale can be disregarded as their occurrence in a Carboniferous sample clearly predates the evolution of flowering plants.

A higher land-plant source for the bicyclic alkanes in Fig.4.41c is also unlikely. Series of C_{14}-C_{16} bicyclics based on the drimane skeleton are of widespread geological and geographic occurrence, suggesting a derivation from ubiquitous precursors (Alexander *et al.* 1983, 1984b). This factor, coupled with the incidence of drimanes in oils and sediments whose age precludes an input of higher-plant matter (pre-Ordovician), points to a microbial origin for drimane-related bicyclics. A microbial derivation is also considered valid for the C_{16}-C_{24} bicyclics (including non-drimane related members) found in the Athabasca oil sands and for a C_{21} bicyclic alkane which is a prominent constituent of many oils from the Taranaki Basin, New Zealand (Weston *et al.* 1989).

The occurrence of the novel bicyclic, tricyclic and tetracyclic components with major m/z 97 ions and the bicyclics which do not show the base peaks at m/z 123 in Fig.4.41b is restricted to sample Q. Since the specimen is petrographically unique because of its content of clasts comprising layered lamalginite enveloping carbonate grains, it seems likely that the compounds referred to above are derived from the algal-containing clasts. Unsubstituted and monomethyl-substituted cyclohexanes with isoprenoid side chains have been documented in carbonate-sourced oils (Barbe *et al.* 1988). The source material is thought to have accumulated in a highly reducing, hypersaline environment where it was subjected to intense microbial reworking, principally by anoxygenic sulphur bacteria and archaebacteria. Despite the abundance of carbonate grains in the clasts in Q, any well-established geochemical signatures indicating that they, or the associated algal matter, were deposited under a hypersaline regime (e.g. Pr/Ph ratio <1, presence of long-chain acyclic isoprenoids, marked EOP) are not apparent. Furthermore, intense microbial activity might be expected to be reflected by a high hopane to sterane ratio (Connan *et al* 1986). The ratio of 12 for the Q shale is not excessive in comparison with ratios for other Midland Valley samples. It is therefore unlikely that intense microbial activity in a hypersaline environment accounts for the presence of terpanes containing methylcyclohexyl structures in sample Q.

The reported occurrence of methyl-*n*-alkylcyclohexanes in sediments and oils with ages ranging from the Precambrian to Recent geological time has been taken to be consistent with the contention that "they probably came from ubiquitous precursors present in a wide range of organisms" (Hoffmann *et al.* 1987). Early suggestions that the cyclisation of straight-chain fatty acids, which occur widely in eukaryotic and prokaryotic organisms, can produce the methyl-*n*-alkylcyclohexanes (Johns *et al.* 1966; Rubinstein and Strausz 1979) have been further substantiated by the recent thermal maturation experiments of Hoffmann *et al.* (1987).

Homologous series of *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes can be detected in nearly all the samples studied throughout the course of this project, suggesting that a general "background" level of these compounds exists as the result of an input of fatty acids derived from ubiquitous microbes. The enhanced concentrations of monocyclic alkanes observed in algal-rich sediments lend support to the suggestion that algal-derived fatty acids can be important precursors in geological samples (Johns *et al.* 1966; Rubinstein and Strausz 1979; Fowler and Douglas 1984; Fowler *et al.* 1986). Thus, although the abundance of compounds containing cyclohexyl and methylcyclohexyl moeties in sample Q seemingly correlates with the presence of algal clasts, whether these compounds derive from specific fatty-acid precursors in the layered lamalginite *per se* or even from a unique microbial community associated with these algae is not known.

The occurrence of bicyclic alkanes with carbon numbers exceeding C_{16} has been attributed to microbial activity, as has the presence of the commonly occurring C_{14}-C_{16} bicyclanes (Alexander *et al.* 1983, 1984b; Dimmler *et al.* 1984; Weston *et al.* 1989). A microbial origin may therefore explain the incidence of the bicyclic components which do not show prominent m/z 97 ions that occur in sample Q. Compounds of the latter type which are exclusive to Q could originate from microorganisms (different from those contributing the hopanes) which specifically reworked the algal matter in the clasts. Alternatively, it is possible that the unusual bicyclics may originate from the algal matter itself.

From the foregoing account it is apparent that an algal or microbial origin for the novel components in sample Q is equivocal, but what is reasonably certain is that the compounds are derived from organic matter associated with the rare algal-containing carbonate clasts.

Samples Psh, Q, SM17 and SM18 all contain the same suites of regular and rearranged steranes that were observed in the *Botryococcus*-rich shales and lamosites, with the $C_{29}\alpha\alpha\alpha 20R$ sterane being the most abundant component. The sterane signatures of Psh and Q are similar (Fig.4.48a) and resemble those of the lamosites. Accordingly, both samples plot in the same general field occupied by low-rank lamositic shales in the ternary plot of Fig.4.19.

The enhanced concentrations of $C_{29}\alpha\alpha\alpha 20R$ and $C_{27}\alpha\alpha\alpha 20R$ steranes in SM18 (Fig.4.48c) and SM17 (Fig.4.48b) respectively, confer similarities with the distributions seen in the torbanite and Westfield Oil Shale, and consequently the east Fife samples plot in the extreme regions of the field encompassing these deposits (Fig.4.19).

Diasteranes are low in abundance relative to the regular steranes although enhanced concentrations occur in SM17. The $\alpha\beta\beta$ steranes are present in minor amounts, if at all.

4.3.3.1.4.2 Aromatic Hydrocarbons

The distributions of aromatic components in samples SM17,18 and Psh are all very similar and are typified by the TIC chromatogram of SM18 (Fig.4.49a). The high molecular-weight "hump" is a major feature of the distributions as are many of the peaks previously identified in the lamosites and *Botryococcus*-rich shales. Homologous series of alkylated naphthalenes and phenanthrenes are of relatively minor abundance.

A typical monoaromatic steroid hydrocarbon distribution (m/z 253) for the above samples is shown in Fig.4.49b. Rearranged structures are more abundant (relative to the non-rearranged components) than in the lamosites, but less so than for the torbanite and torbanitic shales. Little or no interference with parent PAH is observed.

The carbon-number distribution of the triaromatic components mirrors that of the saturated steroid hydrocarbons and the methyltriaromatic steroids are similar to the distribution in Fig.4.23b. The ratio of non-methylated to methyltriaromatics is close to or exceeds unity.

The TIC chromatogram of the algal-rich Q shale (Fig.4.49d) differs from that of the other algal-rich shales because of the relatively large quantities of non-alkylated (parent) PAH and their alkylated homologues which are superimposed on the distribution of aromatic components described in the other shales discussed so far. Interference between rearranged monoaromatic compounds and parent PAH is evident from Fig.4.49d. Non-methylated triaromatic steroids exceed the methylated triaromatics in abundance. The compounds eluting between 56 and 60

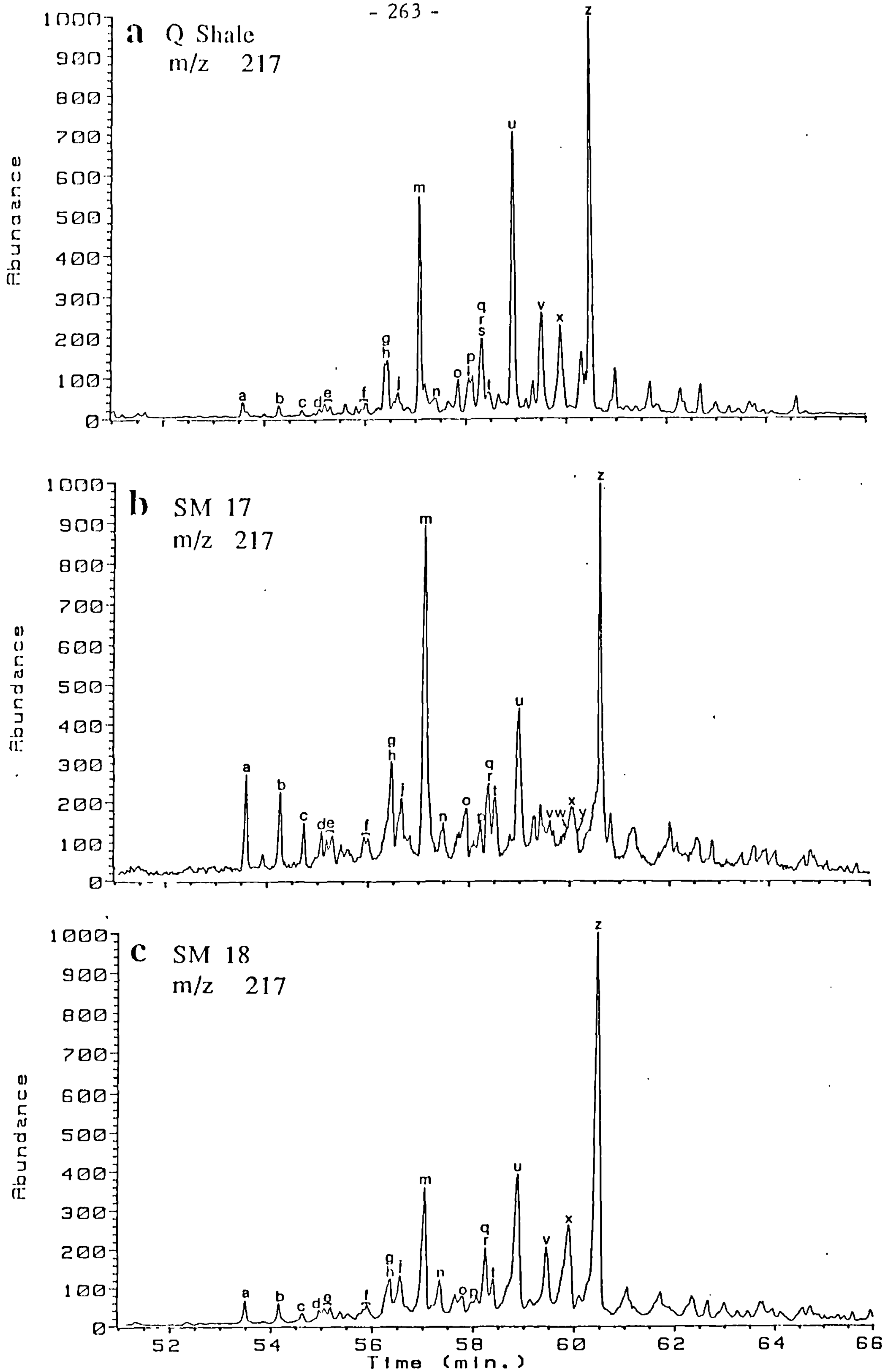


Fig.4.48 Typical distributions of steranes in the algal-rich samples from Fife (see Table 4.6 for peak assignments).

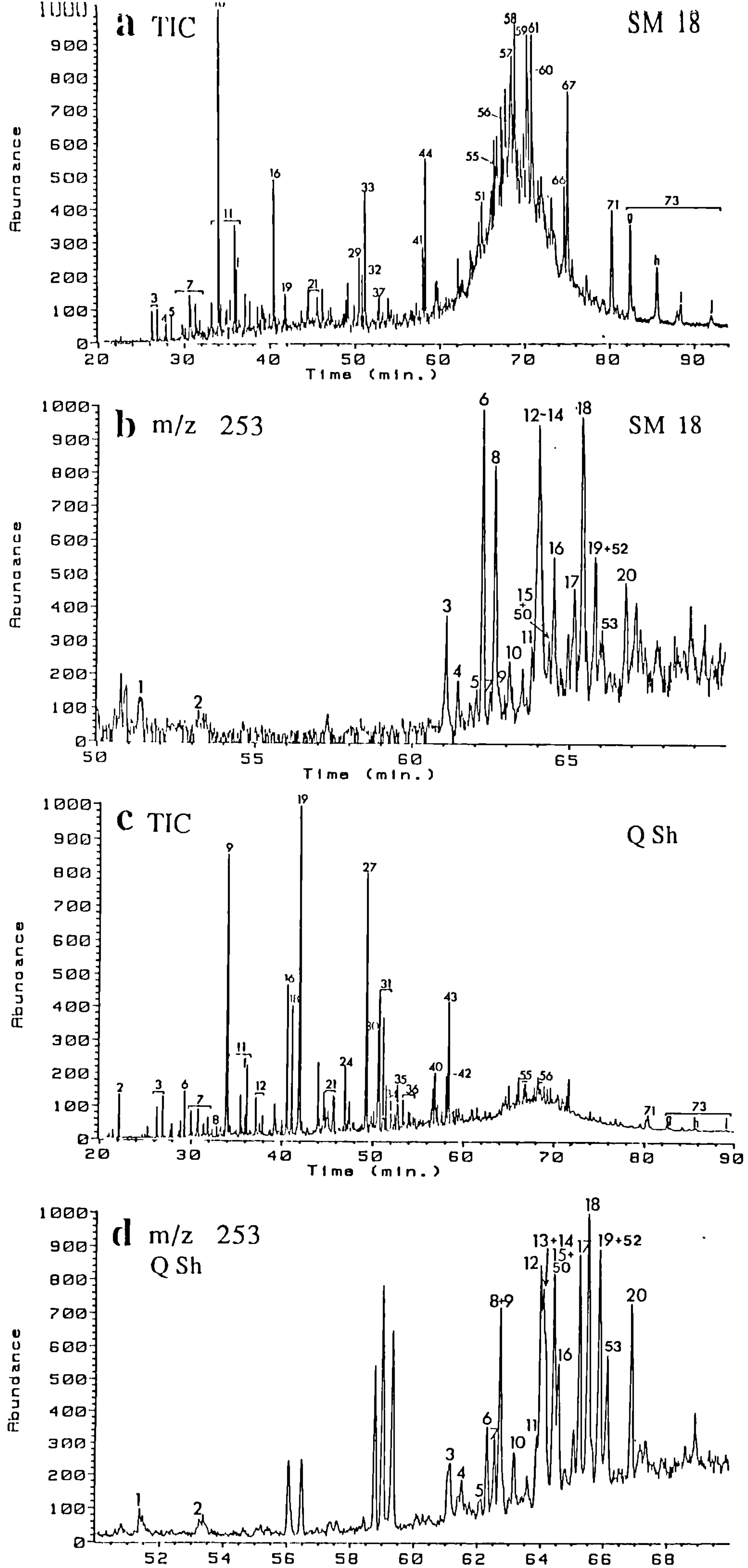


Fig.4.49 Distributions of aromatic hydrocarbons in algal-rich shales from Fife (see Tables 4.7 and 4.8 for peak assignments).

minutes could not be identified, but the simplicity of their mass spectra and prominence of the presumed molecular ions (also the base peaks) suggests that they are parent PAH.

The predominance of parent PAH over alkylated components is characteristic of many aromatic distributions reported in recent sediments in diverse depositional environments in which the compositional uniformity of the PAH distribution has been taken as being indicative of a common origin where the major source has been attributed to the anthropogenic combustion and pyrolysis of fossil fuels (Hites *et al* 1977; Lee *et al* 1977; Laflamme and Hites 1978; Wakeham *et al* 1980b). Natural combustion processes, for example fossil fires, have also been invoked as sources of parent PAH in recent sediments (Blumer and Youngblood 1975; Youngblood and Blumer 1975).

In recent sediments, hydrocarbon distributions dominated by parent PAH are often termed "pyrolytic-like" regardless of whether the compounds derive from pyrolysis or combustion of organic matter. Pyrolytic-like distributions have also been detected as part of the natural background of marine sediments far from industrialised areas, but the ultimate source is still thought to be anthropogenic combustion and/or pyrolysis, with additional contributions from diagenetically-derived compounds (Tissier and Saliot 1983). The source of these distributions in Q and in the other Midland Valley samples is considered later.

4.3.3.2 Coals and Related Materials

Type variation in the humic-derived materials was investigated by considering the hydrocarbon distributions in samples SM6, StA6 (east Fife), M1, M2 (Musselburgh No.1 Borehole), RIG1, RIG2 (Righead Borehole), QMBX, 2583 and W15.85, all of which have reflectances in the range %R_o=0.54-0.71. The last three-named samples are represented in the "miscellaneous humic coals" section of the data tables. The samples from the Righead and Musselburgh boreholes were extracted as part of the rank investigation (Chapter 5), but data from the low-rank samples are included here for comparison. The majority of samples prefixed "M" and "RIG" refer to composites which were made to ensure that sufficient extract was obtained from the little material that was available.

The cannel coals extracted were SMW14 (east Fife coast), BC (Best Cannel) and M4194 (Rum Coal). The exact locations of the last two samples are not known, but they are in the West Wemyss area: data for these specimens are found in the tables incorporating "miscellaneous samples".

The samples categorised as "woody" or "vitrinitic" were all from volcanic terrains as described in Section 4.2.2.3.

4.3.3.2.1 Extract Yields and Gross Compositions

The yields of EOM are all high and generally over 1%. The very high value of 43.9% for sample M2 (Table A.2) suggests the presence of migrant hydrocarbons or impregnated vitrinite, although no evidence for either was evident from microscopical examination. The EOM yields for the Orrock and East Kirkton samples were comparable with those of the other coaly materials analysed, but the yield from the Coalyard wood was relatively low.

Fractionation of the EOM revealed a marked enrichment in polar compounds (Fig.4.50). The cannel coals showed a slight enrichment in aliphatic hydrocarbons compared with the other humic samples. Although petrographic examination indicated that the coal above the Westfield Oil Shale was a "normal" humic coal, its EOM has a relatively high aliphatic hydrocarbon content given its low rank (%R_o 0.55). This fact may indicate the ingress of hydrocarbons from the aliphatic-rich Westfield Oil Shale which lies only 4 feet below the coal analysed. Alternatively, it is possible that the incorporation of aliphatic matter may have occurred

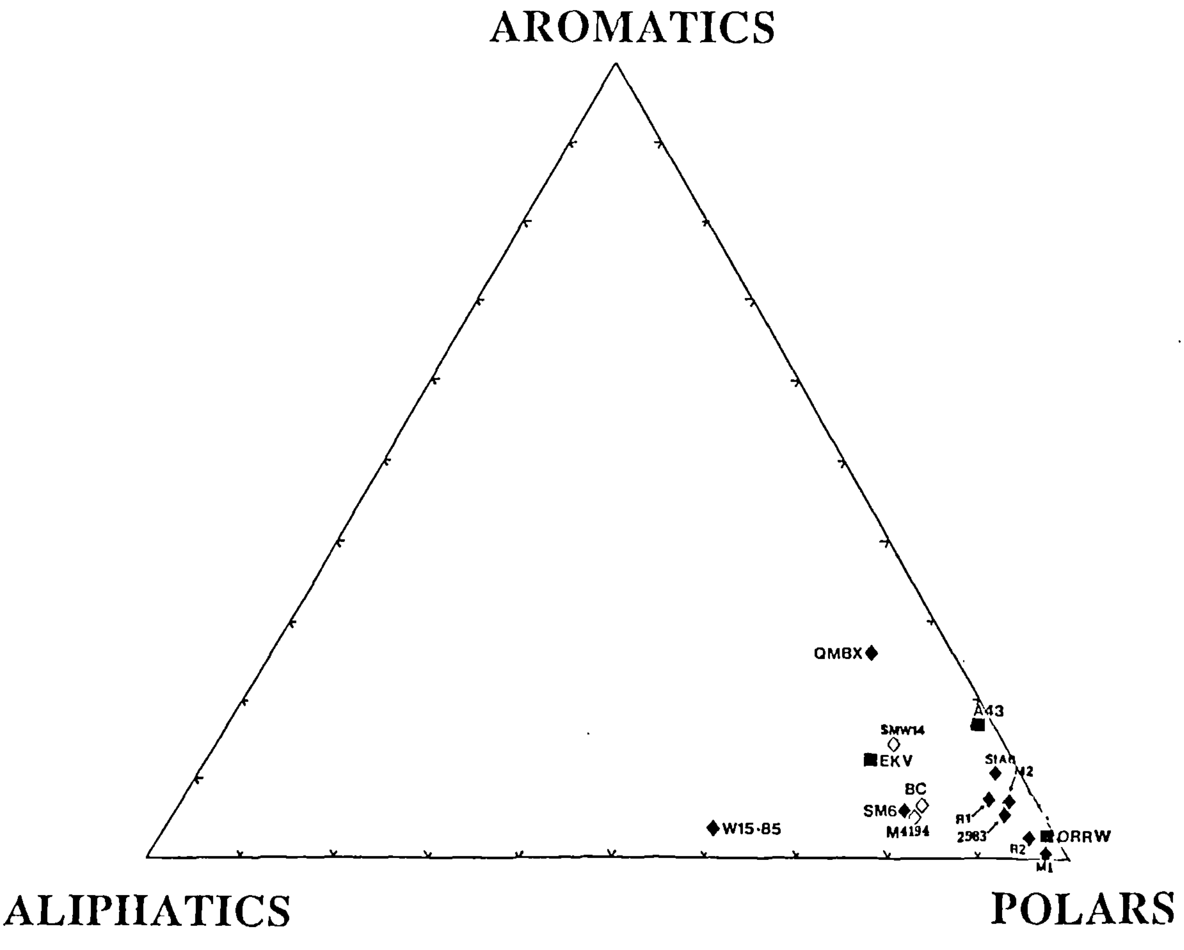


Fig.4.50 Ternary plot showing compound-class constitution of EOM from coals and related materials investigated. ◆ humic coals; ◇ sapropelic coals; ■ woody and vitrinitic materials.

during or shortly after coal formation, giving rise to a perhydrous vitrinite. As discussed in Section 4.2.2.1, the surfaces of such vitrinites are markedly inhomogenous, and since exceptionally "scruffy" vitrinites are found in the Westfield Basin, it is not unlikely that the extracted coal sample above is of this kind. The unusual nature of the coal was indicated by the fact that, during Soxhlet extraction, it expanded causing the rupture of the cellulose thimble. This phenomenon was not observed during the extraction of any other humic or sapropelic coals.

4.3.3.2.2 Humic Coals

4.3.3.2.2.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Representative gas chromatograms illustrating the variations in hydrocarbon distributions that are thought to reflect predominantly organic-matter type variation are shown in Fig.4.51.

Gas chromatograms of the saturate fractions of most of the samples analysed are of the form shown in Fig.4.51a and b. *N*-alkanes are generally present in the range C_{10}-C_{36} with odd-carbon-number preferences extending from C_{15} or C_{19} to C_{27} or C_{29}. The hydrocarbon distributions fall within two categories. The *n*-alkanes may be biased towards the high molecular-weight homologues which show a particularly marked OEP in the C_{23}-C_{27} range (StA6; Fig.4.51a). A similar distribution is recorded in SM6. These observations are in general agreement with those reported within *n*-alkane distributions in sediment extracts in which the parent organic matter is of terrestrial origin (Kvenvolden 1962; Bray and Evans 1965). The *n*-alkane envelope may alternatively take the form shown in Fig.4.51b, where it is skewed towards lower carbon-numbered alkanes . CPIs in the high molecular-weight range are lower than those in distributions of the type shown in Fig.4.51a and no carbon preference below C_{19} is evident. The latter fact, coupled with the failure to recognise any algal matter in the coals using microscopy (which could lead to an OEP in the C_{15} to C_{19} range) suggests that algal lipids are not likely to be the cause of the medium molecular-weight skew of the type in Fig.4.51b.

Bacteria have been reported to contain relatively large amounts of medium length, straight-chain hydrocarbons, often showing no OEP (Han *et al.* 1968b; Han and Calvin 1969a; Albro 1976). It is therefore possible that the enrichment in medium molecular-weight *n*-alkanes is due to an output of bacterial lipids which is swamping contributions from long-chain alkanes. Alternatively, the relatively

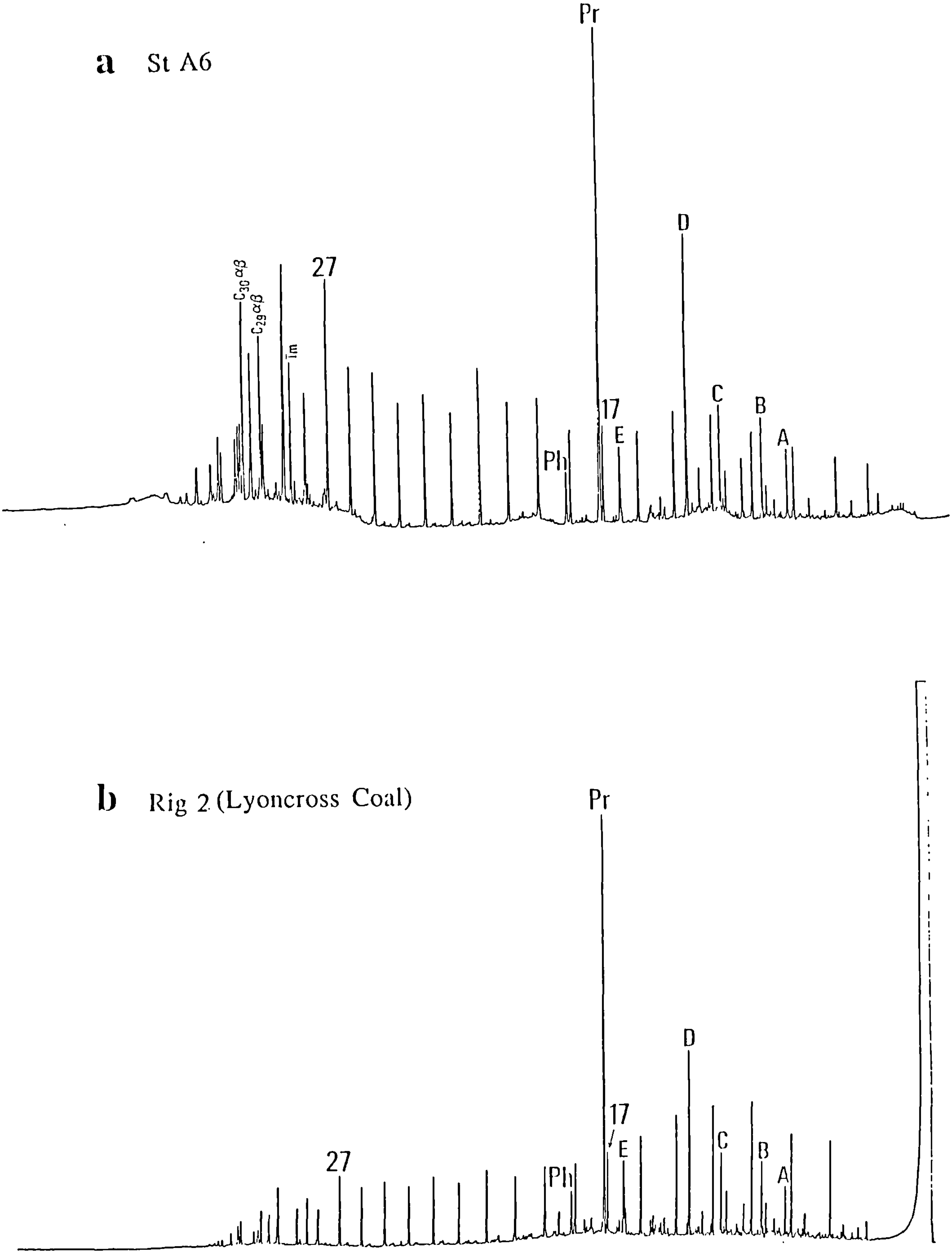
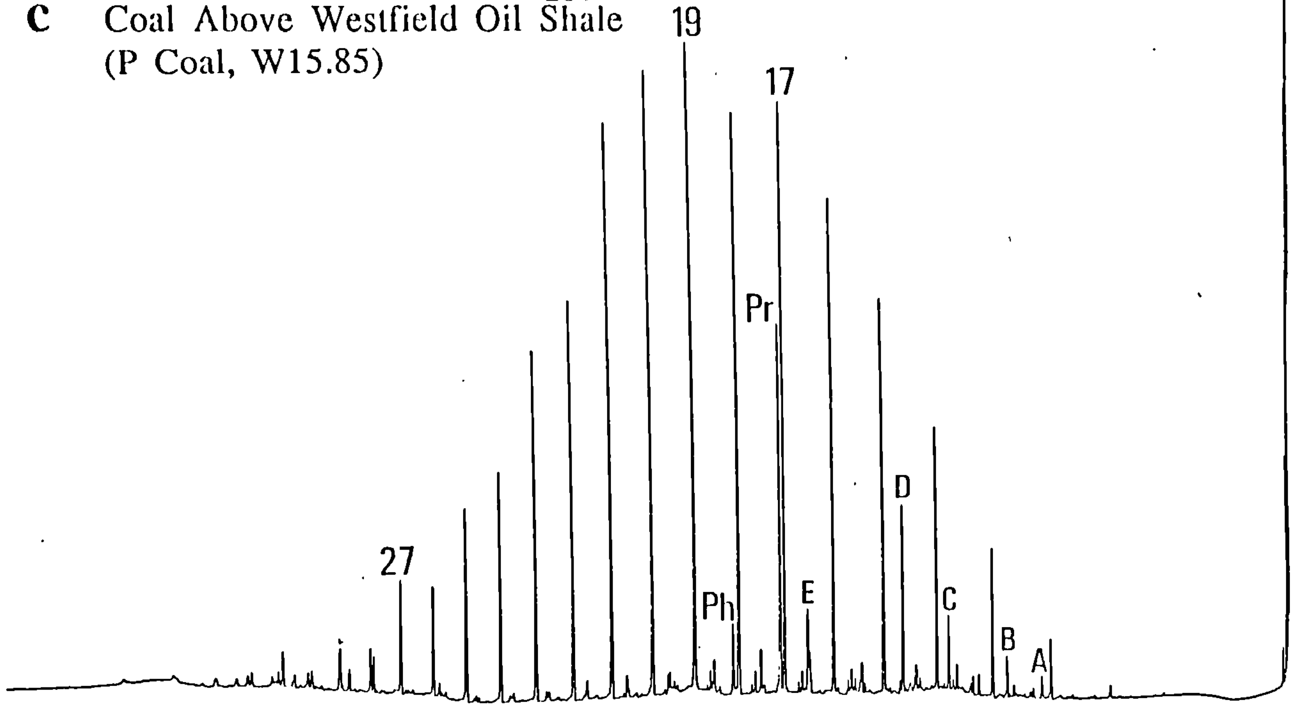
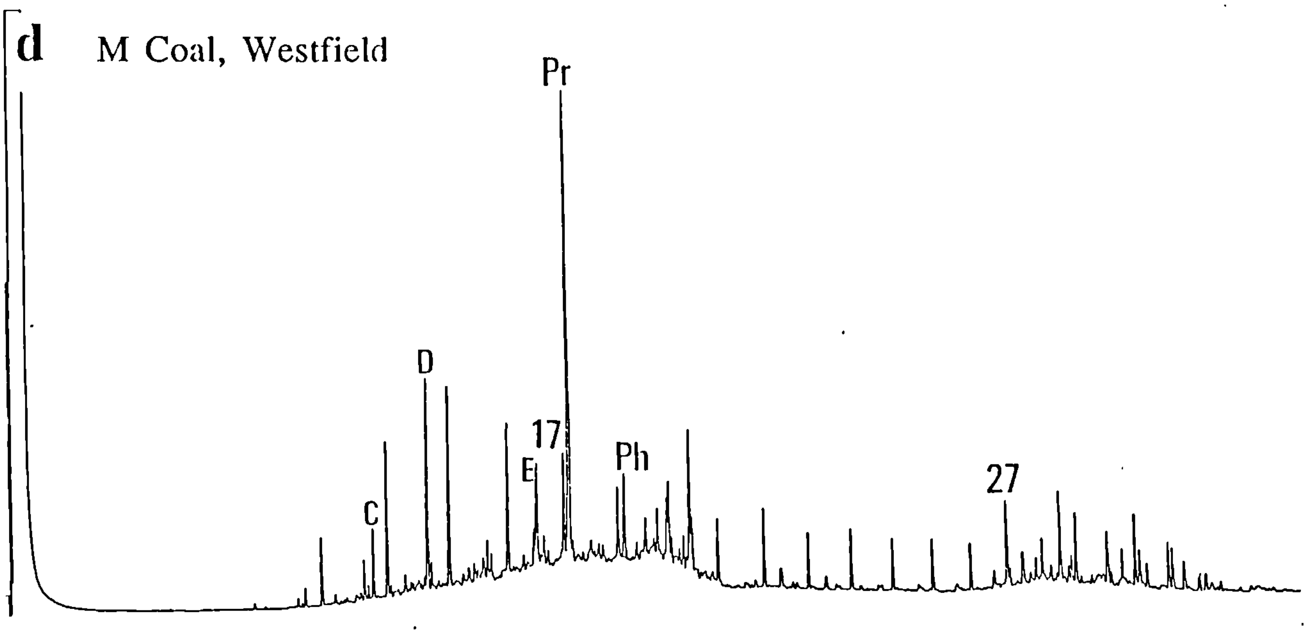


Fig.4.51 Gas chromatograms of the saturated hydrocarbon fractions of humic coals (M coal run on Perkin Elmer 8310 gas chromatograph with 25mx0.32mm i.d. OV1 column; on column injection; all other conditions as described in Section 3.3.5).

c Coal Above Westfield Oil Shale
(P Coal, W15.85)



d M Coal, Westfield



e Pyotshore Coal
(QMB X)

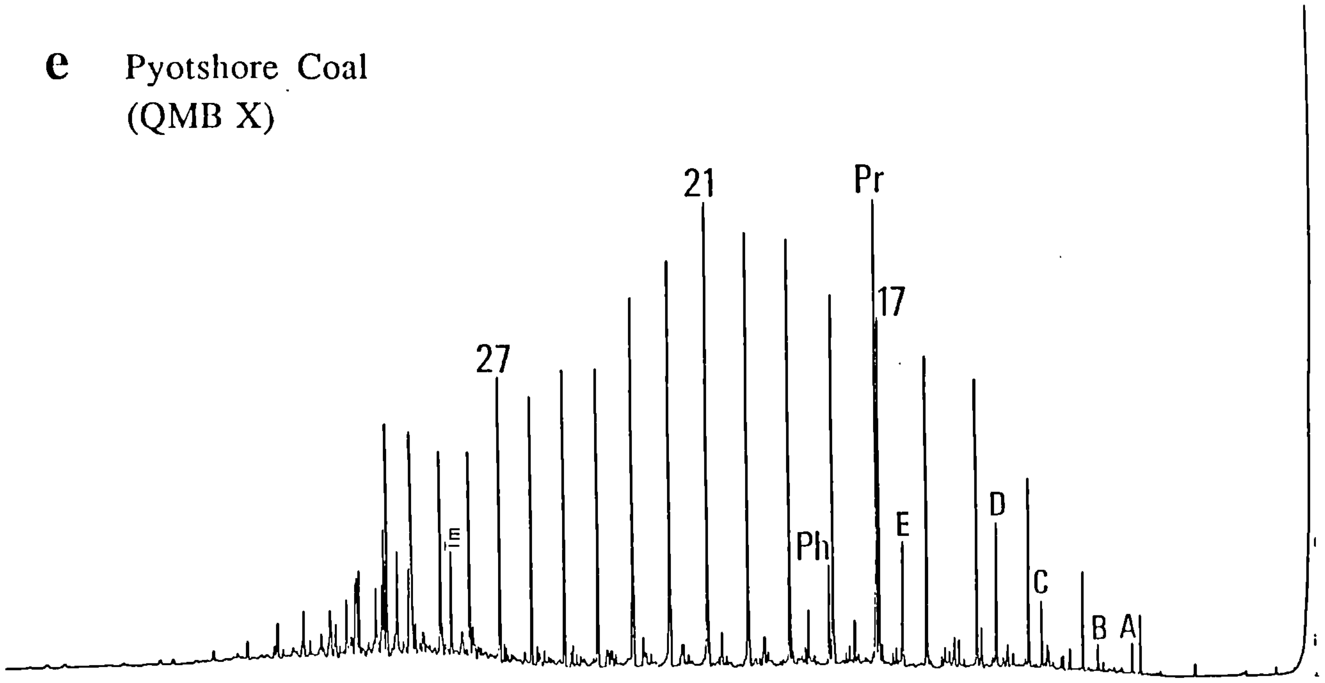


Fig.4.51 (cont.).

low concentrations of high molecular-weight alkanes could be reflecting a reduced contribution from waxy cuticular matter, which is known to contain significant quantities of high molecular-weight *n*-alkanes with a pronounced OEP (Eglinton *et al.* 1962; Eglinton and Hamilton 1963). Such an explanation seems likely in view of the fact that samples with *n*-alkane profiles of the type shown in Fig.4.51b were vitrinite concentrates in which the waxy exinitic materials had been floated off. All vitrinite concentrates do not display *n*-alkane distributionas similar to Fig.4.51b: the concentrate represented by sample 2583 shows an *n*-alkane envelope similar in overall shape, but has a marked OEP in the high molecular-weight range. Conversely, the spore-containing Pyotshore coal (Fig.4.51e) did not show any enhanced concentration of high molecular-weight *n*-alkanes and its CPI is less than that of the vitrinites concentrates (Table A.3). Observations of enhanced concentrations of high molecular-weight *n*-alkanes with a marked OEP, often attributed to an input of waxy cuticular components, can obviously occur independently of any microscopically-discernible exinitic input. A further difference in the two types of hydrocarbon distribution is that high molecular-weight polycyclic alkanes are not as prevalent, relative to the straight-chain alkanes, in distributions of the type shown in Fig.4.51b.

Figs 4.51c and e show saturated hydrocarbon distributions which are atypical of the suite of humic coals analysed. The gc trace of the coal in Fig.4.51c bears a marked resemblance to that of the Westfield Oil Shale lying only 4ft below it (*cf.* Fig.4.29a). Despite the overall similarity in the shape of the *n*-alkane envelope, differences lie in the position of the *n*-alkane maximum, which is at *n*-C_{19} in the Westfield coal (W15.85), as opposed to *n*-C_{21} in the Westfield Oil Shale, and the much-reduced OEP range in the coal (C_{17}-C_{19} rather than C_{21}-C_{27}). Given the disparity between the hydrocarbon distribution in W15.85 and those of the other humic coals studied, and the similarity between the former distribution and the gas chromatogram of the Westfield Shale, it is possible that the aliphatic matter from the oil shale has impregnated the overlying coal resulting in the overprinting of the original hydrocarbon distribution. Absorption of hydrocarbon material by the vitrinite in the Westfield Shale is thought to have occurred resulting in its anomalously low reflectance value. That the saturated hydrocarbon distribution in W15.85 is not representative of all the Westfield coals is provided by Fig.4.51d which is a gas chromatogram trace of a coal not juxtaposed with liptinite-rich sediments (M Coal, sample W1.6). The hydrocarbon distribution is clearly of the type shown in Fig.4.51b. The trace is included for comparative purposes only as the sample was not extracted as part of the present project. The similarity between the gc traces of sample W15.85 and the Westfield Oil Shale lends support to the suggestion of migration made in the foregoing section on the basis of the similarities in the compound-class constitution of the extracts.

The hydrocarbon distribution in the Pyotshore coal also differs from that of other humic coals investigated. The *n*-alkane envelope is more similar in shape to that of the Westfield Oil Shale than that of sample W15.85. Whether the *n*-alkane distribution is reflecting type variation or an input from migrated, possible *Botryococcus*-sourced aliphatic matter is not known as strata above and below the sample were not available for analysis.

The Pr/Ph ratios of humic coals in this sample suite are high (4.73-9.37), as are the Pr/*n*-C_{17} ratios (apart from sample W15.85). The values are consistent with the accumulation of terrestrial debris in oxidising peat-swamp environments.

Gas Chromatography-Mass Spectrometry (GC-MS)

The content of tricyclic and tetracyclic terpanes in the low-rank coals and vitrinites investigated is negligible in comparison with pentacyclic components (e.g. Fig.4.52a). With the exception of the distribution seen in the coal above the Westfield Oil Shale (W15.85), the m/z 191 fragmentogram of the Pyotshore coal is typical (Fig.4.52b). The tetracyclic secohopanes are present in slightly higher abundance than the other tri- and tetracyclic compounds: only one C_{20} tricyclic component (peak 3) can be readily discerned.

The distribution seen in the Westfield coal sample differs in that an additional C_{20} tricyclic (peak 2) is relatively prominent and there is a decrease in the abundance of tricyclics $>C_{20}$. A C_{23} tetracyclic (peak 9) is also relatively prominent. The tri- and tetracyclic terpane distribution in the coal above the Westfield Oil Shale (Fig.4.52c) matches that of the underlying Westfield Oil Shale itself (*cf.* Fig.4.30c) lending further support to the suggestion that migrant hydrocarbons may be present in the coal.

Pentacyclic-terpane distribution patterns in the coals and vitrinite concentrates are qualitatively similar to that shown in Fig.4.52a and consist of the commonly-occurring hopane and moretane families which are supplemented by ββ hopanes in the most immature samples. The unknown C_{29} pentacyclic component eluting after to C_{30}αβ hopane (peak 34) is particularly conspicuous within the sample suite. Small quantities of the 28,30-bisnorhopane were detected in two samples (RIG1 and M1). Out of the nine samples under consideration, the m/z 191 fragmentograms of four show hopane distributions dominated by the C_{29}αβ hopane as opposed to the more commonly-observed dominance of the C_{30}αβ component (see parameter e in Table A.4).

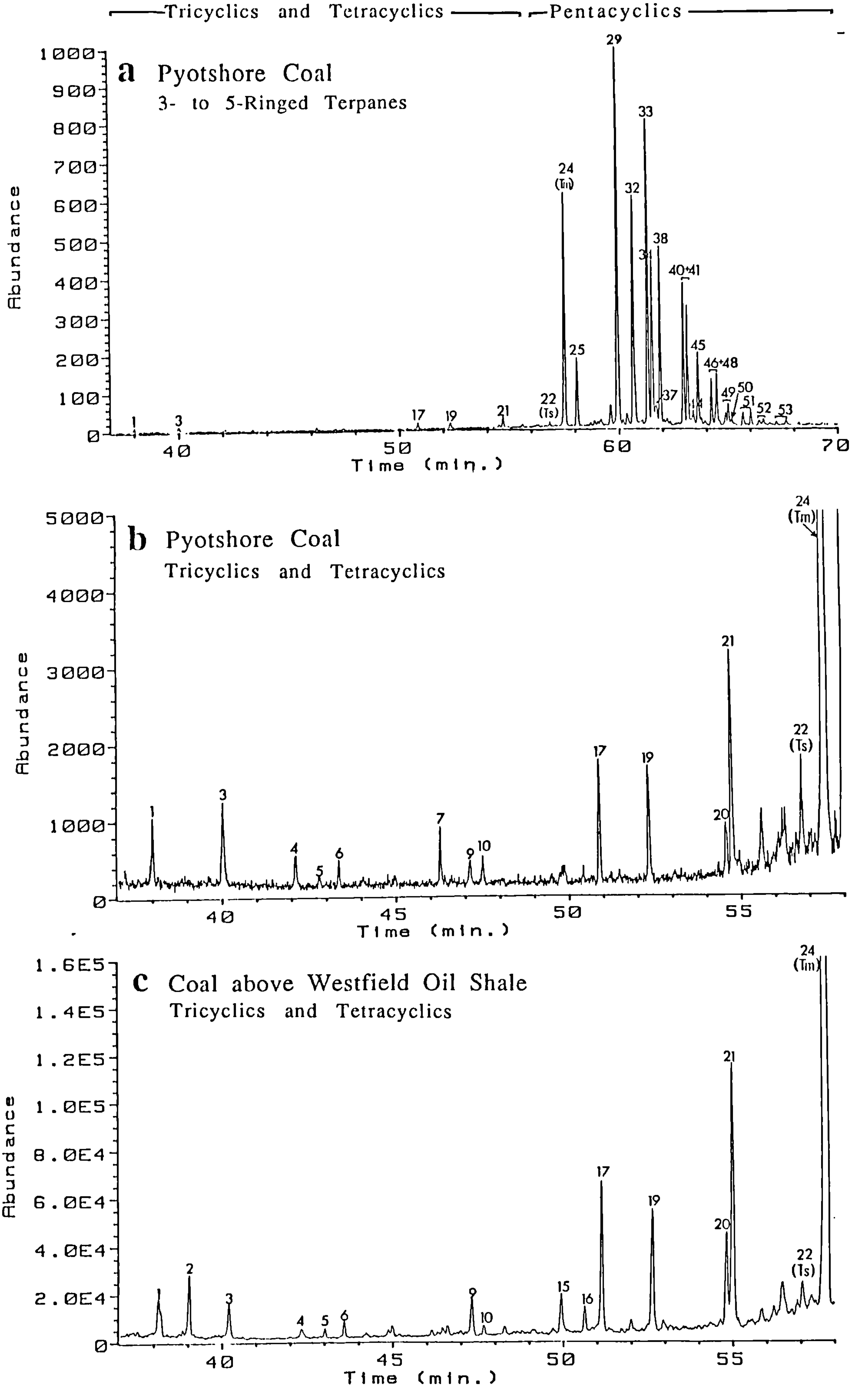


Fig.4.52 M/z 191 fragmentograms showing the distribution of 3- to 5-ringed terpanes in humic coals (see Table 4.5 for peak assignments).

The sterane distributions of all the coals and vitrinites are similar and are dominated by C_{29} steranes. Except for sample W15.85, the $C_{29}\alpha\alpha\alpha20R$ component is at least c.4 times more abundant than the $C_{27}\alpha\alpha\alpha20R$ component, with the consequence that the samples all plot in the lower part of the "terrestrial" zone, as shown in Fig.4.53.

The enhanced concentration of C_{27} steranes in the coal above the Westfield Oil Shale mimics that observed in the underlying shale and results in the coal plotting in the same general field as the shale. As alluded to earlier, the plot position may reflect contamination of the hydrocarbons in the coal by those derived from the shale.

Diasterane distributions parrallel those of the regular steranes in all samples, with abundance decreasing in the order $C_{29}>C_{28}>C_{27}$. Diasterane contents, expressed by the diasterane/sterane ratio, range from zero to 0.88.

A typical sterane distribution for the low-rank coals is represented by the m/z 217 fragmentogram of RIG2 (Fig.4.54). Because of the relatively high hopane to sterane ratio of this sample (20), and of several others (values lie in the range 5-28), peaks due to hopanes, as well as steranes, are observed in the m/z 217 mass fragmentograms.

4.3.3.2.2.2 Aromatic Hydrocarbons

TIC chromatograms illustrating the variation in the distribution of components in the aromatic fractions of the humic coals studied are shown in Figs 4.55a and b. Fig.4.55a typifies the aromatic distributions in samples StA6, W15.85 and 2583 whilst Fig.4.55b closely resembles the TIC traces of samples M1, M2, RIG1 and RIG2.

The aromatic hydrocarbon distributions of the resolved components in the humic coals are more complex than those observed in the algal-rich shales. The high molecular-weight "hump" is less prominent relative to the other compounds, and there is a greater contribution from naphthalenes and phenanthrenes. Alkyltetralins (peaks 5 and 10) are detectable in all samples, but they are lower in abundance compared with their occurrence in the algal-rich shales. 1,2,5,6-Tetramethylnaphthalene (peak 16) is conspicuous, as are the alkylbiphenyls (peaks 8 and 12). Cadalene (peak 14; Fig.4.56) was detected in all samples, but achieves its maximum abundance in the Pyotshore coal (Fig.4.55b).

8,14-monoaromatic secohopanes and benzohopanes were identified in the high molecular-weight region of the TIC traces, their abundance being greatly reduced, relative to other components, in comparison to that in the algal-rich shales. Aromatic steroids were still readily discernible from gc-ms analysis.

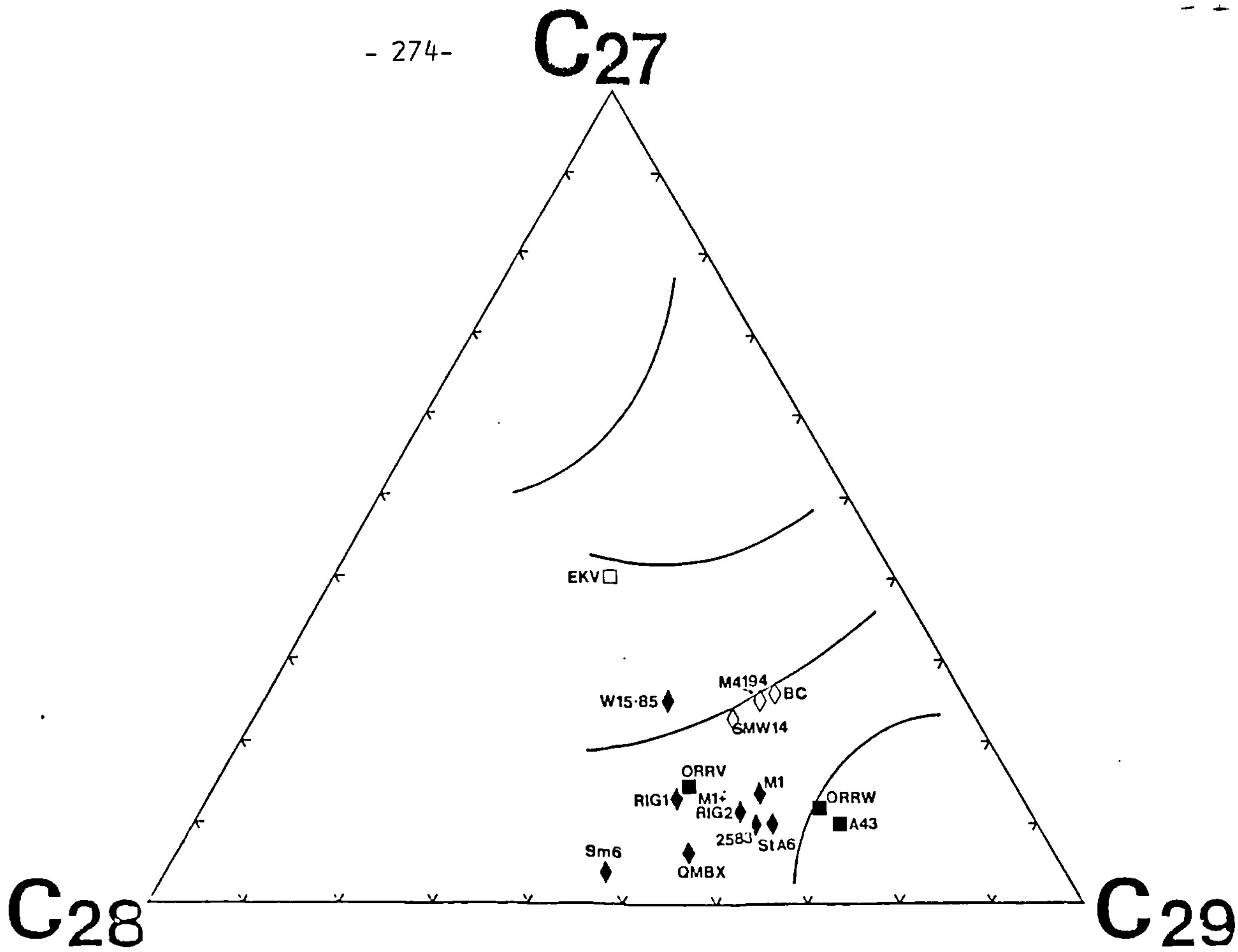


Fig.4.53 Carbon-number distribution of steranes in the coals and related materials analysed. ◆ humic coals; ◇ sapropelic coals; ■ woods and vitrinitic materials. Refer to Fig.4.18 for designation of fields.

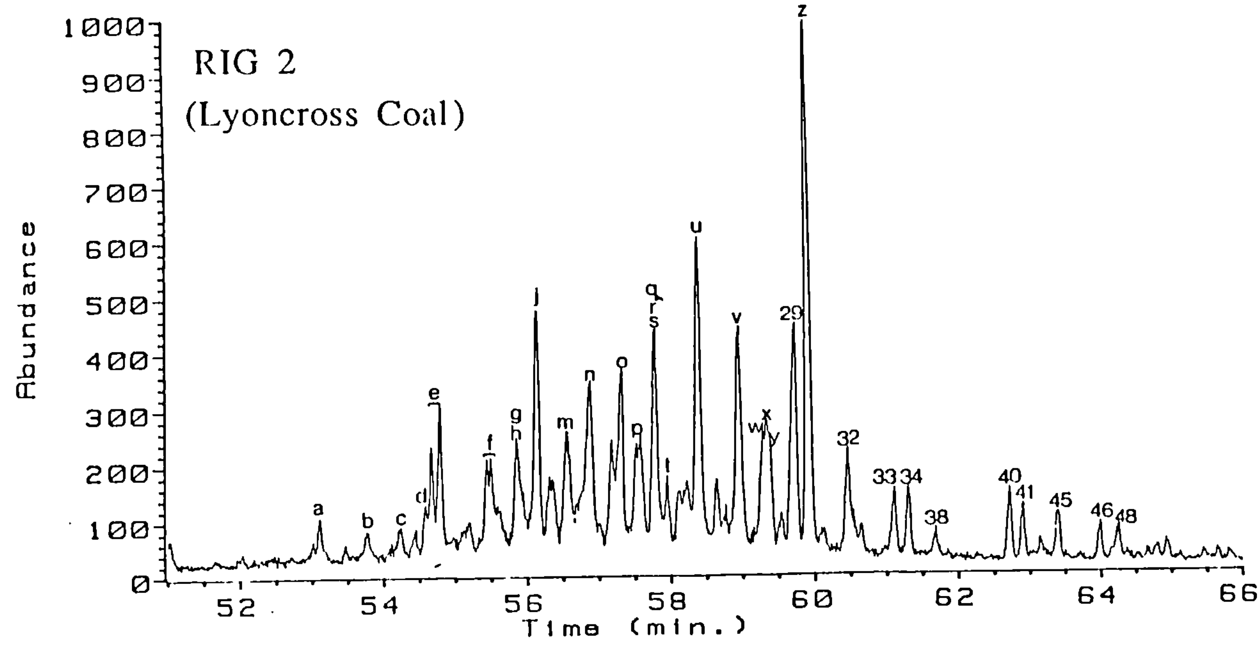


Fig.4.54 M/z 217 fragmentogram showing the typical distribution of steranes in the humic coals (peaks 29-48 are hopanes). Peak assignments are given in Tables 4.5 and 4.6.

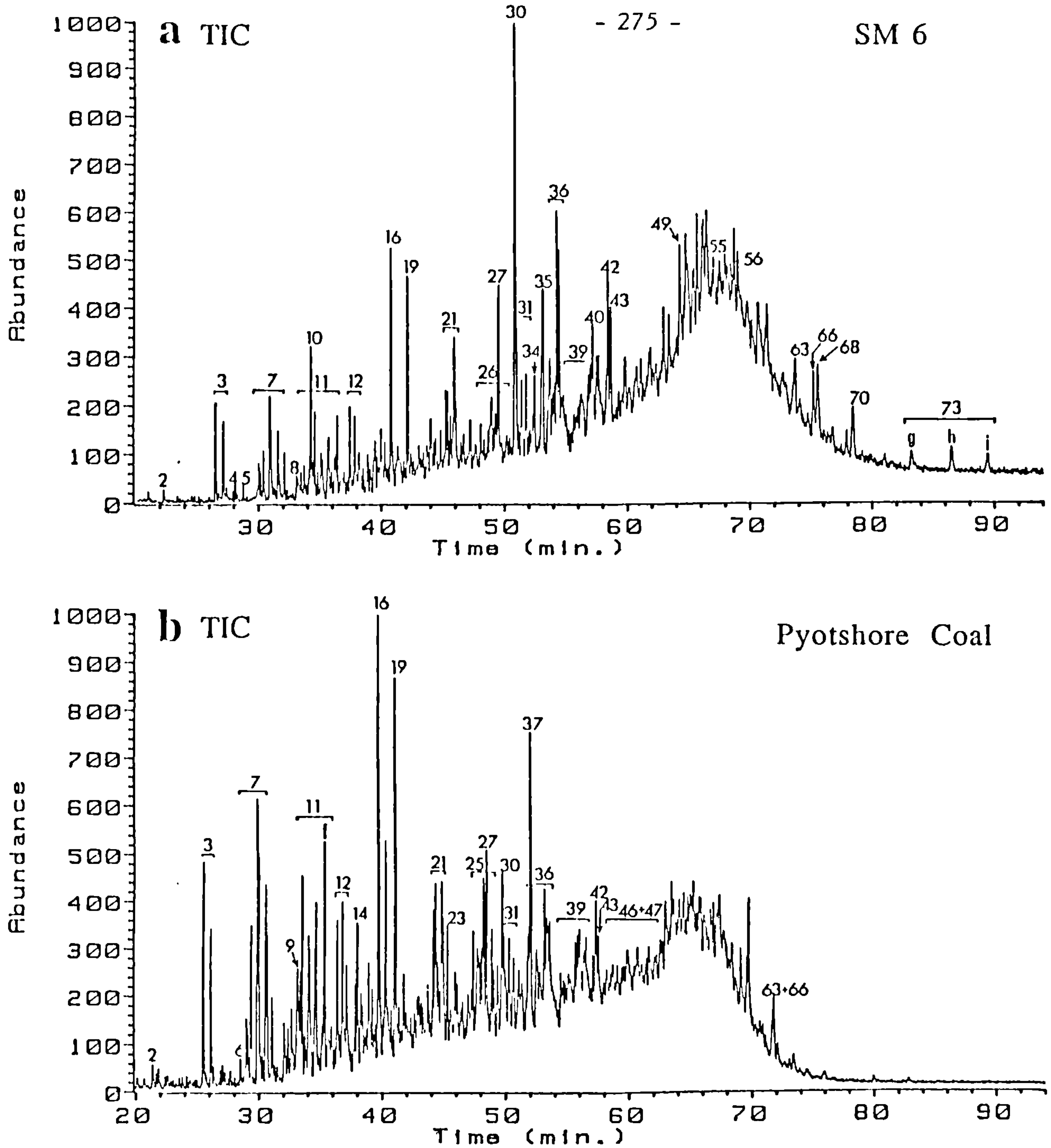


Fig.4.55 Chromatograms showing typical distribution of aromatic hydrocarbons in the humic coals. Peak assignments are given in Table 4.13.

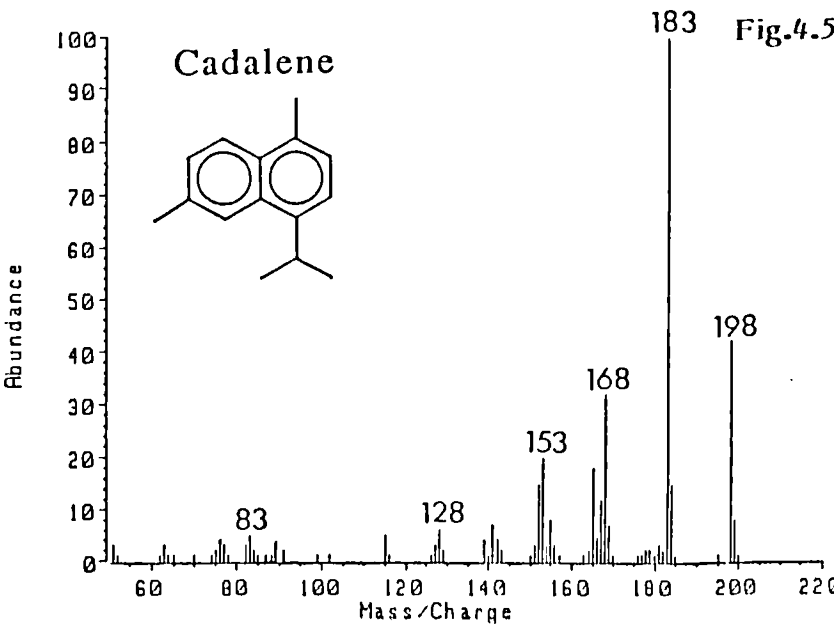


Fig.4.56 Mass spectrum of peak 14

A typical distribution of the monoaromatic components is shown in Fig.4.57a. Rearranged components are present in amounts comparable with the non-rearranged structures, and interference with benzofluoranthenes and benzopyrenes ($[M+1]^+$=m/z 235) was observed in all samples studied.

The distributions of the methyl-substituted triaromatics are the same in all the humic coals investigated, but differ markedly from those of the algal-rich shales because peak 6 is greatly enhanced and peak 4 is markedly reduced in abundance relative to the other components (compare Fig.4.57b with Fig.4.23c). Peaks 6 and 4 are both thought to be 4-methyl substituted. A further significant difference is that, unlike the majority of algal-rich shales investigated, the low-rank humic coals show a marked dominance of methyl-substituted triaromatics over non methyl-substituted triaromatics.

Recognisable in the TIC traces of all the coals and vitrinites are one or more members of a series of compounds with base peaks of m/z 259 in their mass spectra which, in conjunction with their molecular ions, suggests they belong to a series of dimethyl- or ethyl-nuclear-substituted triaromatics. A typical distribution of these compounds is shown in Fig.4.57c, and the mass spectra of two members are shown in Figs 4.57d and e.

The multiplets of peaks eluting after *c.*40 minutes comprise unsubstituted (parent) PAH and, to a lesser degree, their alkylated homologues. Although phenanthrenes and alkylphenanthrenes can have a dual diagenetic and pyrolytic origin (Lee *et al.* 1977; Wakeham *et al.* 1980b), the higher molecular-weight parent PAH are of the type commonly reported in recent sediments where their major source is attributed to the combustion/pyrolysis of organic matter, referred to previously.

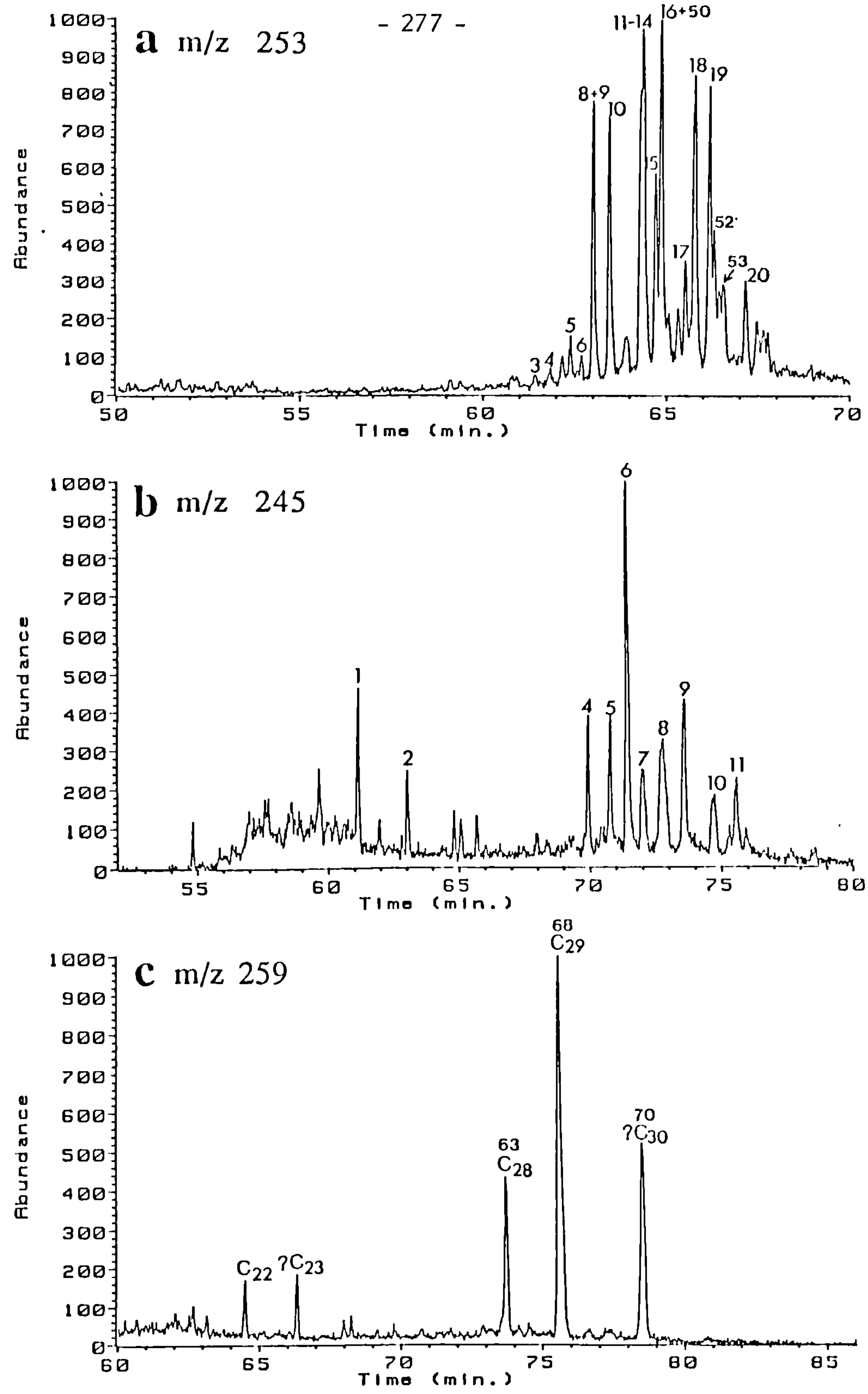
4.3.3.2.3 Sapropelic Coals (excluding torbanite)

4.3.3.2.3.1 Aliphatic Hydrocarbons

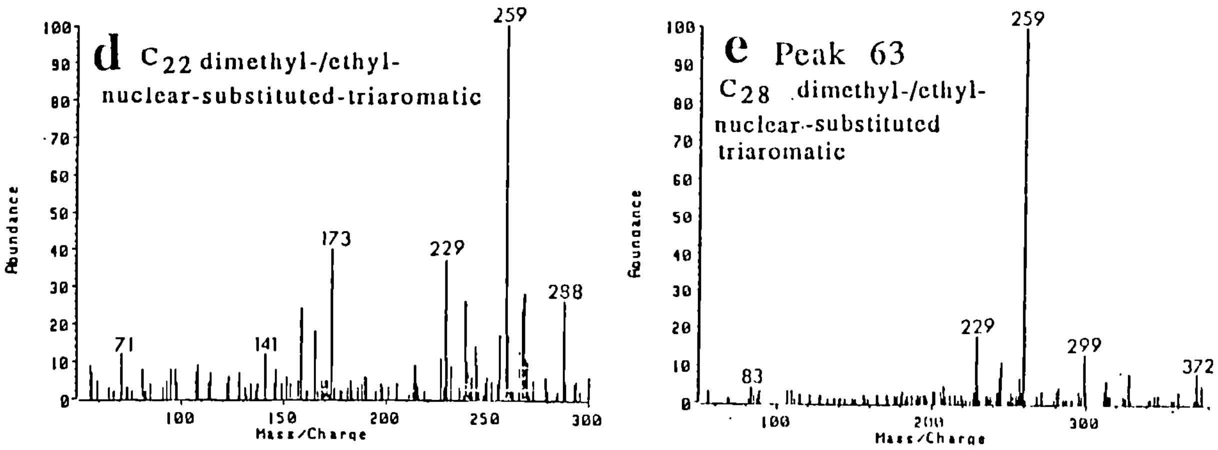
Gas Chromatography (GC)

Gas chromatograms of the hydrocarbon fractions of the sapropelic coals extracted are shown in Fig.4.58.

All three samples contain straight-chain alkanes lying in the range C_{10}-C_{36}. The *n*-alkane envelopes of SMW14 (Fig.4.58a) and the Rum Coal (Fig.4.58b) are similar as they both show enhanced concentrations of long-chain alkanes in the C_{21}-C_{27} range in which there is also an odd-carbon-number preference. These distributions reflect the input of waxy, exinitic matter observed through microscopy.



Figs 4.57a–c Typical distributions of aromatic steroids in humic coals (assigments shown in Tables 4.7, 4.8 and 4.9).



Figs 4.57 d and e Mass spectra of peaks in Fig 4.57c

The "smooth" *n*-alkane distribution beyond C_{17} in the Best Cannel (Fig.4.58c), coupled with the relatively low concentrations of acyclic isoprenoids and also biomarker data, suggest that the level of sample maturity indicated by vitrinite reflectance is erroneously low due to reflectance suppression brought about by the absorption of large quantities of liptinitic matter. The form of the *n*-alkane envelope in Fig.4.58c may therefore reflect predominantly rank, rather than type, control although an input of *Botryococcus*-derived aliphatics could have contributed to the shape of the *n*-alkane envelope since microscopical analysis indicates that 50% of the total organic matter present is represented by the remains of this alga. Saurian-type *n*-alkane contributions appear to be characteristic of *Botryococcus*-rich shales (*cf.* Fig.4.29).

Pr/Ph ratios are also high (3.00-4.51), but are all lower than those recorded in the humic coals discussed in the last section. They are indicative of a more reducing depositional environment. The ratios are of the same order of magnitude as those determined on the torbanite and torbanitic shales which is not surprising since these samples are also the products of deposition in sapropelic environments.

Pr/*n*-C_{17} ratios for SMW14 and the Rum Coal are lower overall (average=2.06) than the average calculated for the humic coals (3.26). They are consistent with the more open-water conditions of sedimentation experienced in peat-swamp pools in which the sapropelic coals accumulated. The low Pr/*n*-C_{17} ratio for the Best Cannel may be a consequence of the inferred higher rank of the sample, but, as already stated, could also be related to the abundance of *Botryococcus* telalginite in the sample since low isoprenoid/*n*-alkane ratios have been recorded in the torbanitic shales (see Table A.3).

Gas Chromatography-Mass Spectrometry (GC-MS)

Variations in the terpane distributions of the three sapropelic coals investigated are reflected in the distributions occurring in the Best Cannel from W.Wemyss (Fig.4.59a) and in sample SMW14 (Fig.4.59b) from the Pathhead Beds in the section west of St.Monance. The terpane pattern of the Rum Coal is virtually identical to that of the Best Cannel.

As in the humic coals, tricyclic and tetracyclic terpanes are minor components compared with the pentacyclics, although enhanced concentrations of the C_{24} secohopane (peak 17) are evident in the Best Cannel and Rum Coal. Three- and four-ringed terpanes are barely detectable in SMW14.

The Best Cannel and Rum Coal are notable for their exceptionally high abundances of hopanes relative to steranes; in fact the hopane to sterane ratio of 130 for the former is the highest value for this parameter recorded in any

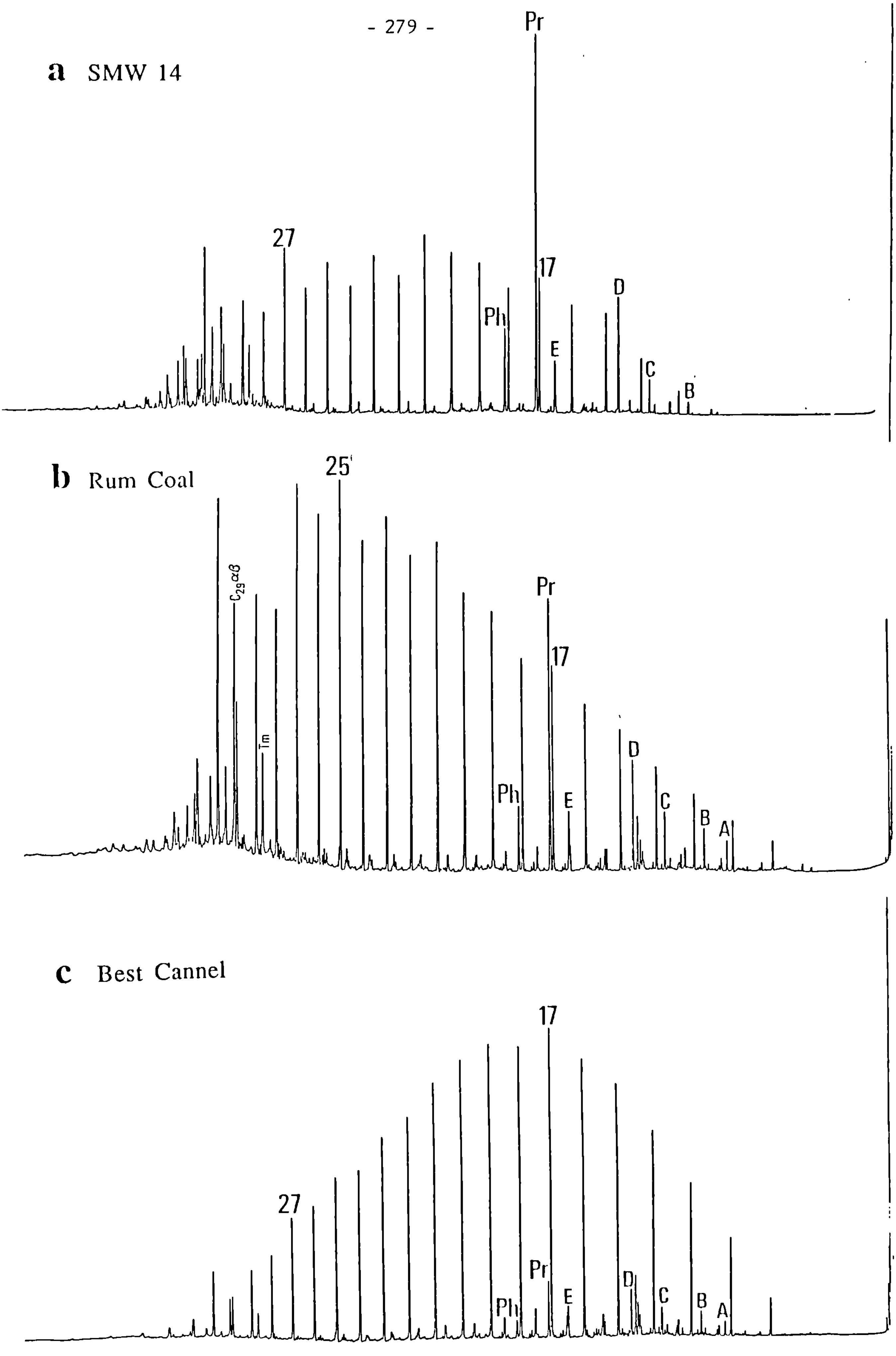


Fig.4.58 Gas chromatograms of the saturated hydrocarbon fractions of the sapropelic coals (isoprenoid assignments are given in Table 4.4).

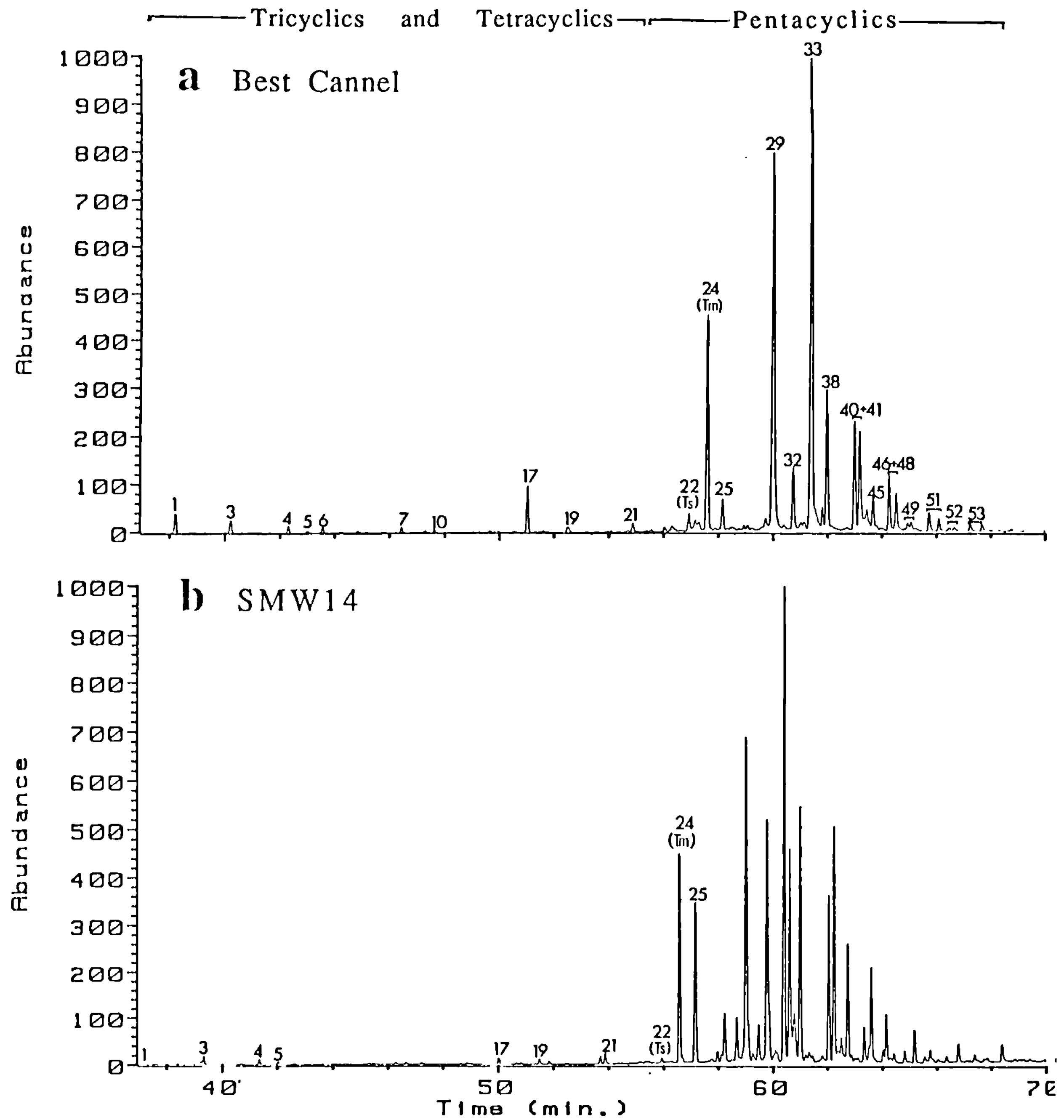


Fig.4.59 M/z 191 fragmentograms illustrating the distribution of 3- to 5-ringed terpanes in the sapropelic coals (peak assignments given in Table 4.5).

Midland Valley sample during the present study. The high hopane concentrations are also reflected in a strong methylhopane contribution, typified by that of the Best Cannel (Figs 4.60a,b). Two series of peaks corresponding to the prominent methylhopane series observed in the Serpiano Oil Shale (McEvoy and Giger 1986), thought to represent 2α-methylhopanes (Summons and Jahnke 1990), and the suite elucidated in the algal-rich shales (see Section 4.3.3.1.4.1), which are thought to correspond to hopanes with a 3β stereochemistry, are present. Distributions of methylhopanes similar to that in Fig.4.60b are also seen in the humic coals, but the fragmentograms are noisy and the methylated components are not sufficiently abundant to allow adequate mass spectral characterisation.

The typical sterane distribution seen in the sapropelic coals is represented by the m/z 217 fragmentogram of the Rum Coal (Fig.4.60c). All three samples show a predominance of the $C_{29}\alpha\alpha\alpha20R$ over the $C_{27}\alpha\alpha\alpha20R$ sterane although the greater abundance of the former is not as large (approximately twofold) as in the majority of humic coals (approximately fourfold). The sapropelic coals therefore plot in the upper half of the "terrestrial" field in Fig.4.53. As for many of the humic coals, the high hopane to sterane ratios mean that part of the hopane distribution is manifested in the m/z 217 fragmentogram.

4.3.3.2.3.2 Aromatic Hydrocarbons

The distributions of aromatic hydrocarbon compounds in the Rum Coal and SMW14 are very similar and are typified by the TIC trace of the former (Fig.4.61a). Overall, the distribution profile resembles those characterising the majority of lamalginite-rich shales. Alkyltetralins (peaks 5 and 10), 1,2,5-Trimethylnaphthalene and 1,2,3,4-Tetrahydroretene are prominent, as is a compound (peak 38) whose mass spectrum is suggestive of a C_3 alkylphenanthrene.

Prominent peaks in the high molecular-weight region of the TIC trace are attributable to monoaromatic 8,14-secohopanes, benzohopanes, monoaromatic steroids and 1- and 4-methyltriaromatic steroids. Distributions of the secohopanes and aromatic steroids are similar to those in the lamosític shales. Dimethyl- or ethyl-substituted triaromatics (m/z 259) were not detected. Analysis of the monoaromatic steroids revealed the presence of rearranged components in proportions equivalent to those noted in the miscellaneous algal-rich shales (Section 4.3.3.1.4.2).

Although containing a similar suite of compounds to the above samples, the aromatic profile of the Best Cannel (Fig.4.61b) is biased towards lower molecular-weight components, but this bias may reflect rank rather than type influence as the maturity of the sample, from biomarker data, probably exceeds $\%R_o$av 0.70. Monoaromatic steroids were not detected. In contrast to the Rum Coal and

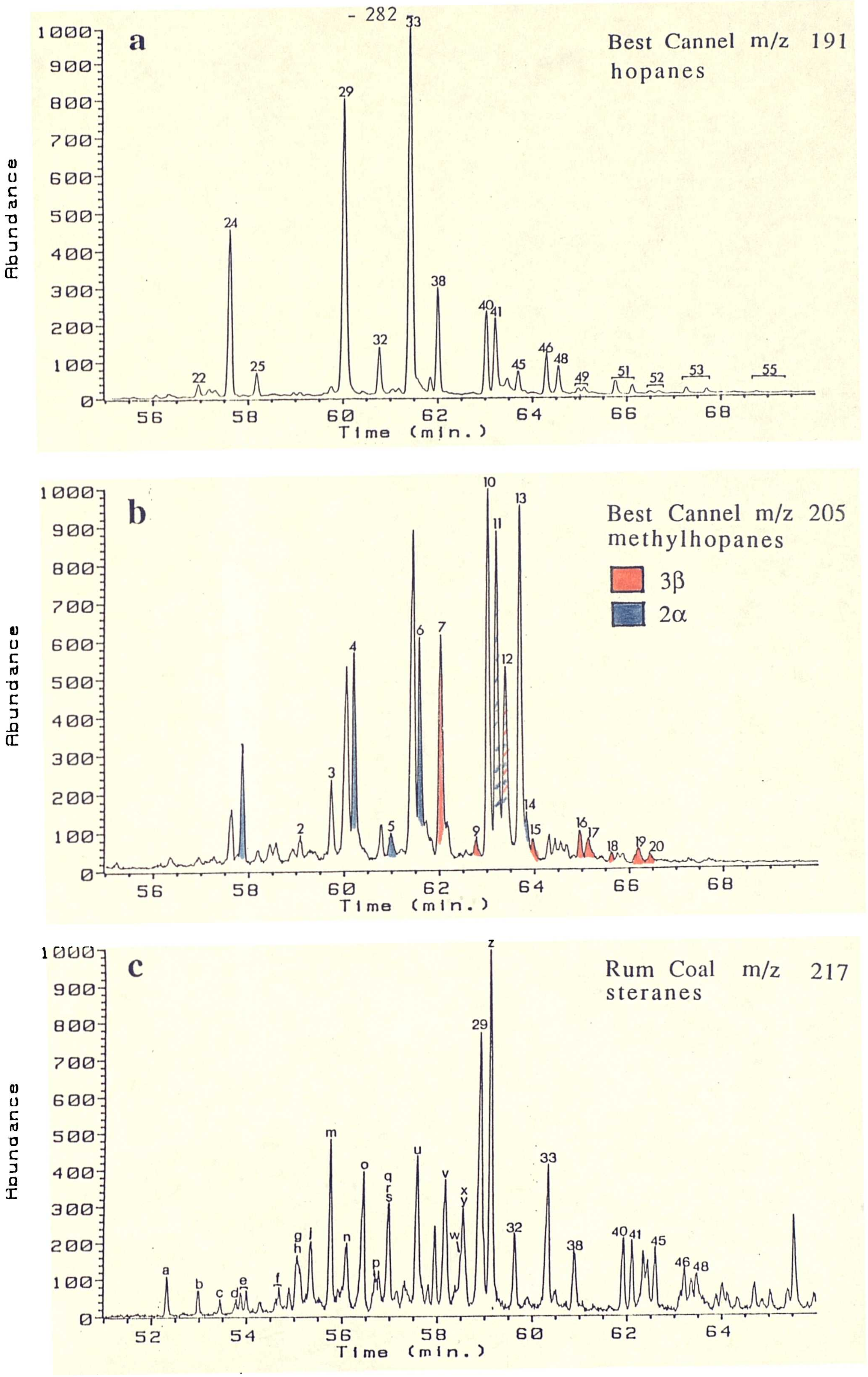


Fig.4.60 Distribution of hopanes, methylhopanes and steranes in the sapropelic coals (peak assignments in Tables 4.5, 4.6 and 4.10).

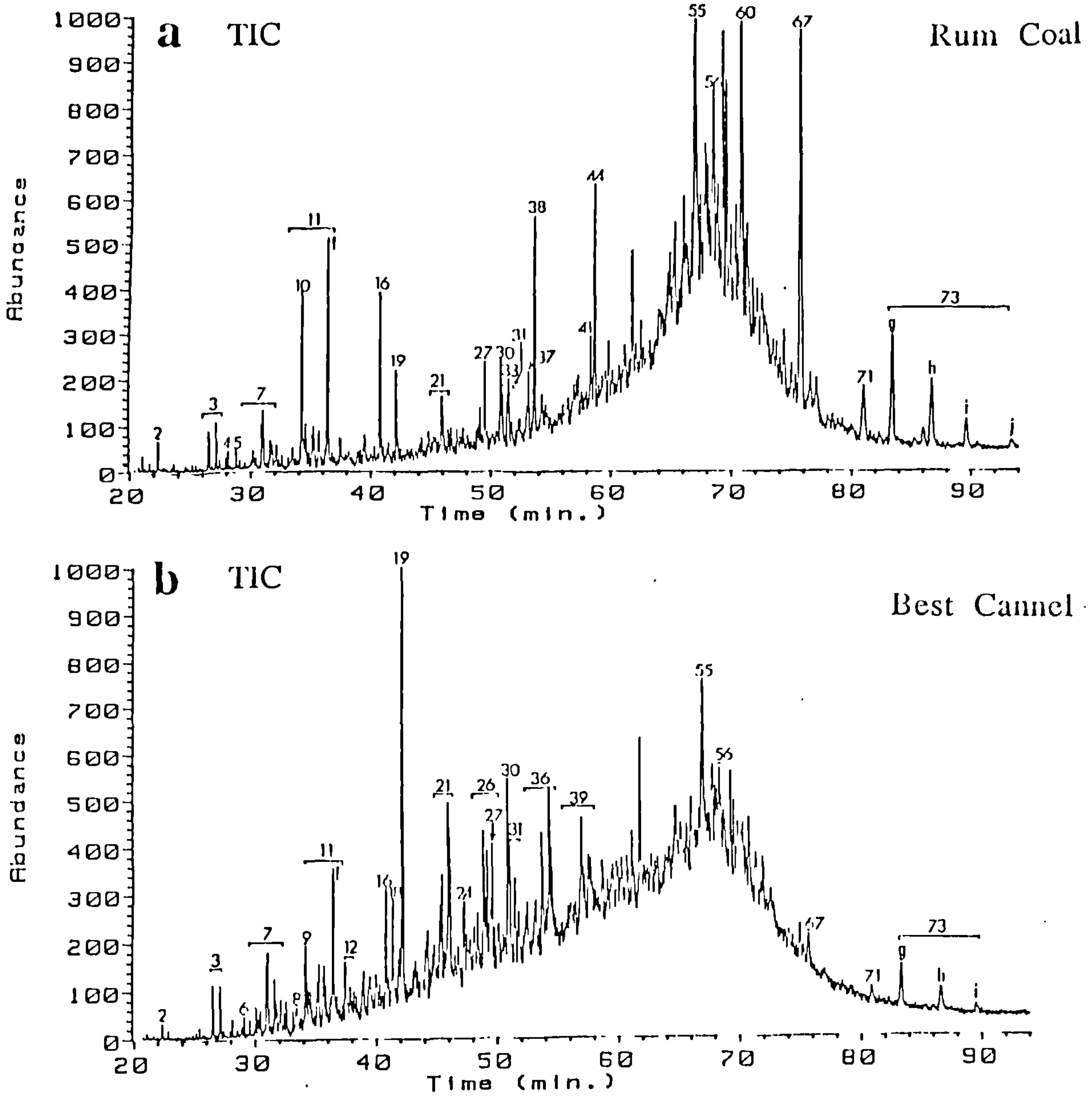


Fig.4.61 Distribution of aromatic hydrocarbon compounds in the sapropelic coals (peak assignments shown in Table 4.7).

SMW14, biphenyl and alkylbiphenyls could be identified, albeit in relatively minor amounts.

All three sapropelic coals contain a suite of pyrolytic-like PAH distributions akin to those noted in the humic coals.

4.3.3.2.4 Woody and Vitrinitic Materials

4.3.3.2.4.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of the wood and "vitrinite" from Orrock Quarry and of vitrinitic matter from East Kirkton Quarry and the Coalyard Hill neck are shown in Fig.4.62.

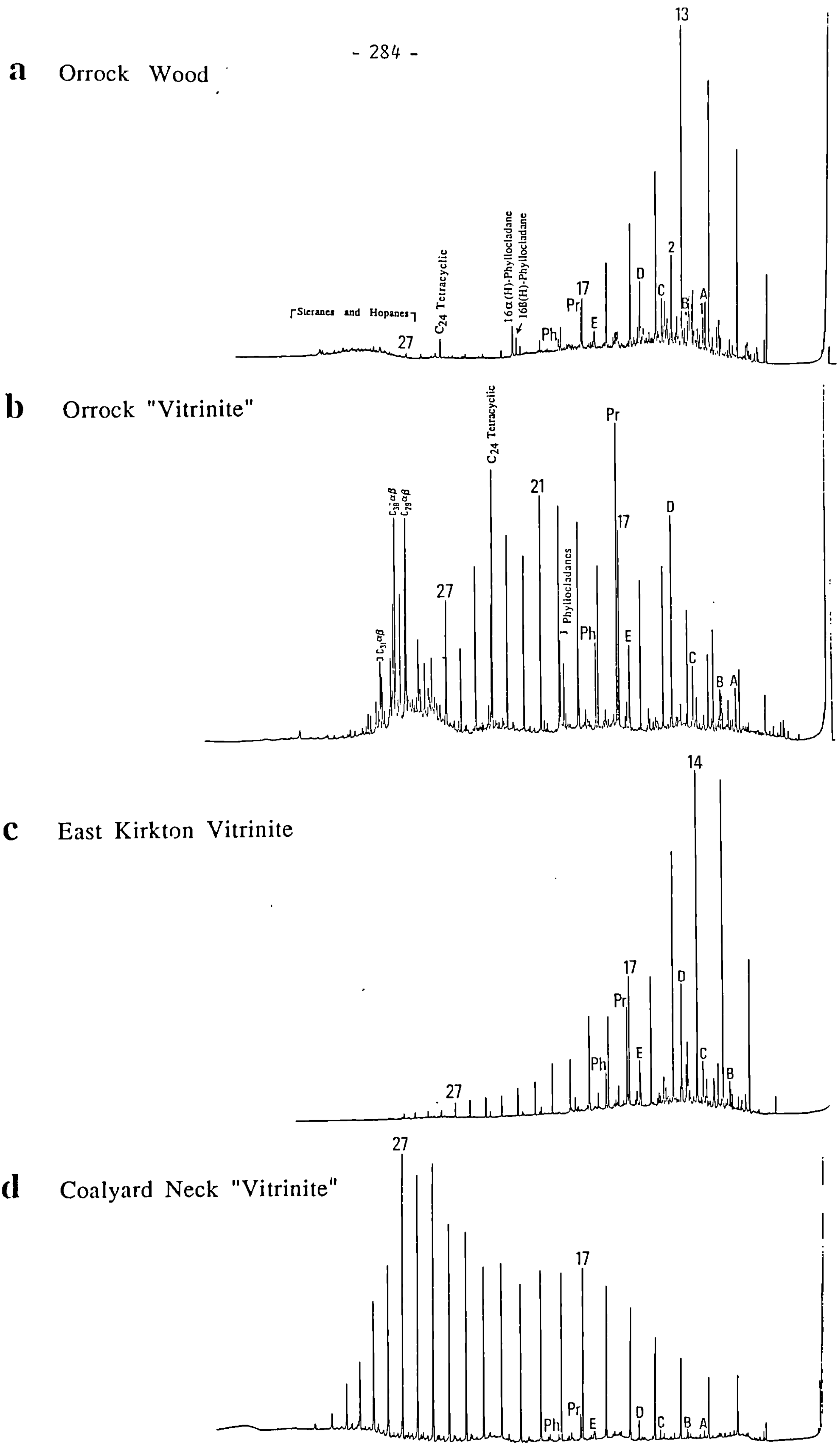


Fig.4.62 Gas chromatograms of the saturated hydrocarbon fractions of woody and vitrinitic materials (see Table 4.4 for isoprenoid assignments).

Although the Orrock samples are of very low maturity (%$R_o$av=0.39), no unsaturated hydrocarbons were detected following chromatographic separation of the aliphatic hydrocarbon fractions using argentation TLC. Despite the similarity of their petrographic characteristics and rank, the hydrocarbon distributions of the Orrock samples differ markedly. The saturated hydrocarbon fraction of the Orrock wood (Fig.4.62a) shows a smooth *n*-alkane distribution, in the range C_{10}-C_{27}, which is heavily skewed towards the low molecular-weight end of the gas chromatogram and maximises at *n*-C_{13}. The very low concentration of *n*-alkanes beyond *n*-C_{18} is unusual since this distribution does not conform to the pattern of *n*-alkane components observed in higher-plant extracts (Douglas and Eglinton 1966) or in extracts of sediments which are known to have received a contribution from vascular-plant matter (Bray and Evans 1965). In such extracts, long-chain *n*-alkanes with marked OEPs are often major constituents of the saturated hydrocarbon fractions, where they are considered to originate from the protective wax-rich cuticular layers in plants. It should be noted, however, that there have been reports of hydrocarbon distributions in higher-plant extracts in which *n*-alkanes $<C_{25}$ constitute a significant part of the total fraction and, furthermore, have no odd-carbon-number preference (Kaneda 1969; Hardman and Brain 1971). Saurian-type *n*-alkane distributions encompassing significant quantities of medium molecular-weight *n*-alkanes showing no OEP have also been documented in heartwoods (Grice *et al.* 1968). Given the above caveats to the "conventional" vascular-plant *n*-alkane distributions, it is possible that the Orrock wood represents a heartwood in which there is no waxy cuticular material to provide large amounts of long-chain *n*-alkanes with pronounced OEPs.

Although the alkane distribution in Fig.4.62a may represent a primary geochemical signature inherited from humic percursor material, the dominance of *n*-alkanes over the C_{10}-C_{20} range could also indicate a bacterial contribution because extant bacteria contain straight-chain hydrocarbons and fatty acids with comparable carbon-number distributions, which often show no odd-over-even preference. (Han and Calvin 1969a; Han 1970; Albro 1976; Nes and Nes 1980). Iso- and anteiso alkanes are also prominent within the same range as the major *n*-alkanes and, in association with the "hump" of unresolved components, provide further evidence of the bacterial activity (Han 1970) which was clearly demonstrated by TEM examination. Other compounds eluting between *n*-C_{12}-C_{15} were identified as bicyclic alkanes from gc-ms analysis. The peaks eluting between *n*-C_{20} and *n*-C_{21} correspond to the tetracyclic diterpanes 16β(H)- and 16α(H)-phyllocladane whilst the peak eluting between *n*-C_{24} and *n*-C_{25} is a C_{24} tetracyclic compound. The basis of identification for these compounds and their significance is discussed later.

The sample of vitrinitic matter from the lower floor of Orrock Quarry (ORR V) has a broadly saurian-type *n*-alkane distribution with no marked skew and a pronounced OEP throughout most of the range C_{15}-C_{27} (Fig.4.62b). The *n*-alkane distribution complies more with the general pattern usually observed in higher-plant materials than does the saturated hydrocarbon distribution of the Orrock wood. Straight-chain alkanes are difficult to resolve in the gas chromatogram beyond *n*-C_{29} because they are swamped by the very high concentrations of polycyclic alkanes present. As in the Orrock wood gas chromatogram, additional components discernible in the trace are large quantities of phyllocladanes, a C_{24} tetracyclic alkane and bicyclanes.

The highly skewed *n*-alkane trace of the coal ball-type vitrinite from East Kirkton Quarry (Fig.4.62c) resembles that shown in Fig.4.62a although in the former the *n*-alkanes >C_{18} are more prominent, there is an OEP (C_{15}-C_{19} range), and the distribution maximises at *n*-C_{14}. Like the Orrock wood, the distribution points to a lack of components derived from waxy cuticular material and/or a bacterial contribution. The lower *n*-alkane/isoprenoid ratios may reflect the slightly higher maturity of the sample than that of the Orrock wood.

Of the four samples investigated in this suite, the *n*-alkane distribution of the Coalyard "vitrinite" conforms most closely to the distributions recorded in extracts from sediments known to have had significant higher-plant input (e.g. Bray and Evans 1965): there is a marked bias in the alkane distribution defined by enhanced concentrations of *n*-C_{21}-C_{27} alkanes, coupled with an odd-carbon-number preference. Also evident is the low abundance of isoprenoids relative to the *n*-alkanes.

From the gc analysis of the above samples it is apparent that extracts of organic matter derived from humic precursors can display a marked variation in the shape of the *n*-alkane envelope. Although the presence of high molecular-weight *n*-alkanes with an OEP is often reported as indicating a terrestrial input to sediments, the lack of this signature should not automatically be taken to indicate a lack of input of land-plant debris unless backed up by other evidence. Relatively low concentrations of straight-chain alkanes in the C_{25} range may indicate a lack of waxy cuticular material in the sediment and/or a contribution from the bacterial biomass.

Gas Chromatography-Mass Spectrometry (GC-MS)

Mass fragmentograms showing the distribution of terpanes in the samples from Orrock Quarry are shown in Figs 4.63a and b. The mass spectra of selected tetracyclic components are shown in Fig.4.64.

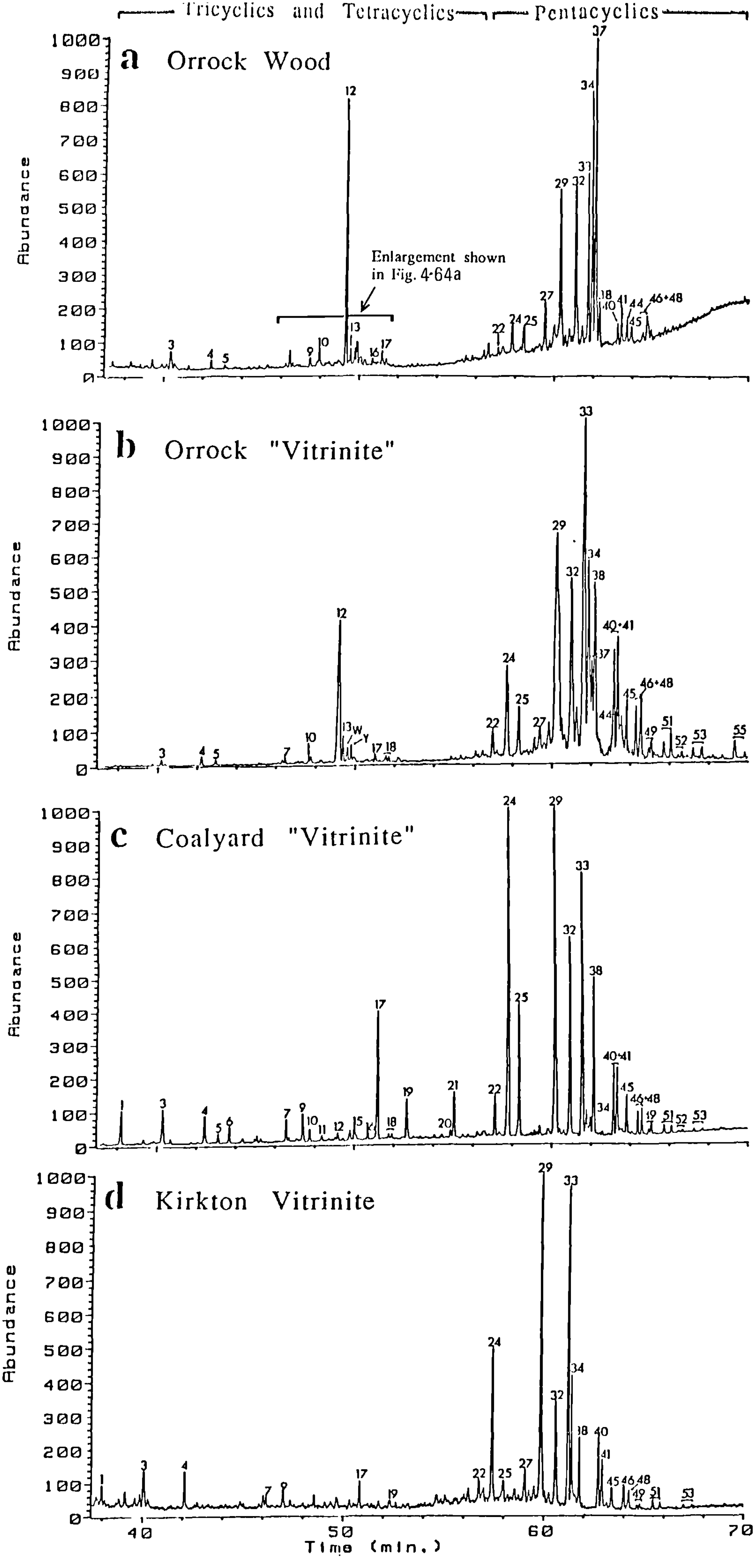


Fig.4.63 M/z 191 fragmentograms showing distribution of 3- to 5-ringed terpanes in the woody and vitrinitic materials analysed (peak assignments in Table 4.5).

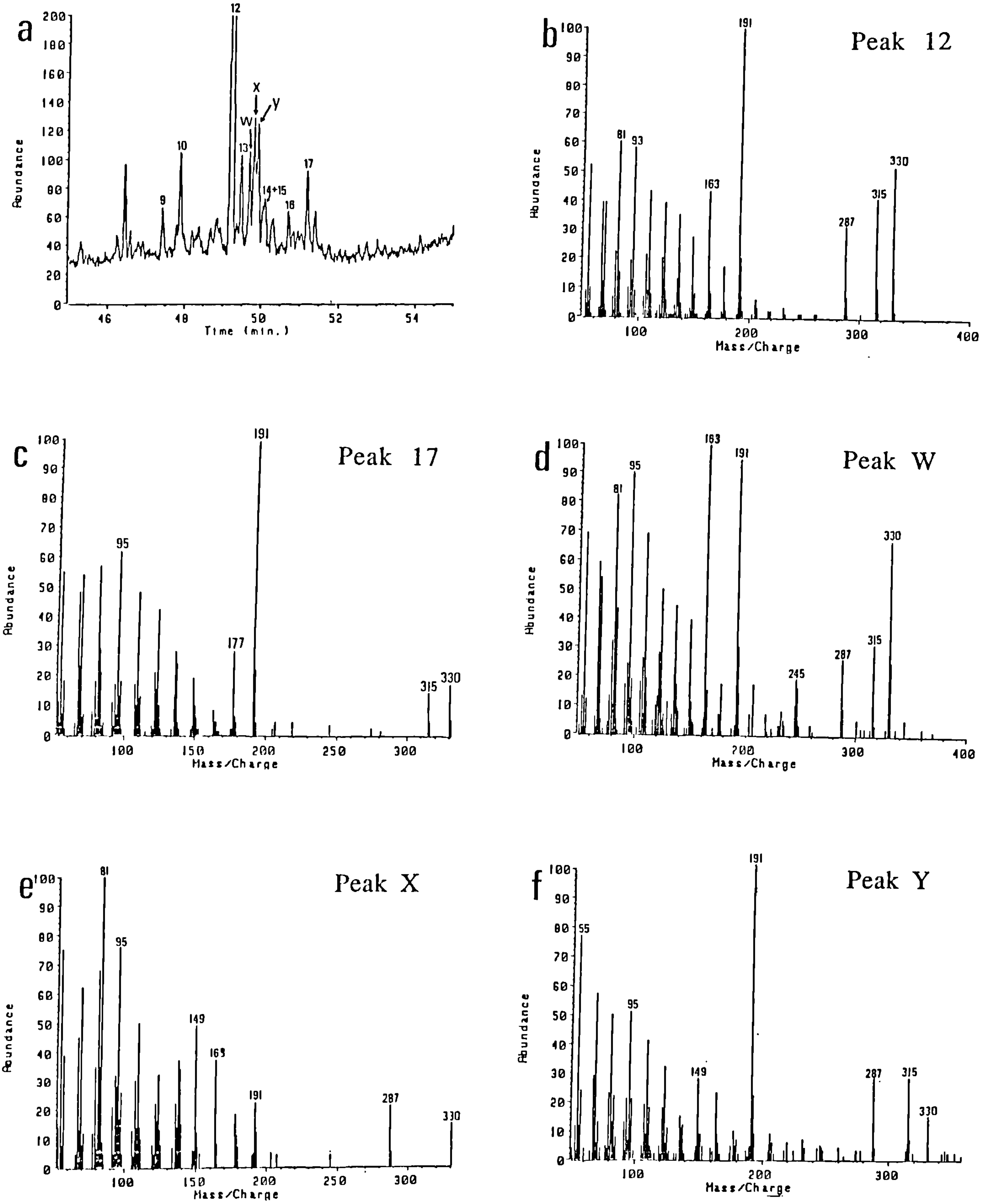


Fig.4.64 Mass spectra of tetracyclic terpanes occurring in the Orrock wood. Fig.4.64a is an enlargement of the 45-55min time range of Fig.4.63a (peak assignments in Table 4.5).

Apart from the prominent C_{24} tetracyclic component (peak 12; Fig.4.64b), which is present in sufficient abundance to be readily discernible in the gas chromatograms, the content of tri- and tetracyclic terpanes with major fragment ions of m/z 191 is low in the Orrock samples, relative to the pentacyclics. In addition to the C_{24} secohopane (peak 17; Fig.4.64c) and peak 12, four other tetracyclic components were identified in the Orrock wood, three of which (W,X,Y) appear to be novel compounds as a literature search failed to reveal any previously published mass spectra of tetracyclic terpanes similar to those in Figs 4.64,d,e and f. Peaks W and Y were also recognised in the Orrock "vitrinite".

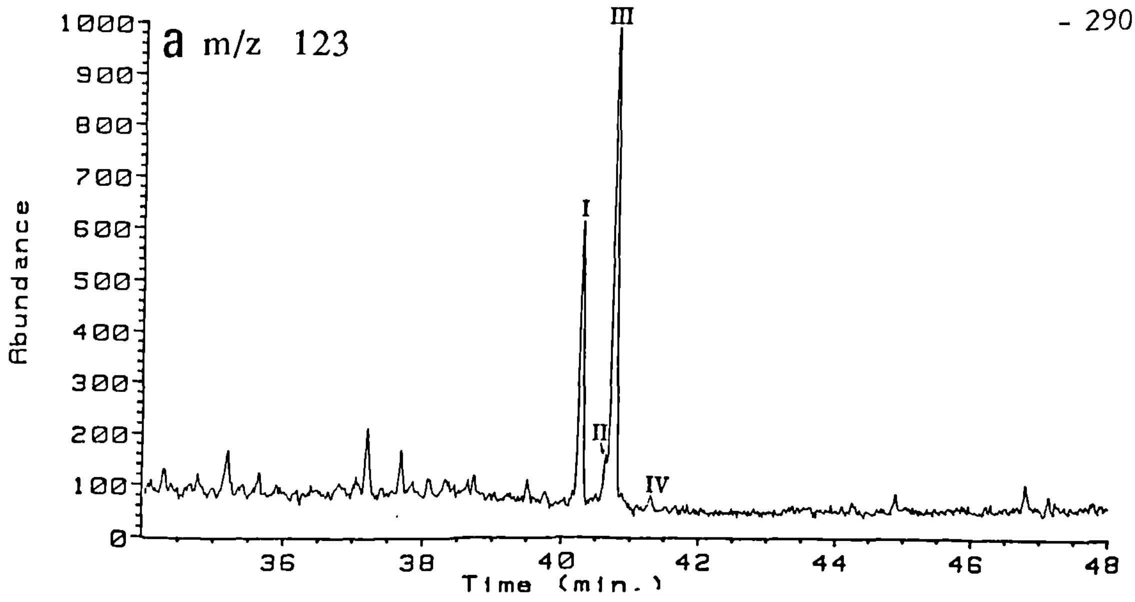
The hopane distributions in the Orrock samples are qualitatively similar. The dominance of 22R epimers in the extended αβ hopane series, coupled with the presence of 17β(H), 21β(H) hopanes, confirms the immature nature of the samples. The unknown C_{29} pentacyclic triterpane which elutes after the $C_{30}\alpha\beta$ hopane (peak 34) is in relatively high abundance in both samples. The 28,30-bisnorhopane (peak 27) is also present in both samples, but is particularly pronounced in the Orrock wood.

Tetracyclic and tricyclic components are more prominent in the m/z 191 fragmentograms of the vitrinite materials from East Kirkton and the Coalyard Hill neck (Figs 4.63c,d). The 17,21-secohopanes are relatively prominent in the latter sample while enhanced concentrations of the C_{19}-C_{21} tricyclics are observed in the former. Several of the tetracyclics present in the Orrock wood are also found in the Coalyard "vitrinite". No C_{24} tetracyclics other than the C_{24} 17,21-secohopane (peak 17) could be recognised in the Kirkton sample.

The hopane distributions in the Kirkton and Coalyard samples are simpler than those occurring in the Orrock samples, which is consistent with the higher rank of the former samples. In contrast to the Orrock samples, the $C_{29}\alpha\beta$ hopane in the Coalyard and Kirkton samples dominates over the $C_{30}\alpha\beta$ homologue.

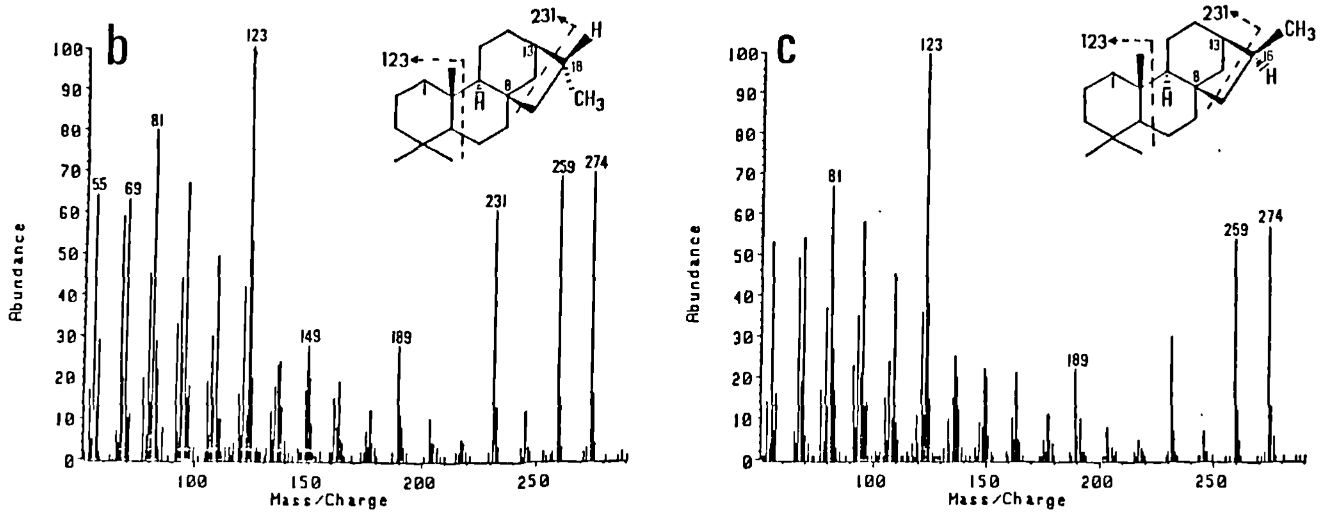
The two peaks eluting between *n*-C_{20}-C_{21} and *n*-C_{19}-C_{20} in the gas chromatograms of the Orrock wood and "vitrinite" respectively were identified as the tetracyclic diterpanes 16β(H)- and 16α(H)-phyllocladane, based on the similarities of their mass spectra (Figs 4.65b,c) and retention times (Fig.4.65a) with those of Noble *et al.* 1985a,b). These compounds were also identified in the Coalyard and Kirkton samples, but they were not present in sufficient quantities for them to be major constituents in the gas chromatograms.

Phyllocladanes have been recognised in a variety of geological materials: hard coals, sediments and oils (Noble *et al.* 1985a,b, 1986; Noble 1986), lignites (Hagemann and Hollerbach 1980) and, in the case of the 16α(H) epimer, as the mineral bombiccite (Serantoni *et al.* 1978). In biological materials, the precursor phyllocladene has only been identified in the resins of conifers (Aplin *et al.* 1963;



Peak I 16β(H)-Phyllocladane

Peak III 16α(H)-Phyllocladane



Peak II *ent*-16β(H)-kaurane

Peak IV *ent*-16α(H)-kaurane

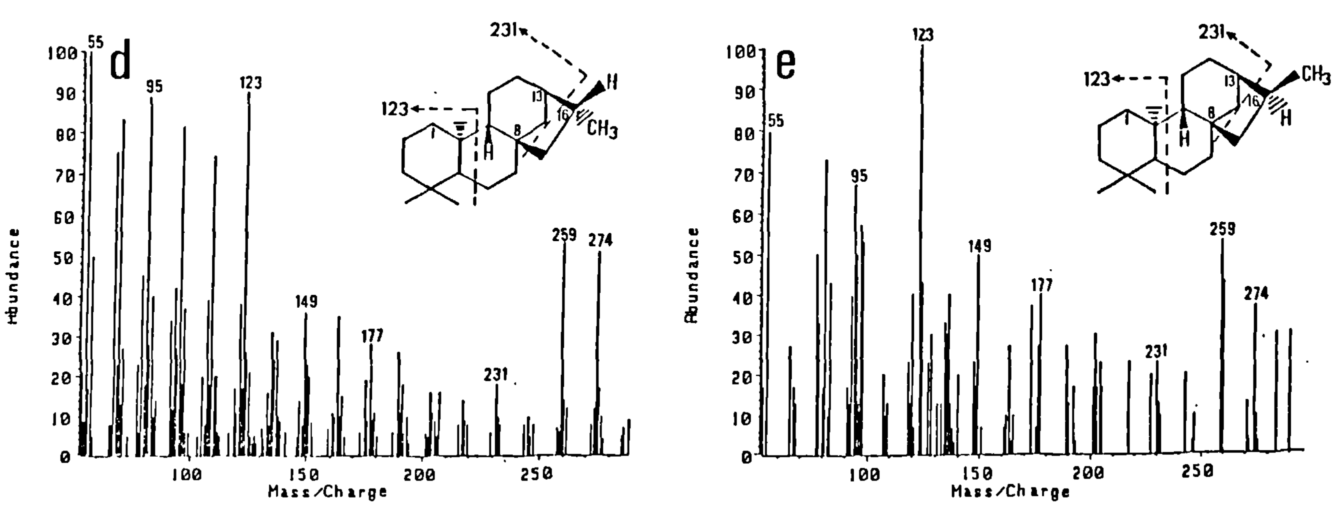


Fig.4.65 Distribution and mass spectra of tetracyclic diterpenoids in the Orrock wood.

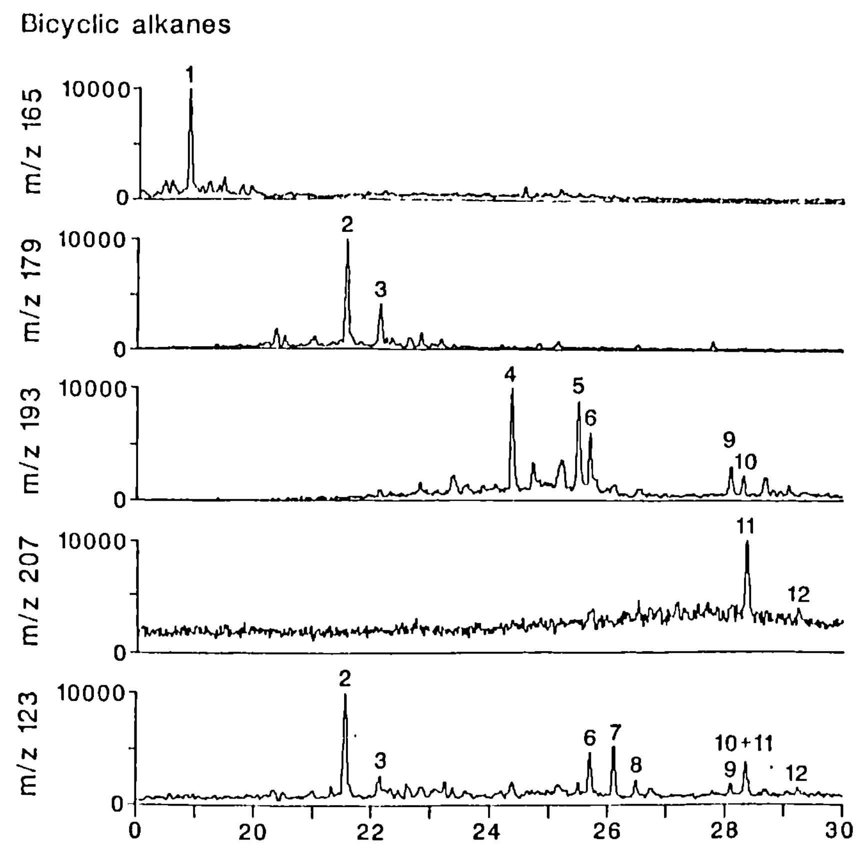
Hanson 1972). The presence of the saturated derivatives of phyllocladene in the four samples points to their organic matter originating in a resin-bearing precursor of the conifers, possibly *Cordaites*, a widespread primitive genus in the Carboniferous.

Noble (1986) and Noble *et al.* (1985a) have reported diterpenoids varying in structural type in coals and sediments of widely differing ages. Phyllocladane and kaurane appear to be the two diterpenoids dominant in samples older than the Mesozoic, although the oldest sediments in which Noble (1986) has found these diterpenoids are of Permian age. The present work cites the occurrence of these diterpenoids in Carboniferous samples although only trace amounts of the kaurane epimers were identified (in the Orrock wood only; Fig.4.65a). None of the other diterpenoid classes (e.g. rimuanes,labdanes, beyeranes, abietanes, pimaranes) is represented in the Orrock or Coalyard samples, but two small peaks with relative retention times identical to those of the inferred pimarane-related compounds in Fig.4.41c were detected in the Kirkton sample, although satisfactory mass spectra could not be acquired to prove their identities.

Gc-ms analysis revealed the presence of a series of bicyclic sesquiterpenoids in all four samples, the compound distributions all being very similar. The bicyclane content of the Orrock wood was very high, relative to other components, so that some members of the series could be readily discerned among the branched and cyclic compounds in the gas chromatogram. The distribution of bicyclic components is exemplified by that for the Orrock wood (Fig.4.66a). The C_{14}-C_{16} members of the series have previously been reported in oils and sediments of different ages from diverse regions of the world (Bendoraitis 1974; Kagramanova 1976; Philp *et al.* 1981; Richardson and Miller 1982; Alexander *et al.* 1983, 1984b; Dimmler *et al.* 1984; Weston *et al.* 1989). The mass spectrum of peak 1 (Fig.4.66b) is consistent with a C_{13} bicyclic sesquiterpenoid which has not, to the author's knowledge, been previously recorded in the literature. This compound was also detected in the Orrock and Kirkton samples, but not in the Coalyard "vitrinite", although its absence could be due to evaporative loss.

Sterane (m/z 217) fragmentograms for the four samples are shown in Fig.4.67. The marked dominance of the $C_{29}\alpha\alpha\alpha 20R$ sterane over the C_{27} homologue in all samples except the Kirkton vitrinite places them within the "terrestrial-higher plant" region of the ternary plot in Fig.4.53. The predominance of the $20\alpha\alpha\alpha R$ isomers is consistent with the low maturity of the samples as indicated by microscopy.

The high concentration of $\alpha\beta\beta$ steranes in the Orrock wood is inconsistent with the low maturity of the sample. Anomalously high abundances of $\alpha\beta\beta$ steranes a



Peak assignments for bicyclic alkanes

1	C_{13} bicyclic alkane	5	C_{15} bicyclic alkane	9	C_{16} bicyclic alkane
2	C_{14} bicyclic alkane	6	8β(H)-drimane	10	C_{16} bicyclic alkane
3	C_{14} bicyclic alkane	7	C_{15} bicyclic alkane	11	8β(H)-homodrimane
4	C_{15} bicyclic alkane	8	C_{16} bicyclic alkane	12	8α(H)-homodrimane

Fig.4.66a Mass fragmentograms of C_{13}-C_{16} bicyclic alkanes (peak 2 corresponds to the C_{14} bicyclic alkane of Vorob'eva *et al.* 1978; peaks 3-5 are the C_{14} and C_{15} bicyclics of Bendoraitis 1974).

b

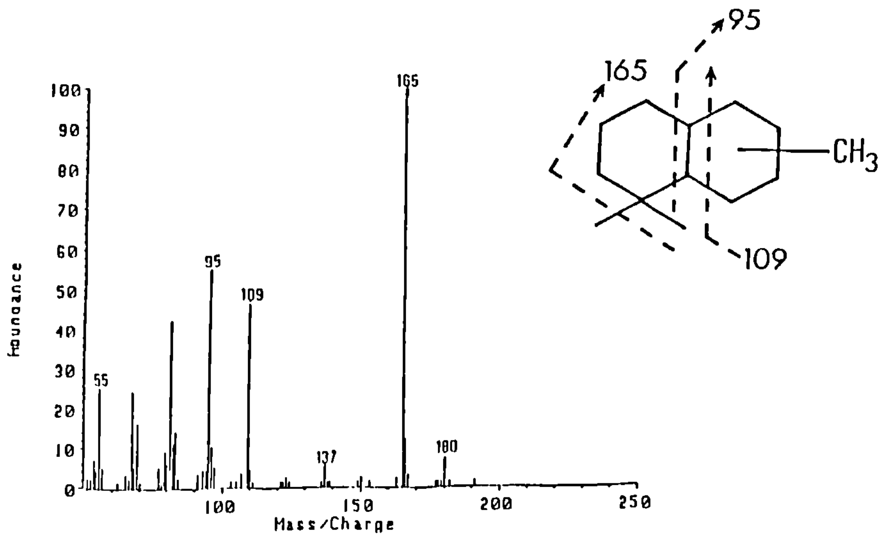


Fig.4.66b Mass spectrum and possible structure of peak 1, a C_{13} bicyclic alkane.

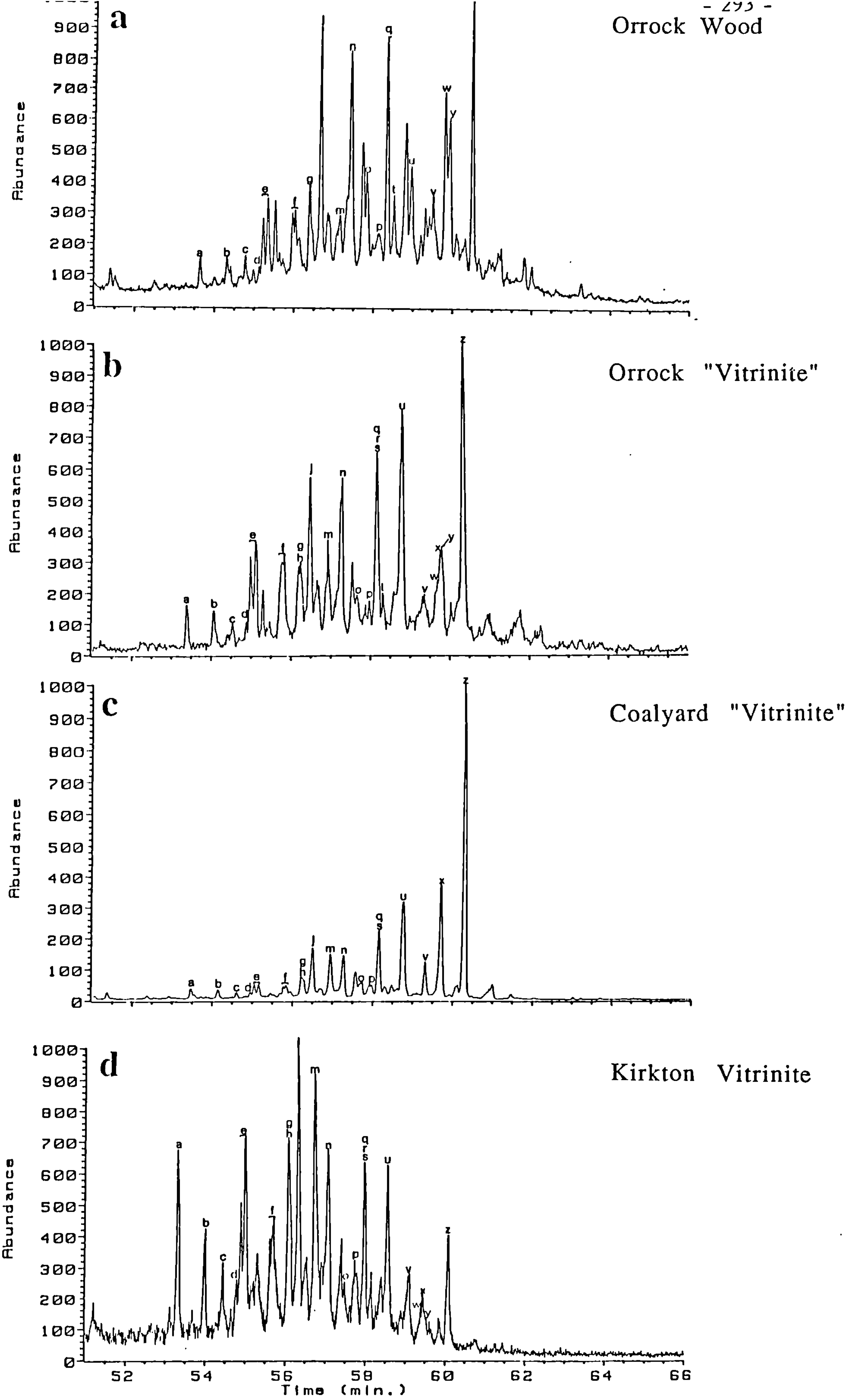


Fig.4.67 M/z 217 fragmentograms showing the distribution of steranes in the woody and vitrinitic materials (peak assignments in Table 4.6).

have been observed by other workers in low-rank samples which were deposited in hypersaline environments (Ten Haven *et al.* 1985, 1986). Such large amounts of αββ steranes, given the low rank of Orrock wood, contradict the traditionally accepted view that maturation-induced isomerisation is the source of αββ steranes (Mackenzie *et al.* 1980). Input from specific precursor sterols present in hypersaline environments has been proposed as an alternative source of αββ steranes (Rullkötter *et al.* 1984; Ten Haven *et al.* 1985, 1986; Peakman and Maxwell 1988), although the mode of occurrence of the wood makes this suggestion highly unlikely. An alternative explanation may lie in the volcanoclastic matrix, which has been highly altered to a montmorillonite-chlorite mixture set in a matrix of calcite (D.A.C.Manning, *personal communication*). Catalytic isomerisation and rearrangement reactions at acid sites in the clay minerals, perhaps enhanced when the matrix was still warm, may have promoted the formation of αββ steranes from suitable precursor sterols. Although the host-rock mineralogy of the other samples was not investigated, the low abundance or absence of αββ steranes in the "vitrinites" may reflect a difference in the chemical constitution of the matrices enveloping the organic matter. The catalytic effects of the matrix could also account for the high concentrations of diasteranes present in the Orrock and Kirkton samples. The catalytic effects of clay minerals on organic matter in tuffaceous sediments (where the clay minerals originate from the breakdown of igneous materials) are likely to be much greater than the rearrangements induced by active clay minerals in argillaceous sediments (D.A.C.Manning, *personal communication*). This situation arises because of the higher concentrations of active acid sites present in the altered tuffaceous matter which is also in close proximity to the organic clasts because it envelopes them. In argillaceous sediments active clay minerals are dispersed throughout the matrix in which organic matter is invariably present in the form of small phytoclasts; thus the potential for clay-catalysed rearrangement of steroidal precursors is greatly diluted.

That the diasterane contents of the Orrock and Kirkton samples are amongst the top ten highest levels recorded in samples from the Midland Valley lends further support to the suggestion that the intimate mixing of volcanic and organic matter may have an important influence on controlling the distributions of steranes whose presence is dependent on clay mineral-organic interactions.

Low concentrations of suitably active clay minerals in the host-rock matrix of the Coalyard "vitrinite" may explain the relatively low abundance of diasteranes in the sample and also the absence of αββ steranes.

4.3.3.2.4.2 Aromatic Hydrocarbons

TIC chromatograms showing the variation in the distribution of aromatic hydrocarbons in the woody and vitrinitic materials analysed are shown in Fig.4.68. The chromatogram of the vitrinitic material from Orrock Quarry is not included since, apart from the preponderance of the high molecular-weight "hump", it is very similar to that of the Orrock wood.

Despite the Carboniferous age of the sample, the relative simplicity of the aromatic distribution of the Coalyard Hill sample (Fig.4.68a) is characteristic of the PAH distributions recorded in recent soils, sediments and airborne particulates in which the components derive from natural (forest fires) or anthropogenic combustion and/or pyrolysis processes. Parent PAH dominate the distribution, with greatly reduced contributions from their corresponding alkyl homologues. No high molecular-weight compounds based on steroid or terpenoid skeletons were detected. It therefore seems likely that the aromatic distribution in the Coalyard sample is entirely pyrolytically- or combustion-derived. Additional support for this suggestion stems from the overall dominance of compounds with three or more condensed rings, this distribution being highly characteristic of combustion-derived PAH suites (Prahl and Carpenter 1983). Furthermore, the presence of members of the 4H-cyclopenta[*def*]phenanthrene series (peaks 22, 24, 31) is also indicative of a high-temperature origin for the PAH suite in the Coalyard material, since these compounds, possessing a sterically-strained 4,5 position, are recorded in much greater abundance in high-temperature combustion products than in fossil fuels (Youngblood and Blumer 1975; Lee *et al.* 1976b). It is thought that rapid quenching of pyrolysis gases preserves the strained 4,5 position in the former case, while extended equilibration in the subsurface leads to its partial elimination during coalification and petroleum formation (Youngblood and Blumer 1975).

The aromatic distributions in the Orrock and East Kirkton samples (Figs 4.68b,c) are compositionally more complex than that of the Coalyard "vitrinite", but still contain a prominent pyrolytic-like PAH suite, which is superimposed on a "hump" of unresolved components.

Alkylated naphthalenes and phenanthrenes are more abundant, relative to their corresponding parent compounds, than in the Coalyard "vitrinite", suggesting that these may, in part, be diagenetically-derived components. Other compounds deriving from the aromatisation of biogenic precursors were identified, e.g. mono- and triaromatic steroids, terpenoids (excluding benzohopanes) and naphthalene and phenanthrene derivatives such as retene, simonellite and cadalene. The last three named compounds were present in only minor quantities.

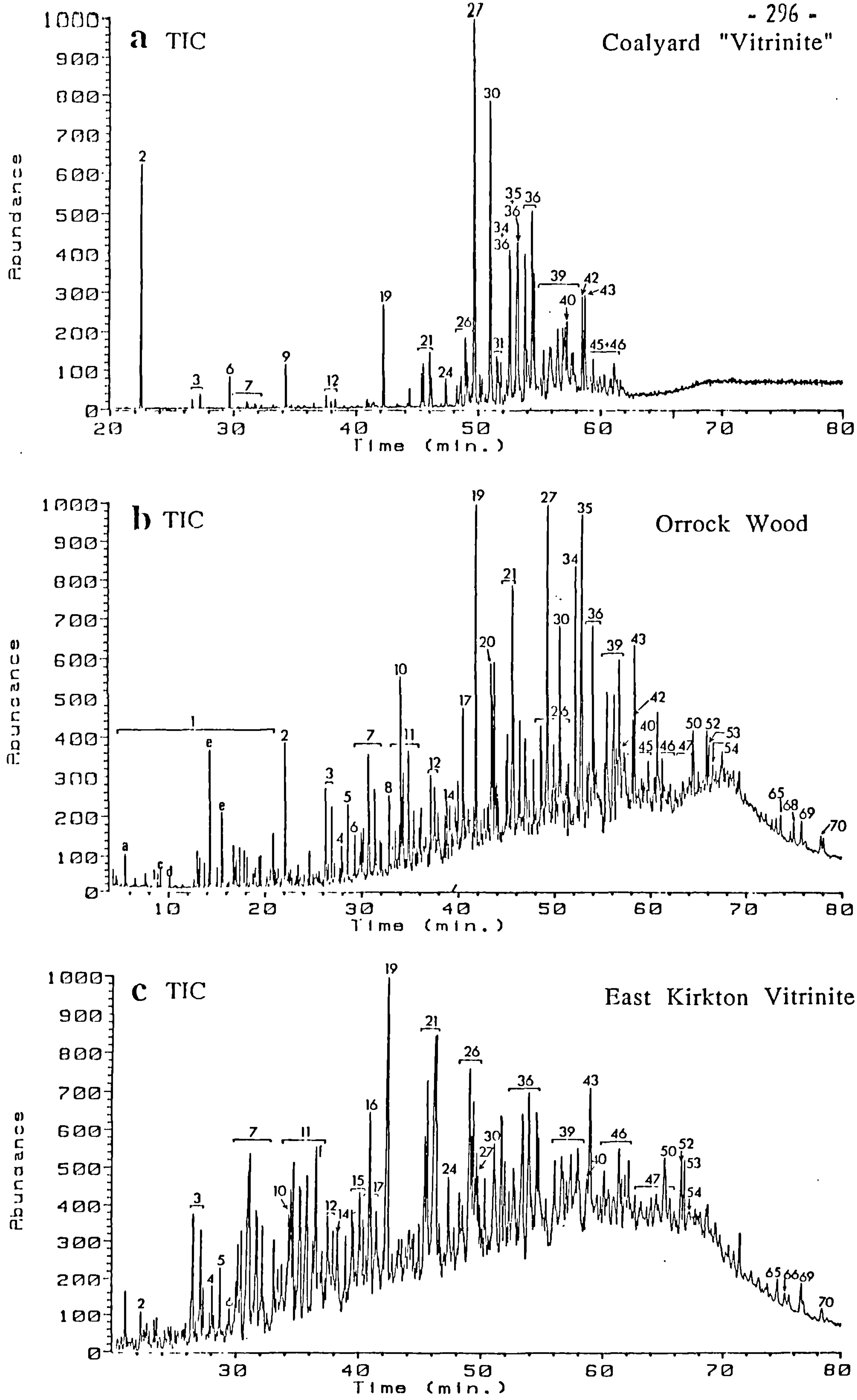


Fig.4.68 Distribution of aromatic hydrocarbons in the woody and vitrinitic materials (peak assignments in Table 4.7).

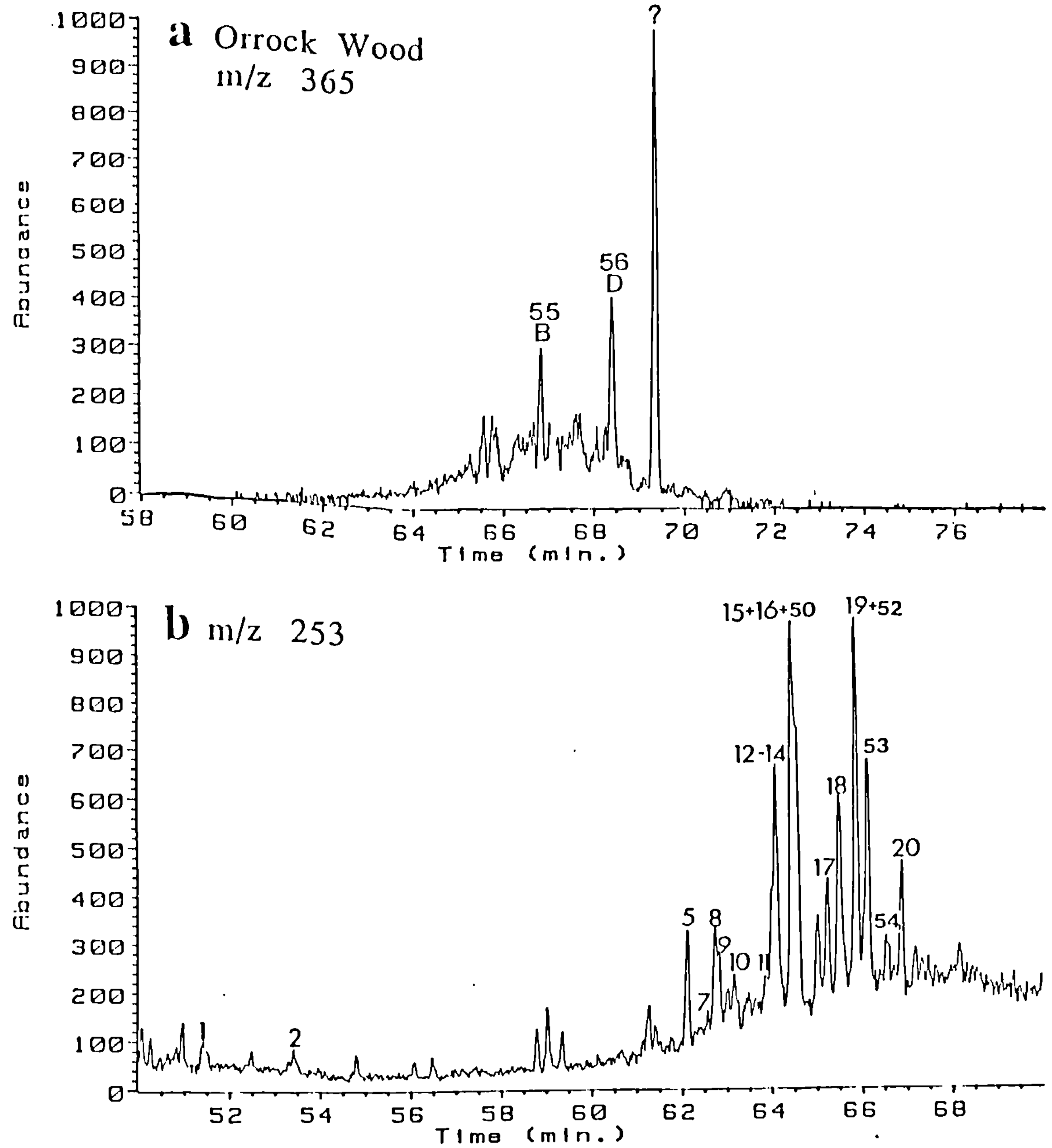


Fig.4.69 Distribution of 8,14-secohopanes (a) and monoaromatic steroids (b) in the Orrock wood (peak assignments in Tables 4.7 and 4.8).

The distributions of the 8,14-secohopane series in the samples from Orrock Quarry (Fig.4.69a) differ from the patterns seen in other coals and sediments in that only the later-eluting components in the doublets shown in Fig.4.25 are present. Considering the very low rank of these samples, it is possible that peaks 55B and 56D have a structural configuration inherited from the natural-product precursors while peaks 55A and 56C are isomerisation products which develop in response to increased thermal stress.

Monoaromatic steroid profiles for the Orrock and East Kirkton samples closely resemble that shown in Fig.4.69b. Rearranged components are relatively less abundant than in the humic coals and vitrinites discussed in the last section. Major interference from benzofluoranthenes, benzopyrenes and perylene can be seen in the m/z 253 fragmentograms. The pattern of methyltriaromatics in all samples is similar to that found in the humic coals and sediments *viz.* enhanced concentration of peak 6 in the m/z 245 fragmentograms. The 1- and 4-methyltriaromatics exceed the non-methylated triaromatics in abundance in the Orrock wood and "vitrinite", but the reverse is true for the East Kirkton sample. Peaks belonging to the dimethyl- or ethyl-substituted triaromatic series, discernible on the m/z 259 fragmentograms, were prominent in the high molecular-weight regions of the TIC traces.

4.3.3.3 Marine Horizons

The localities of the samples extracted from the laterally-extensive named marine horizons are shown in Fig.4.70. Additional samples whose rank is less than $\%R_oav \approx 0.70$ and known, from palaeontological evidence, to be marine are SM1, 4 and 5 from the Lower Limestone Group succession near Pathhead, SM15 (Pittenweem Marine Band), SM29 (Wormistone Lower Marine Band), CO6 (*Lingula* shale), StA8, StA9 (part of the St.Andrews Castle Marine Band), FOF1b and samples AB2 and MK2 from the Kinghorn-Kirkaldy field section.

4.3.3.3.1 Extract Yields and Gross Compositions

Bitumen yields for the marine samples analysed vary from less than 1% to 8.6%. Yields for the Kelty Blackband suite are higher, overall, than for the other marine samples investigated and probably reflect their higher organic contents. TOC data, to which the yields should be normalised for comparative purposes, were only available for the Kelty Blackband samples. Carbon-normalised yields show that two samples (KBBI 185 and KBBI 385) have extract yields commensurate with those cited for samples lying in the zone of peak hydrocarbon generation (Tissot and Welte 1984). The vitrinite reflectance values of these two samples are $<\%R_oav=0.40$ and are not consistent with such high EOM yields. The Tmax value for KBBI 382 (445°C) places the sample within the oil window, thus the measured vitrinite reflectance is anomalously low, possibly due to suppression effects. Tmax data and observations from fluorescence microscopy indicate that the maturities of the remaining Kelty Blackband samples are relatively low, less than $\%R_oav=0.65$ (supported by biomarker evidence) and that the range of normalised EOM yields is principally reflecting variations in organic-matter type.

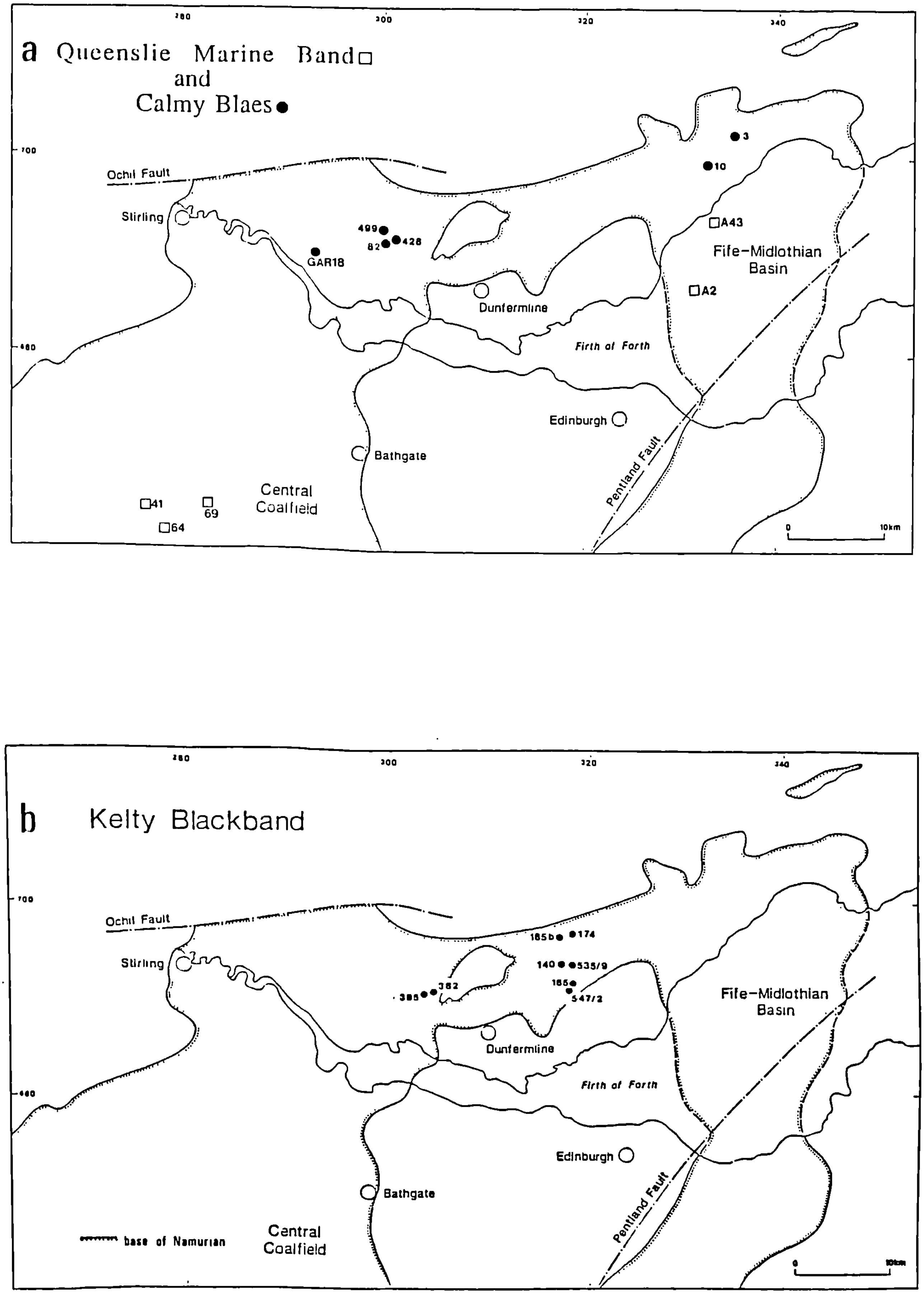


Fig.4.70 Locations of extracted samples from named marine bands.

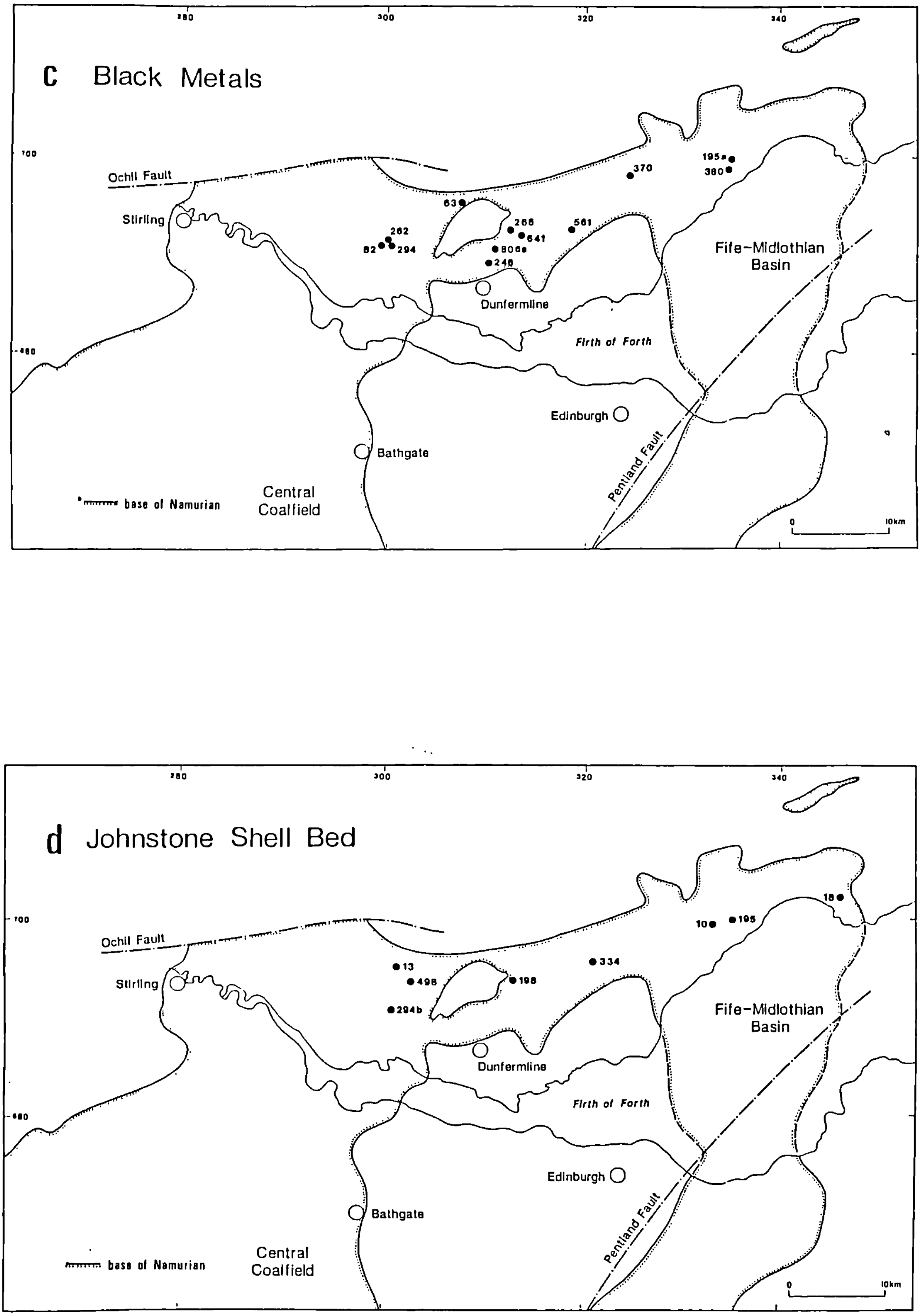
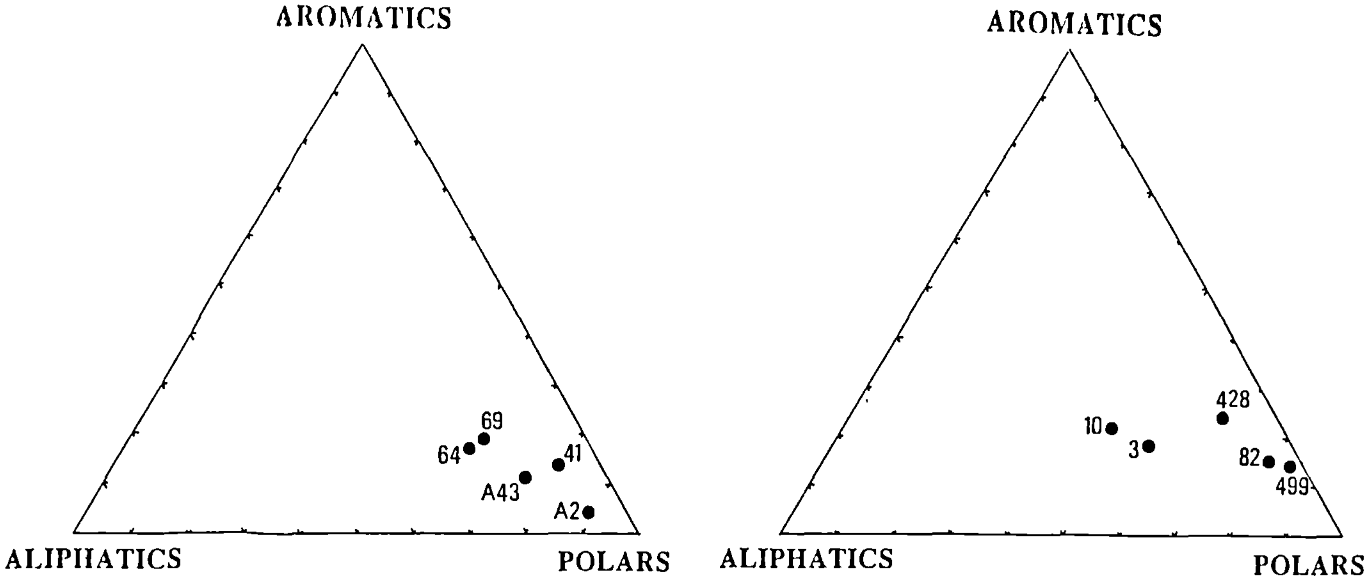
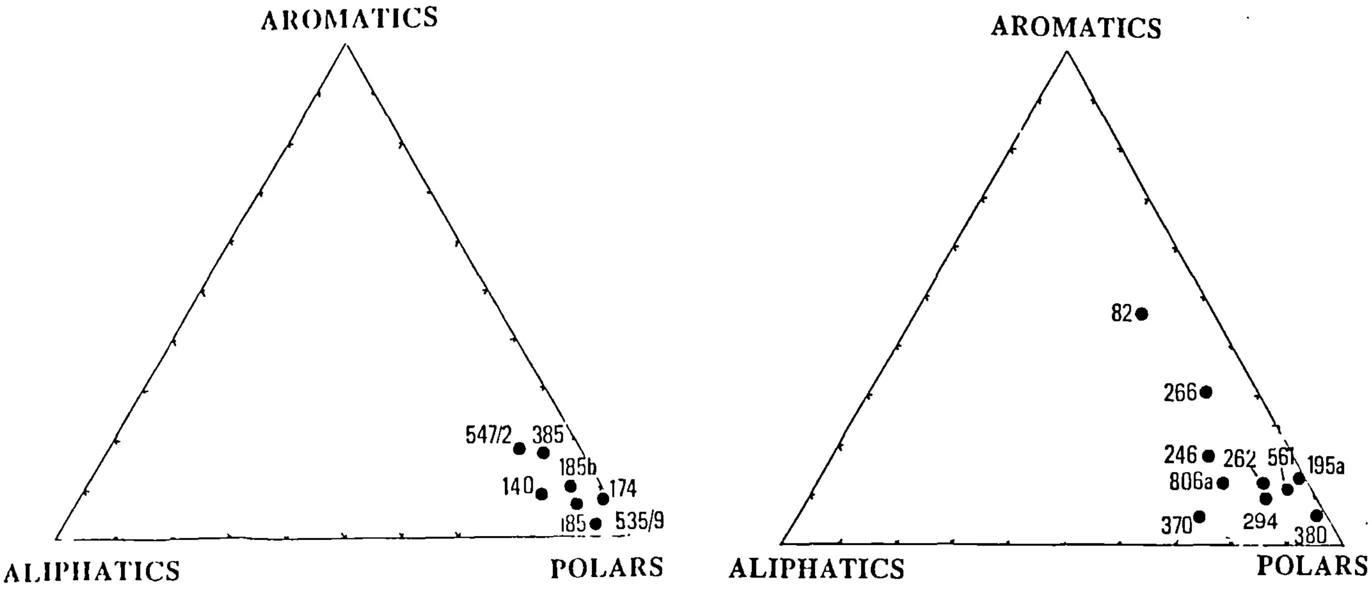

c Black Metals
280
300
320
340
700
680
Ochil Fault
Stirling
63
262
82
294
266
641
806a
246
561
370
195a
380
Dunfermline
Fife-Midlothian
Basin
Firth of Forth
Edinburgh
Bathgate
Pentland Fault
base of Namurian
Central
Coalfield
0
10km
d Johnstone Shell Bed
280
300
320
340
700
680
Ochil Fault
Stirling
13
498
294b
198
334
10
195
18
Dunfermline
Fife-Midlothian
Basin
Firth of Forth
Edinburgh
Bathgate
Pentland Fault
base of Namurian
Central
Coalfield
0
10km

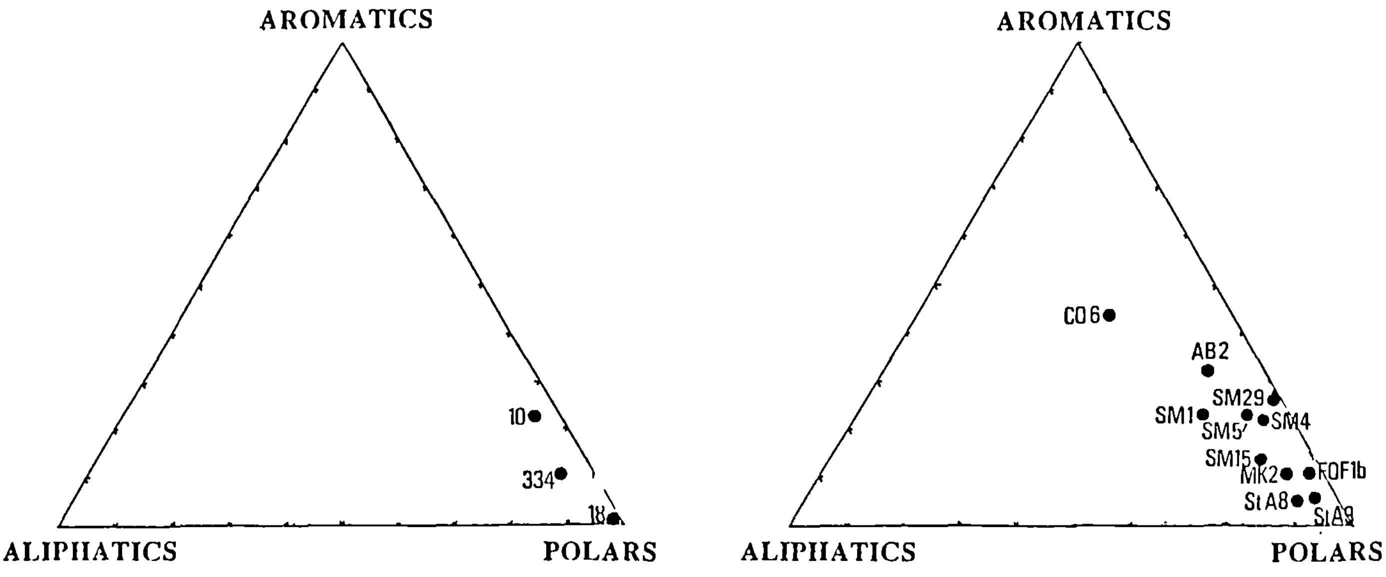
Fig.4.70 (cont.).



a Queenslie Marine Band **b** Calmy Blaes



c Kelty Blackband **d** Black Metals



e Johnstone Shell Bed **f** Miscellaneous

Fig.4.71 Ternary plots showing variation in gross composition of EOM in the low-rank marine samples analysed.

Ternary plots showing variations in EOM composition are given in Fig.4.71 from which it is evident that the majority of samples is enriched in polar compounds.

4.3.3.3.2 Queenslie Marine Band

4.3.3.3.2.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of the Queenslie Marine Band samples extracted are shown in Figs 4.72a-e. The samples were selected to see if the differences in lithological facies and maceral composition determined microscopically were reflected in different geochemical signatures.

The gas chromatograms are all similar in that there is a dominance of medium molecular-weight *n*-alkanes in the C_{15}-C_{19} carbon-number range, giving rise to a pronounced skew in the unimodal *n*-alkane envelopes in Figs 4.72a-d. The distributions maximise at *n*-C_{15} or *n*-C_{17}. Enhanced concentrations of C_{15}, C_{17} and C_{19} *n*-alkanes, sufficiently high to give a marked OEP within the medium molecular-weight range in samples QMBA2, A43 and 41 reflect a contribution from algal lipids (Clark and Blumer 1967; Han *et al.* 1968b; Blumer *et al.* 1971) which is consistent with the inference of an algal affinity for the liptodetrinite and cyst-like bodies made in Section 4.2.3.1.

A marked OEP extends over most of the carbon-number range in the shales from the Fife-Midlothian Basin, but is less noticeable in samples from the Central Coalfield, suggesting differences in source input between the two basins although more samples would obviously have to be investigated to verify these differences. The higher CPI values for samples QMBA2, A43 and 41 correlate with the higher content of vascular-plant material in these samples. An even-over-odd carbon preference (EOP) is evident in the C_{18}-C_{22} *n*-alkane range in the marl (Fig.4.72e). Unlike other calcareous sediments in which OEPs have been reported (e.g. Welte and Waples 1973), sample QMB64 is not thought to have been deposited in a highly reducing environment because of its high Pr/Ph ratio (1.71). Sample QMB64 is also unusual in that it has a bimodal *n*-alkane envelope which is defined by enhanced concentrations of *n*-C_{25} and *n*-C_{27}. These hydrocarbons are probably not derived from waxy matter of terrestrial origin since the vascular plant-derived material in the marl consists almost entirely of inertinitic debris. Furthermore, a terrestrial imprint might be expected to produce an OEP range that extends over a range comparable with that seen in other samples containing abundant vascular-plant matter (e.g. QMBA43), rather than the restricted high molecular-

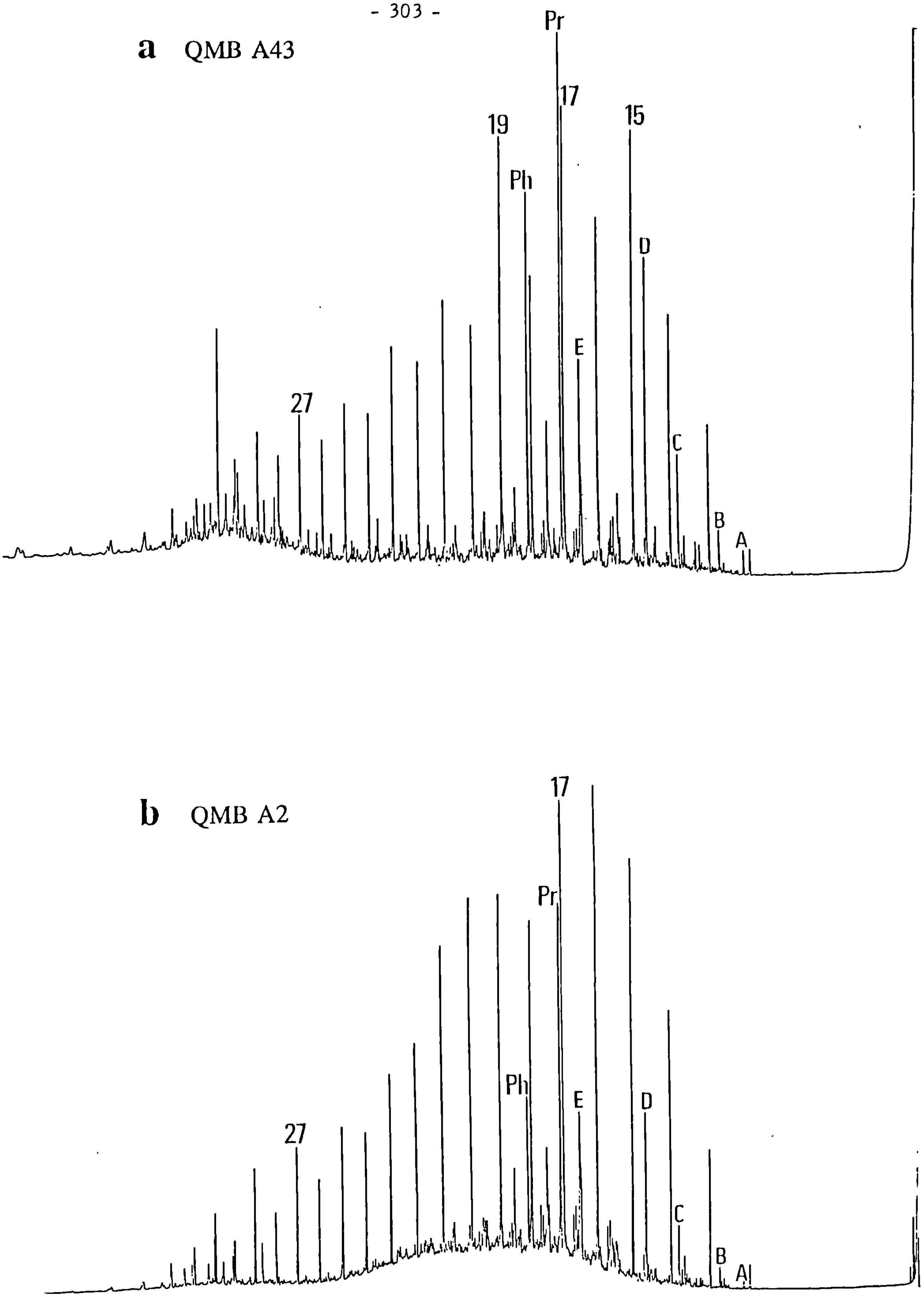
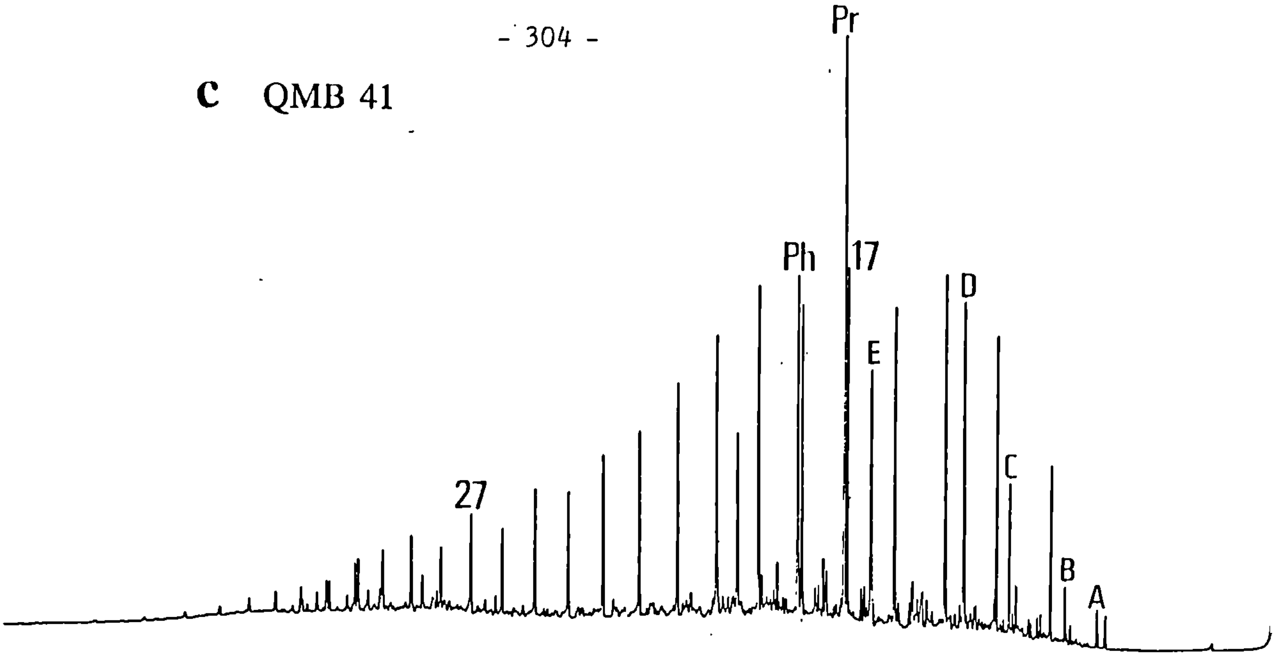
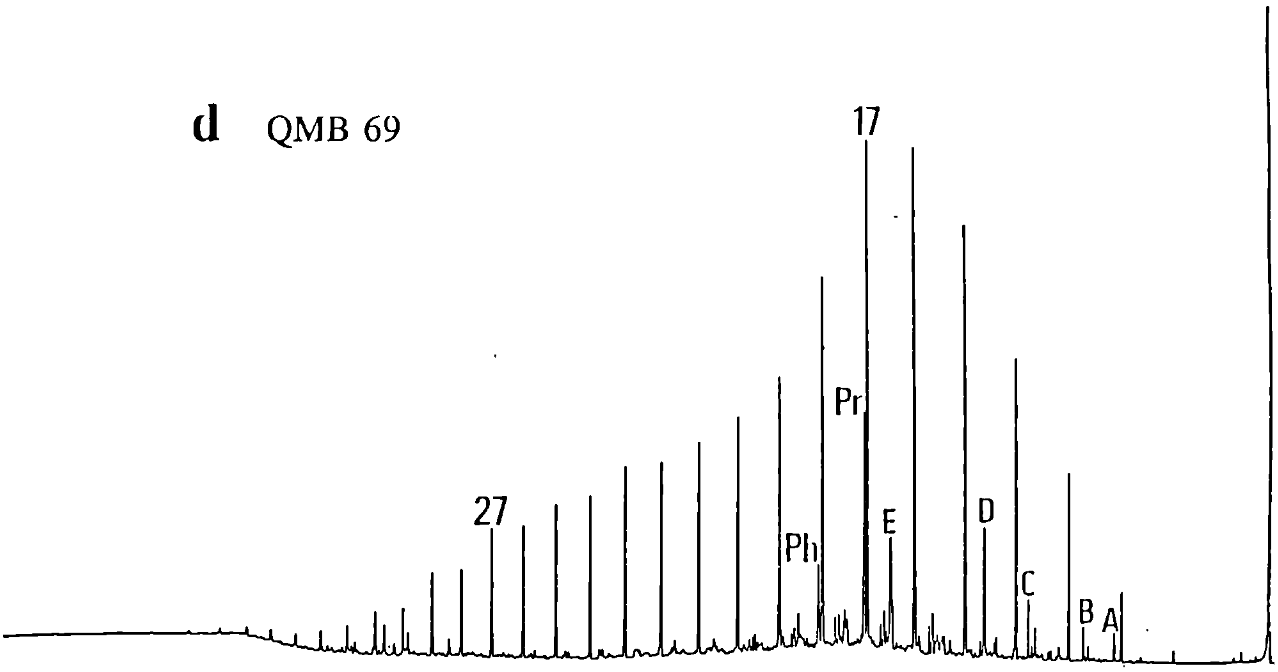


Fig.4.72 Gas chromatograms of the saturated hydrocarbon fractions of samples from the Queenslie Marine Band (isoprenoid assignments in Table 4.4).

c QMB 41



d QMB 69



e QMB 64

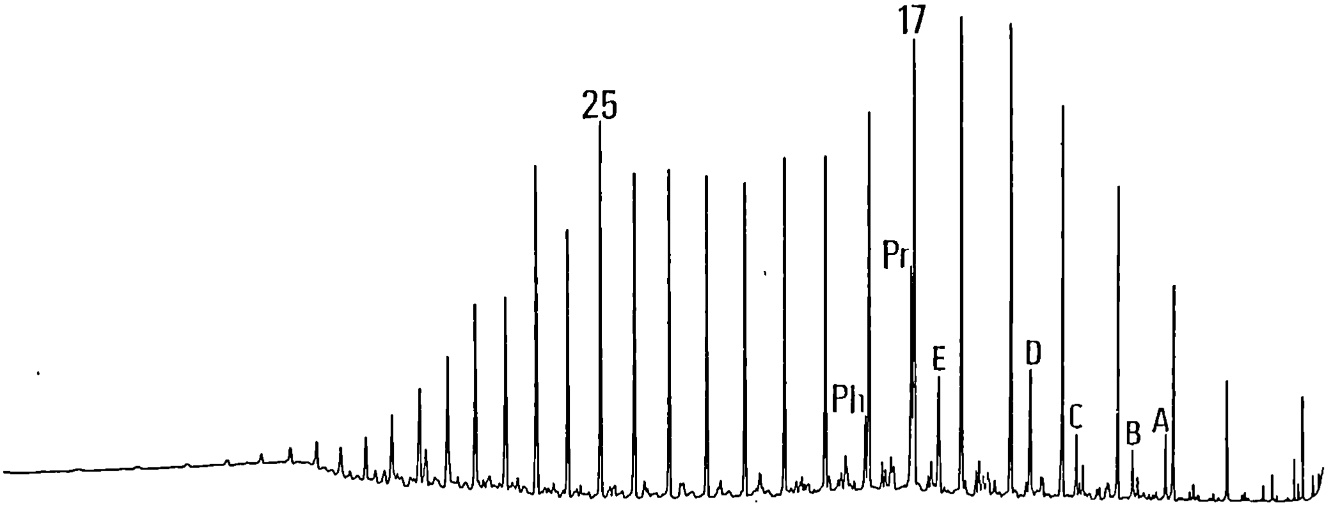


Fig.4.72 (cont.).

weight range seen in the marl. In view of the abundance of liptodetrinite flecks and wisps in the sample, it is likely that the long-chain *n*-alkanes in the marl are inherited from algal precursors. Further reference to this possibility is made later.

Pr/Ph ratios in the range 1.53-3.00 point to oxic depositional environments for the samples analysed. Pr/*n*-C_{17} ratios in the range 0.46-0.77 indicate relatively open-water conditions of sedimentation for samples QMBA2, 69 and 64 while the value of 1.14 for sample A43 indicates a more marginal depositional regime, possibly reflecting the proximity of the sample to the edge of the basin. The Pr/*n*-C_{17} ratio of 1.67 for QMB 41 is anomalously high in view of its relatively close geographical association with sample QMB69 and its location in what is considered to be a deep-water facies (Brand 1977), in which a lower Pr/*n*-C_{17} ratio might be expected (see Figs 4.1 and 4.2). It is possible that the high pristane content reflects a direct input from organisms restricted to the deep-water facies of the Queenslie Marine Band and may even be derived from percursors of the mosaiced, bituminous-looking material found exclusively in this facies (Section 4.2.3.1).

Gas Chromatography-Mass Spectrometry (GC-MS)

Of the five samples analysed, variations in terpane distributions are exemplified by considering the m/z 191 mass fragmentogram of QMB69 (Fig.4.73a) and QMBA2 (Fig.4.73b). The contribution of tri- and tetracyclic terpanes, relative to the pentacyclics, in QMB9 is typical of that seen in QMBA43, 64 and 41. The enhanced concentrations of these components in QMBA2 do not appear to be related to rank since inspection of the biomarker ratios shows QMBA2 to be the most immature sample in the suite. It is also difficult to rationalise the terpane distributions on the basis of variations in microscopically-discernible organic input because low concentrations of tri- and tetracyclics are also seen in other samples containing algal cysts and wisps where, moreover, these moieties are present in greater amounts.

Despite quantitative differences in the tricyclic and tetracyclic terpanes, the distributions for all Queenslie Marine Band samples studied are qualitatively similar. Apart from the 17,21-secohopanes, tetracyclic compounds are barely detectable. The abundance of the tricyclics is either comparable with that of the secohopanes or, as in samples QMBA2, 41 and A43, exceeds it.

The pentacyclic distribution (Fig.4.73a) is also seen in samples QMB64 and 41. Peak 31 is evident in these samples, but, unlike its occurrence in the lamosites, the accompanying C_{29} pentacyclic (peak 30) is not seen in the m/z 191 mass fragmentogram. Its presence in all the above samples was, however, confirmed

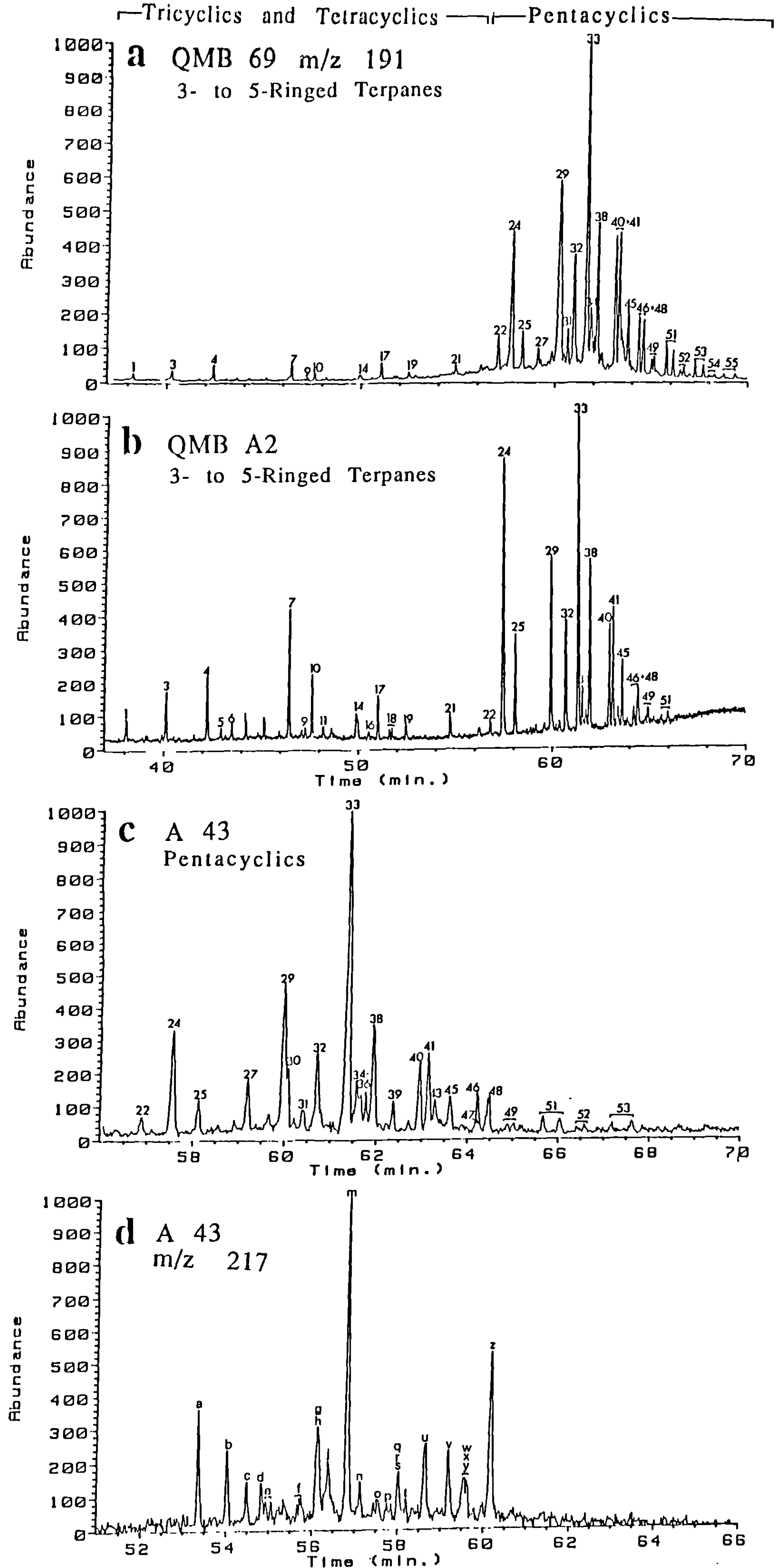


Fig.4.73 Mass fragmentograms showing distributions of terpanes (a-c) and steranes (d) in samples of the Queenslie Marine Band (peak assignments in Tables 4.5 and 4.6).

through inspection of the m/z 177 mass fragmentograms where a "split" peak was observed at the position of the $C_{29}\alpha\beta$ hopane. A mass spectrum of the later-eluting peak corresponded to the spectrum shown in Fig.4.13a, thus verifying the presence of the compound in the Queenslie samples. The compound corresponding to peak 30 is present in sufficient abundance in QMBA43 (Fig.4.73c) to produce a shoulder on the $C_{29}\alpha\beta$ hopane. The hopane distribution of the latter sample differs from that seen in the other samples since it contains the two compounds (peaks 39 and 47) with major m/z 232 fragment ions that were noted in two lamosites. Bisnorhopane (peak 27) also occurs although trace amounts were also recorded in QMB69 and 64.

The m/z 217 mass fragmentograms of QMBA43 (Fig.4.73e) shows a sterane distribution resembling those seen in QMB69,41 and A2. The $C_{27}\alpha\alpha\alpha20R$ sterane dominates the distribution in all the above samples in which the carbon-number distribution is $C_{27}>C_{29}>C_{28}$. These samples all plot in the "open marine" field (Fig.4.74). The marl, QMB64, differs in that the $C_{29}\alpha\alpha\alpha20R$ sterane dominates the distribution placing it in the "terrestrial" field.

Diasteranes are readily discernible in m/z 217 traces where their proportions, relative to the steranes, lie in the range 0.58-0.69.

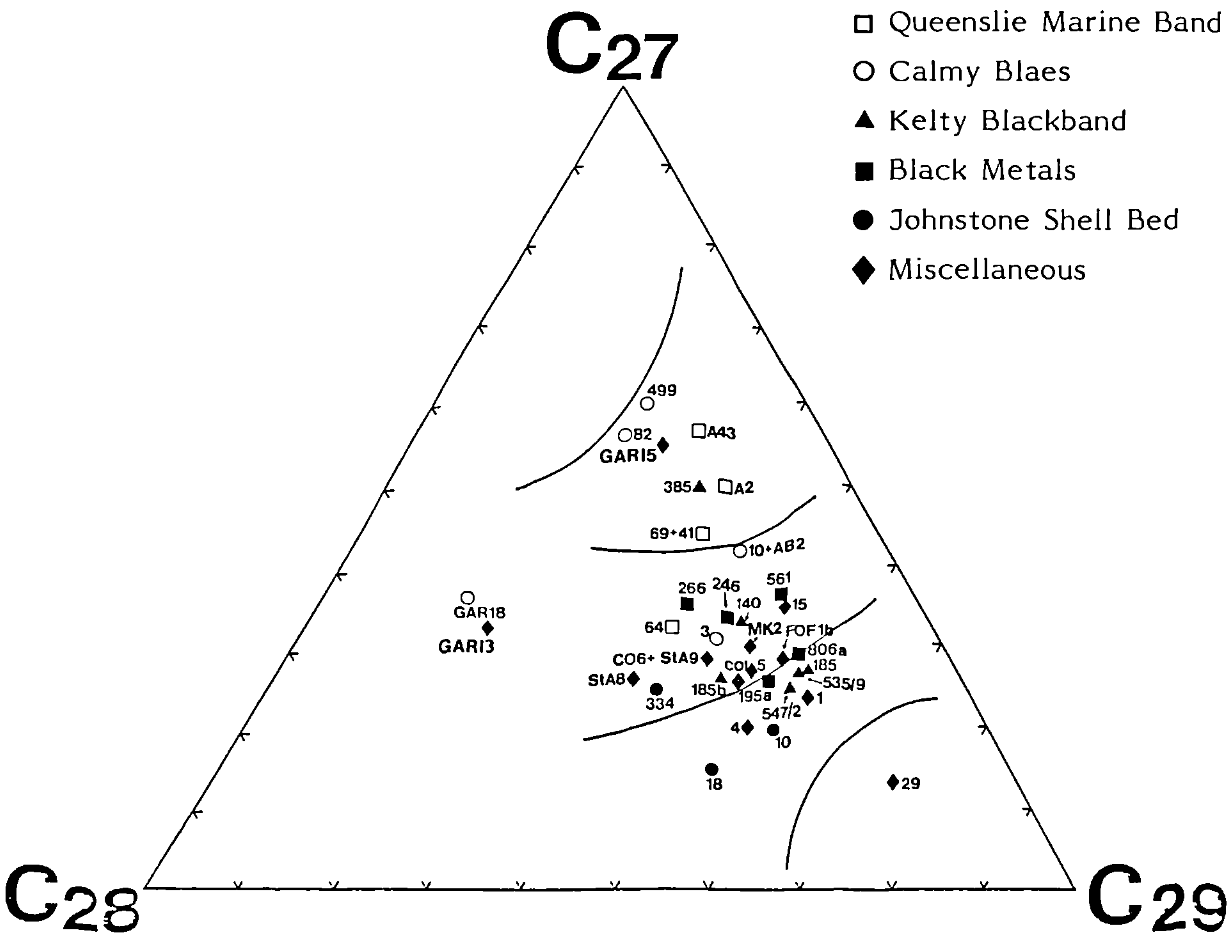


Fig.4.74 Ternary plot showing carbon-number distribution of steranes in the marine samples analysed.

4.3.3.3.2.2 Aromatic Hydrocarbons

Variations in the aromatic hydrocarbon distributions of the samples from the Queenslie Marine Band analysed are shown in Fig.4.75. Two samples (QMB64 and QMB69) were not submitted for gc-ms, but the gas chromatograms of their aromatic hydrocarbon fractions closely resemble that of QMB41 (Fig.4.75c).

Cadalene dominates the aromatic fraction of sample QMBA2 in which 1,2,5,6-Tetramethylnaphthalene (peak 16) is also relatively prominent. Most of the remaining discernible components in the TIC trace comprise PAH with a pyrolytic-like distribution that was discernible in the coaly materials. Apart from peak 69, and the trace quantities of benzohopanes, compounds derived from steroid or triterpenoid precursors could only be detected using mass fragmentography.

In contrast to QMBA2, cadalene is a negligible contributor to the aromatic fraction of the other cyst-bearing sample from Fife (QMBA43). Many of the peaks identified in the lamositic shales occur in the sample, but, unlike the algal shales, dimethyl-/ethyl-substituted triaromatic steroids are prominent in the high molecular-weight fraction.

All the liptodetrinite-rich samples of the Queenslie horizon that were analysed have aromatic distributions of the type shown in Fig.4.75c. Components common to QMBA2 and QMBA43 are recognised. High molecular-weight compounds could only be detected by gc-ms: their distributions were similar to those of the QMBA2 and QMBA43.

The distribution of monoaromatic steroids found in all samples is exemplified by Fig.4.75d from which it is apparent that rearranged structures form a significant contribution and that interference from pyrolytic PAH occurs. The carbon-number distributions of the mono- (m/z 253 fragmentograms) and triaromatic components (m/z 231) mirrors that of the saturated steroidal components, while the profile of the m/z 245 fragmentogram is similar to that shown for the Dunnet Shale (Fig.4.23c).

4.3.3.3.3 Calmy Blaes

4.3.3.3.3.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of low-rank samples of the Calmy Blaes are shown in Figs 4.76a-e.

Straight-chain alkanes are present in the range C_{10}-C_{36}, and the relatively high abundance of homologues in the medium molecular-weight range (C_{15}-C_{19}) leads to the skewing of the *n*-alkane envelope. Apart from sample C10, whose

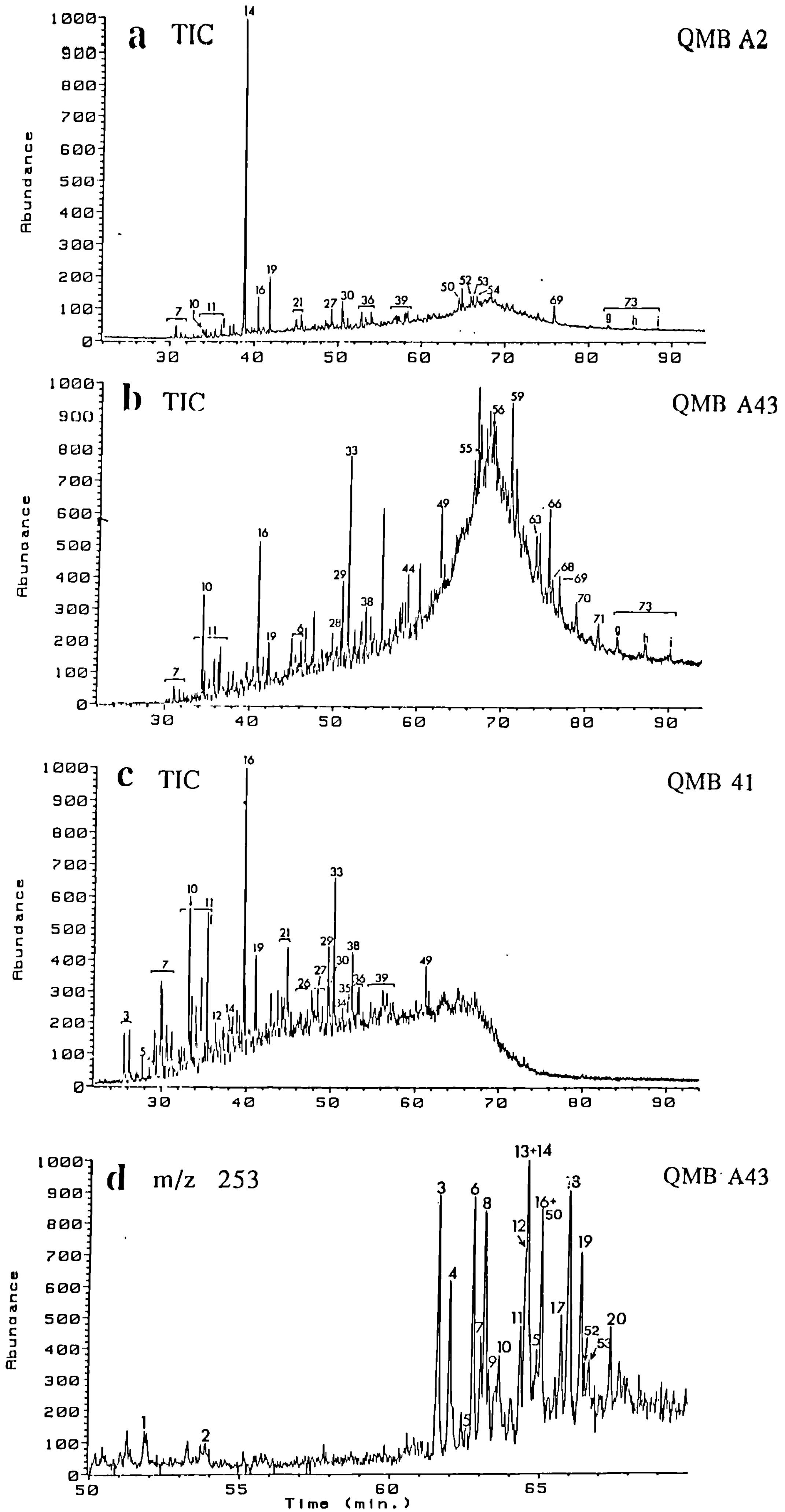


Fig.4.75 Distribution of total aromatic hydrocarbons (a-c) and monoaromatic steroids (d) in the Queenslie Marine Band (peak assignments in Tables 4.7 and 4.8).

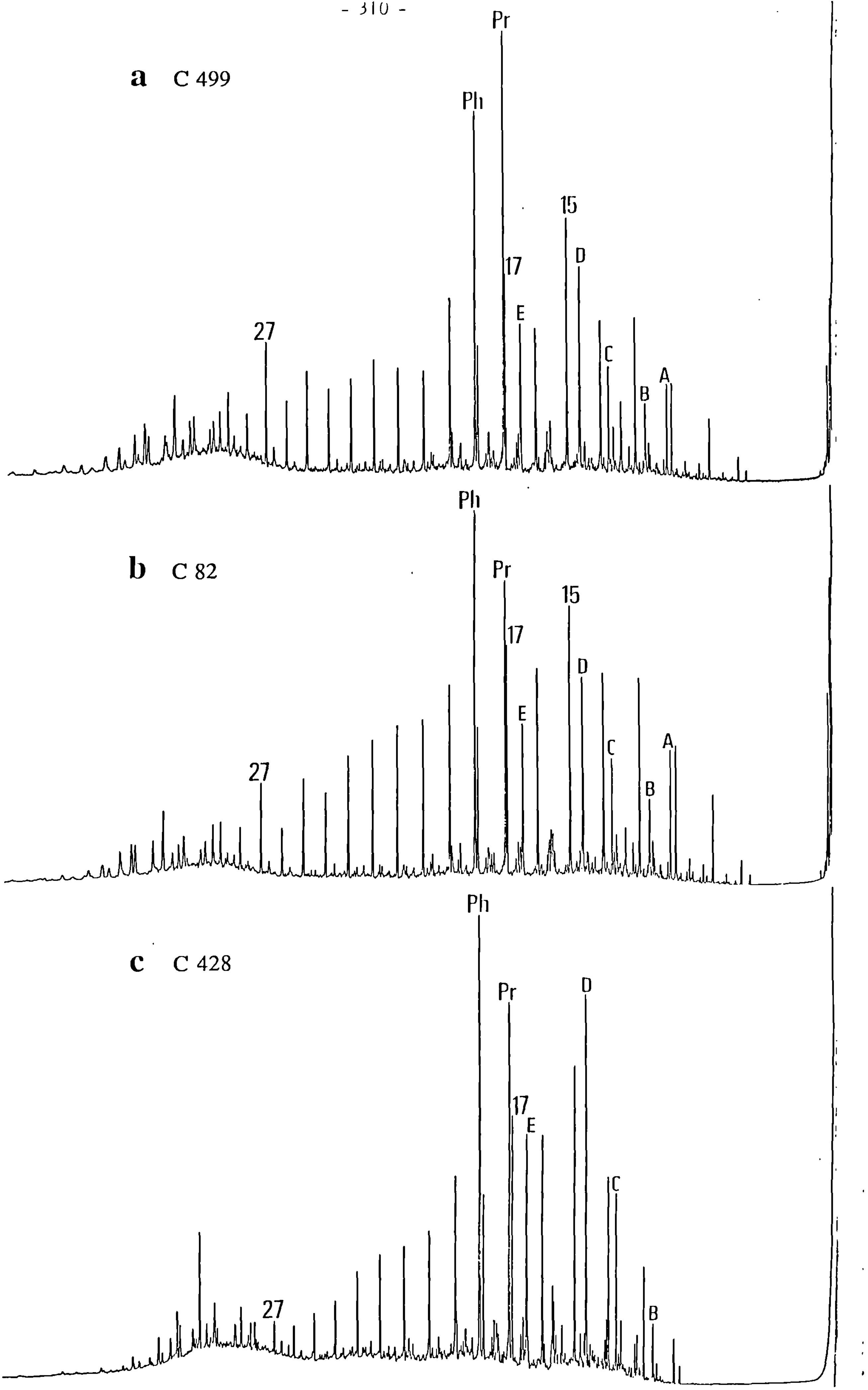


Fig.4.76 Gas chromatograms of the saturated hydrocarbon fractions of samples from the Calmy Blaes (isoprenoid assignments given in Table 4.4).

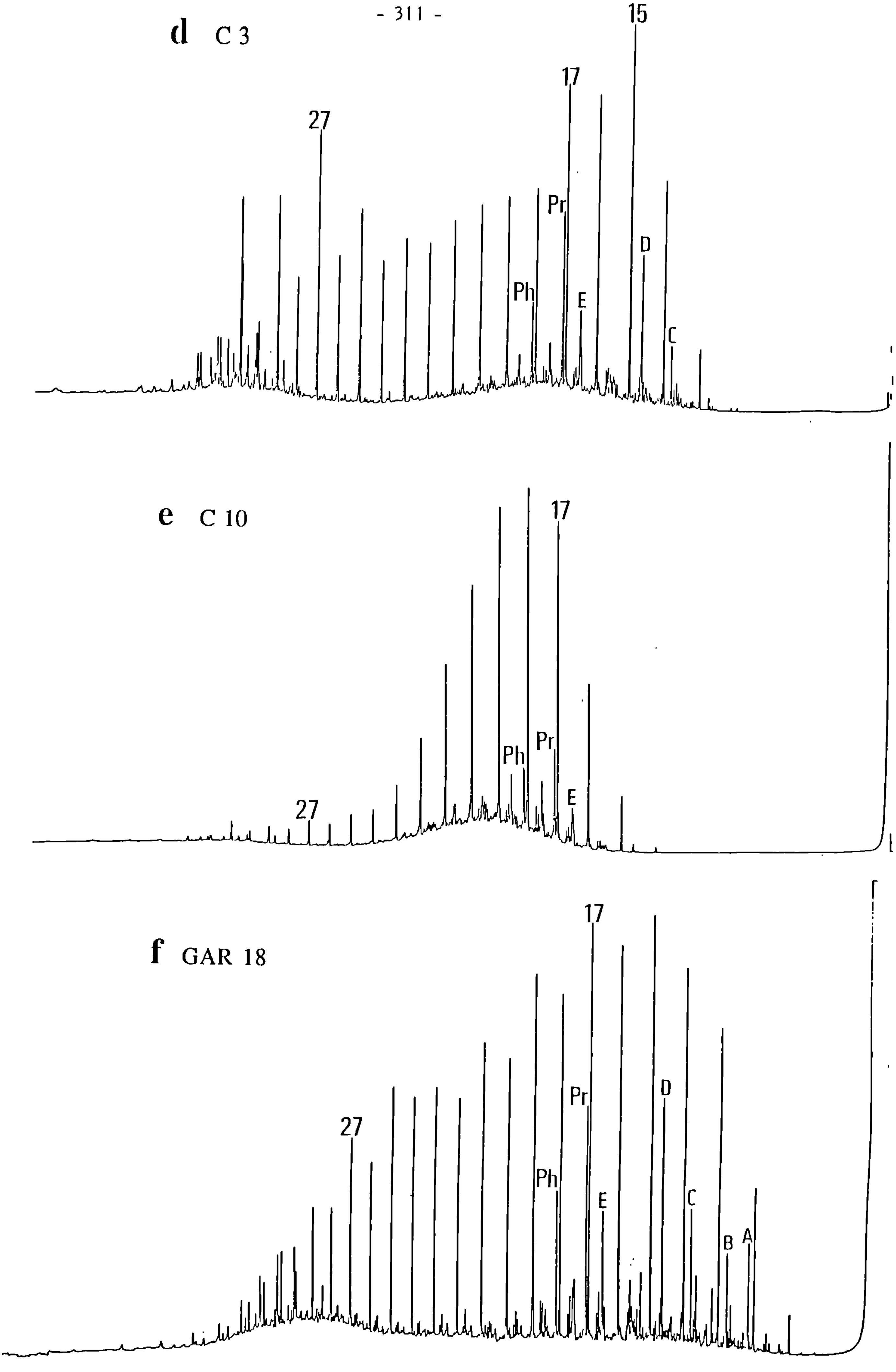


Fig.4.76 (cont.).

shortened *n*-alkane range may be due to evaporative loss of low molecular-weight alkanes during laboratory fractionation, the peak maximum is at *n*-C_{15}. A secondary maximum occurs at *n*-C_{27} in C3 which results in a bimodal *n*-alkane envelope. (Fig.4.76d). The relatively high concentrations of *n*-C_{15} and *n*-C_{17} indicate an algal input (Clark and Blumer 1967; Han *et al.* 1968b) which was seen from optical examination (Section 4.2.3.2). Enhancement from *n*-C_{15} and *n*-C_{17} in the west Fife samples is more pronounced than in samples further to the east and could be related to different algal constituents: in the west Fife samples, the algal matter occurs in the form of discrete lamalginite while in central Fife the algal matter comprises liptodetrinite flecks and wisps. The marked predominance of acyclic isoprenoids over *n*-alkanes in the west Fife samples may also reflect the different nature of the algal components. Relatively high concentrations of isoprenoid's are still evident in west Fife samples at increased levels of maturity (Fig.4.76f; unsuppressed reflectance is %$R_o$av=0.90).

All the Calmy Blaes samples analysed show an OEP over the high molecular-weight range, consistent with the input of vascular-plant matter observed microscopically. Although the level of higher-plant input in sample C10 is comparable with that in C3, the latter has relatively large concentrations of *n*-C_{25}, *n*-C_{27} and *n*-C_{29} which impart a bimodal shape to the *n*-alkane envelope. The high molecular-weight "hump" may reflect an input of *n*-alkanes from sporinite. Although samples from west Fife contain equal or greater amounts of sporinite, the absence of relatively large contributions from long-chain alkanes may be due to swamping by the medium molecular-weight alkanes derived from algae, which are present in much greater abundance in these samples than in those from central Fife. An alternative possibility that the secondary maximum in Fig.4.76d may be due to hydrocarbons derived from the *Botryococcus* telalginite in the sample is considered less likely. Despite the presence of relatively large contributions of C_{25}, C_{27} and C_{29} *n*-alkanes in the gas chromatograms of the torbanite and torbanitic shales studied (Fig.4.29), their CPIs in the high molecular-weight range (1.08-1.17) are considerably lower than the value recorded in sample C3 (1.43).

Pr/Ph ratios for the Calmy Blaes samples extracted vary from 0.80-2.10. Two of the three low-rank samples from west Fife (C82 and C428) have ratios of 0.80, indicating reducing depositional environments. A value of 1.22 for C499 indicates that, a relatively small distance to the northwest (see Fig.4.70), environmental conditions were more oxic, but less oxic than during the deposition of C10 and C3, in the Fife-Midlothian Basin, as suggested by their ratios of 1.50 and 2.10 respectively. Although likely to have been influenced by maturation, the Pr/Ph ratio of 1.54 for the Calmy Blaes sample in the Gartarry Toll borehole suggests that an oxidising depositional environment persisted to the westernmost part of Fife. The area around Cattlemoss may therefore have been a "pocket" of anoxicity during the deposition of the Calmy Blaes.

That the enhanced reducing conditions recorded in west Fife were associated with relatively restricted aquatic environments is inferred from the relatively high Pr/n-C_{17} ratios of 1.29-2.25 (Lijmbach 1975). As suggested earlier, the relatively high isoprenoid content of the west Fife Calmy Blaes samples may be a reflection of discrete lamalginite input. The low Pr/n-C_{17} values for C3 and C10 suggest that accumulation of the Calmy Blaes in the Fife-Midlothian Basin occurred in a more open-water regime than did the accumulation of the same horizon in the Kincardine Basin, further to the west.

Gas Chromatography-Mass Spectrometry (GC-MS)

Of the four low-rank samples of the Calmy Blaes submitted for gc-ms analysis, C10 was the only sample in which tricyclic and tetracyclic terpanes were present in relatively large amounts (Fig.4.77a). Despite their exceptionally low abundance (relative to the pentacyclics) in the remaining samples, characterisation of the 3- and 4-ringed terpanes was possible and revealed differences in the distribution of these components in the samples from west Fife (C82 and C499) and those further to the east (C3 and C10). Although there is a pronounced difference in the amounts of tricyclics and tetracyclics present in C3 and C10, the distribution patterns of these samples bear a close resemblance in that the concentration of tricyclics is enhanced relative to the tetracyclics (Fig.4.77a). The only tetracyclic components observed in the above samples are members of the 17,21-secohopane series. In C82 (Fig.4.77b) and C499 the tetracyclics dominate over tricyclics.

Differences in pentacyclic hopane fingerprints are evident by comparing Figs 4.77a, c and d. The hopane signature in C499 is almost identical to that of C82, which is consistent with the similarity in the maceral composition of both samples. Apart from rank-related changes in the distribution of hopane isomers, the difference in the overall pattern of the pentacyclic hopane "envelope" in C3 and C10 probably reflects the different composition of the liptinite fraction. Hopane distributions resembling C3, in which there is a marked prevalence of the $C_{30}\alpha\beta$ hopane, were observed in the majority of sediments containing abundant lamalginite (see Section 4.3.3.1). Sample C3 also contains the unknown compounds with major m/z 232 fragment ions (peaks 39 and 47).

A bipartite division of the sample set is apparent, based on the sterane distributions, which can, again, be related to the geographical location of the samples and their maceral compositions. Examples of "end member" m/z 217

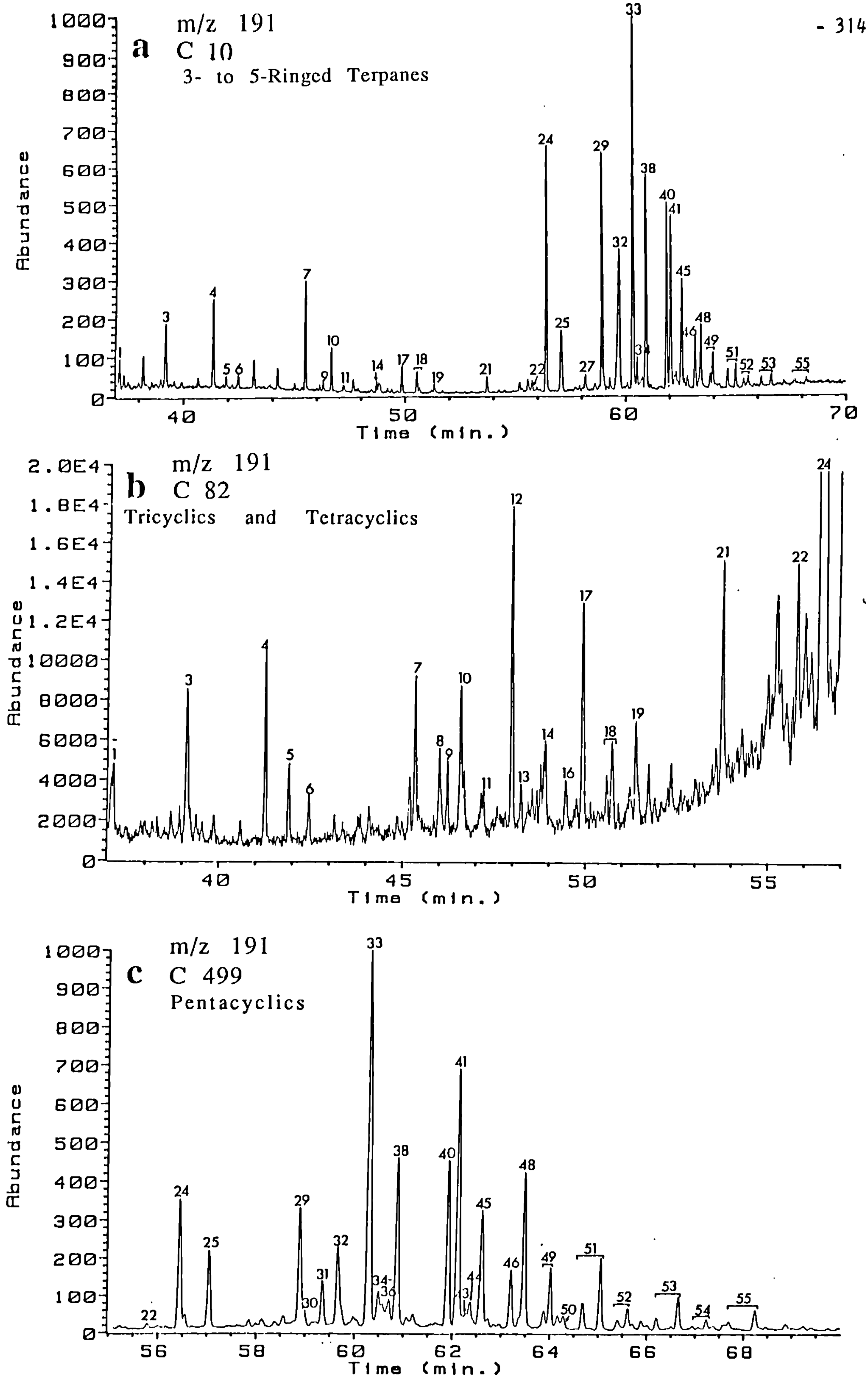


Fig.4.77 Mass fragmentograms showing distribution of terpanes (a-d) and steranes (e,f) in samples of the Calmy Blaes (peak assignments given in Tables 4.5 and 4.6).

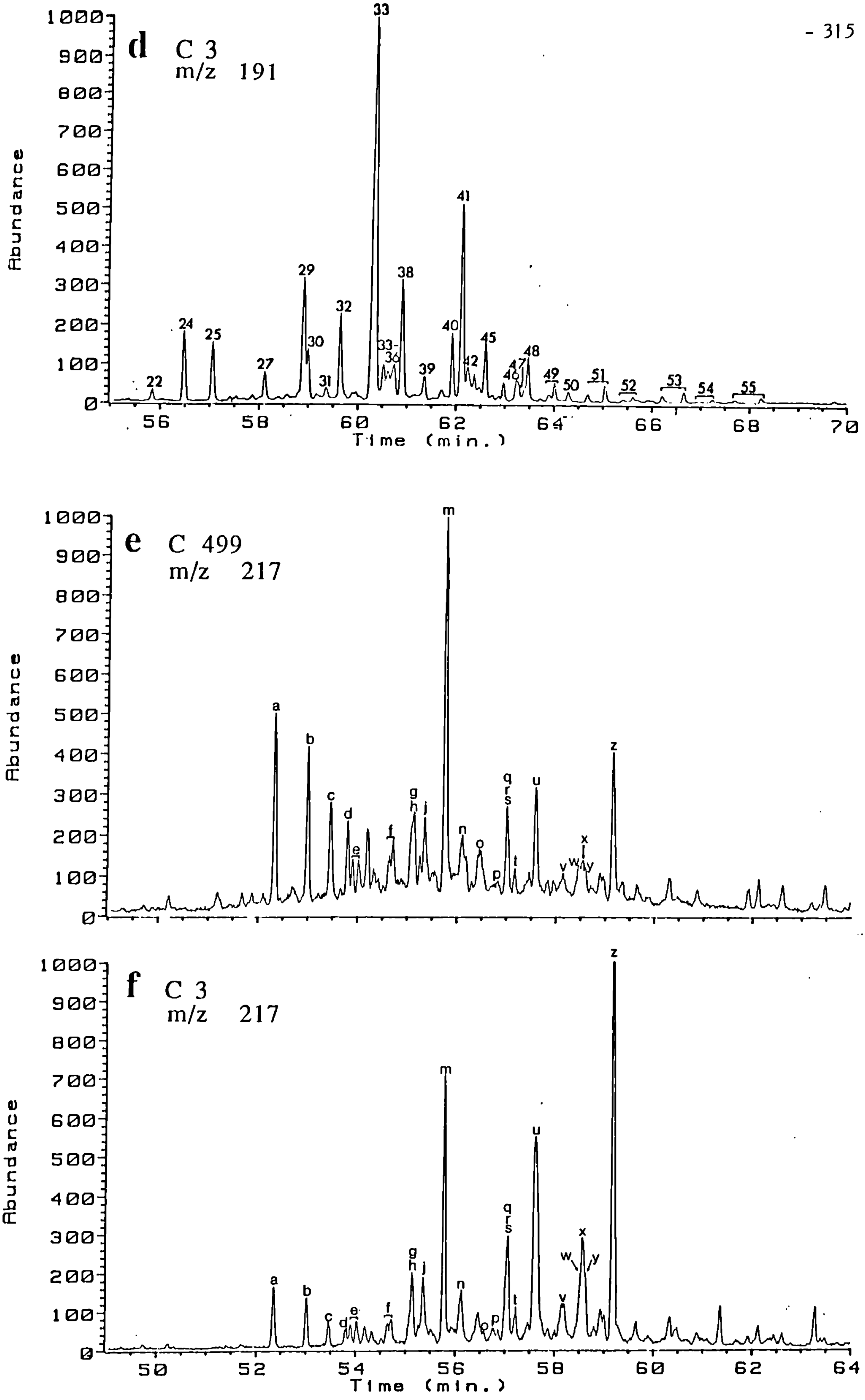

d C 3
m/z 191
Abundance
1000
900
800
700
600
500
400
300
200
100
0
Time (min.)
56
58
60
62
64
66
68
70
22
24
25
27
29
30
31
32
33
33-
36
38
39
40
41
42
45
46
47
48
49
50
51
52
53
54
55
e C 499
m/z 217
a
b
c
d
e
f
g
h
j
m
n
o
p
q
r
s
t
u
v
w
x
y
z
f C 3
m/z 217
50
52
54
56
58
60
62
64

Fig.4.77 (cont.).

mass fragmentograms are shown in Figs 4.77e and f. The fingerprint of C499 (Fig.4.77e) is very similar to that in C82 whilst the sterane distribution of C3 (Fig.4.77f) resembles that of C10, although the latter contains approximately equal proportions of $C_{29}\alpha\alpha\alpha20R$ and $C_{27}\alpha\alpha\alpha20R$ components.

A major input of algal C_{27} sterols (as evidenced by the large amounts of discrete algal cysts) present in the west Fife samples ensures that they plot within the "open marine" field (Fig.4.74). Enhanced concentrations of $C_{29}\alpha\alpha\alpha20R$ are evident in the m/z 217 mass fragmentograms of the east/central Fife samples (C10 and C3) in which vitrinite and inertinite dominate the maceral assemblages. These distributions result in the samples plotting in the "estuarine/bay" field.

The diasterane content in the two sets of samples also shows a marked variation, with diasterane/sterane ratios in west Fife samples being significantly higher than those determined in samples further to the east.

4.3.3.3.3.2 Aromatic Hydrocarbons

The difference in the geochemistry of samples from east and west Fife that was evident from the analysis of their saturated hydrocarbon fractions is paralleled by differences in the distribution of aromatic components. TIC traces of the aromatic fractions of C3 (Fig.4.78a) and C82 (Fig.4.78b) typify those of the samples from east and west Fife respectively. Overall, both types of distribution are qualitatively similar, but differ quantitatively because the aromatic fractions of the west Fife samples show a greater dominance of compounds whose skeletal structures can be related to biogenic precursors. Alkyltetralins are also more prominent and include a probable C_5 member whose mass spectrum is shown in Fig.4.79a.

In contrast to the west Fife samples, those from east Fife contain PAH with a pyrolytic-like distribution which, unlike similar distributions recorded earlier, is biased towards higher molecular-weight members. A compound (peak 65) whose mass spectrum (Fig.4.79b) and relative retention time correlate with those of 1,12-benzoperylene (Wakeham *et al.* 1980a) dominates the higher molecular-weight fractions of all the east Fife samples.

Benzohopanes are readily discernible in the TIC and gas chromatogram traces of all the Calmy Blaes samples analysed, but the presence of aromatic steroids and monoaromatic 8,14-secohopanes could only be confirmed following gc-ms analyses. Distributions of the latter were of the form shown for the Dunnet Shale (Fig.4.23c), while the carbon-number distributions of the former components mirrored those of their saturated analogues. Rearranged C-ring monoaromatic steroids were moderately abundant relative to non-rearranged structures.

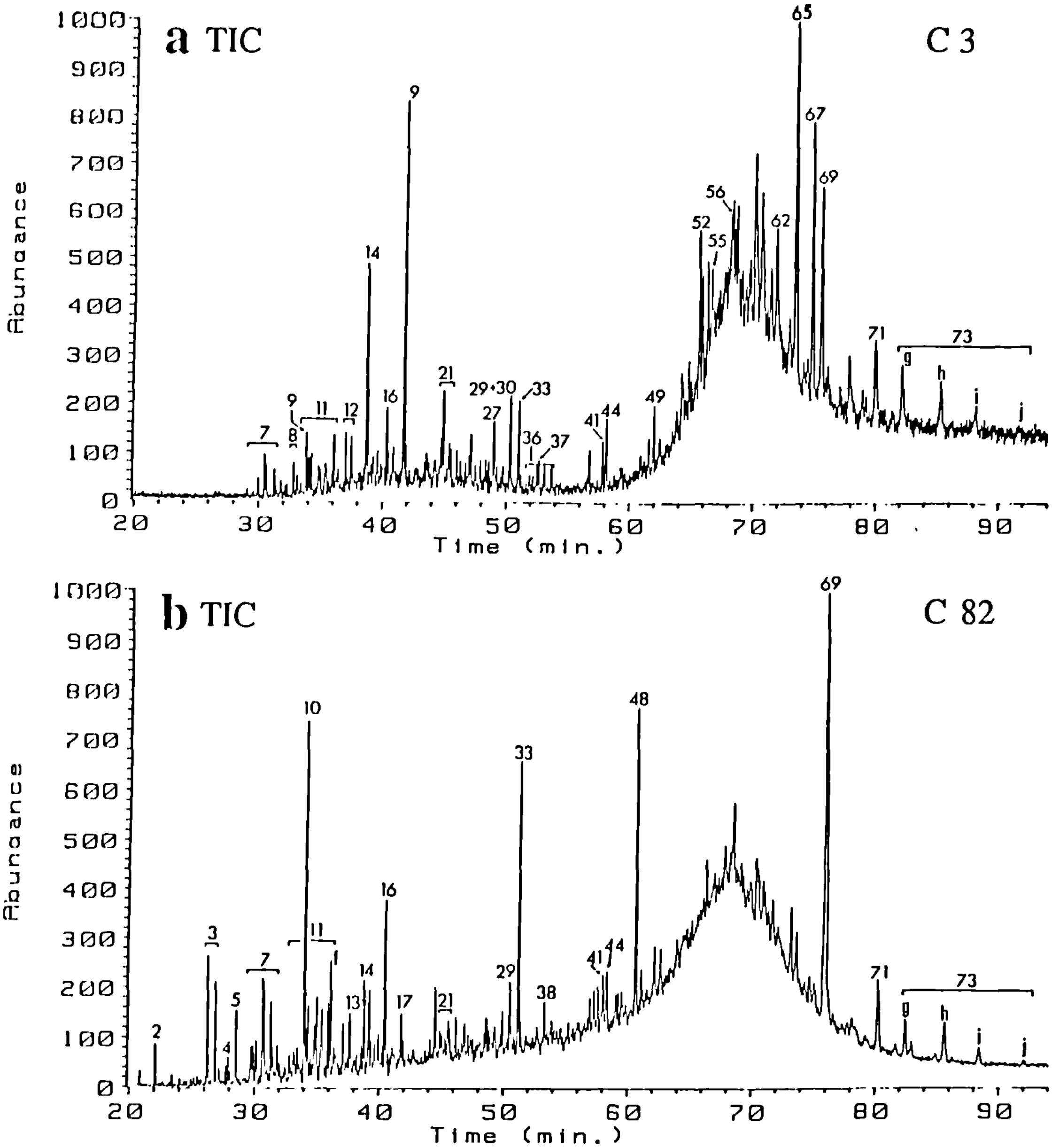


Fig.4.78 Chromatograms illustrating the variation in the distribution of aromatic hydrocarbon components in the Calmy Blaes samples (peak assignments in Table 4.7).

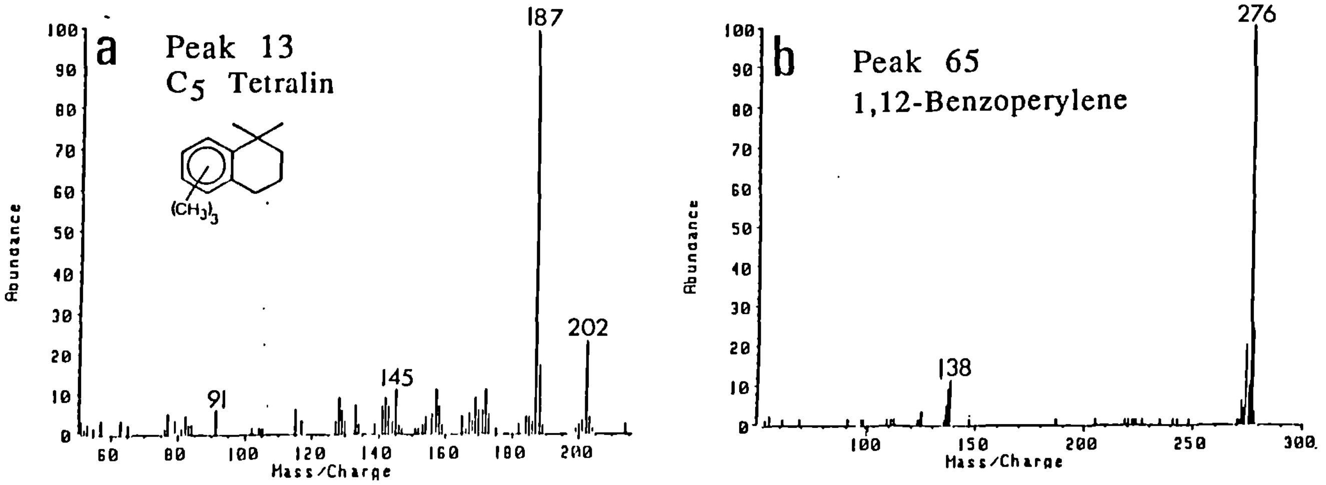


Fig.4.79 Mass spectra of peaks 13 and 65 in Fig.4.78.

4.3.3.3.4 Kelty Blackband

4.3.3.3.4.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Representative gas chromatograms illustrating variation of the saturated hydrocarbon distributions in samples of the Kelty Blackband are shown in Fig.4.80.

N-alkanes lie in the range C_{10}-C_{38} with peak maxima occurring at various carbon numbers between C_{23} and C_{29}. An OEP occurs throughout most of the medium and high molecular-weight range in all samples analysed and is particularly pronounced in the C_{23}-C_{27} range. High CPI values in the latter range corroborate the higher-plant input determined from microscopical examination.

Although algal matter is present in all samples except KBBI547/2 and 535/9, high concentrations of *n*-C_{15} and *n*-C_{17}, indicative of an algal input, are only seen in KBBI 185b (Fig.4.80a) resulting in a bimodal *n*-alkane distribution. This observation suggests that at least some of the liptodetrinite displaying the same fluorescence colour and intensity as sporinite in the same sample (probably liptodetrinite which is yellower in colour and has a stronger fluorescence) is derived from algal matter. A dual input of algal and higher-plant lipids is not evident from the *n*-alkane traces of other algal-bearing sediments, probably because the algae are not present in sufficiently high quantities for their *n*-alkane signatures to overprint those derived from co-existing vascular-plant debris.

The strong skew towards the high carbon-number region of the gas chromatogram in sample KBBI385 (Fig.4.80b; similar to KBBI382) and KBBI140 (Fig.4.80c) appears to correlate more with the calcareous nature of the samples than with a specific organic assemblage. The *n*-alkane distribution of sample KBBI547/2 (Fig.4.80d) typifies that of the remaining samples (KBBI185, 535/9 and 174) in showing far less of a skew of the envelope towards high carbon numbers.

The peaks eluting between *n*-C_{19} and *n*-C_{20} in KBBI547/2 (also seen in KBBI535/9) correspond to tetracyclic diterprenoids (phyllocladanes) already discussed in Section 4.3.3.2.4.1.

Pr/Ph ratios range from 2.96-4.33, indicating oxidising depositional environments. The lowest Pr/*n*-C_{17} ratios (0.44-0.69) occur in the samples containing the greatest quantities of algal-derived liptodetrinite, i.e. KBBI 185b, 382 and 385. These samples probably experienced more open-water conditions of sedimentation than did the remaining samples whose high ratios (1.95-2.91), coupled with significantly higher contents of terrestrial debris, point to accumulation in a more restricted, coastal or inland swamp-type environment (Lijmbach 1975).

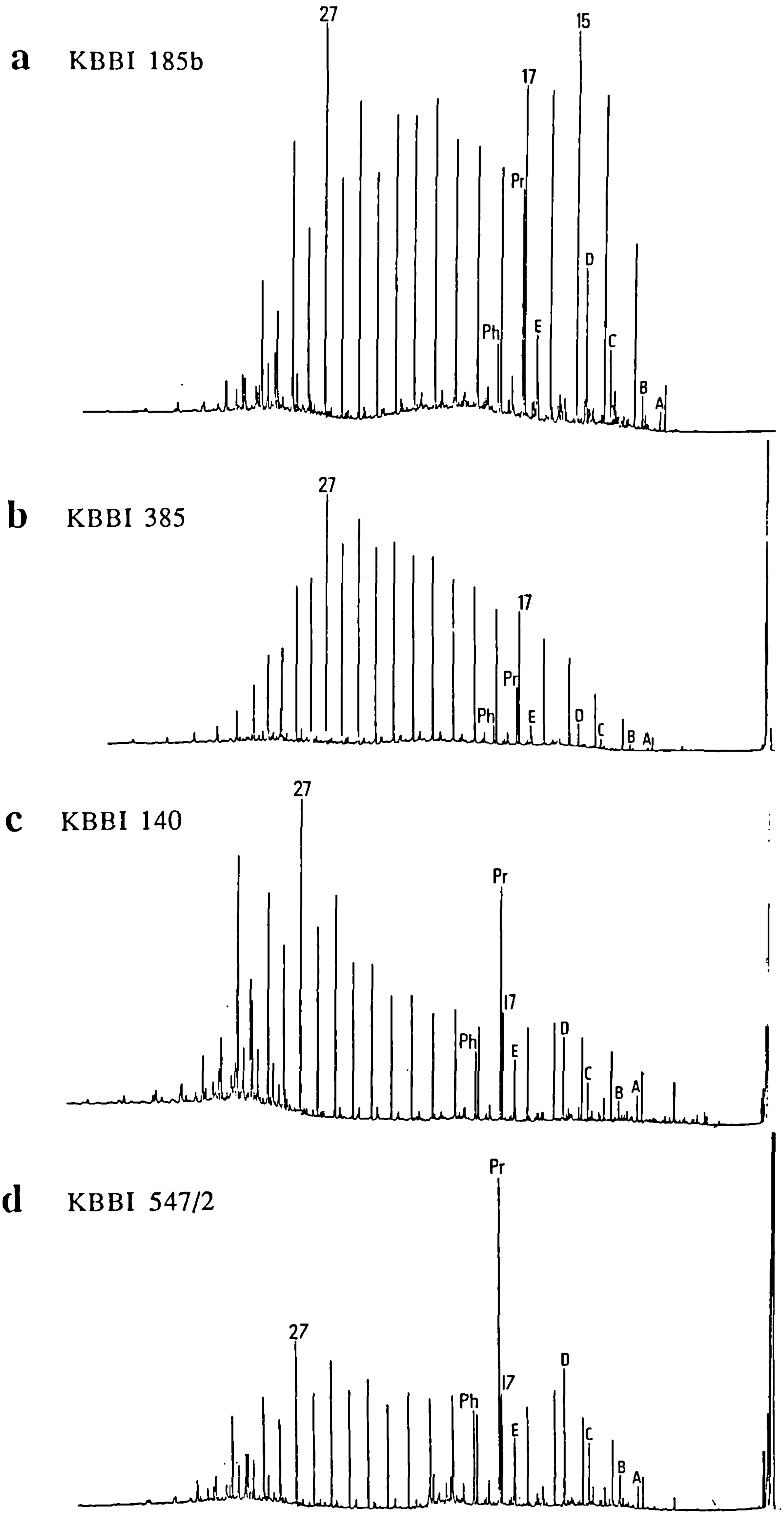


Fig.4.80 Gas chromatograms of the saturated hydrocarbon fractions of samples from the Kelty Blackband (isoprenoid assignments given in Table 4.4).

Gas Chromatography-Mass Spectrometry (GC-MS)

The relative proportion of tricyclic and tetracyclic terpanes to pentacyclics in all the Kelty Blackband samples analysed is illustrated in Fig.4.81a. The distributions of 3- and 4-ringed terpanes are of two types: in samples KBBI185b (Fig.4.81b) and KBBI385, the distributions closely resemble each other, but differ from those of the other samples in the suite which are typified by the m/z 191 mass fragmentogram shown in Fig.4.81c. Comparison of the terpane patterns shows that, in samples KBBI185b and 385, tricyclics are more prominent than the tetracyclics (represented solely by the 17,21-secohopanes) whereas the reverse is true in the case of the remaining samples. The former type of distribution relates to samples whose kerogen comprises $\geq$30% of intensely-fluorescing liptodetrinite, thought to be of algal origin, while the latter sterane patterns are seen in the other samples, in which higher-plant matter and *Botryococcus* are the main constituents.

The distributions of pentacyclic terpanes in the Kelty Blackband are qualitatively similar: Fig.4.81d is an example. Perhaps the most salient feature of the pentacyclic hopane distributions is the prominence of the 28,30-bisnorhopane (peak 27) in all samples except KBBI185b and 385. The compound is present in trace quantities in the former (see Fig.4.81a), but is absent in the latter. In no other samples from the Midland Valley was the bisnorhopane found to be in greater abundance than in the Kelty Blackband. The two C_{29} pentacyclic terpenoids, represented by peaks 26 and 28, were pronounced in samples containing bisnorhopane, suggesting a possible common precursor or mode of formation for these compounds.

The unknown C_{30} pentacyclic (peak 31) is present in all samples where, in all but KBBI185, it co-exists with the compound corresponding to peak 30. Although the latter compound is only seen in the m/z 191 mass fragmentograms of KBBI140 and 385, its presence in other samples is inferred by the observed broadening of the $C_{29}\alpha\beta$ hopane peak, particularly noticeable in the m/z 177 mass fragmentograms. No such peak broadening was observed in KBBI185, suggesting that peak 30 is either absent or is present in such small amounts that it cannot be detected even in the m/z 177 mass fragmentogram.

Except for sample KBBI385, the $C_{29}\alpha\alpha\alpha$20R sterane dominates the Kelty Blackband m/z 217 mass fragmentograms, in which the carbon-number distributions of the steranes is $C_{29}>C_{27}>C_{28}$. A typical trace for the Kelty Blackband samples analysed is shown in Fig.4.81e. In KBBI385, the most algal-rich sample, the order of carbon-number abundance is reversed, and the abundance of the C_{27} steranes is sufficient to allow the sample to plot in the "open marine" field in Fig.4.74.

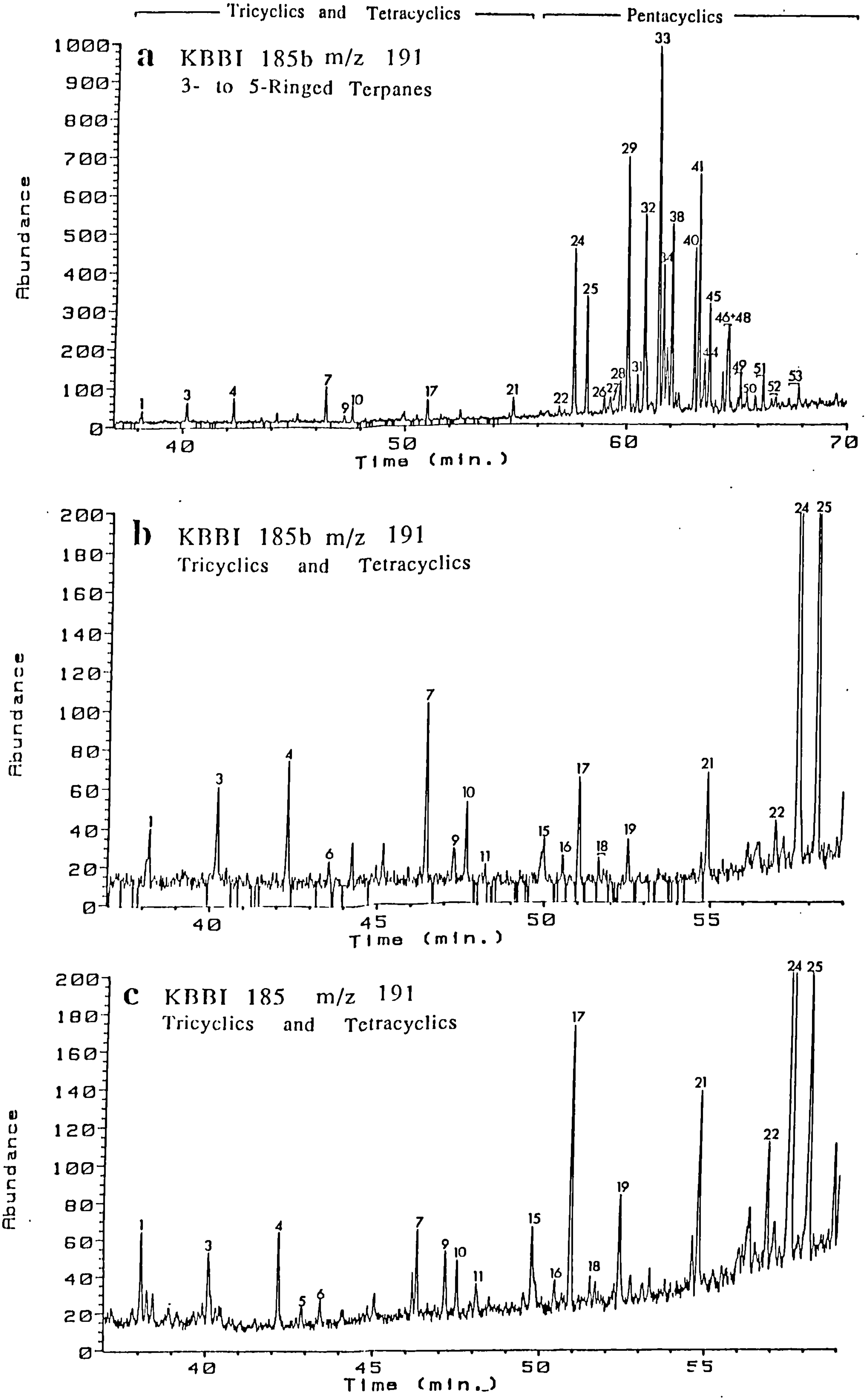


Fig.4.81 Mass fragmentograms illustrating the distribution of terpanes (a-d) and steranes (e) in the Kelty Blackband samples (peak assignments given in Tables 4.5 and 4.6).

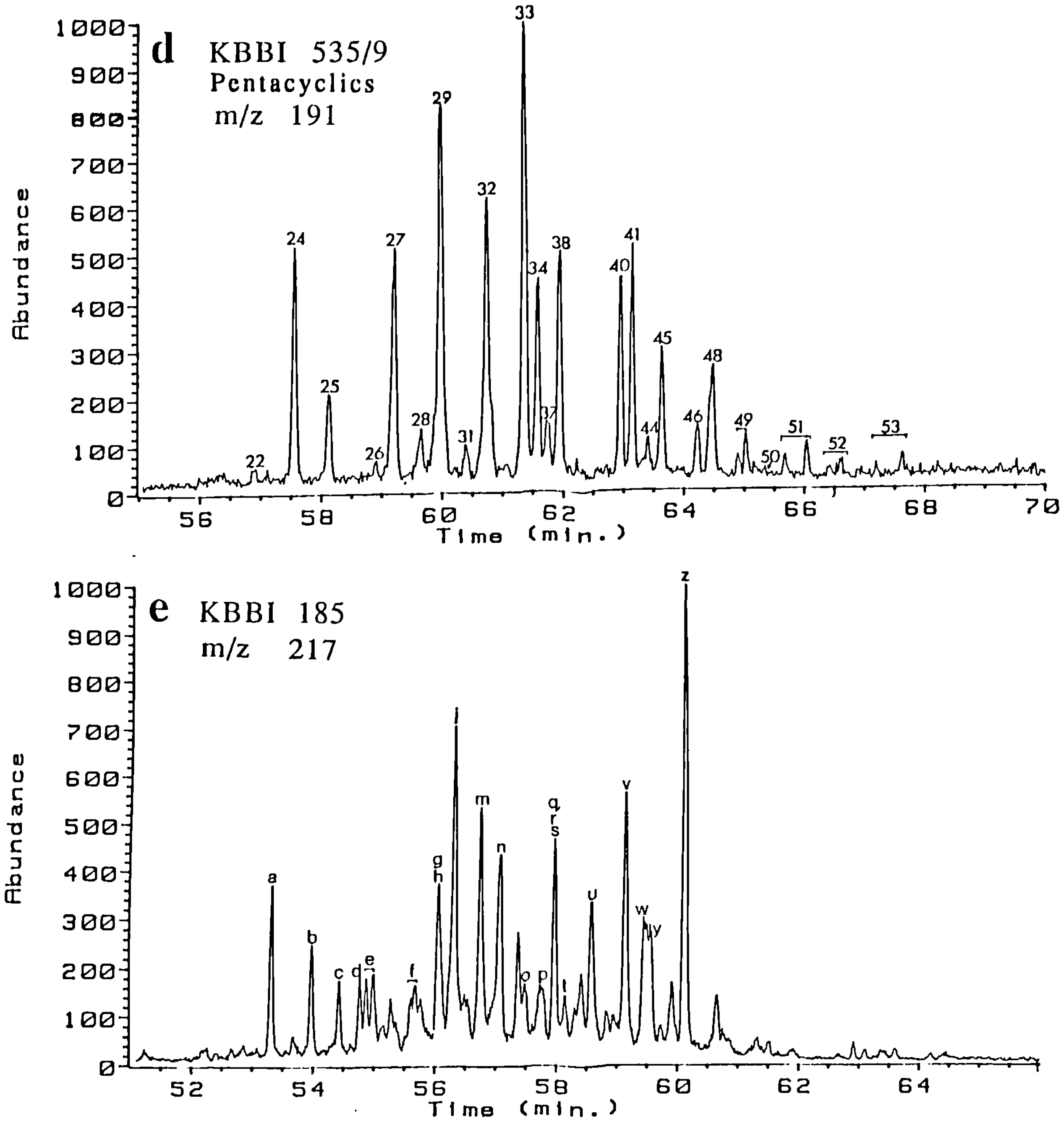


Fig.4.81 (cont.).

Samples containing >20% algal matter (either in the form of liptodetrinite or *Botryococcus*) plot in the "estuarine/bay" field, while those whose maceral assemblages comprise mainly sporinite and humic material plot in the upper half of the terrestrial field.

Diasterane/sterane ratios are variable (0.36-0.76).

4.3.3.3.4.2 Aromatic Hydrocarbons

Representative TIC traces illustrating type-related variations in the distribution of aromatic components in the samples investigated are shown in Fig.4.82. The trace of sample KBBI535/9 (Fig.4.82a) is almost identical to that from KBBI185b, and the traces from the samples analysed from west Fife (KBBI382 ; Fig.4.82d and KBBI385) closely resemble each other.

The aromatic fractions in KBBI535/9 and 185 are qualitatively similar which is not surprising in view of their similar petrographic characteristics. Both samples contain relatively large amounts of alkylated naphthalenes and phenanthrenes of which cadalene (peak 14) is particularly prominent in the latter sample as retene (peak 37) is in the former. Compounds based on the biphenyl skeleton (peaks 6, 8, 12, 20) are conspicuous in the above samples, as is a series of parent PAH, and their alkylated homologues, which display a pyrolytic-like distribution. The mass spectrum and relative retention time of peak 72, not hitherto detected in any of the samples from the Midland Valley, suggest that this peak may correspond to the diagenetically-derived compound 2,9-Dimethylpicene (Wakeham *et al.* 1980a).

As retene is commonly thought to originate from the natural degradation of abietic acid (a major constituent of conifer resins), the prominence of retene in KBBI535/9 and KBBI185b is surprising considering that only trace amounts of resinite were observed in the former sample and no microscopically discernible resinous matter was detected in the latter. Because of the association of large quantities of retene with a pyrolytic-like distribution of aromatics, it is possible that at least some of the retene is also a high-temperature artefact. This possibility arises from the observation of retene as a product of the combustion of resinous softwoods (Ramdahl 1983).

The algal-rich samples from west Fife (KBBI382; Fig.4.82d and KBBI385) and central Fife (KBBI140; Fig.4.82c) differ from the aforementioned samples in that their aromatic distributions contain a prominent high molecular-weight "hump" and show a relatively minor contribution from the commonly-occurring series of alkylated naphthalenes and phenanthrenes. Compounds thought to be partially aromatised triterpenoid derivatives are prominent in the high molecular-weight region of the TIC traces. A feature worth noting is the prominence of cadalene in both spore-rich samples (central Fife) and algal-rich samples (west Fife) suggesting a possible dual origin (discussed later).

Benzohopanes and monoaromatic 8,14-secohopanes are present in all samples, but they are most conspicuous in the algal-rich sediments. In contrast, ethyl- or dimethyl-nuclear substituted triaromatics are more abundant, relative to other components, in the samples rich in higher-plant debris. A parallel observation was

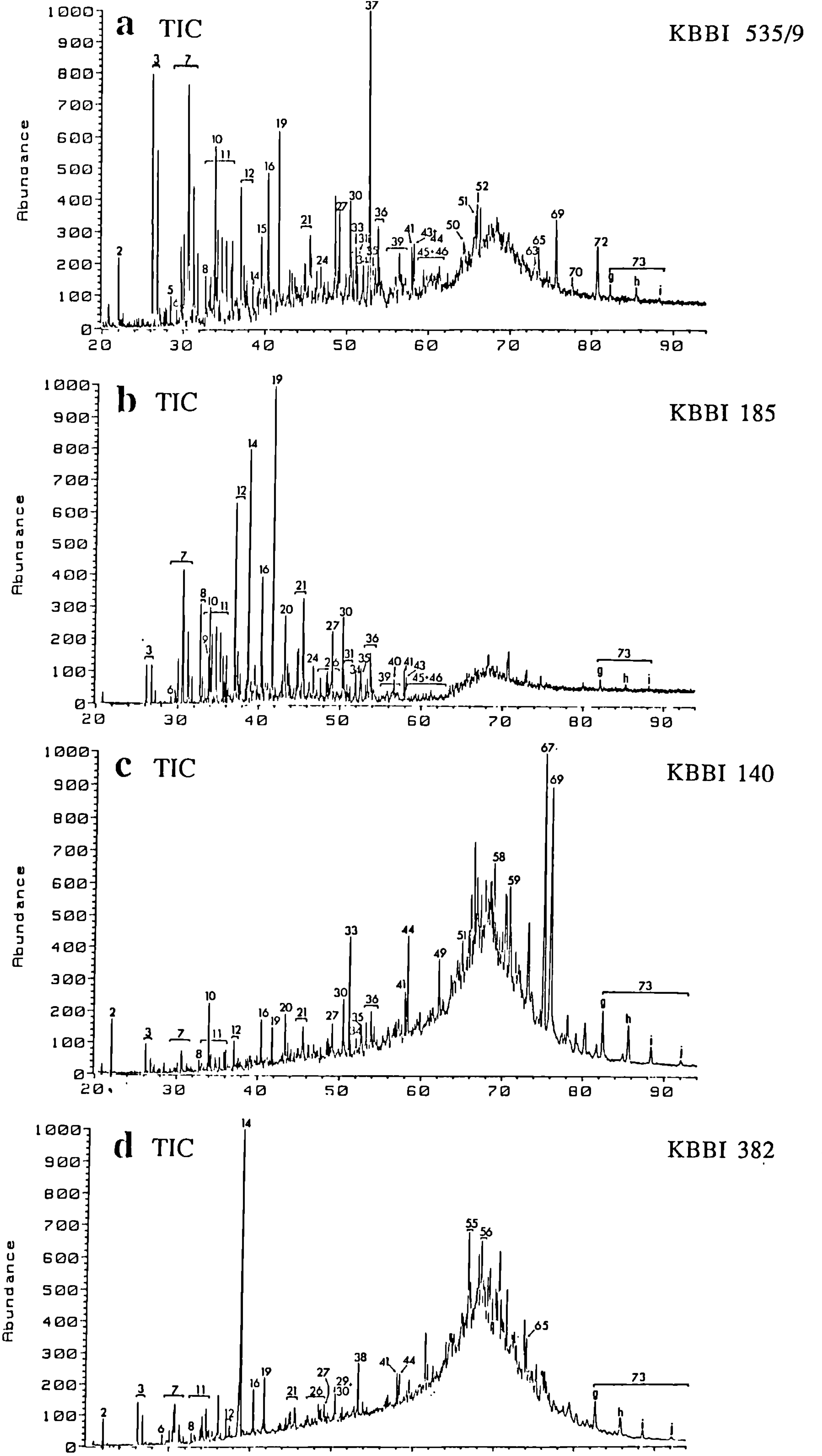


Fig.4.82 Traces showing the variation in aromatic hydrocarbon distributions in samples from the Kelty Blackband (peak assignments in Table 4.7).

made in relation to the enhanced concentration of peaks 6 and 9 noted in m/z 245 mass fragmentograms. The ratio of non-nuclear-substituted triaromatics to 1- and 4-methyl-substituted triaromatics varies (0.18- 1.84).

4.3.3.3.5 Black Metals

4.3.3.3.5.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Representative gas chromatograms illustrating the variation in the saturated hydrocarbon distributions within the Black Metals marine band throughout Fife are shown in Fig.4.83.

Gas chromatograms of the saturated hydrocarbon fractions of samples containing abundant higher-plant matter in which the liptinite fraction is dominated by sporinite and containing subordinate liptodetrinite (Plate 4.85) are shown in Fig.4.83a. The gas chromatogram of BM246 is very similar. *N*-alkanes are evenly distributed, overall, so that no skew of the *n*-alkane envelope is evident. An odd carbon-number preference exists throughout the medium and high molecular-weight ranges.

Samples containing $\geq$30% discrete lamalginite with subordinate sporinite and trace quantities of *Botryococcus* (BM266, 63 and 294; see Plates 4.86 and 4.88) have hydrocarbon distributions similar to that shown in Fig.4.83b. In contrast to Fig.4.83a, Fig.4.83b shows enhanced concentrations of long-chain *n*-alkanes in the C_{21}-C_{29} range which cause a slight skew of the *n*-alkane envelope. An OEP is still apparent, but in two samples (BM266 and 63) it occurs in two separate carbon-number ranges, C_{17}-C_{19}, and then in the high molecular-weight range, rather than uninterrupted throughout most of the *n*-alkane range, as in Fig.4.83a. This split in the OEP range may be a consequence of the dual higher plant and algal input. The presence of an OEP over much of the *n*-alkane range in BM294 could be a reflection of the lower contribution of discrete lamalginite and the higher contribution of sporinite observed in the sample during microscopic analysis, thus giving an OEP distribution more like that of Fig.4.83a.

Gas chromatograms showing hydrocarbon distributions from samples containing virtually no liptinitic matter are shown in Figs 4.83c and d. Sample BM561 (Fig.4.83c) contains only 5% sporinite, but shows an OEP encompassing most of the *n*-alkane range, akin to that of other samples with abundant sporinite (e.g. BM806a; Fig.4.83a). The CPI of BM561 is also close to that of BM806a. The medium molecular-weight bias in the *n*-alkane distributions in Figs 4.83c and d

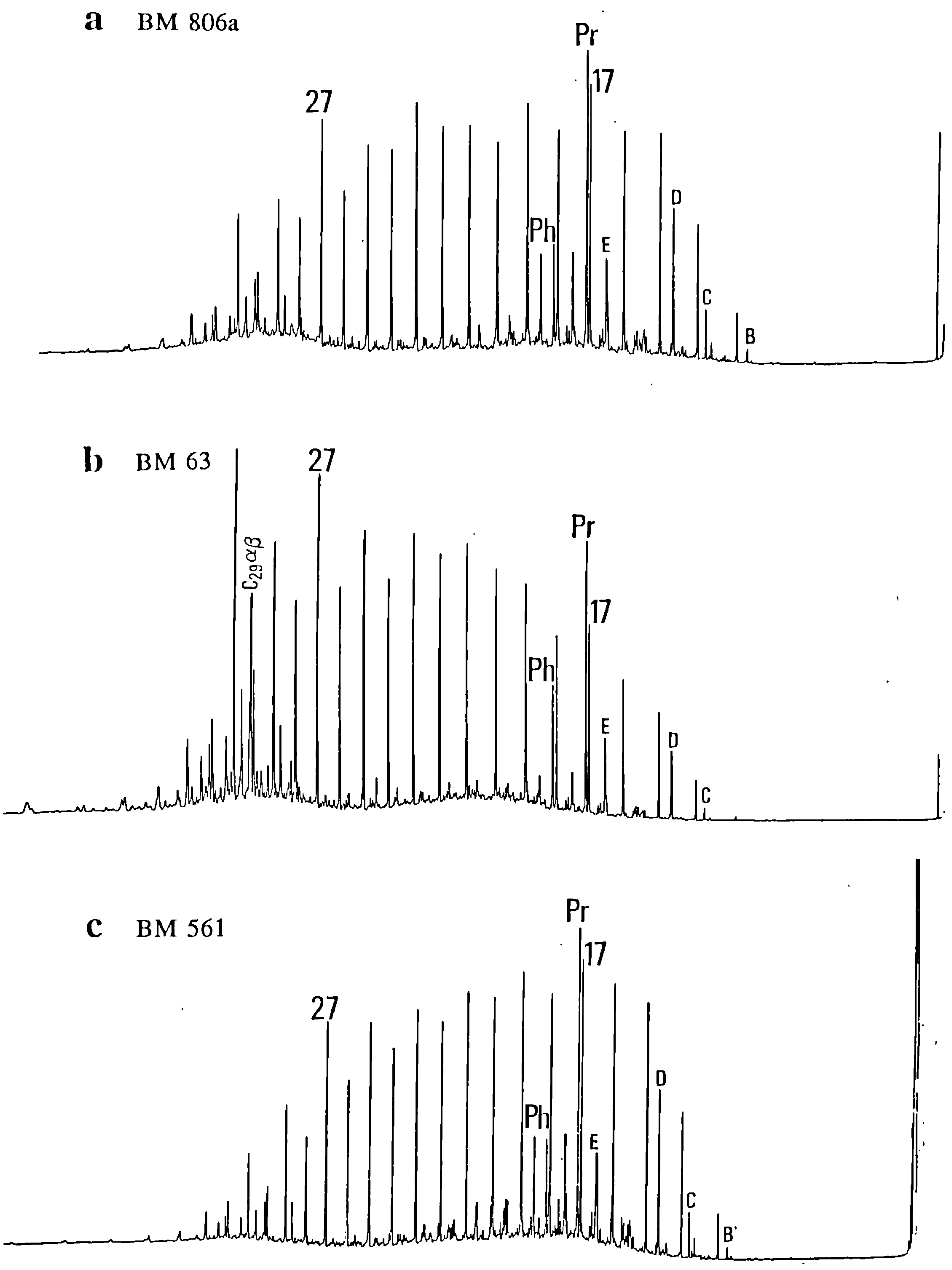
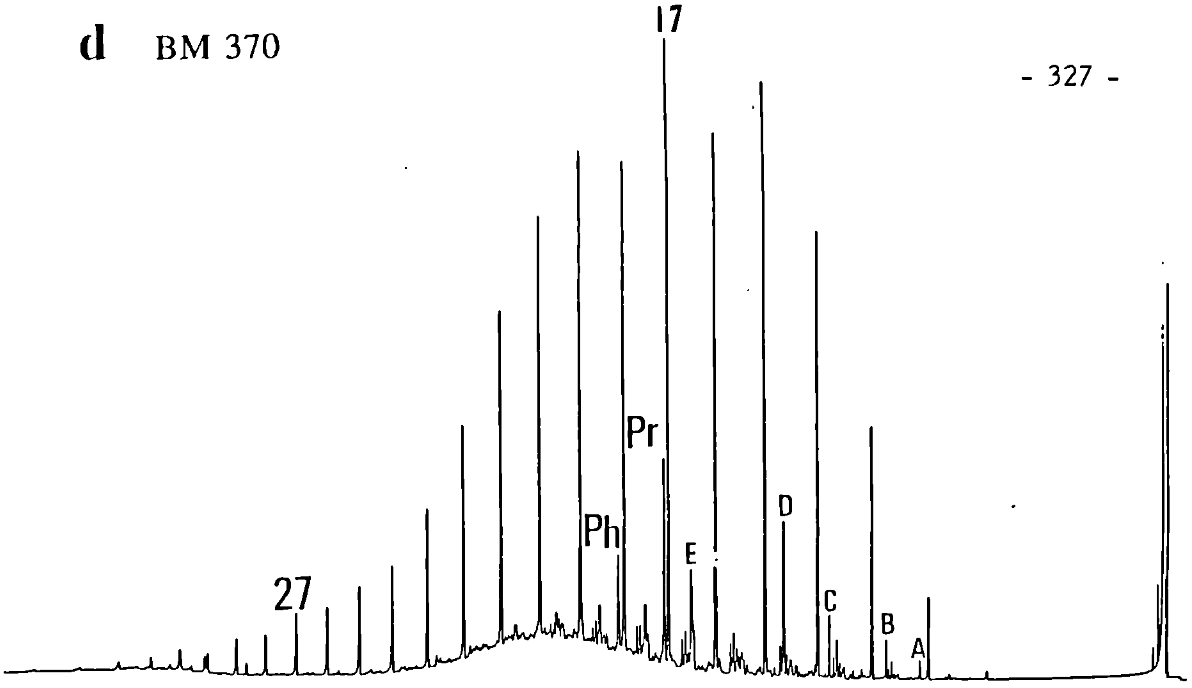
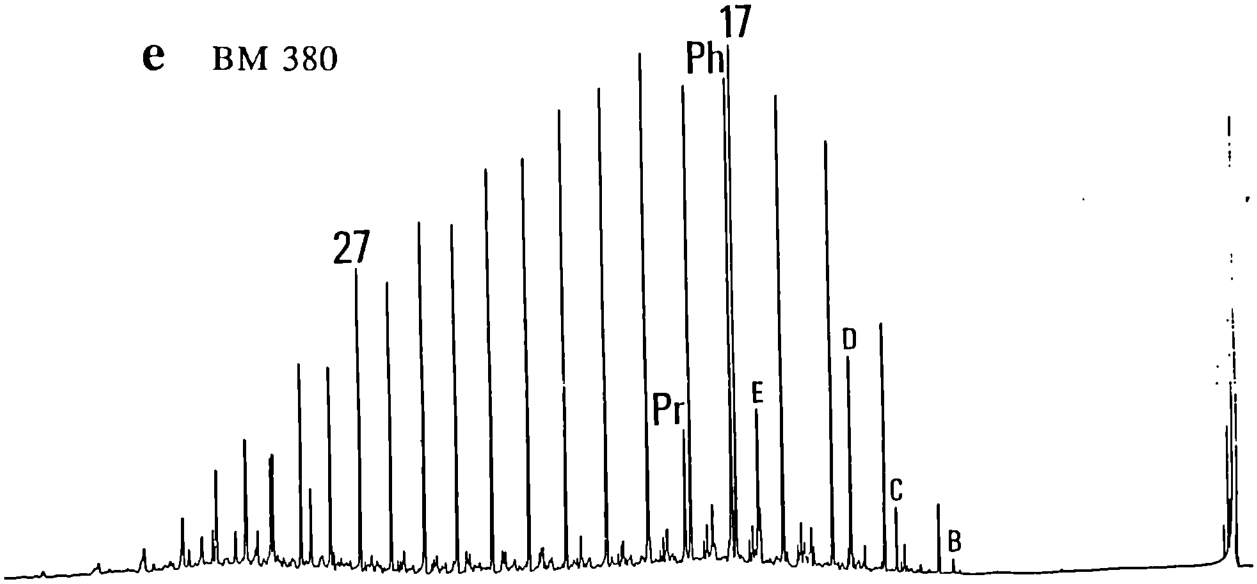


Fig.4.83 Representative gas chromatograms of the saturated hydrocarbon fractions of samples from the Black Metals Marine Band (assignments for isoprenoids given in Table 4.4).


d
BM 370
17
Pr
Ph
27
E
D
C
B
A


e
BM 380
17
Ph
27
Pr
E
D
C
B

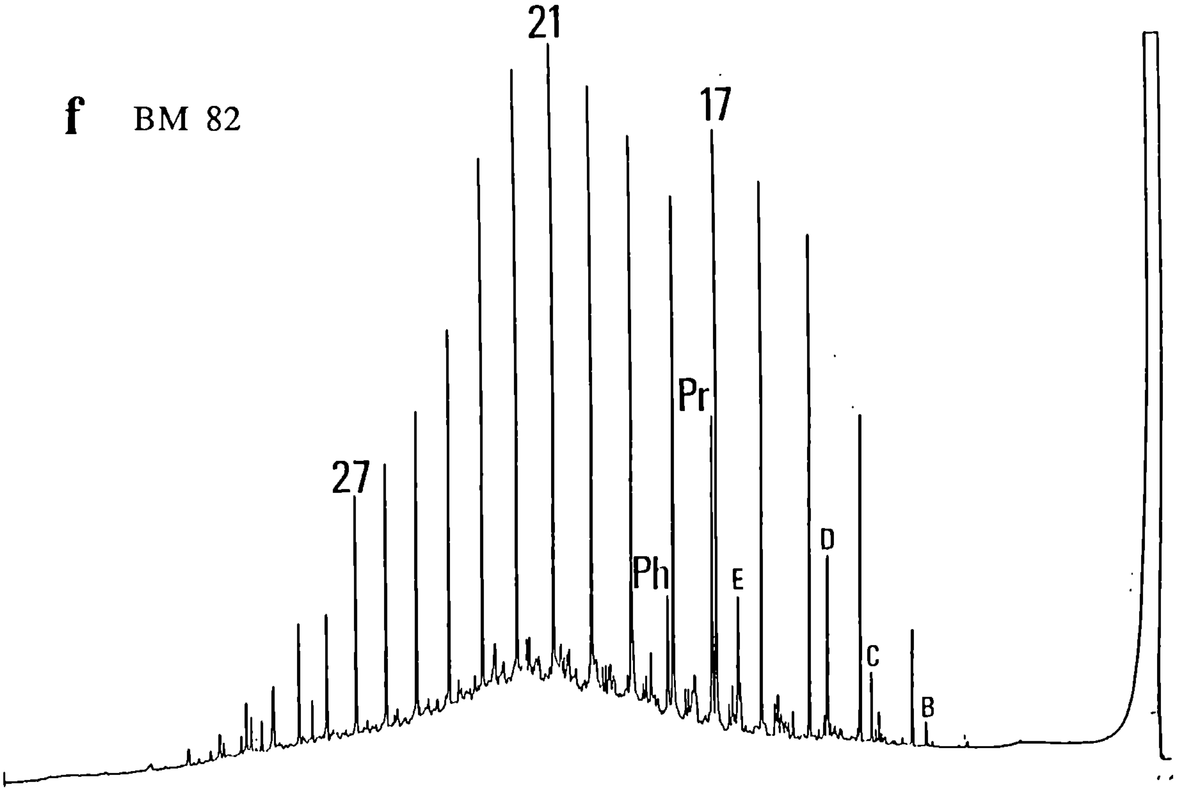

f
BM 82
21
17
Pr
27
Ph
E
D
C
B

Fig.4.83 (cont.).

may reflect the reduced content of spore exines in the samples. The fact that the *n*-alkane distribution in spore-rich BM262 (60% of organic matter) is virtually identical to that of BM370, in which only trace quantities of liptodetrinite are recognised, suggests that the last explanation is not universally applicable.

The *n*-alkane profiles of BM380 (Fig.4.83e) and BM195a closely resemble each other and they are similar in overall form to that of BM561 (Fig.4.83c). Lower OEPs in the first two samples are evident and they correlate with the presence of liptodetrinite thought to be of algal origin.

The increased abundance of C_{15}-C_{17} *n*-alkanes gives a bimodal appearance to the envelope in BM82 (Fig.4.83f) suggesting a joint algal and vascular-plant input, although no algae were seen in the sample. The similarity of the *n*-alkane envelope of BM82 to that of BM370 and BM262 is difficult to explain solely in terms of source input. A common factor is the "smoothness" of the *n*-alkane envelope beyond *n*-C_{21}. Although somewhat tentative, one possible explanation may be that these "mature" *n*-alkane distributions have arisen because of rapid thermal alteration of organic matter in proximity to the Midland Valley Sill. The distributions of the type shown in Figs 4.83d and f may therefore be the net result of an overprinting of biogenic alkanes by migrant, "mature" thermogenic alkanes from adjacent, thermally-altered sediments. Given that the maturation of the Black Metals by the Midland Valley Sill is widespread in Fife and that rank increase can occur over relatively short distances (see Chapter 5), such a scenario seems feasible in this province. Additional support for this idea is provided by the distribution of saturated hydrocarbons in BM641, which is very similar to those seen in BM82, 370 and 262. Although not apparent from microscopical examination, soluble-extract data indicate that the rank of BM641 is higher than $\%R_o$av=0.70. Further evidence pointing to a thermogenic origin for the smooth *n*-alkane envelopes above is apparent from the occurrence of these types of distribution in several bitumens for which a high temperature origin is strongly suggested by geochemical and geological data (see Chapter 6).

Pr/Ph ratios (2.21-4.67) are all indicative of oxidising depositional environments for the Black Metals. Pr/*n*-C_{17} are variable (0.32-2.38). There is a general trend from low Pr/*n*-C_{17} ratios (less than 1) in the Fife-Midlothian Basin and west Fife (Kincardine Basin) to higher values in the intervening E-NE-trending tract joining the two major basinal areas. There are no apparent trends in the petrographic constitution of the sediments which parallel the changes observed in the Pr/*n*-C_{17} ratios. Although the Black Metals horizon throughout Fife contains abundant higher-plant matter, the high Pr/*n*-C_{17} ratios in most of central Fife suggest that the terrestrial run-off occurred into a more restricted aquatic environment here than in the adjacent basinal areas. Isoprenoids would therefore be more likely to have been preserved in what may have been a relatively shallow, brackish, coastal shelf-like area in central Fife than under the more open-water marine regime inferred to have existed in the adjacent Fife-Midlothian and Kincardine Basins.

Gas Chromatography-Mass Spectrometry (GC-MS)

Fig.4.84a is a typical distribution illustrating the relatively low abundance of tricyclic and tetracyclic terpanes observed in the low-rank samples of the Black Metals that were submitted to gc-ms analysis. Tricyclic and tetracyclic terpanes are present in approximately equal amounts, although slightly enhanced concentrations of tetracyclic components are evident in samples containing abundant sporinite.

Differences in the pentacyclic distributions occurring in the Black Metals are evident from the mass fragmentograms (Figs 4.84a and b). Apart from the exclusive presence of peak 39 (showing major m/z 232 ion) in BM266, the hopane distribution (Fig.4.84b) is qualitatively equivalent to those in samples BM806a, BM195a and BM246, all three of which contain discrete lamalginite and/or liptodetrinite, at least some of the latter probably being of algal origin. The compound corresponding to the peak 30 is present in these three samples, but is not well resolved from the $C_{29}\alpha\beta$ hopane in BM266, thus explaining the accentuated width of this peak seen in Fig.4.84b.

When it occurs, bisnorhopane is seen in relatively high abundance in the Black Metals marine band, but it was only detected in samples from central Fife. Sampling bias may account for this observation, since gc-ms analyses were not performed on any specimens from west Fife; of the seven samples analysed, five were from central Fife. As in the Kelty Blackband, the two C_{29} pentacyclic terpenoids represented by peaks 26 and 28 are prominent in the samples containing bisnorhopane.

The sterane distributions of the low-rank Black Metals samples are all qualitatively similar: carbon-number distributions are in the order $C_{29}>C_{27}>C_{28}$ and the samples all plot in, or straddle, the "estuarine/bay" field in Fig.4.74. A m/z 217 mass fragmentogram typifying the distribution in BM266, 246, 195a and 561 is shown in Fig.4.84c.

The main variation in sterane distributions of the Black Metals is in diasterane content. Relatively low values of the diasterane/sterane ratio are recorded in samples BM266, 246 and 561; diasteranes are absent from BM195a: The much higher value of 0.60, determined in BM806a (Fig.4.84d) cannot be correlated with any specific microscopically-discernible organic constituent (the amorphous matter

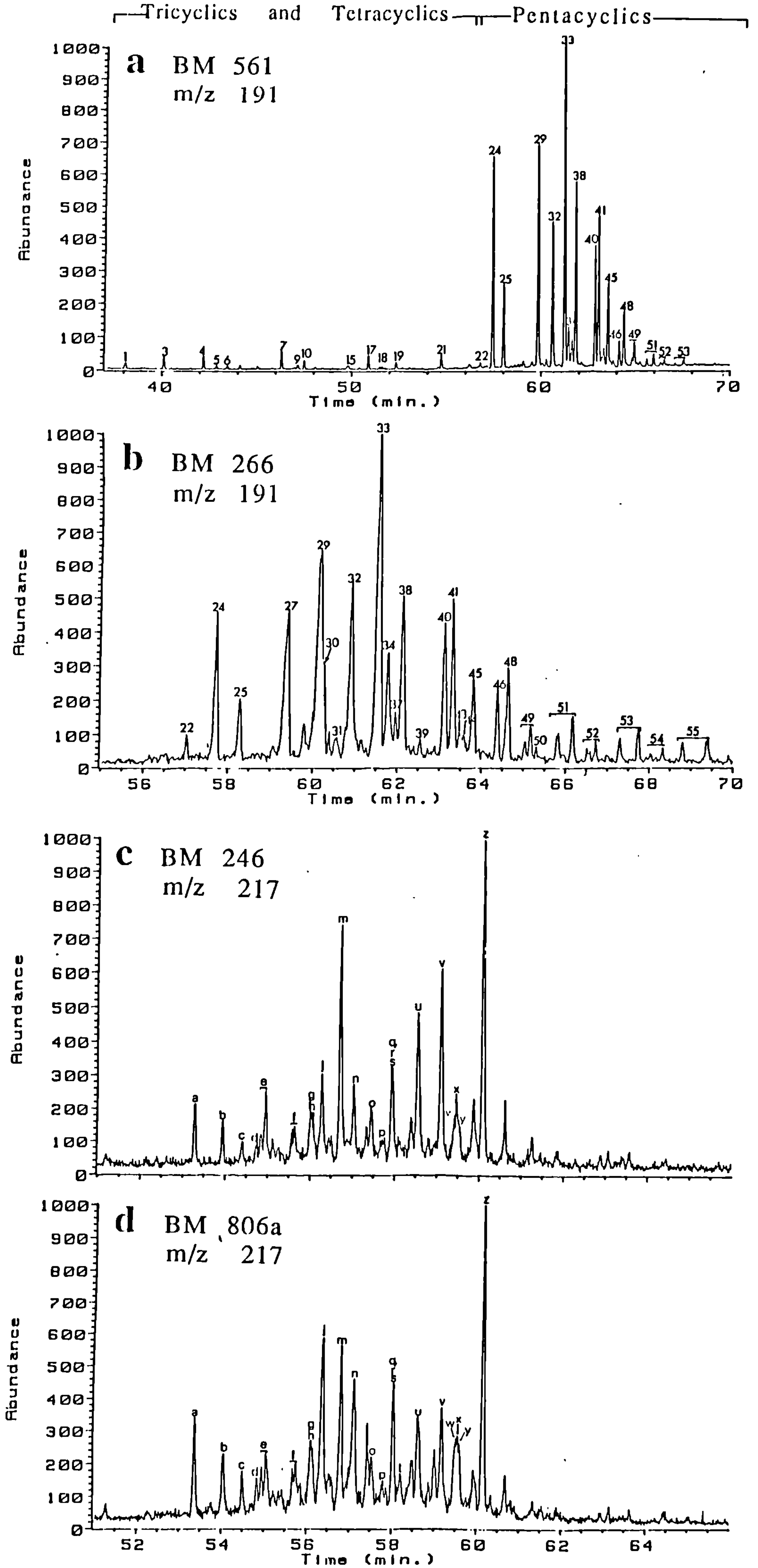


Fig.4.84 Mass fragmentograms showing typical distributions of terpanes (a,b) and steranes (c,d) in samples of the Black Metals (assignments in Tables 4.5 and 4.6).

present has the same fluorescence properties as the accompanying sporinite and therefore probably derives from it) or to any lithological pecularities.

4.3.3.3.5.2 Aromatic Hydrocarbons

TIC traces illustrating the different types of aromatic hydrocarbon assemblage found within the low-rank samples studied are shown in Fig.4.85. Fig.4.85a is virtually identical to the traces obtained from the other lamalginite-rich samples of the Black Metals, BM63 and BM294, while the TIC trace of Fig.4.85b typifies the profiles seen in the other samples investigated in which their maceral assemblages are dominated by higher-plant constituents.

The distribution of aromatics in Fig.4.85a resembles those of many of the algal-rich samples referred to in previous sections. Alkylated naphthalenes and

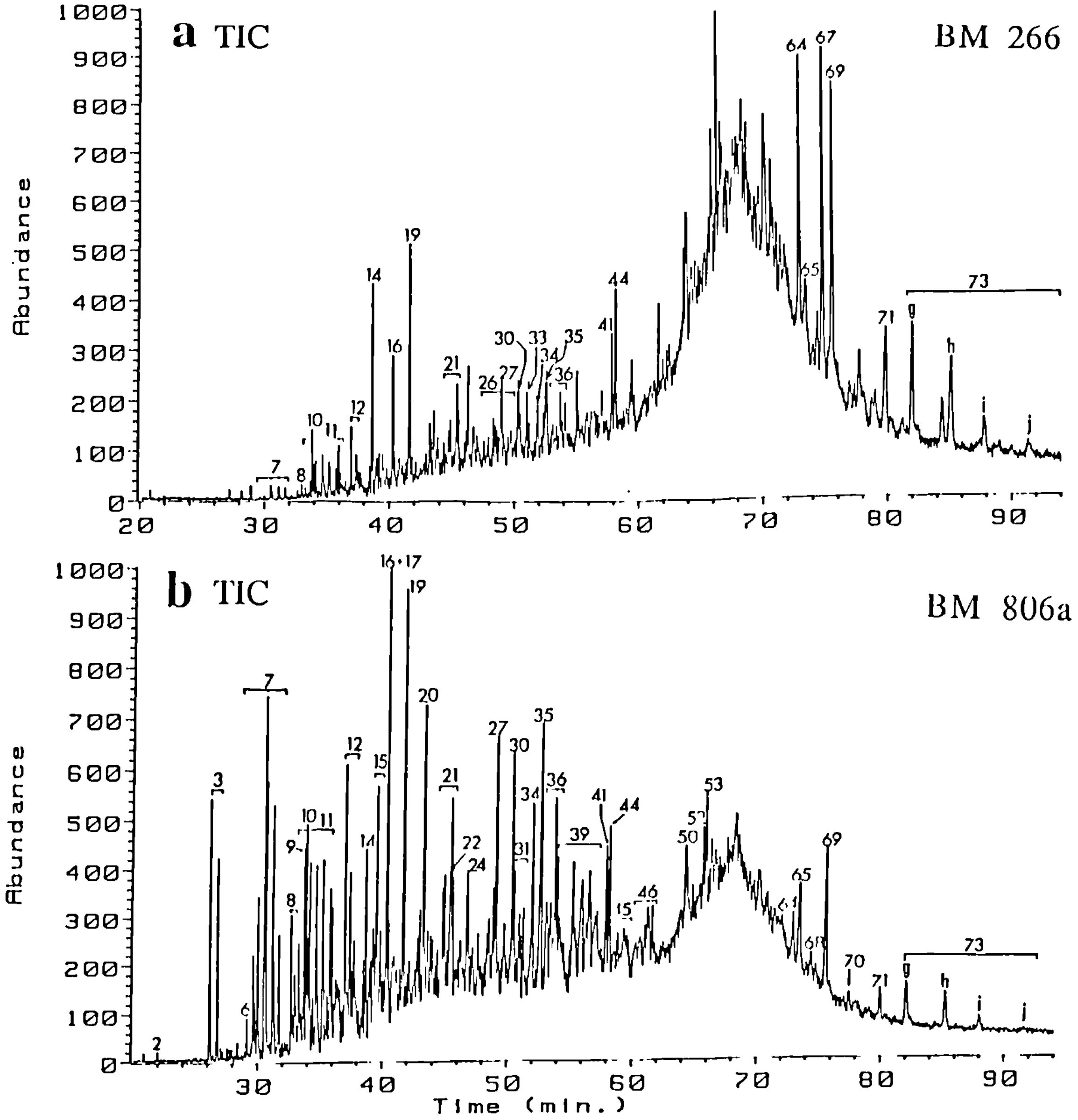


Fig.4.85 Traces illustrating the variation in the distribution of aromatic compounds in the Black Metals marine band (peak assignments shown in Table 4.7).

phenanthrenes are of relatively minor importance, and there is a pronounced high molecular-weight hump from which major contributions of compounds based on triterpenoid structures are resolved. The later-eluting benzohopanes are very prominent. Of the lower molecular-weight constituents, the C_3 alkyl tetralin and alkylated naphthalene derivatives, cadalene (peak 14) and 1,2,5,6-tetramethylnaphthalene (peak 16) are conspicuous, as is phenanthrene. Peaks attributable to pyrolytic/combustion-derived PAH can be discerned in the aromatic fractions of the algal-rich facies of the Black Metals, but are of relatively minor abundance.

Only one algal-rich sample (BM266) was subjected to gc-ms analysis, which revealed the presence of aromatic steroids. Rearranged C-ring monoaromatics are present in relatively small amounts compared with non-rearranged components. Significant interference with benzofluoranthenes and benzopyrenes can be seen in the m/z 253 mass fragmentograms. The profile of the m/z245 mass fragmentogram is similar to that shown for the Dunnet Shale (Fig.4.23c). Non-methyl-substituted triaromatics exceed methyl-substituted components in abundance. Triaromatics with major ions of m/z 259 are present, but are not sufficiently abundant to be identifiable in the TIC trace.

The aromatic fractions of the remaining low-rank samples (rich in terrestrial debris) differ from those of the algal-rich samples because their aromatic distributions are dominated by alkylated naphthalenes and phenanthrenes, alkylbiphenyls (peaks 8, 12, 17, 20) and PAH with a pyrolytic-like distribution (Fig.4.85b). Benzohopanes are less abundant in the latter samples, in contrast to the dimethyl-/ethyl-substituted triaromatic steroids which are found in the high molecular-weight part of the TIC trace. Rearranged C-ring monoaromatics are relatively more abundant than in the algal-rich samples, but they are still subordinate to the non-rearranged components. In the two samples on which gc-ms analysis was performed, the non-substituted triaromatics exceeded the 1- and 4-methyltriaromatics in abundance.

4.3.3.3.6 Johnstone Shell Bed

4.3.3.3.6.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Representative gas chromatograms illustrating the variations in saturated hydrocarbon distributions observed in samples of the Johnstone Shell Bed are presented in Fig.4.86.

The generally invariant nature of the organic assemblages in the Johnstone Shell Bed, which consist almost entirely of vitrinite, inertinite and sporinite,

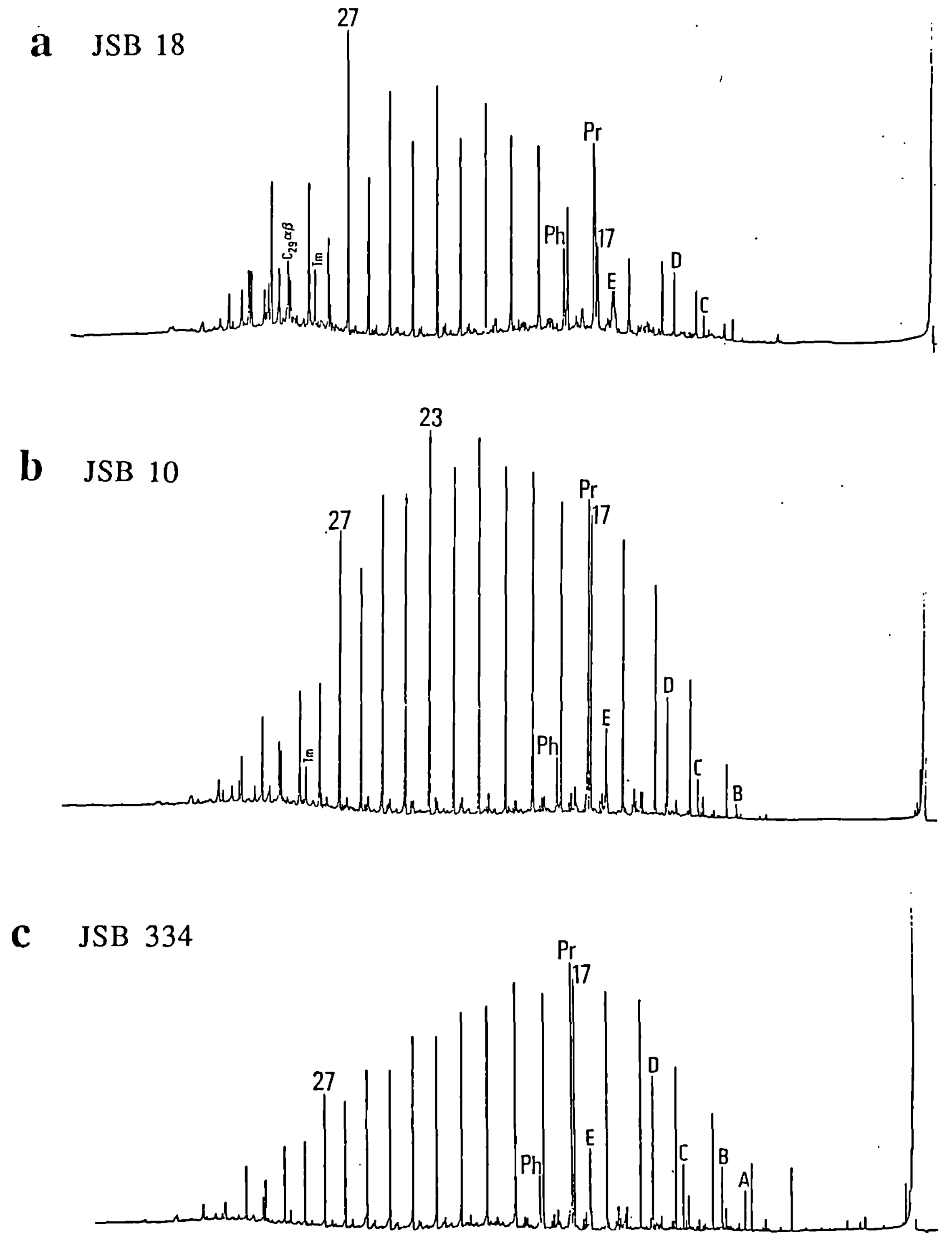


Fig.4.86 Gas chromatograms of the saturated hydrocarbon fractions of samples from the Johnstone Shell Bed (isoprenoid assignments given in Table 4.4).

mean that little variation is evident in the hydrocarbon distributions of the samples analysed. Any such variation might be difficult to detect in any case because of the higher rank of the Johnstone Shell Bed which is due to much of of this horizon lying within the thermal aureole of the Midland Valley Sill. The intrusion exerts a significant control on rank variation in Limestone Coal Group strata in Fife and Stirlingshire. Its effects are discussed more fully in Chapter 5.

The hydrocarbon distribution in JSB18 is consistent with its low rank (Fig.4.86a). The relatively high concentration of long-chain *n*-alkanes, which show a pronounced OEP in the C_{23}-C_{29} range, reflects the higher-plant input observed microscopically (unusual peaks eluting between *n*-C_{16} and pristane are contaminants from septum bleed). Plant-derived OEPs persist at higher ranks, but they are much diluted by thermogenic *n*-alkanes (Figs 4.86b,c). The gas chromatogram of JSB10 (Fig.4.86b) is very similar to that of JSB195, while the *n*-alkane envelope of JSB334 (Fig.4.86c) is very similar to those of JSB498, JSB294b and JSB13, although the isoprenoid/*n*-alkane ratios differ markedly due to rank variation.

Pr/Ph ratios for the samples where type effects can still be detected (JSB18, 10 and 334) lie in the range 2.18-5.88 and are indicative of oxidising depositional environments. The Pr/*n*-C_{17} ratios of these samples (1.06-2.02) indicate that the sediments accumulated in relatively restricted aquatic environments associated with coal swamps.

Gas Chromatography-Mass Spectrometry (GC-MS)

The 3-and 4-ringed terpanes are minor components, compared with the pentacyclics, as shown in a typical mass fragmentogram in Fig.4.87a. The distributions of tricyclics and tetracyclics in the low - rank samples investigated (JSB18, 334 and 10) are all relatively simple and closely resemble each other (Fig.4.87b). The 17,21-secohopanes dominate over the tricyclics in all samples.

Distributions of pentacyclic hopanes are qualitatively similar, the maximum variation being expressed by the differences between the hopane profiles in Figs 4.87a and 4.87c. The trace of Fig.4.87c is similar to the m/z 191 mass fragmentogram of JSB334. The difference in the concentrations of the C_{29} and $C_{30}\alpha\beta$ hopanes in the two types of profile cannot be related to any variation in the petrographic constitution of the sediments which is much the same in all three samples.

Trace quantities of bisnorhopane were detected in only one (JSB334) sample. No compound corresponding to peak 30 was detected in either the m/z 191 or m/z 177 mass fragmentograms of the low (or higher) rank samples of the

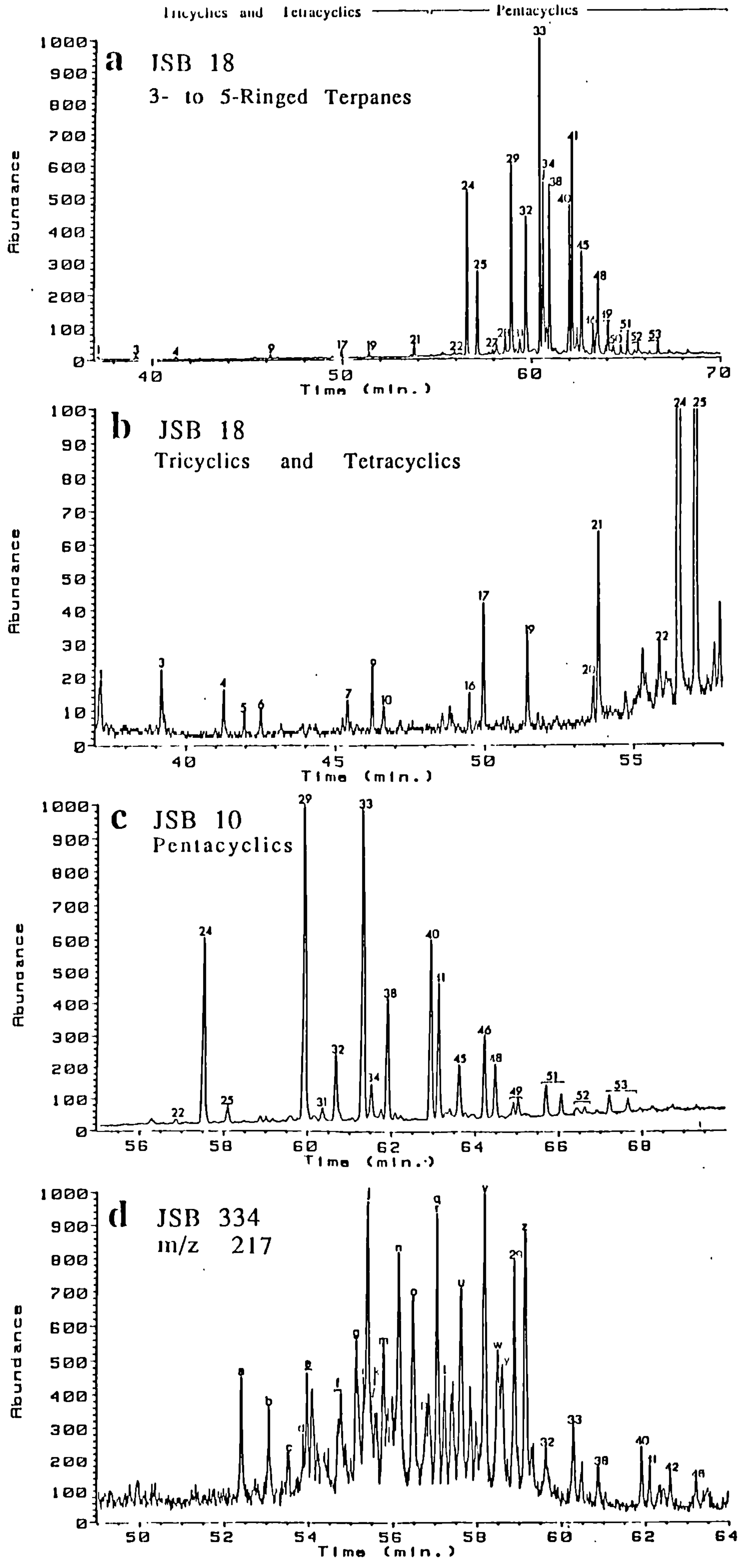


Fig.4.87 Mass fragmentograms showing the distribution of terpanes (a-d) and steranes (d) in samples of the Johnstone Shell Bed (assignments given in Tables 4.5 and 4.6).

Johnstone Shell Bed, despite the fact that the compound corresponding to peak 31, which often accompanies peak 30, was detected in all samples. It is possible that peak 30 was present in such small quantities that it could not be resolved from the $C_{29}\alpha\beta$ hopane.

M/z 217 mass fragmentograms (e.g.Fig.4.87d) show the order of abundance of steranes to be $C_{29}>C_{28}>C_{27}$ in all low-rank samples. The sterane distributions are such that the samples encompass the "terrestrial" and "estuarine/bay" field (Fig.4.74). The prominence of ααα20S isomers in sample JSB334 is considered to be anomalously high in view of the measured reflectance value of $\%R_oav=0.65$. This value is thought to be a true representation of the sample maturity since calculated reflectances, based on the methylphenanthrene index (Table A.6), are close to this value. Furthermore, this rank level is consistent with those attained by other samples from the same horizon located in the area of the Bowhill Mine (see rank-map data in Chapter 5).

Diasteranes are readily discernible in the m/z 217 mass fragmentograms, where they are greatly subordinate to steranes in samples JSB18 and 10. Diasteranes reach their maximum abundance in JSB334 (Fig.4.87d) in which the diasterane/sterane ratio is 0.63.

4.3.3.3.6.2 Aromatic Hydrocarbons

The TIC trace shown in Fig.4.88a illustrates the distribution of aromatic components encountered within JSB18 while profiles of the type shown in Fig.4.88b are characteristic of all the other samples (low and high rank) analysed.

The aromatic distributions of all the samples are marked by a preponderance of alkylated naphthalenes, phenanthrenes and biphenyls. A series of pyrolytic-like PAH is ubiquitous in the sample suite, but is most prominent within JSB18. The latter sample is unique within the Johnstone Shell Bed samples studied because of the prominence of a high molecular-weight hump from which steroidal and triterpenoidal compounds can be identified. Benzohopanes are also relatively prominent in the above sample, but they could not be detected at all in other specimens. Given the overall similarity in the petrography of the extracted samples, it is not readily apparent why the aromatic distribution of JSB18 differs from those characteristic of the other samples.

Steroidal components were only detected in JSB334 and 18. C-ring monoaromatics are confined to the latter: the rearranged components are very pronounced, although coelution with compounds with a molecular weight of 252 occurs (Fig.4.88c). Dimethyl- or ethyl-substituted triaromatic steroids are also restricted to JSB18 and can be discerned in the TIC trace. 1- and 4-methyl triaromatics

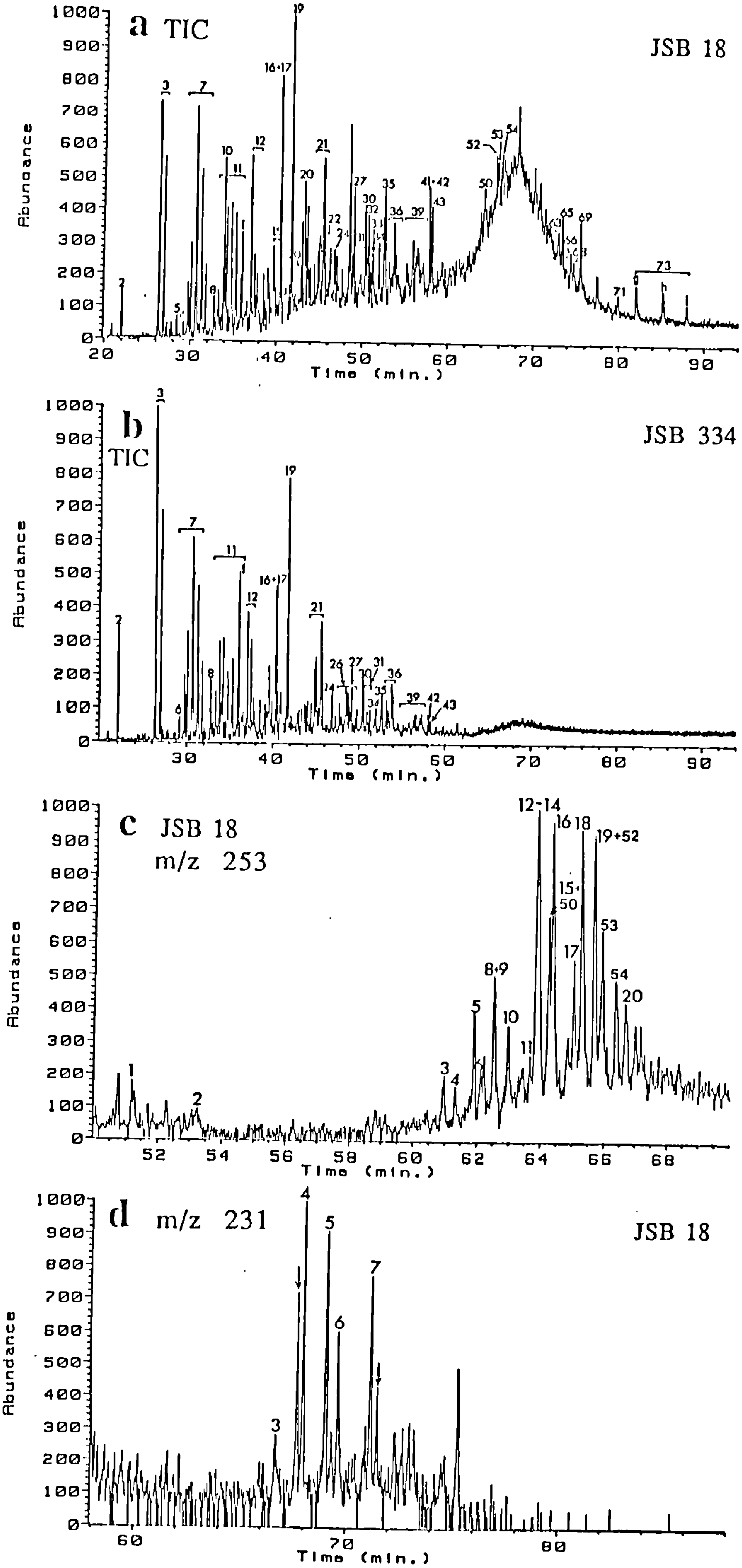


Fig.4.88 Distribution of total aromatic hydrocarbons (a,b) and aromatic steroids (c,d) in samples of the Johnstone Shell Bed (assignments in Tables 4.7, 4.8 and 4.9).

occur in the above samples, with the distributions being similar to that observed in the Dunnet Shale (Fig.4.23c). Unlike the m/z 231 mass fragmentograms of any of the other samples discussed so far, those of the Johnstone Shell Bed differ because of the occurrence of the arrowed peaks in Fig.4.88d. These components, also showing a base peak with m/z 231, may represent triaromatics with a different side-chain configuration (G.D.Abbott *personal communication*).

4.3.3.3.7 Miscellaneous Marine Horizons

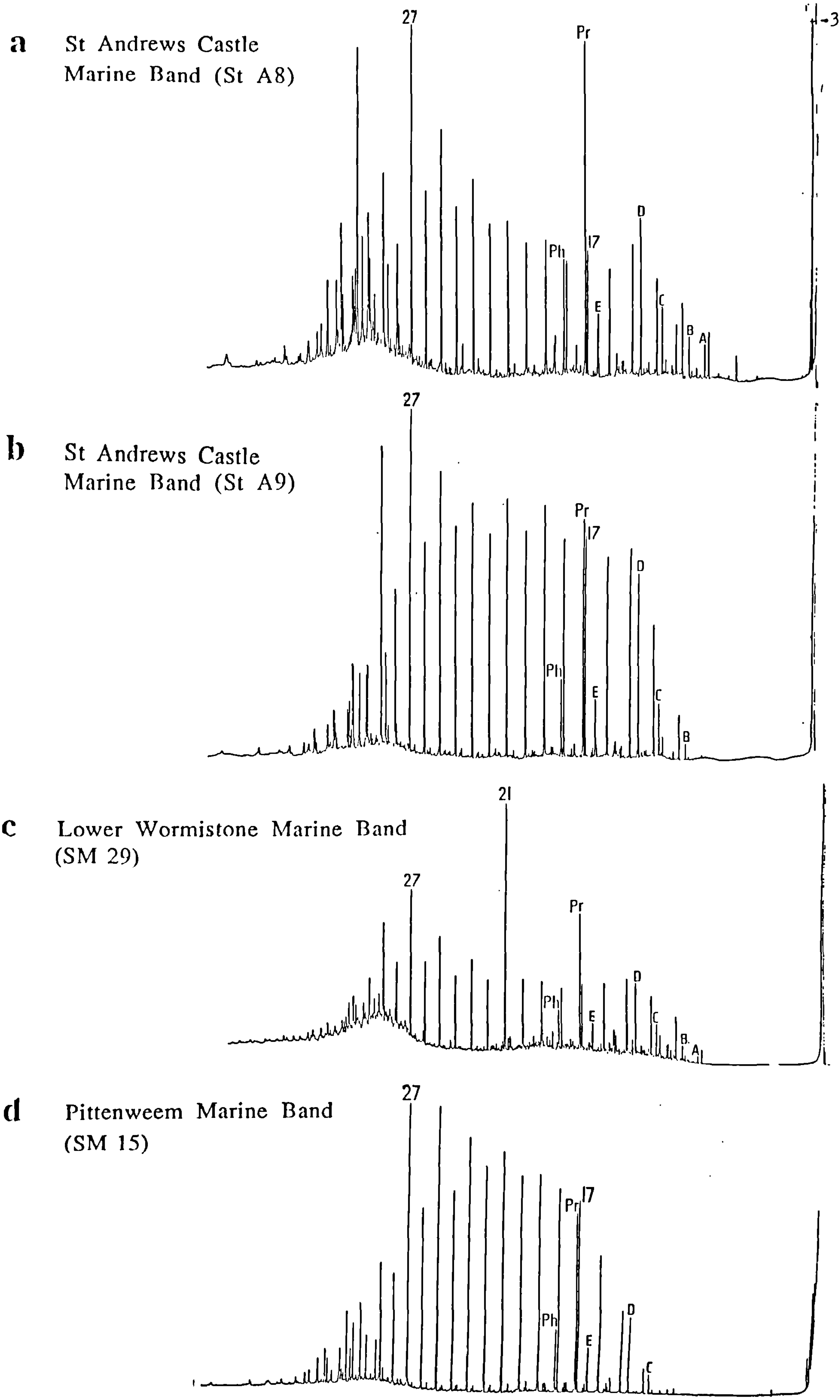
4.3.3.3.7.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of shale samples known to be marine on the basis of faunal content are shown in Figs 4.89a-k. The gas chromatograms of SM1, 4 and 5 are not included here as the *n*-alkane distributions are very similar to that of SM15 (Pittenweem Marine Band; Fig.4.89d). The ranks of samples CO1, GAR13, GAR15 exceed $\%R_o av=0.70$, but their chromatographic traces still retain characteristics attributable to source input and are therefore included here.

There is clearly a marked variation in the hydrocarbon distributions of the miscellaneous marine samples analysed. Most of the *n*-alkane envelopes are unimodal, with peak maxima occurring in the medium (at C_{15} of C_{17}) or high (C_{27} or C_{29}) molecular-weight range, reflecting a predominance in the extracts of algal or terrestrial lipids respectively. Despite their undisputed deposition in marine environments, there is a marked terrestrial imprint on the hydrocarbon distributions of all samples, defined by the presence of relatively large concentrations of long-chain *n*-alkanes which display a marked odd-carbon-number preference. This terrestrial fingerprint is consistent with the observations of significant amounts of terrigenous material in the samples, as determined by microscopy, and is particularly pronounced in the marine shales from east Fife (Figs 4.89a-d). The major peak at *n*-C_{21} in the Lower Wormiston Marine Band (Fig.4.89c) has not been observed in any other marine (or non-marine) samples analysed and may reflect the input of a specific organism. Alternatively, the very low concentration of aliphatic matter in the sample, coupled with the low EOM yield, means that there is a possibility that the major peak is a contaminant.

Samples in which the kerogen comprises $\geq$20% of the wispy and/or flecky liptodetrinitic matter have enhanced concentrations of *n*-alkanes in the C_{15}-C_{19} range and show a pronounced OEP (e.g.Figs 4.89e,h,i,j). This distribution confirms the inferred algal affinity of the liptodetrinitic material which was proposed on the basis of fluorescence properties.



a St Andrews Castle Marine Band (St A8)

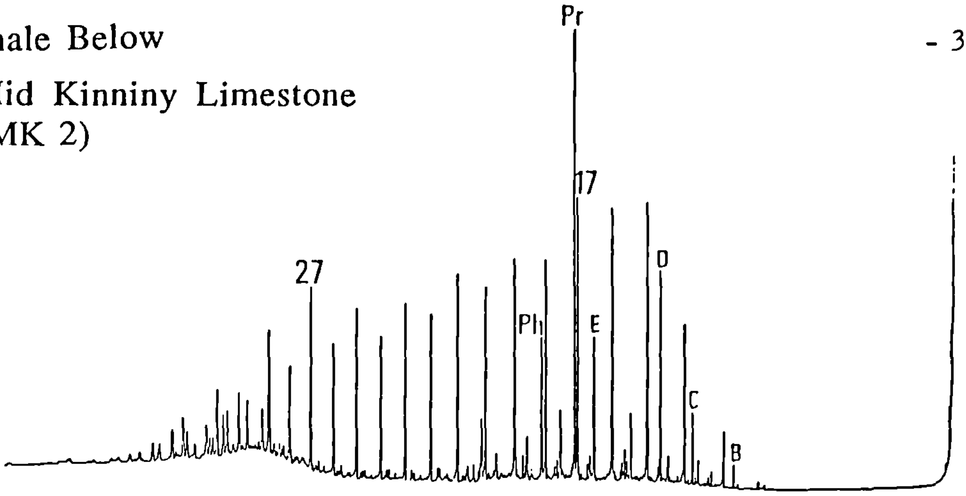
b St Andrews Castle Marine Band (St A9)

c Lower Wormistone Marine Band (SM 29)

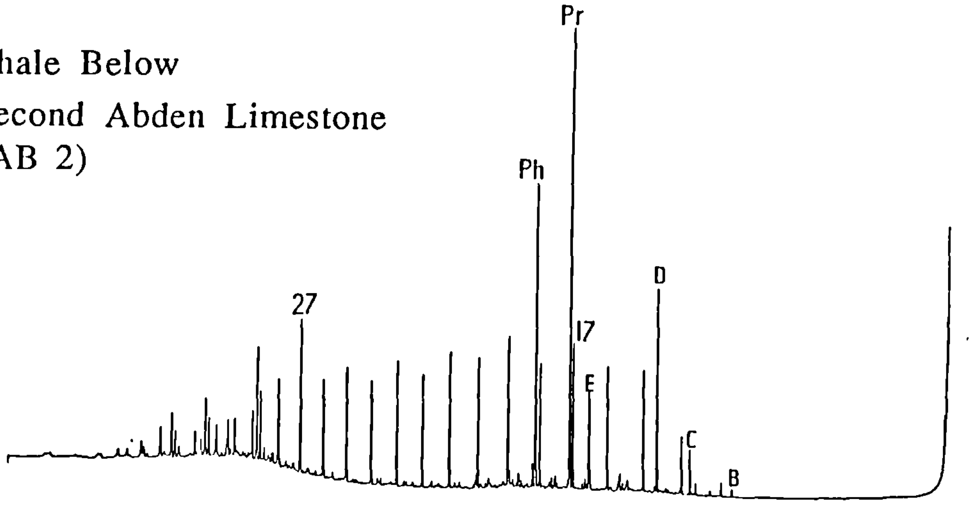
d Pittenweem Marine Band (SM 15)

Fig.4.89 Gas chromatograms of the saturated hydrocarbon fractions of miscellaneous marine samples (isoprenoid assignments given in Table 4.4).

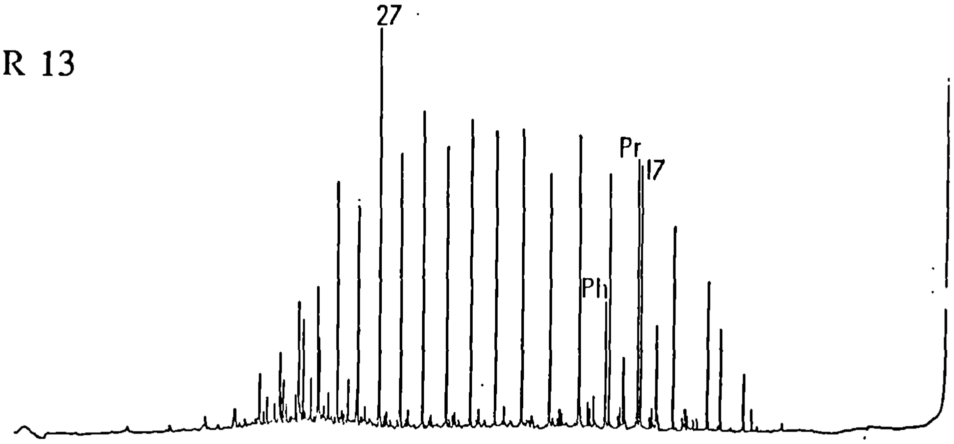
e Shale Below
Mid Kinniny Limestone
(MK 2)



f Shale Below
Second Abden Limestone
(AB 2)



g GAR 13



h GAR 15

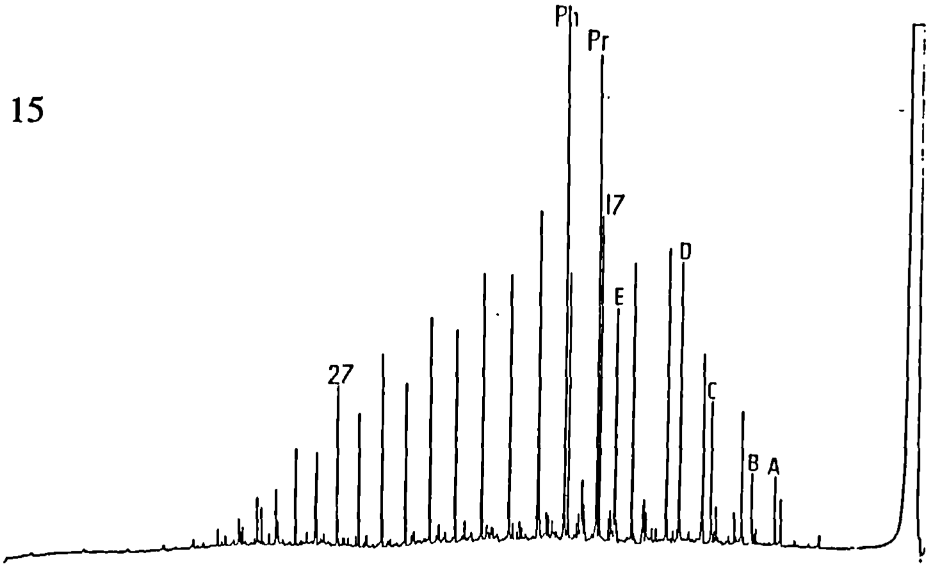


Fig.4.89 (cont.).

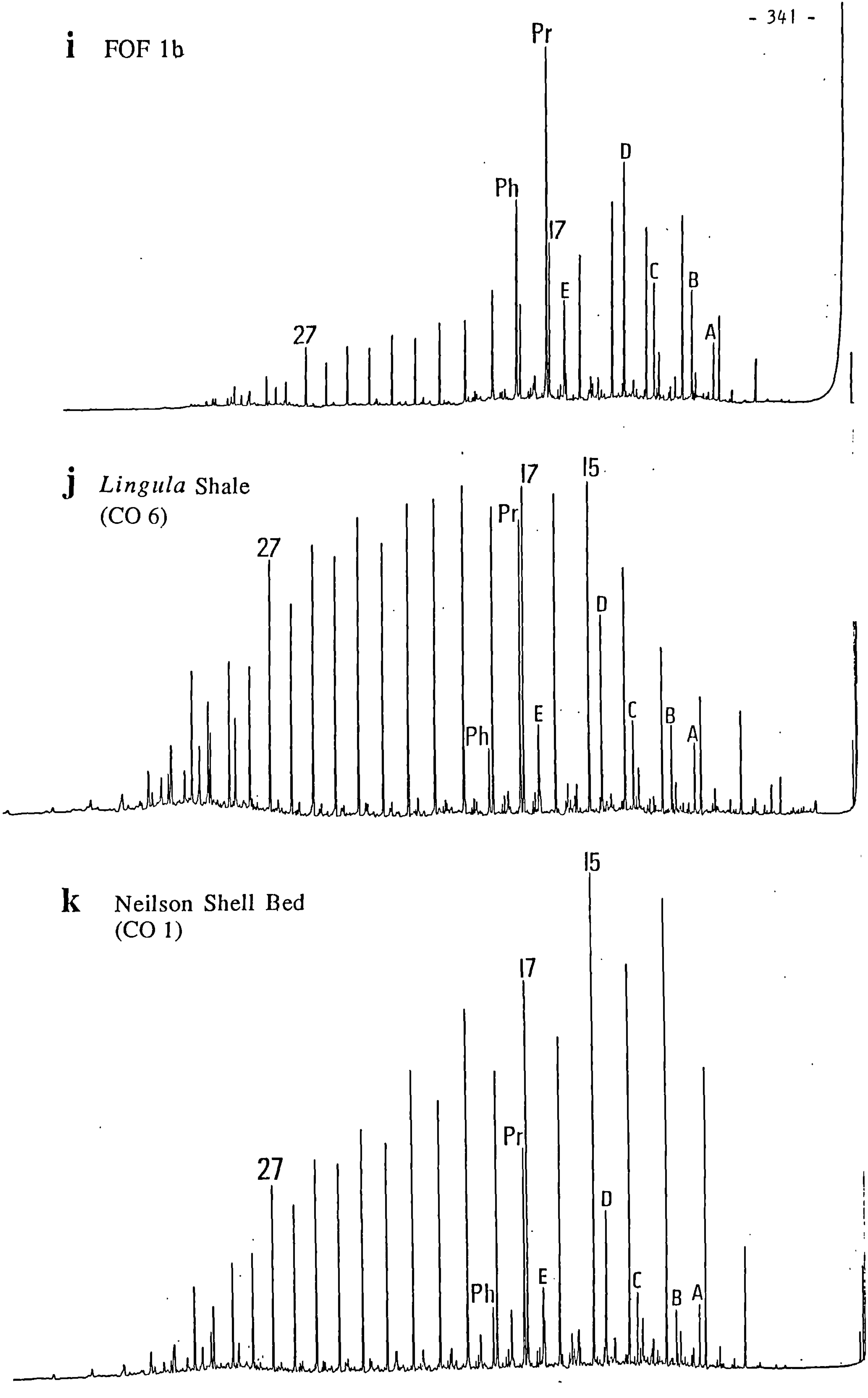

i
FOF 1b
Pr
D
Ph
17
E
C
B
A
27
j
Lingula Shale
(CO 6)
17
15
Pr
27
D
Ph
E
C
B
A
k
Neilson Shell Bed
(CO 1)
15
17
Pr
27
D
Ph
E
C
B
A

Fig.4.89 (cont.).

Apart from sample GAR15 (marine shale above the Plean No.1 Limestone in the Gartarry Toll Borehole; Fig.4.89h), Pr/Ph ratios are high (1.52-3.63) and are indicative of oxic depositional environments. The ratio of 0.92 for GAR15 suggests a greater prevalence of sedimentary anoxia during the deposition of this horizon. Other samples from the Upper Limestone Group in west Fife possess very similar hydrocarbon distributions to that of Fig.4.89h (*cf.* C82 and C428 in Fig.4.74), suggesting that anoxic environments may have been prevalent during the accumulation of some of the marine strata within this group, at least in west Fife.

Isoprenoid/*n*-alkane ratios are highly variable within the suite of samples investigated. The samples in which relatively high concentrations of Pr and Ph are preserved may have been deposited in marine environments that were rather more restricted than those in which the samples with relatively low ratios accumulated, as the latter environments are not thought to be as conducive to the repression of bacterial oxidation of the phytol precursor as the former sedimentary regime (Lijmbach 1975).

Gas Chromatography-Mass Spectrometry (GC-MS)

Tricyclic and tetracyclic terpanes are present in extremely low concentrations, with respect to the pentacyclics, in the miscellaneous samples considered and they could not be detected at all in StA9 (part of the St.Andrews Castle Marine Band) or in SM29 (the Lower Wormistone Marine Band). Despite the "noisy" traces obtained for most samples, a distribution of 3- and 4-ringed terpanes was established in all the samples that was qualitatively similar to that shown in Fig.4.87b. The 17,21-secohopanes are present in higher abundance than the tricyclics in all samples except FOF1b and those from the Gartarry Toll Borehole (GAR13 and GAR15). The terpane distribution in the Gartarry samples may be a consequence of rank rather than type control since their unsuppressed reflectances are both $\%R_oav=0.85$.

Fig.4.90 illustrates differences in the hopane distributions in the suite of miscellaneous marine shales investigated. The mass fragmentogram of *Lingula* shale (Fig.4.90a) is similar to that of FOF1b (and the higher-rank Neilson Shell Bed). The hopane profile in Fig.4.90b closely resembles those seen in samples SM1, 4 and MK2, while the distribution in Fig.4.90c typifies those of SM29 and StA9. No marked changes in the shape of the hopane envelopes are evident in the different samples, but variations in the type and distribution of components present are apparent. They relate to differences in rank as opposed to organic input. This factor will be discussed further in Chapter 5.

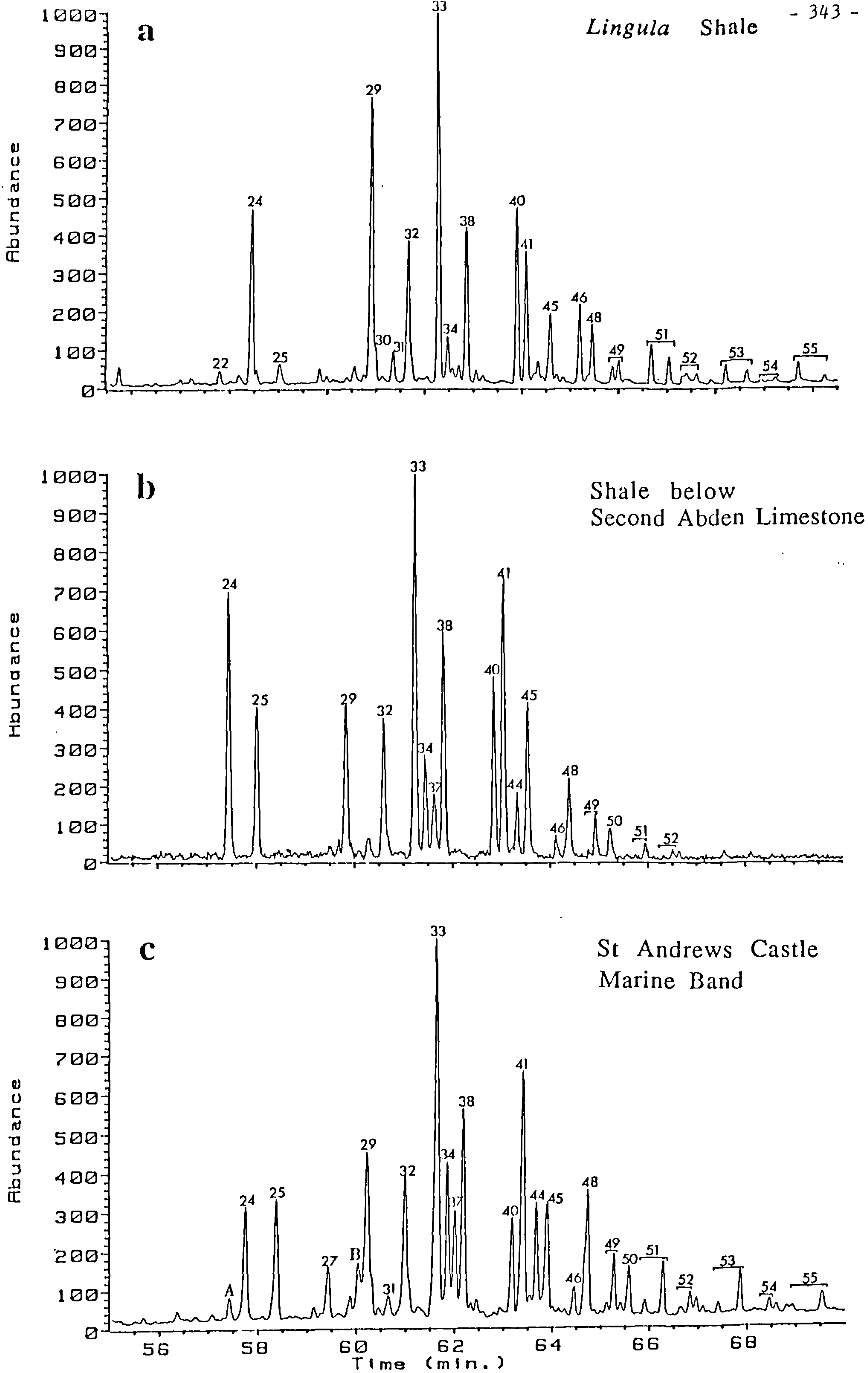


Fig.4.90 M/z 191 fragmentograms illustrating the differences in hopane distributions in the miscellaneous marine samples analysed (peak assignments shown in Table 4.5).

Samples SM29, StA8, StA9, and StA6 (a coal from the same field section as StA8 and StA9 and referred to in Section 4.3.3.2.2) are the only samples encountered in the present project in which hopenes were recognised. Peaks A and B in Fig.4.90c were tentatively identified as C_{27}22,29,30-trisnorhop-13(18)-ene and C_{29}30-norhop-13(18)-ene respectively on the basis of mass spectral characteristics.

The unknown C_{29} pentacyclic triterpane corresponding to peak 30 was detected in the *Lingula* shale, the shale below the Second Abden Limestone and also in the two higher-rank samples from Gartarry Toll Borehole. Bisnorhopane occurs in greatest abundance, relative to the $C_{30}\alpha\beta$ hopane, in StA8, but also occurs in much smaller concentrations in StA9, SM29, FOF1b and GAR13.

The $C_{29}\alpha\alpha\alpha$20R sterane dominates the m/z 217 mass fragmentograms in all but one sample in the suite of miscellaneous low-rank samples studied. The $C_{27}\alpha\alpha\alpha$20R sterane is slightly more abundant than the $C_{29}\alpha\alpha\alpha$20R sterane in the shale below the Second Abden Limestone. The relative abundance of the C_{27} and C_{28} steranes varies, but C_{27} steranes invariably prevail, giving rise to a distribution of the type already seen in Fig.4.84d. The majority of samples plot in the "estuarine/bay" field of Fig.4.74. Although their ranks are higher than $\%R_o$av=0.70, the liptinite-rich samples from the Gartarry Toll Borehole and a sample from the Neilson Shell Bed (CO1) are included in the plot for comparison. Although the increased rank of Gartarry samples ($\%R_o$av=0.85) may have influenced the carbon-number distribution of the steranes to some degree, the disparity between the C_{27} and C_{28} sterane content in these samples and that of the other marine shales is probably too great to be attributed to rank alone, particularly since the high-rank sample CO1, with a reflectance of $\%R_o$av=0.78, plots in the centre of the field occupied by the other marine samples.

The diasterane/sterane ratios of the samples varied from zero to 0.52 for samples with $\%R_o$av<0.70. The high ratios recorded for GAR13 (0.75) and GAR15 (1.34) may reflect some rank influence, but since CO1 has a diasterane/sterane ratio of 0.24, type control is probably prevalent.

4.3.3.3.7.2 Aromatic Hydrocarbons

The distributions of aromatic components in the majority of low-rank samples from Fife (SM1,4,15,29, MK2, TK2, AB2) and in FOF1b and the *Lingula* shale all closely resemble those shown in Fig.4.88a. Although the aromatic profiles of the samples from the St.Andrews Castle Marine Band (StA8 and StA9) are similar to those of the other samples, enhanced concentrations of simonellite (peak32) are apparent.

Monoaromatic 8,14-secohopanes, benzohopanes and aromatic steroids were identified in all samples. Rearranged C-ring monoaromatic steroids are prominent constituents in the m/z 253 mass fragmentograms of all the above samples and they are present in amounts comparable with the non-rearranged components. Profiles of the m/z 245 mass fragmentograms resemble those seen in coals, although peaks 4, 6 and 9 are not so pronounced. Components thought to be dimethyl- or ethyl-substituted triaromatics, showing a base peak of m/z 259, can be discerned in all the above samples. For samples on which gc-ms was performed, most values of the m/z 231/245 ratios are less than 1 (average value is 0.90).

Although of a rank greater than that taken as the upper limit for inclusion in the study of type variation, the aromatic distribution of sample AB3 (marine shale below the 3rd Abden Limestone) is worth noting because a similar distribution of aromatics was observed in the algal-rich Q shale. The distribution in AB3 (Fig.4.91) is relatively simple and is pyrolytic-like, with distributions of alkylated naphthalenes and phenanthrenes swamped by parent PAH.

4.3.3.4 Fife Coastal Sections

Because of proximity to the Fife coastal exposures and penetration of the same parts of succession, the following borehole samples have been included within this sample suite: CS4177 (Braefoot E15 bore; Pittenweem Beds), CS (Sypsies Bore, Crail; Anstruther Beds), CS7 (Newburgh Bore; Ballagan Beds) and samples SBO7516, SBO7517 and ANSTF from the Anstruther Borehole (Anstruther Beds).

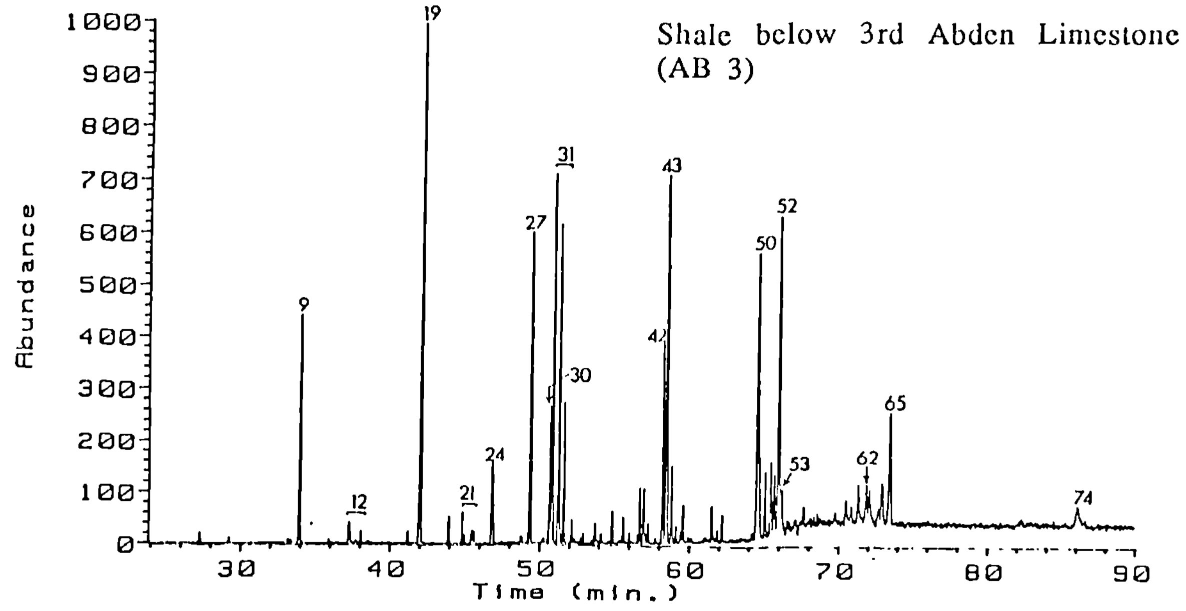


Fig.4.91 Total Ion Current (TIC) trace showing the distribution of aromatics in the shale below the 3rd Abden Limestone (peak assignments in Table 4.7).

4.3.3.4.1 Extract Yields and Gross Compositions

EOM yields vary from <0.1% to 2.4%, increased yields generally paralleling increases in organic content of the samples. Carbon-normalised yields for those samples for which TOC data are available vary from 9.1-93.6mgEOM/gTOC. No depth-related trend in EOM yield is evident within the Pathhead to Anstruther Wester sections; thus the variation in EOM yields appears to be reflecting organic-matter type variation. The highest carbon-normalised yields correspond to the algal-rich samples in the Pittenweem and Anstruther Beds, referred to in Section 4.3.3.1.4. The highest yield recorded was from SM25 in the Randerston section. Given the relatively low rank of the sample (estimated "true" reflectance value is c.$R_o$av=0.54), the high yield may indicate a significant contribution from bituminous matter seen to exude from the vitrinite in this sample.

Variation in EOM composition is shown in the ternary plot of Fig.4.92. There is a general trend towards an increase in the proportion of aliphatics and aromatics in the extracts as the amount of liptinite matter in the sample increases. Extracts containing over c.20% aliphatics are those from samples in which the maceral assemblages are dominated by algal components.

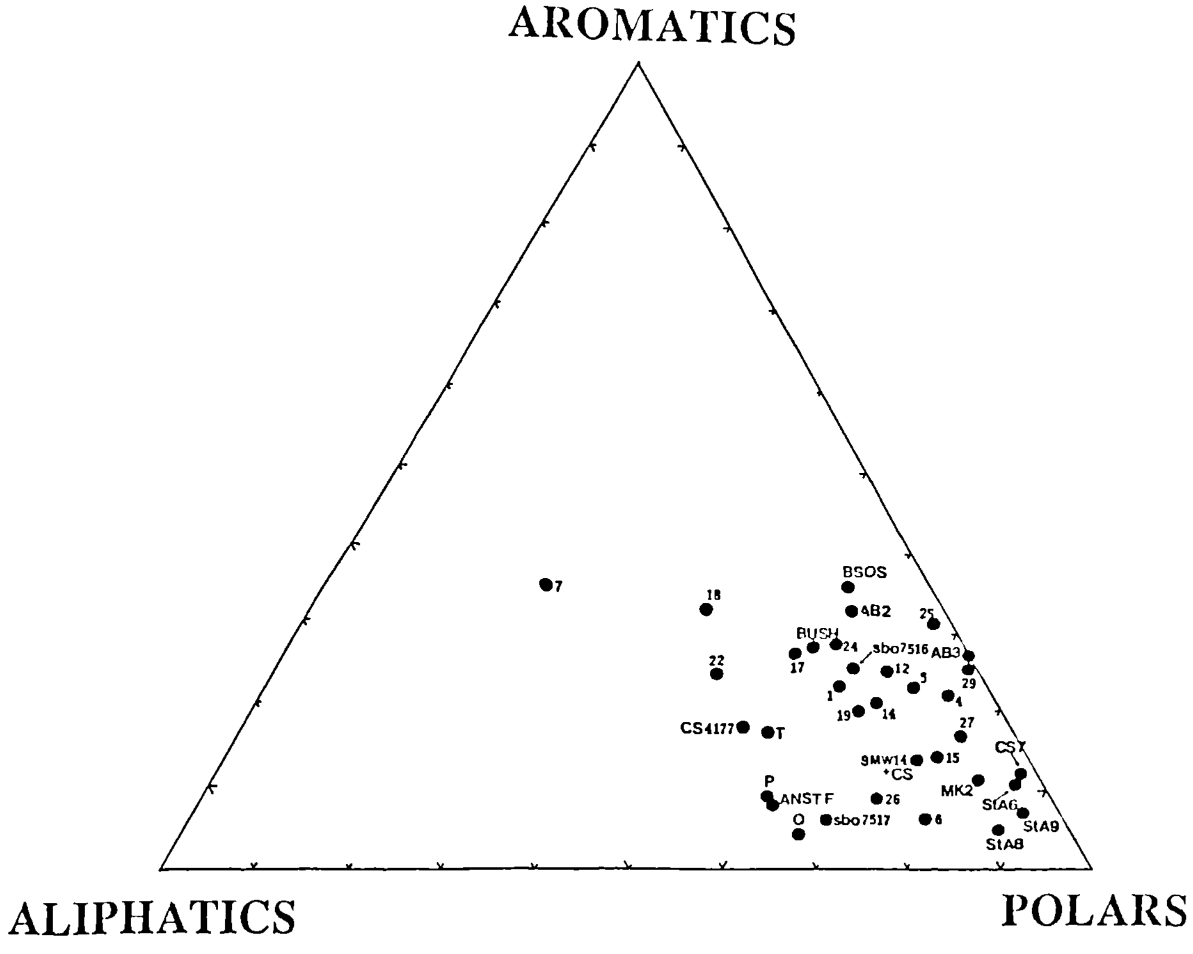


Fig.4.92 Ternary plot showing compound-class constitution of EOM from samples from Fife coastal successions.

4.3.3.4.2 East Fife

4.3.3.4.2.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of samples taken from the various field sections are shown in Fig.4.93. Strata belonging to the Lower Limestone Group conformably overlie the Pathhead Beds at St.Monance, and gas chromatograms of samples selected for extraction from this interval (SM1, 4, 5 and 6) are included in Fig.4.93 for completion. Although the geochemical characteristics of most of the samples have been discussed in other sections, the chromatograms are presented together here to illustrate the variations in hydrocarbon distribution that occur through the Viséan succession in east Fife. The chromatograms are arranged in order of increasing age. Figs 4.93p, q and r are from the Anstruther Borehole, and Figs 4.93t, u, v and w are from the Randerston Section. The stratigraphic levels at which the samples were taken were shown in Fig.4.3. Additonal samples from boreholes penetrating the Calciferous Sandstone Measures in east Fife are presented in Fig.4.94, which also includes a sample from the lowermost facies of the Carboniferous, the Ballagan Beds (Fig.4.94c).

Despite the marked variation in the petrographic constitution of the samples, their hydrocarbon distributions show a general similarity because they all contain abundant sraight-chain alkanes in at least part of the C_{21}-C_{29} range, giving a high molecular-weight bias to the *n*-alkane profiles for the majority of samples, in which there is also a marked OEP. As stated earlier, such distributions are commonly associated with terrestrial input where the alkanes are considered to derive from the cuticular components of leaves and spores. While the terrestrial fingerprint can be correlated with the presence of vascular-plant matter in east Fife samples, there are some algal-rich sediments containing no sporinite, or very little, and also relatively little humic material, in which high molecular-weight *n*-alkanes are prevalent and show OEPs that are comparable with or even higher than those found in coals or other sediments whose kerogens are dominated by higher-plant debris: compare for example the CPIs and hydrocarbon distributions of SM7 (Fig.4.93e), CS4177 (Fig.4.94a), Q (Fig.4.93n) and SBO7517 (Fig.4.93q) with those of SM6 (Fig.4.93d), StA6 (Fig.4.51a), SM14 (Fig.4.93g), SM19 (Fig.4.93k) and SM26 (Fig.4.93v). These geochemical similarities and petrological discrepancies raise the possibility that not all long-chain *n*-alkanes with a pronounced odd-carbon-number preference necessarily derive from higher-plant matter.

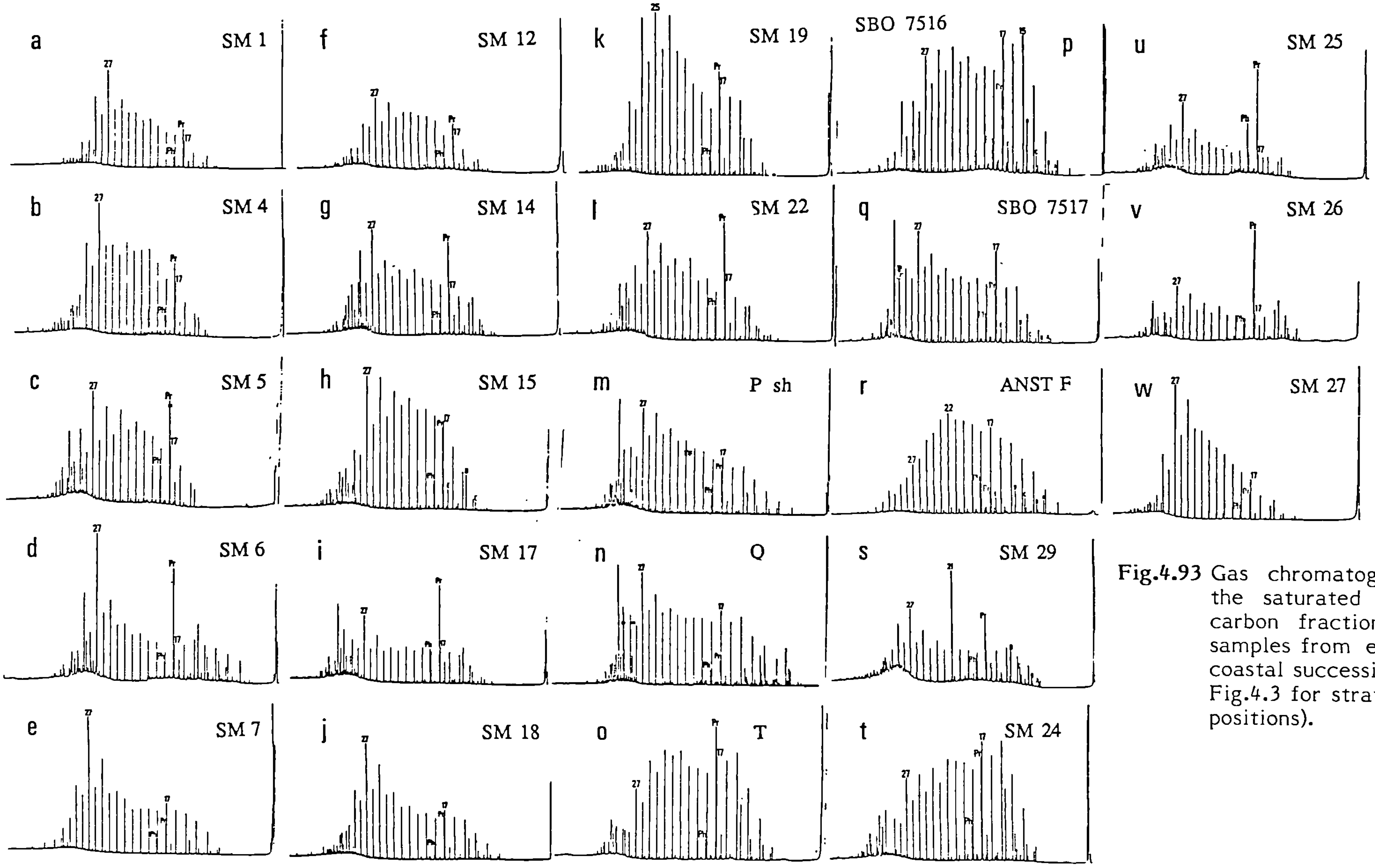


Fig.4.93 Gas chromatograms of the saturated hydrocarbon fractions of samples from east Fife coastal successions (see Fig.4.3 for stratigraphic positions).

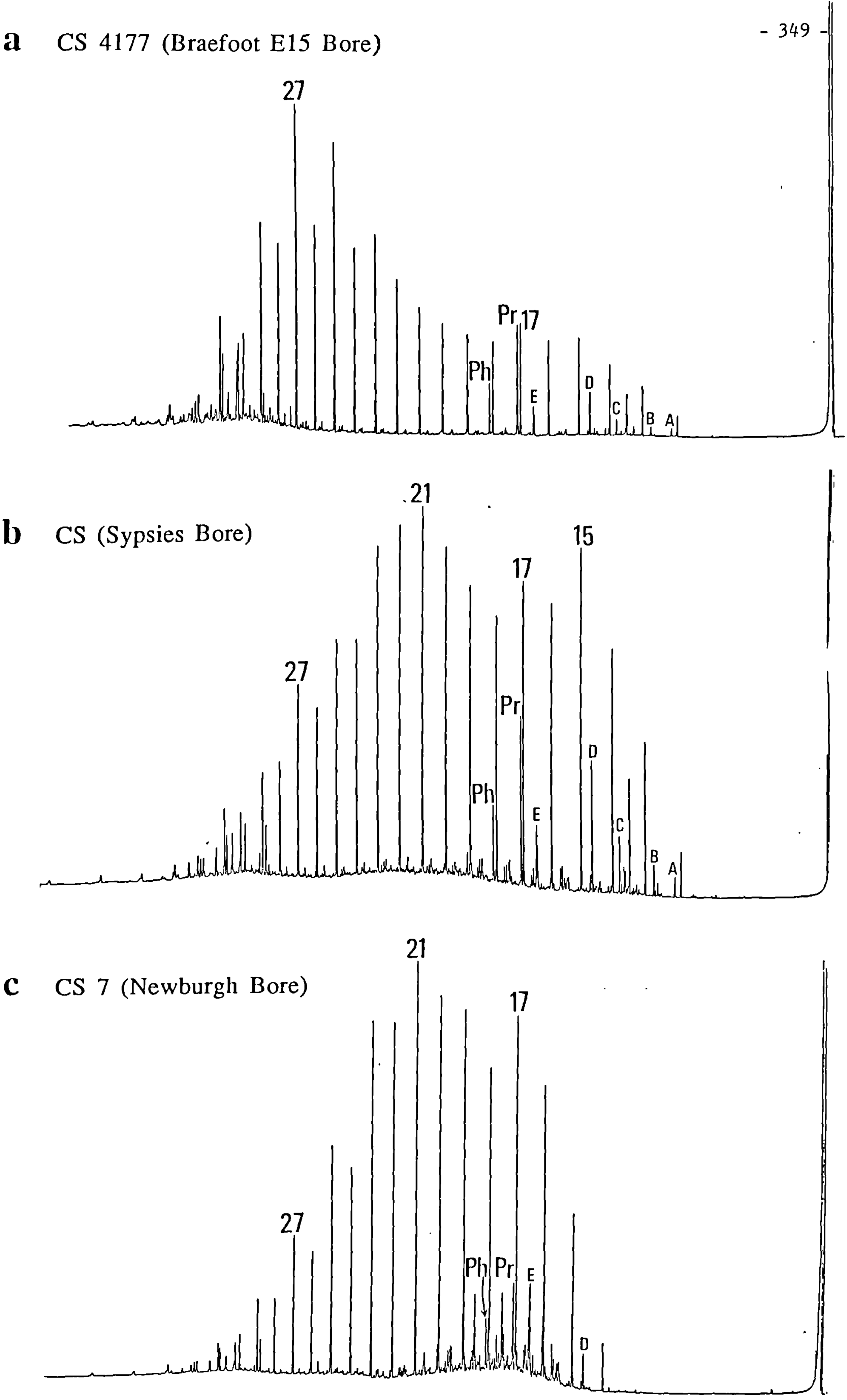


Fig.4.94 Gas chromatograms of the saturated hydrocarbon fractions of borehole samples from the Calciferous Sandstone Measures succession in Fife (isoprenoid assignments given in Table 4.4).

Any contribution from marine algal lipids, which might have been expected in the marine shales analysed, is not evident in the gas chromatograms of most samples, as these bear a marked terrestrial imprint that is consistent with the observed abundance of vascular-plant debris (Figs 4.93a, b, c, h, s).

Despite the presence of abundant algal matter in sediments lying stratigraphically above the upper half of the Anstruther Beds, algal signatures (enhanced concentrations of *n*-C_{15} and *n*-C_{17}) are only evident in samples lying at and below the level of sample Q. The petrographic characteristics of the extracted samples from the Anstruther Borehole are very similar to those shown in Plate 4.95, with prolific flecky liptodetrinite giving the samples a distinctly "marine" appearance. Like many other samples of known marine provenance which contain abundant intensely-fluorescing liptodetrinite, accentuated peaks at *n*-C_{17} and/or *n*-C_{15} are seen in Figs 4.93p and q. A slightly enhanced peak at *n*-C_{17} is also apparent in the gas chromatogram of the lowest extracted sample from the Anstruther Borehole (Fig.4.93r). Although no marine fossils have been found in the upper 550ft of the Anstruther Borehole (Forsyth and Chisholm 1968), the flecky appearance of the samples SBO7516 and SBO7517 (at 91ft and 167ft in the borehole respectively) is suggestive of a marine influence. The marine regime may not have been sufficiently well developed to permit the colonisation of the environment by a marine macrofauna. Whether the sample at 810ft (ANST F) contains marine fossils is not known, but again, its microscopical appearance suggests that a marine influence may have been operative during the deposition of this sediment. That the *n*-alkane profile of ANST F (Fig.4.93r) is much smoother than those of the two samples at 91ft and 167ft is thought to be type- rather than rank-related, since unsuppressed vitrinite reflectance data indicate the rank of the sample at 810ft to be $\%R_o av=0.85$, at which level the *n*-alkane envelope might be expected to show a greater skew towards lower carbon numbers than that shown in Fig.4.91r.

A further point of interest in relation to *n*-alkane distributions is that peak maxima in the high molecular-weight range lie between *n*-C_{21} and *n*-C_{23} in samples lying stratigraphically below (and including) sample T whereas peak maxima in samples higher than T in the succession occur at *n*-C_{25} or *n*-C_{27} (almost exclusively the latter). Unsuppressed reflectance data, in conjunction with biomarker data, indicate a progressive increase in sample maturity moving from the Lower Limestone Group sequence near St.Monance to the Anstruther Beds in the Anstruther Borehole, but rank data for the samples from the Randerston and Wormistone sections, however, point to lower maturity levels for the Anstruther Beds in these localities. Despite their lower maturities, samples SM29 and

SM24 from the Wormistone and Randerston sections, respectively, still show relatively high concentrations of *n*-C_{21} (see Figs 4.93s and t). Furthermore, although the exact stratigraphic level within the Anstruther Beds of sample CS from the Sypsies Borehole is not known, petrographic observations and biomarker data for this sample and CS7, from the Ballagan Beds in the Newburgh Borehole (both have peak maxima at *n*-C_{21}), indicate that the rank of these sediments is no higher than that of other samples in the middle of the Anstruther Beds sequence in the Cuniger Rock to Anstruther Borehole sections (Fig.4.3). This evidence strengthens the view that a C_{21}-C_{23} *n*-alkane prevalence in samples lying stratigraphically below sample Q is related to organic-matter type and not to rank.

The lower carbon-number *n*-alkane maxima in most of the algal-rich sediments lying below the middle of the Anstruther Beds unit may reflect a major difference in the type of organic input to the sediments, although no such difference was recognised from microscopical examination. Alternatively, the different distributions in the lowermost Carboniferous strata could be related to the algae being at a lower evolutionary level than those later in the Carboniferous, with a change in organisational level (not detected microscopically) occurring midway through the Anstruther Beds sequence. Shifts in *n*-alkane maxima towards higher carbon numbers have been reported in extant plant extracts with increasing phylogenetic level: maxima in the C_{15}-C_{23} range have been reported in lower plants such as mosses, lichens, liverworts, marine grasses and algae (Stransky *et al.* 1967; Attaway *et al.* 1970; Corrigan *et al.* 1973), prominent *n*-alkanes in the C_{23}-C_{29} range are documented in gymnosperms (Stransky *et al.* 1967; Herbin and Robins 1969) while *n*-C_{29}-C_{33} alkanes are major hydrocarbons in the extracts of angiosperms (Stransky *et al.* 1967; Herbin and Robins 1968,1969). Shifts towards higher molecular-weight *n*-alkane maxima, thought to be related to floral evolutionary level rather than to sample maturity, have also been recorded in progressively younger geological samples (Tissot *et al.* 1972,1977). Assuming that there is an evolutionary control on the *n*-alkane distribution in the Fife samples, one might expect Devonian sediments in the Midland Valley to display *n*-alkane maxima at $\leq C_{21}$. Although no Devonian samples were extracted in the current project and no published gas chromatograms are available for Devonian samples from the Midland Valley, the *n*-alkane distributions of low-rank Devonian sediments in the Orcadian Basin conform to the above expectation (peak maxima are in the C_{17}-C_{21} range; Duncan and Hamilton 1988), lending further support to the possibility that the *n*-alkane distributions in the Fife samples are influenced by the evolutionary level of the contributing organic matter.

Other extracted samples from Fife were selected from sampled horizons in the Sandy Craig Beds in the Maiden Rock to Kinkell Ness section near St.Andrews (Fig.4.4). The gas chromatogram of the coal StA6 was shown in Fig.4.51 while the hydrocarbon distributions of StA8 and StA9 were presented in Fig.4.98. These last samples were collected from a series of strata which together comprise the St.Andrews Castle Marine Band (MacGregor 1968 p.164; Forsyth and Chisholm 1977 p.40). Sample StA8 was collected from a shelly horizon in a black shale band and StA9 was collected from a horizon 2ft below, in the fossiliferous "grey and black shales" of MacGregor (1968). The *n*-alkane distribution of StA6 is similar to that found in other whole coals and type III-rich sediments in Fife, i.e. it shows enhanced concentrations of long-chain homologues which have a pronounced odd-carbon-number preference. This high molecular-weight bias is also evident in StA8 and StA9, despite their marine origin, and is consistent with the higher-plant input observed microscopically. Any algal signature deriving from the intensely-fluorescing liptodetrinite (thought to be of algal origin) is not seen in the gas chromatograms due to overprinting by terrestrially-derived hydrocarbons.

In all but two samples, Pr/Ph ratios for the extracted samples from east Fife lie in the range 1.65-9.00 (average value is 3.65), indicating that an oxidising depositional regime prevailed during Viséan times in this province. Interludes of environmental anoxicity are suggested by the low Pr/Ph ratios in samples ANST F (0.79; Anstruther Beds) and in the lamosite from Claremont Burn (0.96; Pathhead Beds).

The isoprenoid/*n*-alkane ratios in the east Fife samples show a marked variation, but, akin to the *n*-alkane distributions, show no depth-related maturity trend. The ratios can be related to organic input. The lowest ratios are generally present in the most algal-rich samples, possibly indicating that algae accumulated in more open-water environments than did the sediments containing abundant vascular-plant matter which show higher Pr/*n*-C_{17} ratios.

Although StA8 and StA9 (Fig.4.89) are from the same marine band, their isoprenoid/*n*-alkane ratios differ significantly (2.72 and 1.07 respectively). The abundance of the fresh/brackish water bivalve *Naidites* in StA8 (the sample is from a shell-bed) supports the interpretation of a more restricted, near-shore depositional environment for this sample, made on the basis of Pr/*n*-C_{17} ratio, than the more open-water offshore environment that is inferred for the deposition of StA9.

Gas Chromatography-Mass Spectrometry (GC-MS)

Tricyclic and tetracyclic terpanes are present in such low concentrations, relative to the hopanes, in the coastal samples from east (and central) Fife that displaying the full terpane fragmentograms is not felt to be worthwhile. Reference to the distribution of 3- and 4-ringed terpanes in certain samples has already been made in preceding sections. The "standard" suite of C_{19}-C_{26} tricyclics is recognised in all samples, as are the C_{24}, C_{25} and C_{27} 17,21-secohopanes. The distributions of the tricyclics and tetracyclics can be divided into two types which are related to differences in organic input. Terpane patterns in samples containing abundant lamalginite and/or liptodetrinite thought to be of algal origin (i.e. the samples from the Anstruther Borehole, SM7, 17, 22, Psh and Q) are all of the type shown in Fig.4.84a where tricyclics are of comparable abundance to the tetracyclics. The remaining samples have distributions akin to that presented in Fig.4.87b in which the tetracyclics predominate.

Hopane distributions of the samples from east Fife coastal sections are presented in Fig.4.95. Inspection of the biomarker data reveals trends in many of the ratios over the sample range SM1-SM29 which are rank-related (see next chapter). A salient feature of the hopane distributions, which appears to be type-related, is the relatively low intensity of the extended hopanes, relative to the $C_{30}\alpha\beta$ hopane, often observed in samples containing abundant lamalginite. This phenomenon is well illustrated by comparing the mass fragmentograms of the coal and type III-rich sediments SM6 and SM12 respectively (Figs 4.95d and f) with that of the intervening lamosite (SM7; Fig.4.95e). The concentration of the extended hopanes, relative to the $C_{30}\alpha\beta$ hopane, in the lamalginite-rich samples SM22, Psh and Q are lower than those observed in T and SM19, both of which contain larger amounts of higher-plant debris.

Hopane to moretane ratios (parameter d, Table A.4) show a marked variation within the Fife coastal successions studied which is not solely related to rank. Values of the ratio in lamalginite-rich shales (e.g. SM7, 18, 22, Psh and Q) are significantly higher than the ratios recorded in type III-rich lithologies of similar maturity in the succession (e.g. SM6, 12, 19 and T). The hopane to moretane ratios are particularly high in SM7, Psh and Q (0.81-0.85) and they lie close to the end-point value of c.0.90 (Seifert and Moldowan 1980). High hopane to moretane ratios are also recorded in SBO7517 (0.84), in which 80% of the kerogen comprises liptodetrinite wisps thought to be of algal origin, while SBO7516, of similar rank and whose kerogen comprises larger amounts of higher-plant matter, has a much

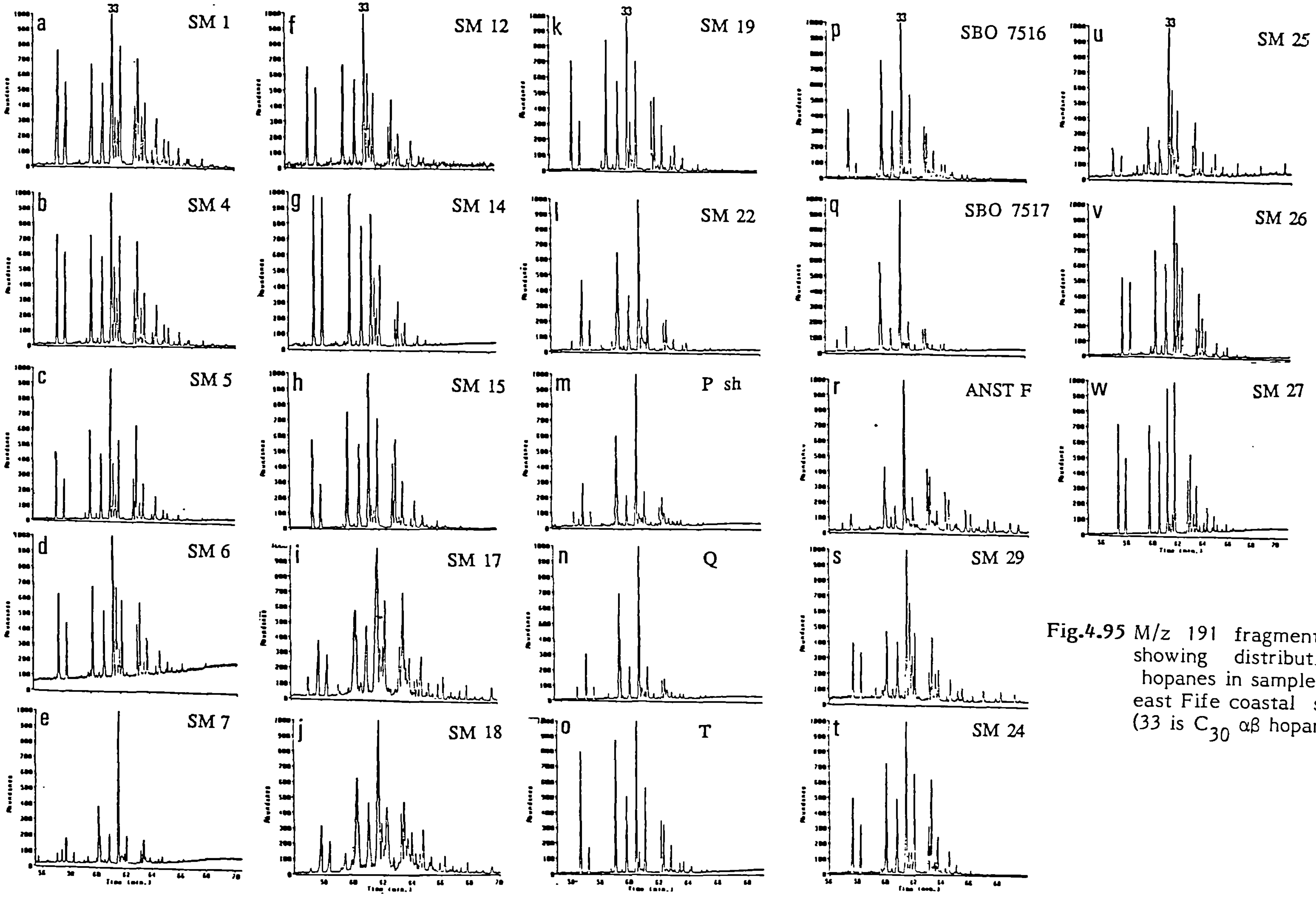


Fig.4.95 M/z 191 fragmentograms showing distribution of hopanes in samples from east Fife coastal sections (33 is C_{30} αβ hopane).

lower ratio (0.65). The disparities in the relative abundance of moretanes in sediments rich in vascular-plant debris and those rich in lamellar algal matter clearly points to a type influence on the hopane/moretane ratio.

Although a depth-related trend towards a decrease in the concentration of peak 34 is seen in the sequence encompassing samples SM1-ANST F, the concentrations of this compound relative to the $C_{30}\alpha\beta$ hopane (ratio f in Table A.4) are much lower in the algal-rich shales than in samples of similar maturity comprising abundant vascular-plant matter. This difference is illustrated by comparing the mass fragmentograms of samples SM1, 4, 5, 6 and 12 with that of SM7 and the higher hopane distribution in T with that of Psh and Q (see Fig.4.95).

Peak 30 occurs in varying quantities in samples from east Fife successions. The sediments in which it occurs all contain large amounts of algal matter either in the form of lamalginite, *Botryococcus* telalginite or liptodetrinite flecks and wisps thought to have been derived from algal precursors. An abundance of algal matter does not implicitly guarantee the presence of compound 30 as illustrated by its absence in T and SBO7516 (Anstruther Borehole). Peak 30 could not be identified in SM18 (Fig.4.95j), but this may be due to poor chromatography.

Bisnorhopane is recorded sporadically within the east Fife coastal sequences. Its presence does not appear to correlate with any particular type of lithology or organic assemblage.

The tricylic and tetracyclic terpanes of the other samples from the Calciferous Sandstone Measures (CS4177, CS and CS7) are present in exceptionally low concentrations relative to the pentacyclics, and their distributions do not differ qualitatively from those shown in Fig.4.84a. In quantitative terms, enhanced concentrations of 3- and 4-ringed terpanes are found in the sample from the Newburgh borehole (Ballagan Beds; Fig.4.96c).

There are no particular pecularities in the hopane distributions of the three samples above (Figs 4.96a-c), except perhaps for the relatively high concentrations of Tm (peak 24) in the Newburgh sample (Fig.4.96a).

The terpane distributions in the other samples analysed from the Calciferous Sandstone Measures in the Maiden Rock to Kinkell Ness field section (StA6, StA8, StA9) have been referred to in previous sections. The distributions in these samples differ from that of SM14 (in the same stratigraphic unit in the Pathhead to Fife Ness section; Fig.4.3) in that hopenes could be detected (*cf.* Fig.4.90c with Fig.4.95g).

Sterane distributions in the samples from the stratigraphic sections shown in Fig.4.3 are presented in Fig.4.97. In all but one sample (SM6), the $C_{29}\alpha\alpha\alpha 20R$ sterane is the dominant component in the m/z 217 mass fragmentograms. The

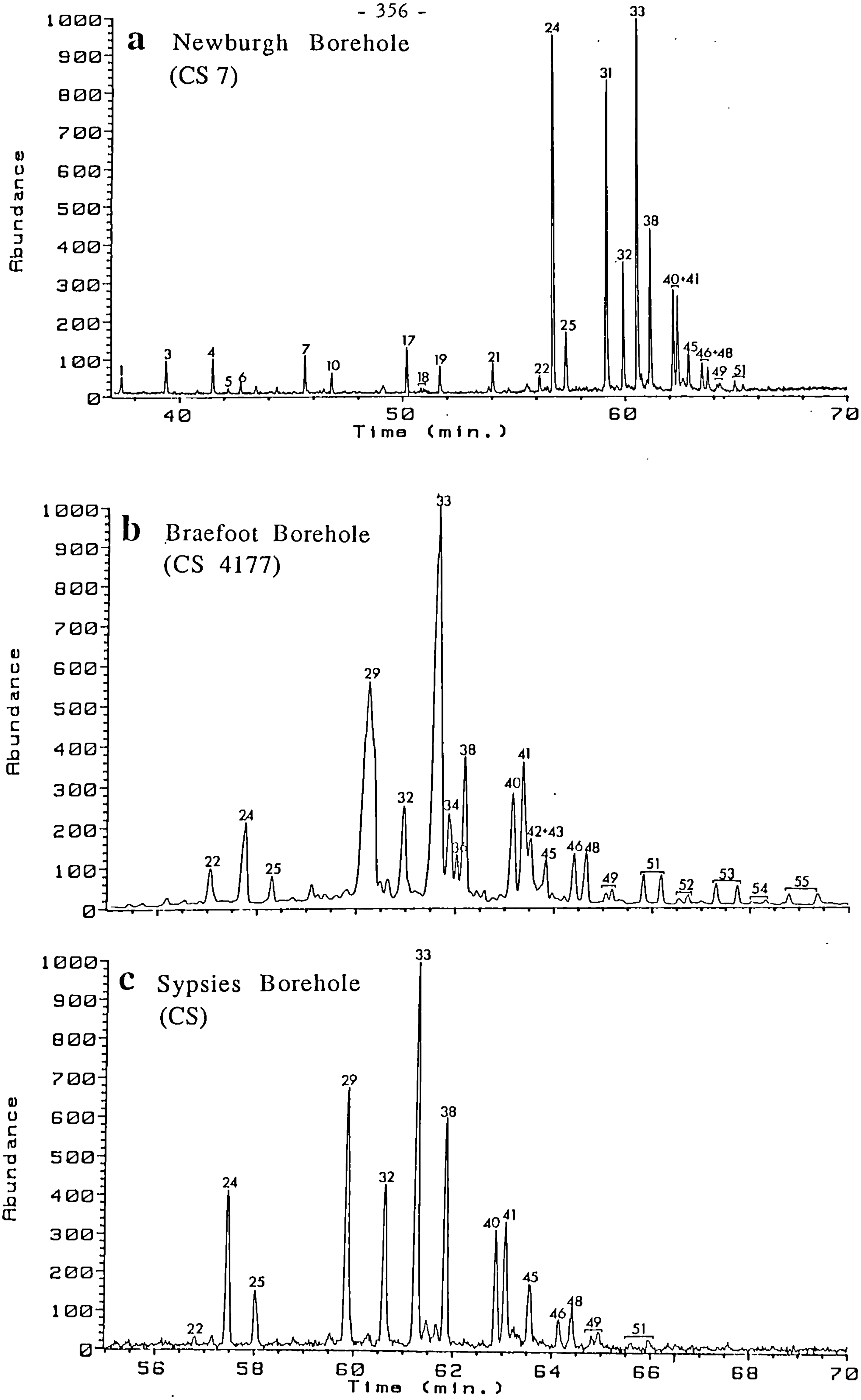


Fig.4.96 M/z 191 fragmentograms showing the distributions of terpanes in miscellaneous samples penetrating strata of the Calciferous Sandstone Measures (peak assignments in Table 4.5).

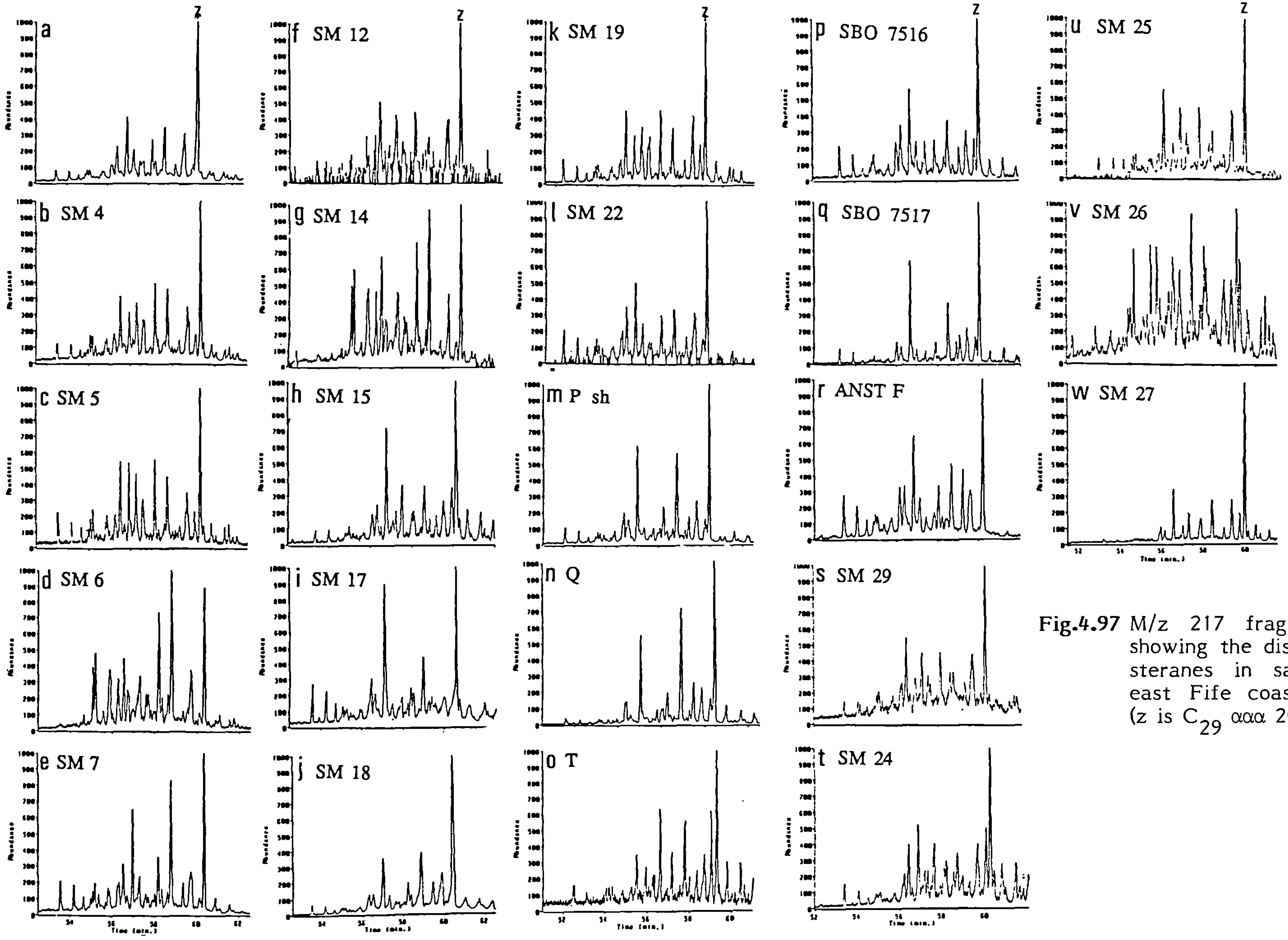


Fig.4.97 M/z 217 fragmentograms showing the distribution of steranes in samples from east Fife coastal sections (z is C_{29} $\alpha\alpha\alpha$ 20R sterane).

proportion of C_{27} and C_{28} steranes varies in different samples, but, in general, those containing abundant algal matter show enhanced concentrations of C_{27} steranes as indicated by their positions in, or straddling, the "estuarine/bay" field in Fig.4.98. The more humic-rich lithologies, either of terrestrial of marine origin, plot in the "terrestrial/higher-plant" fields.

Diasterane/sterane ratios display a marked variation in the east Fife samples analysed, but no correlation with any specific type of organic input could be ascertained. Very low diasterane contents (diasterane/sterane ratios <0.16) are found in calcareous samples (e.g. Psh, Q and SBO7517) or in samples that are closely associated with carbonate lithologies (e.g. SM27, lying directly above the nodular Randerston IX Limestone). The overall simplicity of the sterane mass fragmentogram of the sample from the Newburgh borehole (CS7) is due to the lack of diasteranes (Fig.4.99). The sample is not calcareous *per se*, but lies within the Ballagan Beds, a facies renowned for its abundance of marly horizons ("cementstones"). Although the alginite-rich marl from the Braefoot bore (CS4177) has a low diasterane content, its distribution of regular steranes closely resembles that of SM4 (Fig.4.97b). The sterane profile of the sample from the Sypsies bore (CS) is similar to that of SM24 (Fig.4.97t).

The sterane distributions in samples from the Calciferous Sandstone Measures from the Maiden Rock to Kinkell Ness exposures (Fig.StA6, StA8 and StA9) have been mentioned in a previous section and they are also included in Fig.4.98. Diasteranes were only detected (in small amounts) in the marine sample StA8.

Steranes are always present in higher concentrations than hopanes in the east Fife samples analysed, with hopane/sterane ratios lying in the range 5-39. No correlation between this ratio and organic-matter type and lithology is evident. A hopane-rich interval exists within the Anstruther Beds and is bounded by the samples Psh and SBO7517. Although the samples are algal-rich, a correlation between high algal content and high hopane/sterane ratios is not apparent since similiar high ratios were also recorded for some coals and type III-rich sediments (e.g. StA6, SM19) as well as for marine shales containing little or no algal matter (e.g. SM4,5,15).

4.3.3.4.2.2 Aromatic Hydrocarbons

Gas chromatograms showing distributions of aromatic hydrocarbons in the traverse throughout the Carboniferous succession are shown in Fig.4.100. Many of the samples (and others petrographically similar) have been included within the sample suites described in previous sections. The aromatic profiles of the east Fife samples are complex, but type-related trends can be discerned.

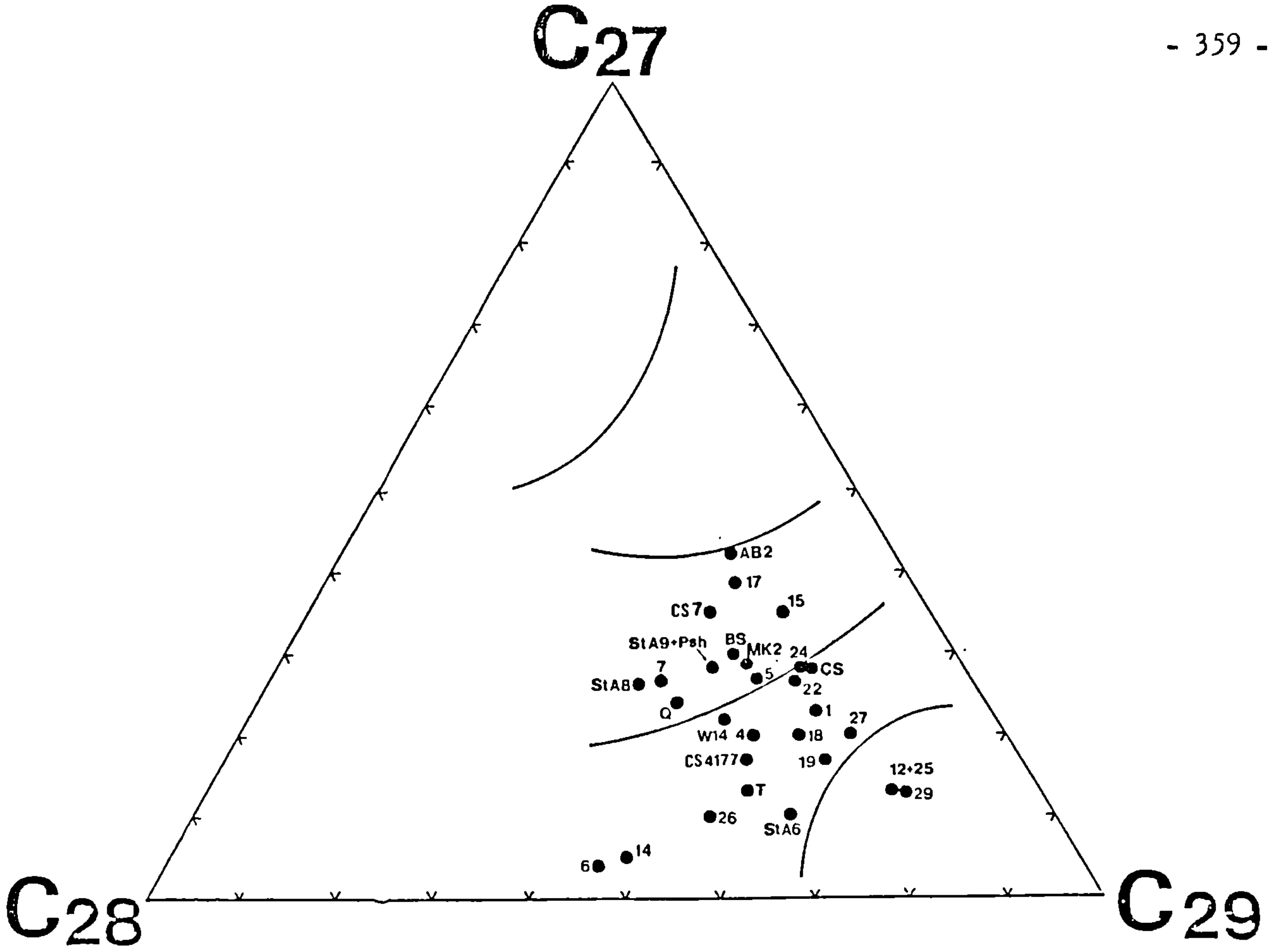


Fig.4.98 Ternary plot showing carbon-number distribution of steranes in samples from Fife coastal exposures (field assignments shown in Fig.4.18).

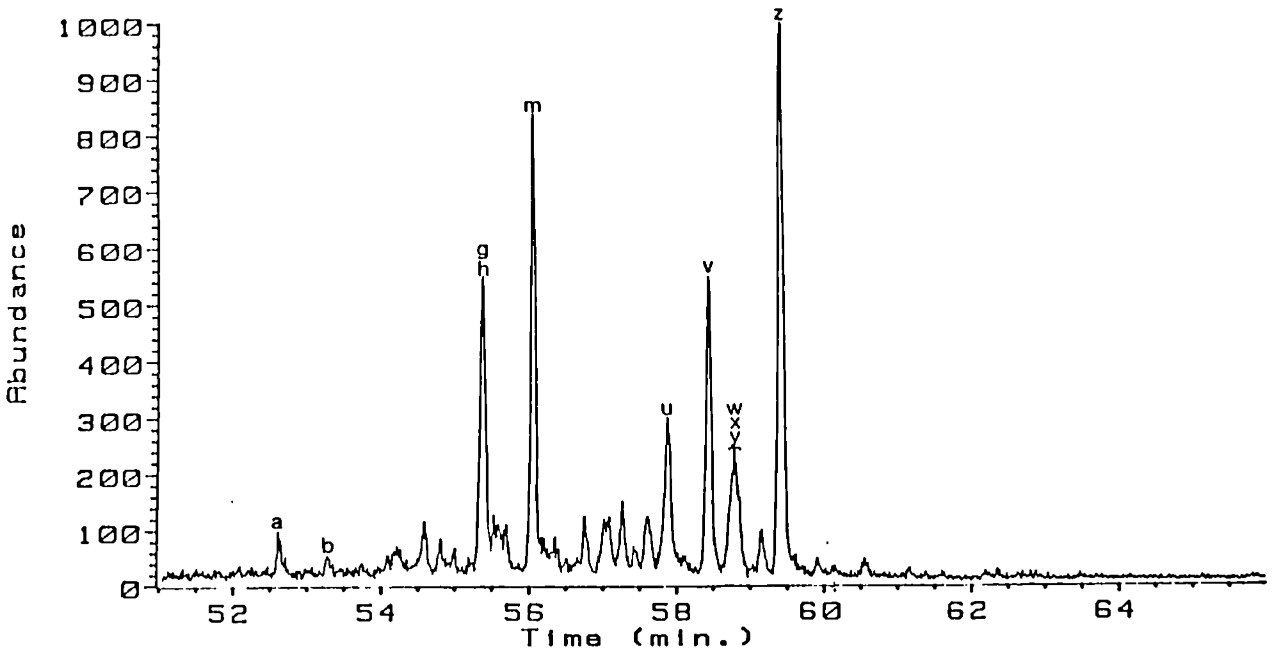


Fig.4.99 M/z 217 fragmentogram showing distribution of steranes in CS7 from the Ballagan Beds, Newburgh borehole (peak assignments in Table 4.6).

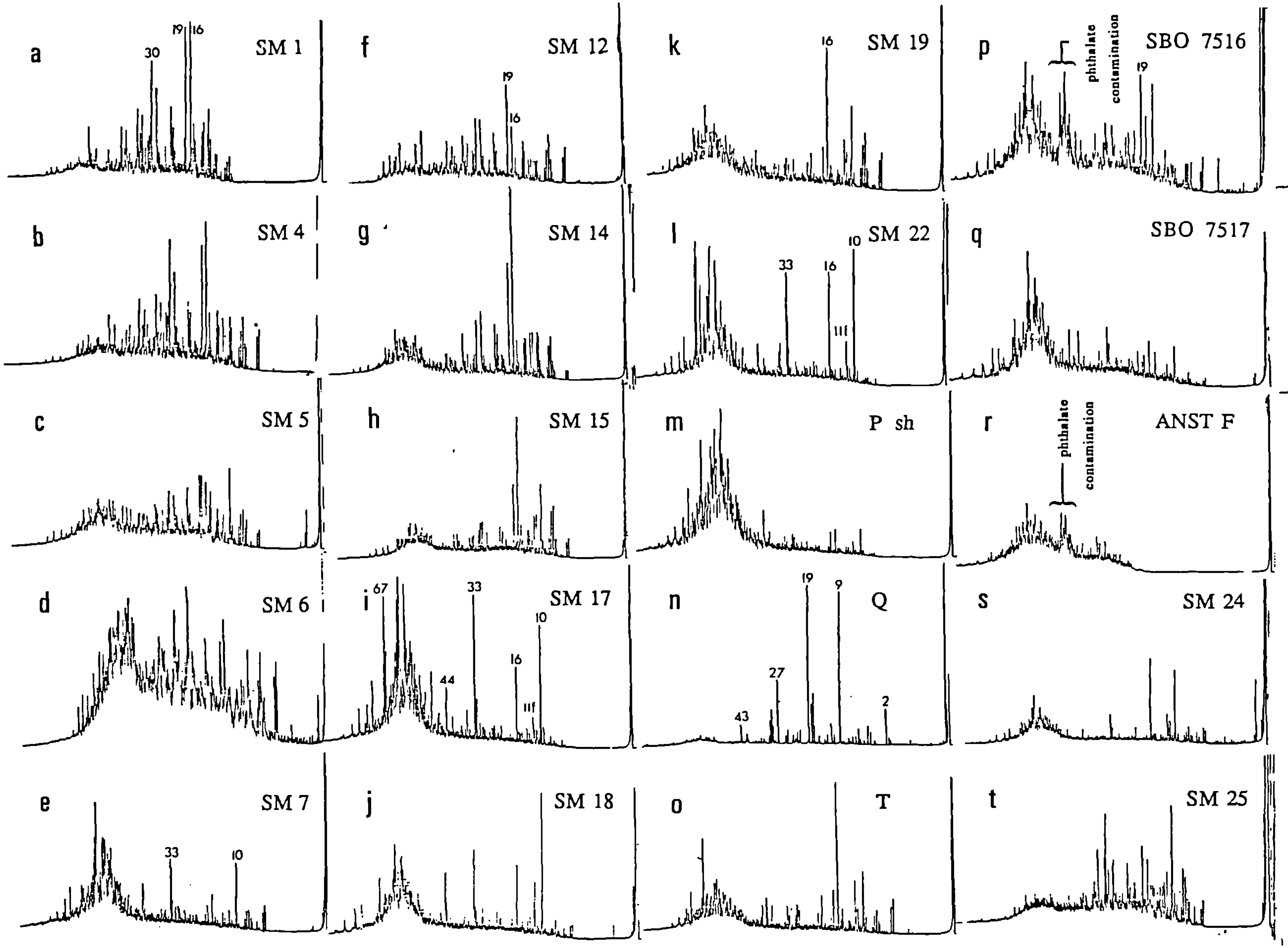


Fig.4.100 Gas chromatograms of the aromatic hydrocarbon fractions of samples from the east Fife coastal sections (see Table 4.7 for assignments).

Regardless of whether sediment accumulation occurred in marine or non-marine environments, the aromatic fractions of sediments containing predominantly higher-plant debris contain a marked contribution from homologous series of alkylated naphthalenes and phenanthrenes and also show a relatively reduced high molecular-weight "hump". In contrast, the salient features of the aromatic distributions in the algal-rich horizons (particularly noticeable within the Anstruther Beds) are a pronounced high molecular-weight "hump" and the prominence of alkyltetralins and specific diagenetically-derived components based on phenanthrene and naphthalene skeletons. Homologous series of the phenanthrenes and naphthalenes are of relatively minor abundance.

PAH displaying pyrolytic-like distributions are ubiquitous within the east Fife succession: they are most abundant, relative to other components, in coals and sediments rich in higher-plant matter and are of low or negligible abundance in algal-rich lithologies.

Aromatic distributions in the samples analysed from the Braefoot and Sypsies boreholes were of the type found in other algal-rich shales in the sequence. The aromatic fraction of the sample of the Ballagan Beds from the Newburgh borehole was dominated by parent PAH whose distribution closely resembled the pyrolytic-like distribution seen in Fig.4.91.

4.3.3.4.3 Central Fife

4.3.3.4.3.1 Kinghorn-Kirkaldy

4.3.3.4.3.1.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Of the four samples extracted from this field section (TK3, MK2, AB3 and AB2), only the marine shales MK2 and AB2 showed any variation in hydrocarbon distribution that could be attributed to organic-matter type variation: sample AB3 yielded no aliphatic hydrocarbons and is also of high rank; any type-related hydrocarbon distribution in TK3 had been masked by the thermal effects of an overlying sill. The gas chromatograms of samples MK2 and AB2 were presented in Fig.4.89. The Pr/Ph ratios for these two samples (1.52 and 3.21) are below the average value cited for the Viséan samples extracted from east Fife, but do, nevertheless, indicate deposition in oxidising environments.

Gas Chromatography-Mass Spectrometry (GC-MS)

Terpane and sterane distributions of the marine shales below the Second Abden and Mid Kinniny limestones have been referred to in Section 4.3.3.3.7. Their sterane distributions have been included in Fig.4.98.

4.3.3.4.3.1.2 Aromatic Hydrocarbons

The distributions of aromatic components present in samples extracted from this field section were referred to in Section 4.3.3.3.7.2. All samples showed a marked contribution from PAH with pyrolytic distributions. The latter components formed the bulk of the aromatics present in the shale below the Third Abden Limestone (AB3; Fig.4.91).

4.3.3.4.3.2 West Wemyss

4.3.3.4.3.2.1 Aliphatic Hydrocarbons

Gas Chromatography (GC)

Of the few samples that were collected from West Wemyss (see Appendix p.125-126) two shales from the Middle Coal Measures (BUSH SH, a pyritic shale 1.5ft above the Bush Coal, and BSOS, a carbargilite between the Wall and Pilkembare coals) were selected for extraction. No biogenic imprint was apparent in the chromatograms of BUSH SH because of its elevated rank.

Despite its higher stratigraphic level, the hydrocarbon distribution in sample BSOS is very similar to that of the coal SM6 (Section 4.3.3.2.2.1). The high CPI (1.73) in the C_{23}-C_{27} range is consistent with the carbargilitic nature of the sediment and its immaturity. The high isoprenoid/*n*-alkane ratios are also a reflection of the low rank of the sample and indicate the accumulation of organic matter in an oxidising peat-swamp environment.

Gas Chromatography-Mass Spectrometry (GC-MS)

Tri- and tetracyclic terpanes are negligible components in the m/z 191 mass fragmentograms of the carbargilite examined from West Wemyss (sample BSOS). The hopane distribution closely resembles those of the Lower Limestone Group sediments in the Pathhead section (Figs 4.97a-d). No distinctive features are evident in the m/z 217 mass fragmentogram of the sample which, apart from showing a lower diasterane contribution, is similar to that shown in Fig.4.97c for SM5.

4.3.3.4.3.2.2 Aromatic Hydrocarbons

The carbargilitic shale BSOS has an aromatic hydrocarbon distribution akin to those of other sediments from Fife which contain abundant higher-plant debris. The aromatic distribution of the high-rank, reddened shale lying above the Bush Coal is identical to that of AB3 (Fig.4.91). Inclusion of the high-rank samples mentioned earlier in the present chapter is justified since the occurrence of pyrolytic-like PAH in these samples lends support to the proposed origin of these distributions in Midland Valley coals and sediments, as discussed in the next section.

4.4 DISCUSSION

4.4.1 Source Input

The earlier sections of this chapter show that there is a tremendous variation in the nature of the organic constituents contributing to the sediments in the Carboniferous succession of the Midland Valley. The variation in organic-matter type is manifested both petrologically and geochemically and is a reflection of the diversity in depositional regimes which existed, both spatially and temporally, as a consequence of the relatively rapid cyclothemic changes which occurred in the Midland Valley through Carboniferous times. The great array of organic components present in the Carboniferous necessitated the inclusion of various points of discussion relating to particular samples or sample suites in the appropriate parts of the preceding text. The following sections comprise a synthesis of the information presented in the foregoing sections. Organic materials, and their precursors, which occur in the Midland Valley Carboniferous are reviewed and geochemical signatures which appear to be characteristic of specific source inputs in the province are identified. Modifications to existing depositional environmental models are made in the light of the results presented in this thesis.

4.4.1.1 Higher Plants

Despite the differing facies which have been defined using long-established macropalaeontological techniques, organic petrological examination has shown that, regardless of provenance, the majority of sediments analysed contain abundant vascular-plant matter, highlighting the overriding importance of terrestrial sedimentation during the Carboniferous. The marked terrestrial imprint is invariably expressed by organic assemblages in which vitrinite and inertinite are the main constituents. Higher-plant input is particularly pronounced in the Black Metals, Johnstone Shell Bed and Kelty Blackband marine horizons, with the latter becoming coaly in places. Had a marine depositional environment not been known (from macrofauna) for these horizons prior to examination, a terrestrial provenance would have been inferred for many samples since their petrological constitution (as for many samples from other marine horizons) is more akin to that seen in the majority of known non-marine sediments.

Evidence for the type and evolutionary level of the plant matter contributing to the sediments was apparent from the analysis of diterpenoids. Although detailed mass spectral investigations were not undertaken on the "diterpenoid region" of the m/z 123 mass fragmentograms in all samples in the project, observations of the overall "fingerprint" suggest that diterpenoid contributions in the Midland Valley Carboniferous are restricted mainly to these components based on the phyllocladane and pimarane skeletons. Components based on the abietane, beyerane, rimuane and labdane skeletons (Noble *et al.* 1986) were not observed. The detection of compounds with the phyllocladane skeleton in the Carboniferous is indicative of input from coniferous precursors as the unsaturated progenitor phyllocladene is restricted to extant genera of this group (Aplin *et al.* 1963; Hanson 1972).

The relatively restricted range of diterpenoid components observed in the extracts of materials rich in vascular-plant matter may reflect an evolutionary trend. Investigations of diterpenoid occurrence and distribution in Australian sediments and oils have shown that diterpenoids are not only more abundant in post-Permian organic materials, they also encompass a much broader range of structural types than those in the Palaeozoic (Noble 1986). The wider range of diterpenoid types in post-Palaeozoic sediments seems to mirror the diversity of flora in Mesozoic and later times and possibly also the ability of individual "higher" gymnosperms to synthesise a greater diversity of diterpenoids as the resin-bearing systems of the plants became more advanced.

The limited scope for resin production by the Carboniferous flora is supported by the scarcity of resinite in coals and sediments rich in terrestrial matter.

4.4.1.2 Algae

4.4.1.2.1 Telalginite

(i) *Botryococcus*-related

Notwithstanding the abundance of terrestrial material in the succession, algal remains are common within the Carboniferous. *Botryococcus*-related telalginite remains are, overall, the most common algal constituents and occur throughout the succession. This telalginite can occur in association with all other types of organic matter in both marine and non-marine sediments.

The progenitor alga for *Botryococcus* telalginite in geological materials has long been recognised as being related to the extant freshwater planktonic, chlorophycean alga *Botryococcus braunii* (Blackburn and Temperley 1936). These authors observed both *Pila* and *Reinschia* morphologies in the Torbanehill torbanite, but only the *Pila* form was recorded in the sediments analysed throughout the course of the current project.

(ii) *Tasmanites*-related

Tasmanites-related telalginite is rare in the Midland Valley Carboniferous, having only been recorded in a handful of samples in which, at most, only a few cysts were seen. Apart from a shale containing abundant vascular-plant material, in the section west of St.Monance (sample SMW9), *Tasmanites* was only found in samples known from palaeontological evidence to be marine.

The precursor alga from which *Tasmanites* derives is related to the extant, marine, planktonic chlorophycean alga *Pachysphaera pelagica* (Hutton *et al.* 1980). The occurrence of tasmanitids in sediments is therefore indicative of a marine influence.

4.4.1.2.2 Lamellar Alginite (Lamalginite)

Sediments in which the bulk of the organic matter comprises lamellar alginite are largely restricted to horizons within the Lower Carboniferous *viz.* the Lothians Oil-Shale Group and its correlatives in east Fife (Pathhead to Fife Ness Beds), and certain marine samples, particularly within the Calmy Blaes and Queenslie Marine Band. Layered lamalginite appears to be confined to the Lower Carboniferous, Calciferous Sandstone Measures (Strathclyde Group) sequence and (apart from sample Q from the Anstruther Wester coastal section) more specifically to lamositic shales.

The precursors for the lamalginite recorded in the Midland Valley succession are less easy to define than those for the telalginites, but the different morphologies are indicative of different precursors. Three types of lamellar algal material are recognised: layered lamalginite, discrete lamalginite and liptodetrinite, each of which is now considered.

(i) Layered Lamalginite

The often sheet-like habit and pervasive nature of the long algal filaments observed in some Scottish lamosites place it within the classification of "layered lamalginite" of Hutton (1987). The highly anastomosing characteristics of this material and the manner in which it envelops mineral gains are morphological features which are markedly similar to those observed in many Tertiary lamosites from the Green River Formation (see Plate 4, Fig.18 in Hutton *et al.* 1980 and Fig.6 in Alpern 1981). These features also resemble, in part, those of laminated algal matter in the Mae Sot shales from Thailand (Sherwood *et al.* 1984). Further comparisons between the cohesive, often mesh-like and finely laminated algal fabrics of the Scottish shales containing lamalginite with similarly structured rocks from other ancient and modern environments (Walter 1976; Williams 1983; Hutton 1987) point strongly towards a source from benthonic, mat-forming, precursor organisms which were probably derived from blue-green algae. Evidence supporting the presence of benthonic algae in Scottish oil shales comes from sedimentological studies of the Petershill Limestone Formation (Lower Limestone group: Jameson 1980, 1987) and the Burdiehouse Limestone Formation (Oil-Shale Group: Loftus 1985; Loftus and Greensmith 1988). The Petershill Formation is a shallow-water sequence comprising carbonates and clastics which occur on the flanks of a volcanic high near Bathgate. Filamentous, mat-forming algae are abundant throughout the lower part of the formation which also includes oil shales. Many of the limestones are thought to have accumulated as a result of the trapping action of calcareous forms of benthonic algae. Algal fabrics are more difficult to detect in the carbonaceous shales, but the remains of non-calcareous, filamentous forms are found (Jameson 1980).

The Burdiehouse Limestone Formation is a fresh-water, cyclothemic sequence of limestones, oil shales, shales and clastics marking the division between the Upper and Lower Oil-Shale Group in the Lothians. Lamositic shales are intimately associated with the Burdiehouse limestones and, in the deep-water (profundal) facies, some limestones darken as a result of increased organic content and pass into oil shales. Filamentous algae exerted a major influence on sedimentation during the deposition of the limestones by adopting an important role as rock-building organisms. The algae not only provided the calcareous substrate, their filamentous habit ensured sediment binding and stabilisation. Most of the algae in the Burdiehouse limestones have been identified as mat-forming cyanophytes (blue-greens). Benthonic algae were not considered to be contributors to the darkened, deep-water limestones or to the oil shales. Descriptions of the organic matter in the darkened limestone lithologies and the Lothians oil shales refer to "anastomosing bituminous films" which are (correctly) considered to resemble lamalginite by Loftus and Greensmith (1988). Later in the above paper, and without any explanation or reference to other work, the authors contradict their previous statement by concluding that the organic matter originates from the "mass accumulation of planktonic algae analogous to the modern form *Botryococcus braunii*" which "collected as flocculent oozes in the low relief bottom of the lake and progressively converted into oil shales". The organic petrological studies undertaken in this thesis using reflected-light and fluorescence microscopy (not utilised by Loftus and Greensmith) show that the above statement is erroneous. *Botryococcus* remains are relatively minor constituents in Midland Valley lamosites, and, furthermore, any indications that accumulations of these algae have a tendency to form oozes which are subsequently incorporated in sediments and preserved in the form of lamellae were not forthcoming from the investigation of *Botryococcus*-containing shales. Although the internal morphological details of *Botryococcus* telalginite may often be indistinct, the presence of a highly resistant biopolymer (termed PRB) in the cell walls of the living colonies (Berkaloff *et al.* 1983; Kadouri *et al.* 1988), for which a structurally analogous geopolymer exists in torbanites (Largeau *et al.* 1984, 1986), ensures that the ovoid algal bodies retain their overall structural integrity in geological environments. Elliptical *Botryococcus* bodies (consistent with compaction) were observed in some cannel coals and laminated carbargilites, but the peripheries of the algal bodies were still well defined. No ooze-like material was ever seen in association with *Botryococcus* telalginite in Midland Valley sediments.

That the *Botryococcus* colonies could collect as flocculent masses on lake bottoms is also unlikely since the high hydrocarbon content of the extant algae (*c.*76% of the dryweight: Maxwell *et al.* 1968; Brown *et al.* 1969) ensures that the colonies float on surface waters. Incorporation within the sedimentary record is generally believed to occur as a result of the algae becoming stranded on lake shores and then being covered by adjacent sediments (Wake and Hillen 1980; D.M.McKirdy *personal communication*). Although rubbery residues of *Botryococcus* can accumulate in the dried-up basins of lakes (Cane 1969), evidence for desiccation in Midland Valley oil shales is very rare (MacGregor 1938). Thus, evaporation was probably not an important mechanism in promoting the accumulation of *Botryococcus* in these deposits.

The assumption by Loftus and Greensmith that *Botryococcus braunii* is the major contributor to the organic content of the algal-rich Lothians shales has almost certainly led to an overestimation of the extent to which planktonic algae have contributed to these sediments. These authors do not attribute any blue-green algae in the organic-rich facies to benthonic forms although their inferred planktonic mode of life for the cyanophyte *Cayeuxia*, a major component in the oil-shale facies, is inconsistent with the known occurrence and mode of life of the organism elsewhere. In other ancient sediments, in different parts of the world, this alga is invariably found in close association with benthonic algal mats and/or carbonate reefs (Flügel 1977). Although no modern analogue of *Cayeuxia* exists against which to draw comparisons, the highly filamentous and encrusting nature of the alga in the oil shales and in the deep-water, organic-rich Burdiehouse

Limestone facies is suggestive of a sedentary, benthonic lifestyle for this algal form rather than a motile one.

Parnell (1988) has further confused the nature of lamalginite with cyanophycean affinities in the Lothians-type lamosites. He envisages lamalginite as "the deposit of flocculent oozes of blue-green planktonic algae". No evidence supporting this judgement is presented apart from an erroneous comparison with the Tertiary shales of Thailand and Australia in the form of a statement "a comparable combination of benthonic and planktonic algal matter is found". Reference to the papers cited by Parnell in which the organic petrology of the above deposits is described (Hutton *et al.* 1980; Sherwood *et al.* 1984) reveals that the blue-green algae are benthonic and that the planktonic forms are green algae! Furthermore, there are suggestions in the literature that the precursors of algal oozes in lamosites are more closely related to benthonic rather than planktonic organisms (Bradley 1970; Sherwood *et al.* 1984; Hutton 1987). Alternatively, the oozes could be a degradation product of the mat-derived lamalginite, a possibility borne out by the sole occurrence of this material in lamosites containing layered lamalginite. A further inaccuracy in Parnell's paper, albeit not related to lamalginite, but again made in the absence of any corroborating evidence, is the conclusion that *Botryococcus* telalginite in the Oil-Shale Group represents deposits of benthonic algal communities, clearly contradicting the known planktonic habit of this organism.

Earlier work suggests that much confusion exists in the identification of benthonic algae and their precursors as constituents of lamalginite in algal sediments in the Midland Valley and indeed in the chacterisation of algal matter generally. The difficulty of isolating algal filaments from the sediment matrix is undoubtedly one causal factor (noted by other workers besides the present author), as is the difficulty in delineating the different algal types *per se*. Much uncertainty surrounds the identification of algae due to the scarcity of published work concerning Dinantian algae in Britain (particularly Scotland) and the confusion attached to the taxonomy of Palaeozoic algae generally. A further problem inherent in assessing the level of input from benthonic algae lies in the difficulty of recognising the characteristic mat fabrics using the standard sedimentological techniques of transmitted-light and scanning electron microscopy. This is because the detail of the delicate filamentous network is invariably obscured or completely obliterated by diagenesis, weathering or biological reworking. The difficulty in recognising mat fabrics is particularly acute in shales, in which the more calcareous-secreting filamentous algae are not as abundant as they are in carbonates (Jameson 1980). Occurrences of benthonic algal assemblages in shales from the Midland Valley may therefore have been overlooked by previous workers. These oversights have been at least partly rectified through the use of fluorescence microscopy which has revealed (in contrast to the findings of previous workers) that several lamosites contain cohesive, filamentous algal fabrics that are consistent with an input from benthonic, mat-forming cyanophycean algae.

(ii) Discrete Lamalginite

Notwithstanding the presence of highly anastomosing algal fabrics in some lamosites, the bulk of lamalginite in lamosites occurs in the form of less densely packed, discrete filaments *viz.* "discrete lamalginite" of Hutton (1987). The filaments closely resemble the algal material which comprises the bulk of the organic matter in the Condor and Rundle shales of Australia (Hutton *et al.* 1980; Cook *et al.* 1981) and part of the algal assemblage of the Mae Sot shales of Thailand (Sherwood *et al.* 1984). The discrete lamalginite in these Thai and Australian deposits closely resembles the extant fresh-water chlorophycean, planktonic alga *Pediastrum*. No such positive identification of discrete lamalginite at the generic level has so far been achieved for Scottish lamalginite. Because of its morphological similarity to *Pediastrum*, it is possible that the discrete lamalginite in Scottish sediments is also related to this alga. Where extant precursors for other forms of discrete lamalginite in oil shales have been identified, they are affiliated to chlorophycean, planktonic algae (Hutton 1987). The other forms of discrete lamalginite found in Scottish lamosites are therefore likely to be the remains of green, planktonic algae, although any affiliations to living algae were not established.

An early consensus that the laminated algal matter in the Lothians shales derived entirely from the remains of planktonic algae (Conacher 1917; Moore 1968) is only partially borne out by the current work. The view of these earlier authors probably results from their failure to identify benthonic forms because of the limitations of transmitted-light microscopy in elucidating the detailed textural relationships between the algae and the rock matrix rather than from any positive confirmation of the presence of planktonic algal forms (no identifications were made).

More recent publications also suggest that the origin of Scottish lamalginite lies in the accumulation of planktonic algae. They are considered to originate either from oozes comprising the remains of the green alga *Botryococcus braunii* (Loftus and Greensmith 1988) or to flocculent oozes of blue-green planktonic algae (Parnell 1988). These view are conflicting and in error and were discussed (and dismissed) earlier.

Discrete lamalginite occurs in greatest abundance in the Lower Carboniferous lamosites in Fife and the Lothians, but also in other, non-lamositic, sediments throughout the Carboniferous succession, including marine bands. In the non-lamositic sediments it is much less attenuated and more robust in form than in the lamosites, with particularly coarse varieties occurring in some specimens of the Calmy Blaes. Some of the thicker lamellae which are seen as wisps in sections perpendicular to bedding may appear as cysts when viewed parallel to bedding (well displayed in some samples of the Queenslie Marine Band). The differences in morphology of the discrete lamalginite may reflect different precursors, although none of the discrete lamalginite in Scottish sediments other than the lamosites could be correlated with any named algae in the literature. The discrete morphology of these unidentified algae points to an origin from planktonic, chlorophycean precursors.

(iii) Liptodetrinite

Other algal material in Midland Valley sediments falls under the liptodetrinite classification. The strong fluorescence intensity of the wispy and flecky material suggests an algal origin, which is corroborated by the enhanced concentrations of the algal-derived C_{15} and C_{17} *n*-alkanes in sediments containing this material, most notably the Calmy Blaes and Queenslie Marine Band. The wispy and slightly diffuse appearance of this algal matter are characteristics suggesting an affiliation to lamalginite rather than telalginite. The sediments in which the wisps and flecks occur in greater abundance are always marine (determined from macrofossil content). The wisps and flecks may represent highly comminuted remains of marine algae, but the fact that the algal matter occurs in the same form and is approximately the same size in all samples in which it is found indicate that a primary origin may be more appropriate, where the flecks and wisps represent the complete cysts of nanoplanktonic marine organisms (A.C.Cook *personal communication*).

4.4.1.3 Microbes

Microscopical evidence for microbial activity is seen in all types of organic assemblages occurring in the Midland Valley Carboniferous. The variegated fluorescence colours and intensities of liptinitic materials in a given sediment attest to microbial reworking since the degradation of organic matter has been shown to result in a reduction in fluorescence intensity and an increased reddening of organic matter when fluorescing (Spiro and Mukhopadhay 1983). The lack of cellular detail invariably seen in alginites and the common occurrence of degraded terrestrial debris, often associated with abundant pyrite, are all factors indicating microbial reworking. Direct evidence for microbial input was recorded in the humic materials analysed from the Orrock and East Kirkton quarries where TEM analysis showed the presence of non-filamentous and filamentous micro-organisms, the latter including fungi.

An assessment of the degree of microbial input to the sediments in the Midland Valley Carboniferous can be made by considering hopane/sterane ratios. Since eucaryotic algae are the main sources of sterols in geological environments, the hopane/sterane ratio has been used to assess the amount of eucaryotic algal input into sediments, relative to higher-plant material. Relatively few hopane/sterane ratios are cited in the literature against which to compare the values calculated in this project, but a general scale can be constructed. Literature values for sediments and oils in which eucaryotic marine algae are known to have been important contributors are approximately ≤ 2 (Mackenzie *et al.* 1982), whilst values cited for sediments and oils in which higher-plant precursors were dominant lie in the range *c.*3-10 (Hoffmann *et al.* 1984; Philp and Gilbert 1986b). Oils and bitumens sourced from non-marine, algal-rich rocks lie in the range *c.*3-7 (Mackenzie *et al.* 1982; McKirdy *et al.* 1986). The method used for calculating hopane/sterane ratios in this thesis (see Appendix II) permits effective comparisons to be made with data presented in the literature.

Histograms of the hopane/sterane ratios for all the low-rank samples included in the investigation of type variation in this project are shown in Fig.101. To provide a rapid assessment of their overall distribution, the different categories of humic-rich materials are grouped together in Fig.101a, whilst the detailed breakdown is presented in Fig.101b. The marine bands are subdivided in Fig.101c. It is appararent that in all samples the hopanes exceed the steranes in abundance, with the extent of hopane dominance varying greatly. Since hopane/sterane ratios greater than 4 or 5 are considered to be high (Mackenzie *et al.* 1982; McKirdy *et al.* 1986), the ratios for virtually all Midland Valley samples are clearly very high, the majority of these exceeding the upper limit of 10 cited for organic matter in terrestrially-dominated regimes in other parts of the world (Hoffmann *et al.* 1984). That the ratios for the Midland Valley samples studied, (regardless of source) greatly exceed this value suggests that there has been an additional input of hopanoid precursors.

The widespread occurrence of hopanoid structures in a variety of geological materials (Ensminger *et al.* 1972, 1974) is a direct consequence of derivation from equally ubiquitous precursors, namely the bacterial organisms which proliferate

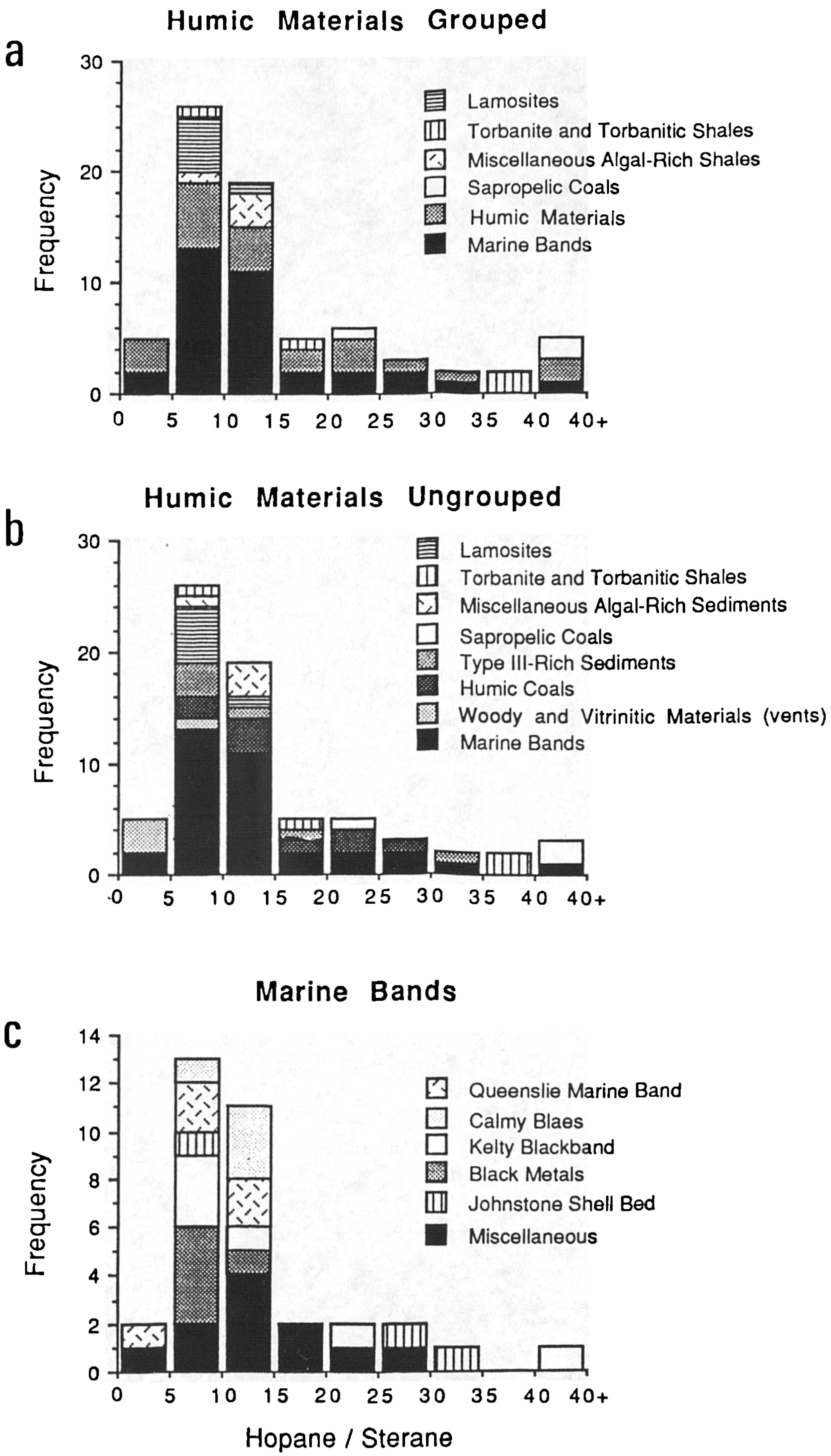


Fig.4.101 Histograms showing the distribution of hopane/sterane ratios.

in the surface layers of virtually all sedimentary environments (Ourisson *et al.* 1979). The input of bacterial lipids would therefore seem to be the most likely explanation for the enrichment in hopanes that has occurred, to varying degrees, in the Midland Valley samples. High hopane/sterane ratios in other sediments and oils have been attributed to bacterial reworking of the source material (Connan *et al.* 1986; McKirdy *et al.* 1986; Derenne *et al.* 1988).

Further evidence for the inferred widespread microbial input stems from the extensive occurrence of qualitatively similar distributions of C_{14}-C_{16} bicyclics based on the drimane skeleton. Although these compounds were particularly abundant in the Orrock wood, and corroborate the prolific microbial activity that was apparent from TEM examination, members of this series were detected in all samples studied from the Midland Valley.

The widespread occurrence of bicyclic sesquiterpanes in crude oils and sediments to which there has been a terrestrial contribution has often led to these compounds being used as markers for land-plant input (Philp *et al.* 1981; Richardson and Miller 1982). In addition to those samples known to have been terrestrially influenced, Alexander *et al.* (1983, 1984b) have recorded 8β(H)-drimane and related compounds in marine samples, some of which are of Lower Palaeozoic age and clearly predate the development of land plants. The ubiquity of sesquiterpanes and the qualitative similarity of their distributions worldwide would seem to require derivation from similarly widespread precursors, and the above authors have proposed the microbial degradation of hopanoid precursors as being a feasible formation mechanism, although Noble (1986) has also suggested an origin through direct bacterial synthesis.

4.4.1.4 Geochemical Signatures for Organic Input in the Midland Valley Carboniferous.

4.4.1.4.1 Algal Markers

Organic geochemical analyses are not as effective as optical methods in elucidating contributions from the different types of organic matter referred to in previous sections because few of the kerogen components can be linked to any specific hydrocarbon distributions or biomarkers. There is a great deal of overlap in the distribution of hydrocarbons in sediments containing different types of organic matter although general trends can be established, based on the parameters listed and discussed below.

(i) EOM Composition

The gross composition of EOM shows that the majority of low-maturity sediments from the Midland Valley are enriched in polar compounds. Nevertheless, ternary plots of compound-class constitution provide a screening method for delineating samples rich in alginite since virtually all these samples have EOM comprising >20% aliphatic hydrocarbons. The aliphatic hydrocarbon contents are particularly high in the Lothians-type lamosites, most of which exceed 40% of the EOM. No further categorisation of algal matter is evident from EOM fractionation data.

(ii) Acyclic Alkanes

Subdivision of alginite into telalginite and lamalginite is possible on the basis of *n*-alkane fingerprints and, in some cases, distinction between marine and non-marine lamalginite is possible.

Telalginite Signatures

The almost symmetrical shape of the *n*-alkane envelope and its maximum at *n*-C_{21} or *n*-C_{23}, which are observed in the torbanite and torbanitic shales in this study, are features that have been noted in other low-rank *Botryococcus*-rich shales from the Midland Valley and other parts of the world (Douglas *et al.* 1969; Allen 1975; Hall 1981). Despite the widespread occurrence of *Botryococcus* remains in Midland Valley sediments, the saurian-type *n*-alkane pattern is only recognised in sediments containing major accumulations of this telalginite, i.e. the torbanite and torbanitic shales; thus it would appear to represent a characteristic fingerprint for these types of deposit. The presence of the above distribution in sediments should not be taken as an unequivocal indication of the presence of abundant *Botryococcus* telalginite however, since similar distributions were also recorded for two coals, although one of these (the coal above the Westfield Oil Shale) was thought to have been contaminated by hydrocarbons derived from the underlying torbanitic Westfield Oil Shale.

Lamalginite Signatures

N-alkane distributions showing enhanced concentrations of *n*-C_{15} and *n*-C_{17}, which give rise to a pronounced OEP in the medium molecular-weight range,occur in sediments containing abundant lamalginite; thus the occurrence of the above distribution can be used as a marker for lamalginite input. Akin to the saurian-type distributions which occur in the torbanite and torbanitic shales, the absence of pronounced *n*-C_{15} and *n*-C_{17} contributions does not necessarily mean that the sample has not had a lamalginite input as exemplified by *n*-alkane distributions in Psh and the Carron Harbour lamosite (CB1). A lack of major peaks at *n*-C_{15} and *n*-C_{17} in lamalginite-containing sediments occurs rarely.

Many marine samples containing discrete lamalginite which is less filamentous and thicker than that in lamosites, and which occasionally may be discerned as cysts in sections parallel to bedding, show *n*-alkane distributions in which *n*-C_{19} is prominent (in addition to *n*-C_{15} and *n*-C_{17}). The OEP in the medium molecular-weight range is also more pronounced than that observed in lamositic shales, and the *n*-alkane envelope shows a pronounced skew towards the low molecular-weight end. Such a distribution is particularly well seen in samples from the Calmy Blaes and Queenslie Marine Band (e.g. QMBA43, C82, C499). The occurrence of this distribution may therefore indicate if the lamalginite in sediments is derived from marine or non-marine algal precursors.

Two additional points relating to acyclic alkanes which merit some comment are first, the origin of the high molecular-weight *n*-alkanes in sediments rich in lamalginite and second, the absence of botryococcane in the Midland Valley Carboniferous.

a) Origin of high molecular-weight *n*-alkanes

Although lamalginite input is invariably associated with a characteristic *n*-alkane signature in the medium molecular-weight range, there are many lamalginite-rich sediments whose *n*-alkane distributions are markedly terrestrial in character. This phenonemon is illustrated by considering the bimodal *n*-alkane distributions in the lamositic shales. Prominent peaks at *n*-C_{15} and *n*-C_{17} in the aliphatic hydrocarbon fractions of sediments have been attributed to contributions from benthonic and/or planktonic algae (Clark and Blumer 1967; Han *et al.* 1968b; Han and Calvin 1969a; Youngblood *et al.* 1971), and, indeed, this assignment does accord with the observed high algal content of the lamositic deposits. Enhanced concentrations of high molecular-weight *n*-alkanes, giving rise to a secondary maximum, accompanied by a marked odd carbon-number preference (C_{23}-C_{27} in the case of the lamosites) are traditionally ascribed to an input from the waxy cuticular components of higher plants (Eglinton *et al.* 1962; Eglinton and Hamilton 1963; Bray and Evans 1965). The range over which the OEPs extend in Carboniferous material from the Midland Valley is very similar for both algal-rich and humic-rich samples. The OEPs in the high molecular-weight range extend from C_{21} or C_{23} to C_{27} or C_{29}, but do not extend beyond *n*-C_{29}. This distribution has been recorded in other Carboniferous organic matter (Allan 1975; Powell *et al.* 1976;

Allan and Douglas 1977). The OEPs in post-Carboniferous successions extend beyond n-C_{29} (usually to C_{33} or C_{35}), which is probably a reflection of the higher evolutionary level of the flora (see Section 4.3.3.4.2.1).

Bimodal n-alkane distributions of the type seen in lamositic shales (particularly those from the Lothians) were found in other organic-rich sediments whose kerogens comprised largely algal matter (e.g. SBO7517, Anstruther Borehole, Fig.4.93q; CS4177, Braefoot Bore, Fig.4.94a; Queenslie Marine Band sample QMB64, Fig.4.72e; Psh, Q, SM17 and SM18 from the east Fife coastal section, Fig.4.37). When reported in the literature, such distributions are invariably attributed to a dual higher plant and algal input (e.g. Tissot *et al.* 1978; Yang *et al.* 1985; Powell 1986). Although it is appreciated that a relatively small input from terrestrial debris could lead to an overprinting of any pre-existing algal or bacterial n-alkane signature, several points arise from the analysis of samples from the Midland Valley from which it is not unreasonable to infer a direct algal source for the high molecular-weight n-alkanes.

First, microscopical examination of the lamosites and the other algal-rich sediments shows that relatively little of the total organic fractions comprise the remains of vascular-plant material, and the greater part of this is inertinitic. The CPI values for the two lamosites from the east Fife coast section (SM 7 and O/SBLA), which contain only trace amounts of vitrinite and sporinite, are higher than for those of lamosites of equivalent rank from the Lothians succession (Carron Harbour, Dunnet) in which vitrinite and sporinite are more abundant. An increase in the content of macerals which could contribute long-chain, waxy hydrocarbons to the sediments is not accompanied by an increase of the CPI in the high molecular-weight range, suggesting that the origin of the marked OEP may be associated with algal input. This point is supported by the observation that the CPIs for the lamosites and other algal-rich sediments are at least comparable with, but frequently in excess of, those for the coals and terrigenous-rich materials studied. This is evident from considering the CPIs cited in Table A.3 and the histograms of Fig.102. The CPI values for two lamosites (SM7 and CBl) and the algal-rich sample Psh are exceptionally high: they greatly exceed the values of all the coalified vascular plant-derived materials of similar rank. The CPIs for the algal-rich samples SBO7517 (1.26) and CS4177 (1.41), from the Anstruther and Braefoot boreholes respectively, are not included in the histograms because it is not known whether their telalginite derives from marine or non-marine algae. The CPI values are, nevertheless, relatively high and exceed the modal class.

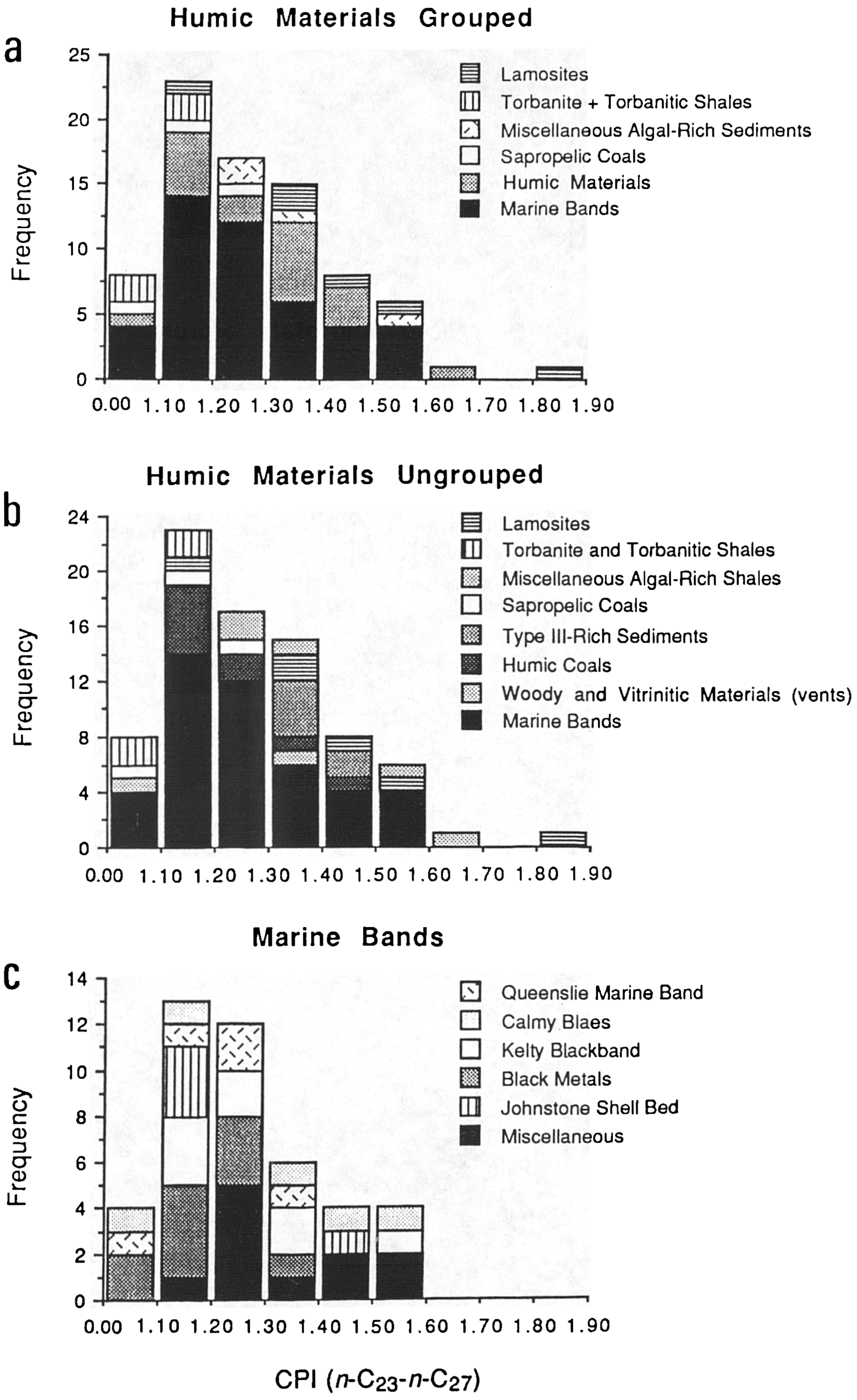


Fig.4.102 Histograms showing the distribution of carbon preference indices (CPIs).

Second, coals and sediments rich in terrestrial components do not display contributions of *n*-C_{25} as pronounced as those seen in the low-rank lamosites; indeed, this alkane defines the high molecular-weight maximum in the lamosites from the Oil-Shale Group succession. *N*-C_{25} occurs as the *n*-alkane maximum in only one type III-rich shale, SM19 (Fig.4.93k), where it is not as prominent as it is in the algal-rich shales of the Lothians succession. The enhanced concentrations of the *n*-C_{25} in the lamosites (also evident, albeit to a lesser degree, in other algal-rich shales) lend further support to the possibility that the high molecular-weight *n*-alkane signatures in these deposits are, at least in part, reflecting algal rather than higher-plant input.

The observations of other workers provide further evidence corroborating the postulated algal provenance of the long-chain *n*-alkanes with pronounced OEPs. Incidences of odd carbon-number preferences in long-chain, *n*-alkane homologues have been documented in sediments of Precambrian and Cambrian age (Smith *et al.* 1976; McKirdy and Kantsler 1980; Fowler 1984) as have bimodal *n*-alkane distributions (Brooks 1971; McKirdy 1974; McKirdy and Hahn 1982; Philp and van der Meent 1983). Given that these ancient sediments predate the appearance of higher plants, their *n*-alkane distributions have been regarded as unusual. Of further relevance (see Section 4.3.3.1.2.1) is the anomalous occurrence of a bimodal *n*-alkane distribution, with a high molecular-weight OEP, in the lamalginite-rich Rundle Oil Shale in which there is no microscopically-discernible higher-plant input (Hutton *et al.* 1980). Bimodal *n*-alkane distributions have also been reported in present-day algal mats (Cardoso *et al.* 1978; Malinski *et al.* 1988) where at least some of the long-chain *n*-alkanes are thought to derive from cyanobacteria.

In an evaluation of lacustrine source rocks and their depositional environments, Powell (1986) noted that a paradox exists if the traditional rationale for the presence of large amounts of high molecular-weight *n*-alkanes in oils and sediments is accepted, *viz.* the defunctionalisation of long-chain, carboxylic acid precursors or the direct input of long-chain hydrocarbons, both of which are derived from higher-plant waxes. The paradox is that the most aliphatic-rich kerogens and those yielding very waxy oils form remote from the source of terrestrial matter, in lake centres. Furthermore, the wax content of the resulting oils is often higher than is encountered in oils derived from coal measures sequences with organic matter generally exclusively of land-plant origin. One possible explanation envisages an environmental control on source-rock formation from higher-plant matter, whereby bacterial and fungal attack results in the destruction of cellulosic and lignaceous materials and the concentration of liptinitic-rich components such as cuticles, spores and resins (Powell 1984).

The hydrogen-rich concentrate is supplemented by the addition of bacterial remains. Extensive microbial degradation of higher-plant matter is thought to have played an important part in the formation of the structureless, highly aliphatic organic matter seen in many organic-rich horizons in the Uinta Basin (Tissot *et al.* 1978).

If severe microbial reworking were to account for the relatively low content of vitrinitic matter in the lamositic shales and for the possibility that there may be higher-plant matter in the shales that is not microscopically discernible, other indicators of intense microbial activity might be expected to be revealed, as outlined below.

(i) Abundant amorphous matter.

Amorphous kerogens are often formed as a result of intense bacterial reworking. Some of the amorphous ooze-like matter in the lamositic shales may arise from microbial reworking of the algal substrate, but if microbial reworking had played an important role in the formation of aliphatic-rich kerogens in the lamosites, amorphous matter should be seen in abundances much greater than those recorded in the lamosites analysed in the present study.

(ii) Abundance of iso- and anteiso-alkanes.

Relatively high concentrations of iso- and anteiso-alkanes have been reported in sediments and oils in which microbial processes are thought to have been important (Tissot *et al.* 1978; Powell 1984; Connan *et al.* 1986; Jackson *et al.* 1986). These components derive from branched acids present in bacterial membranes (Leo and Parker 1966). Enhanced concentrations of iso- and anteiso-alkanes were not recorded in the lamosites (or other algal-rich shales) in the Midland Valley.

(iii) High hopane to sterane ratios.

The rationale behind the use of these ratios was discussed earlier. Although the ratios for low-rank samples from the Midland Valley are high *per se*, excessively high values might be expected in the lamositic shales if microbial reworking had been particularly intense. The histogram in Fig.101 indicates that for the lamosites, and other algal-rich shales containing relatively little higher-plant matter, the ratios are not markedly high in comparison with those of other samples.

The above three points all militate against the occurrence of terrestrial remains that are not microscopically discernible (but could still contribute long-chain *n*-alkanes to the soluble organic fraction) through intense microbial degradation of terrigenous source material. The origin of the high molecular-weight *n*-alkane maximum (and accompanying pronounced OEP) seen in many algal-rich sediments in the Midland Valley is not likely to be due to the microbially-induced enrichment of hydrogen-prone terrestrial components, a mechanism that has been invoked to explain the formation of lacustrine kerogens yielding waxy hydrocarbons in other parts of the world.

The observations of other workers, in conjunction with those made on the Scottish samples, all weigh against a higher-plant origin for the long-chain, waxy hydrocarbons possessing a marked OEP seen in many algal-rich shales. Vascular plants certainly cannot account for the secondary *n*-alkane maximum seen in Precambrian sediments where such an input must be discounted. Other potential sources of long-chain *n*-alkanes with an odd carbon-number preference must therefore be sought. High molecular-weight *n*-alkanes have been found in extant blue-green and higher algae (Clark and Blumer 1967; Han *et al.* 1968a; Gelpi *et al.* 1968,1970; Han and Calvin 1969a; Paoletti *et al.* 1976a) including *Botryococcus* (Brown *et al.* 1969; Gelpi *et al.* 1968,1970; Largeau *et al.* 1980). In addition to the free hydrocarbons present in *Botryococcus*, recent work has shown that the cell walls of this alga are comprised of a highly resistant aliphatic hydrocarbon biopolymer, termed PRB (Berkaloff *et al.* 1983; Kadouri *et al.* 1986) which could yield paraffinic hydrocarbons on maturation. Resistant biopolymers, albeit with different structures to PRB, have been isolated from the cell wall membranes of cyanobacteria (Chalansonnet *et al.* 1988) and from the leaf cuticles of higher plants (Nip *et al.* 1986). Laboratory heating of the cuticular biopolymer has given rise to *n*-alkane distributions which contain abundant high molecular-weight components which show a marked odd-carbon preference (Tegelaar *et al.* 1989). Since cutinite was not observed in any of the algal-rich shales from the Midland Valley in which bimodal *n*-alkane distributions occur (cutinite is rarely seen in any of the Carboniferous coals and sediments analysed), it is unlikely that the high molecular-weight *n*-alkanes in the algal-rich shales originate in the resistant cuticular biolpolymer. The algal-derived biopolymers are therefore more tenable precursors.

Long-chain alkanes may also derive from bacteria (most notably the non-photosynthetic varieties), although these are reported to show no odd carbon-number dominance (Albro and Huston 1964; Davis 1968; Han *et al.* 1968b; Han and Calvin 1969a; Albro and Dittmer 1970; Tornabene 1976). Whilst this fact suggests that OEPs probably do not derive from bacterial hydrocarbons *per se*, bacterial organisms may play an important part in the formation of high molecular-weight OEPs because they may modify cyanobacterial hydrocarbon distributions. This possibility stems from the laboratory studies of Bubela *et al.* (1983) who demonstrated that the microbial reworking of a cyanobacterial mat resulted in a progressive shift in the *n*-alkane distribution towards higher carbon numbers, with the concomitant development of a pronounced OEP which was not present in extracts of the original cyanobacterial substrate. The effects of microbial activity within cyanobacterial mats could therefore be easily mistaken for a higher plant-type fingerprint. Microorganisms are known to constitute an important part of the algal-mat ecosystem (Golubic 1976); thus past assumptions of higher-plant input into recent cyanophycean algal mats, based solely on the presence of high molecular-weight *n*-alkanes (Cardoso *et al.* 1978), some displaying very high OEPs (Malinsky *et al.* 1988), may be erroneous. These authors did not mention the occurrence of vascular-plant matter in the algal mats under investigation, or of the extent to which terrestrial run-off might have contributed higher-plant matter to the mats. These points support the view that the "terrestrial" signatures may have been wrongly assigned.

Fungal extracts have been shown to contain long-chain *n*-alkanes in which there is a marked odd carbon-number preference (Oro *et al.* 1966; Weete 1972). Fungal decomposers are always present in algal-mat communities (Golubic 1976), so the "terrestrial" *n*-alkane signatures that have been recorded from recent mats and from ancient sediments in which the remains of algal mats comprise the bulk of the organic matter (in stromatolites) may, at least in part, be due to an input of fungal hydrocarbons.

From this consideration of earlier literature it is apparent that higher-plant matter is not the sole contributor of long-chain *n*-alkanes to the geosphere. Algae, bacteria and fungi can all impart high molecular-weight *n*-alkanes amongst which, moreover, the odd-carbon numbered homologues can dominate. The importance of vascular-plant material in imparting "terrestrial" fingerprints to geological materials is probably overstated. Green or blue-green algae would appear to be the most likely primary sources of the long-chain *n*-alkanes with marked OEPs in oil shales and Lower Palaeozoic sediments in which, respectively, contributions from higher-plant material are very low or can be completely ruled out. Subsequent modification of the algal-produced *n*-alkane distributions could occur through bacterial activity, resulting in the accentuation of CPI values. Fungal contributions to ancient sediments are difficult to assess.

Since algal-rich samples from the Midland Valley are of Carboniferous age, the possibility of a contribution from highly degraded, waxy, terrestrial debris which is not microscopically discernible cannot be absolutely excluded although, as discussed earlier, a high degree of reworking might be expected to be accompanied by other geochemical signatures and these are not evident. Since the contribution from alginite dwarfs that of vascular-plant debris in the algal-rich shales, at least some long-chain *n*-alkane input from algal constituents seems likely. Eucaryotic green algae are likely to be the main source of long-chain hydrocarbons in the algal-rich shales since these are the presumed precursors of the discrete lamalginite and *Botryococcus* telalginite which together comprise the bulk of the organic components. Input of high molecular-weight components from filamentous, mat-forming, blue-green algae is also inferred in the shales in which layered lamalginite is present. Whilst *Botryococcus*-derived hydrocarbons could contribute to the absolute content of high molecular-weight components, a high molecular-weight "hump" maximising at n-C_{25} or n-C_{27} is thought to reflect lamalginite input, because *Botryococcus* telalginite displays its own characteristic *n*-alkane envelope maximising at around n-C_{21}.

Fungal hyphae have been detected in woody materials by TEM (see Section 4.2.2.3), and fungal remains have been reported in oil shales (Moore 1968). The extent of fungal attack in algal shales is unknown, but it is possible that fungal *n*-alkanes could have contributed to the very high CPIs recorded in some shales. Fungi are often intimately associated with extant, filamentous, mat-forming, blue-green algae (the presumed precursors of layered lamalginite), and fungal hydrocarbons have been reported in recent cyanophycean mats (Cardoso *et al.* 1978). A fungal contribution to *n*-alkane signatures may therefore have been more important in the shales that contain layered lamalginite.

Bacterial reworking of the algal subtrate may have contributed to the high molecular-weight *n*-alkane distributions in algal shales, but much work is required to determine the importance of bacterial activity in modifying primary hydrocarbon distributions in geological environments.

The above discussion illustrates that *n*-alkane distributions can yield information about the types of algal matter contributing to sediments and also highlights the need for caution when interpreting the high molecular-weight "hump" in bimodal distributions.

b) Absence of botryococcane

The C_{34} branched isoprenoid botryococcane is an unambiguous marker for *Botryococcus*-containing kerogens, or the oils sourced from them, since the unsaturated analogue of this compound (and related structures) has only been isolated from extant colonies of *Botryococcus braunii* (Maxwell *et al.* 1968; Cox *et al.* 1973;

Metzger *et al.* (1985). In spite of the abundance and wide-ranging distribution of *Botryococcus*-derived telalginite in the Midland Valley, no botryococcane was identified in any of the *Botryococcus*-containing rocks analysed. Parallel observations have also been made by Derenne *et al.* (1988) from a study involving twelve torbanites from various localities worldwide. On a global scale, *Botryococcus* telalginite is also widespread, yet published data indicate that botryococcane occurrence is very limited, having only been documented from Sumatran oils (Moldowan and Seifert 1980; Seifert and Moldowan 1981), Australian bitumens (McKirdy *et al.* 1986) and the Chinese Maoming oil shale (Brassell *et al.* 1986, 1988). The rarity of botryococcane may be explained in terms of differences in the nature of the *Botryococcus* colonies contributing to the sedimentary organic matter or to oxidative degradation of botryococcane precursors (botryococcenes) during early diagenesis. The former possibility stems from the work of Metzger *et al.* (1985) who demonstrated the existence of two physiologically-distinct strains of *Botryococcus braunii*, termed the A race and B race, both with similar morphologies, but each synthesising different types of hydrocarbons. The A race exclusively synthesises unbranched, non-isoprenoid hydrocarbons (alkadienes and trienes) whilst the B race produces botryococcenes. The absence of botryococcane in Midland Valley sediments may therefore indicate that the *Botryococcus* telalginite in the province was derived solely from the A race although, for the reasons discussed below, this suggestion seems unrealistic. A third "L race" of *Botryococcus braunii* has recently been characterised (Derenne *et al.* 1989). Although morphologically similar to the A and B races, the L race contains a resistant biopolymer (PRB L) which gives rise to the production of the C_{40} isoprenoid hydrocarbon lycopadiene. The relative importance of the different races in the formation of torbanites in the geological record is not yet known.

Work by Dubreuil *et al.* (1989) has shown that the botryococcene content of laboratory-grown cultures of race B algae decreases during atmospheric exposure, since oxidative polymerisation of the various constituents leads to the production of *Botryococcus* rubber. In the light of these data, the same authors invoked subaerial oxidation as an important factor to account for the lack of botryococcenes in an Australian coorongite in which the *Botryococcus* remains comprise colonies belonging to the B race. In this deposit, and in other coorongites, microscopical examination has revealed evidence of intense bacterial activity such as poorly-defined cell structures, abundant amorphous material and the remains of microorganisms (Glikson 1983, 1984; Dubreuil *et al.* 1989). In geological environments, the general lack of botryococcane may therefore be explained by the bacterial degradation and subaerial oxidation of botryococcenes present in the original biomass. In present-day environments, the races of *Botryococcus* are of cosmopolitan distribution, but their co-existence in a given body of water is seldom observed (Wake and Hillen 1981). Assuming that the different races existed in Carboniferous times, it seems unreasonable to assume that all the *Botryococcus*-derived telalginite observed in the Midland Valley sediments originated solely from the A race. The degradation of botryococcene precursors must therefore be considered as a mechanism to explain the lack of botryococcane in the Midland Valley Carboniferous: indeed there is abundant evidence, presented below, for bacterial reworking in the *Botryococcus*-rich shales studied and for the accumulation of this alga in oxidising environments.

The Pr/Ph ratios for the torbanite and torbanitic shales studied are all high (3.90-4.28), as they are in the environmentally related cannel coals (3.00-4.51) which also contain *Botryococcus* remains (10%-40% of the total organic matter). These high ratios are all consistent with the exposure of organic materials to oxic conditions during sedimentation which militates against the preservation of botryococcenes. High Pr/Ph ratios (2.80-6.20) have also been determined for four torbanites extracted by Derenne *et al.* (1988) in which no botryococcane was recorded.

Several petrographic features described in Section 4.2.1.2 point to a marked bacterial involvement during the formation of *Botryococcus*-derived kerogens in the Midland Valley. The dull, brown-fluorescing areas seen on the periphery of many *Botryococcus* colonies (particularly well seen in the Westfield Canneloid Shale due to the exceptional degree of preservation of the organic matter) have also been noted in other *Botryococcus*-rich shales in which TEM has revealed the presence of a significant microbial component (Glikson 1983,1984). Some of the *Botryococcus* telalginite bodies in Australian torbanites have areas devoid of fluorescence (Glikson 1983). Although no completely non-fluorescing *Botryococcus* telalginites were noted in the Midland Valley samples, there are algal bodies (particularly in the Westfield Oil Shale) showing greatly reduced fluorescence intensities and brown/orange fluorescence colours which co-exist with colonies displaying "normal" fluorescence properties, *viz.* intense, yellow fluorescence. Individual colonies may also display variable fluorescence properties. Some of the *Botryococcus* telalginite which shows a dull fluorescence under blue-light excitation appears, in reflected light, to be pseudomorphed by framboidal pyrite, a feature also consistent with bacterial activity. The pseudomorphing phenomenon is well displayed in the highly pyritic cannel coal SMW14 (Plates 4.102 and 4.103) in which there is also abundant degraded plant debris and amorphous material (Plate 4.101).

The microbial degradation of algal matter results in a shift of fluorescence colour towards longer wavelengths (Spiro and Mukhopadhay 1983). The variable fluorescence properties seen in *Botryococcus* telalginites are therefore consistent with the microbial reworking of the algal substrate. That the brown fluorescence is most commonly seen around the margins of *Botryococcus* colonies suggests that the soft thecal tissues were probably more susceptible to microbial decay than the main body of the alga. TEM and carbon-isotope data have shown that at least some of the degradation of *Botryococcus* in torbanites was effected by methanogenic bacteria (Glikson 1983). The discovery of archaebacterial lipids (long-chain regular and irregular isoprenoids) in some Australian torbanites and Australian coastal bitumens which were derived from *Botryococcus*-rich source rocks (McKirdy *et al.* 1986) supports this interpretation. No such compounds were detected in any of the *Botryococcus*-rich sediments analysed from the Scottish Carboniferous (or any other sediment for that matter). Sapropelic environments in the Midland Valley probably never became as anoxic as those in which many of the Australian *Botryococcus* accumulations occurred. Some support for this opinion is provided by the much lower Pr/Ph ratios (0.49-2.20) recorded for the Australian bitumens referred to above.

The presence of the ramifying, low-reflecting, stringers of vitrinitic material in the *Botryococcus*-rich shales from the Midland Valley invites comparison with the "low-reflecting, vitrinite-like matter" that has been described in some Australian oil shales (Cook *et al.* 1981). An origin from filamentous cyanobacteria has been suggested for this material in some marine oil shales (Glikson and Taylor 1986), whilst methanogenic bacteria are considered to be likely precursors for material with similar optical properties found in some torbanites (Glikson 1984). In contrast to the Australian "vitrinitic" material in torbanites, the Scottish stringers do not fluoresce, they fail to show any particular association with algal material and, in transmitted light, do not form an "envelope of translucent amorphous material around degraded colonies" (Glikson 1984). An additional dissimilarity is that the Scottish stringers show the same reflectance as other moeities (wisps and particles) within the matrix: the material in the Australian deposits has a much lower reflectance than the associated vitrinite. These factors, coupled with the observed development of cellular structures in the Westfield stringers, suggests that the Scottish stringers *are* vitrinite, much of which may have permeated the sedimentary matrix in the form of a collinitic gel at the soft-sediment stage.

Geochemical evidence supporting the inference, made on the basis of petrological examination, that the bacterial biomass has contributed significantly to

Botryococcus-rich shales, is provided by the hopane/sterane ratios. The exceptionally high hopane/sterane ratios for two torbanites and for the Rum and Best Cannel coals (35-130) indicate that massive inputs of bacterial lipids may occur in sapropelic environments. The hopane/sterane ratios of the Westfield Oil Shale (35) and Westfield Canneloid Shale (7) are consistent with their petrographic features. Both ratios are relatively high and reflect the bacterial reworking which was deduced from the presence of brown fluorescing areas in both samples. The fine degree of preservation of the *Botryococcus* colonies in the Canneloid Shale correlates with the lower degree of bacterial reworking which is inferred from the lower hopane/sterane ratio of this sample. The exceptionally high value for the Westfield Oil Shale is consistent with the more varied fluorescence properties of the *Botryococcus* telalginite and poorer definition of its internal structure.

(iii) Tricyclic and Tetracyclic Terpanes

Although the abundance of tricyclic and tetracyclic terpanes is greatly subordinate relative to the pentacyclics in the low-rank samples analysed, the relative proportion of 3- and 4-ringed components can yield some source information. In sediments containing abundant lamalginite (regardless of a marine or non-marine origin or its morphology), tricyclic terpanes are present in approximately the same concentration or higher concentrations than the tetracyclic 17,21-secohopanes. Dominance of the 17,21-secohopanes (mostly the C_{24} component) is found in samples whose organic matter mainly comprises land-plant debris and/or *Botryococcus* telalginite.

The biological origin of the tricyclic terpanes is still uncertain, but the ubiquity of these components in Midland Valley samples is consistent with the view that they could derive from microbial precursors (Ourisson *et al.* 1982; Aquino Neto *et al.* 1982, 1983). The enhanced concentrations of tricyclics seen in lamalginite-rich sediments also lends support to the possibility of an origin from algal precursors (Aquino Neto *et al.* 1983). The absence of tricyclic terpanes has been reported in terrigenous-sourced oils from many Australian basins whilst tricyclic components are abundant, relatively to the pentacyclics, in oils sourced from marine rocks (Philp and Gilbert 1986a,b). No such trends were observed in the samples studied from the Midland Valley, although a relatively high tricyclic content was noted in the marine sample taken from the Ballagan Beds in the Newburgh borehole (Fig.4.96a). The tricyclics in this sample may be due to the input of large amounts of tricyclic terpenoid precursors from the unusual, furrowed, algal cysts (Plate 4.114) which were not recorded in any other samples.

The possibility that *Tasmanites* can contribute large amounts of tricyclics to sediments has been suggested (Aquino Neto *et al.* 1989), and it is possible that the cysts in the Newburgh sample are tasmanitids.

Very low concentrations of tricyclics have been documented in marine shales (Connan *et al.* 1986) and torbanites (Derenne *et al.* 1988): thus although a dearth of tricyclics has been used as a marker for terrigenous source materials in Australian basins, such a corrollary is not universally applicable.

(iv) Pentacyclic Terpanes

Despite the overall similarity in the distributions of hopane and moretane families in organic-rich sediments from the Midland Valley, some trends can be discerned. The biomarker patterns in the lamalginite-rich shales, notably the lamosites, are particularly distinctive and can be used as markers for these types of deposit.

Abundance of homohopanes $\geq C_{31}$

The abundance of the C_{31} homohopanes and higher homologous doublets relative to the C_{30} hopane is much lower in lamosites than in the majority of other lamalginite-rich sediments or in sediments containing predominantly vascular-plant debris and/or *Botryococcus* remains. Philp *et al.* (1982) and Philp and Gilbert (1986b) have observed a similar dominance of the C_{30} hopane in many Australian oils which are known to have been sourced from rocks containing abundant higher-plant matter. These authors have suggested that this distribution is characteristic of oils derived from terrigenous source rocks. Relatively low concentrations of hopanes $\geq C_{31}$ also occur in three lamalginite-rich samples from the east Fife coastal sections (Psh, Q and SM22) which are thought to be non-marine (Fig.4.95). Whilst the observations from the current work agree with those of the above authors in that relatively low concentrations of hopanes $\geq C_{31}$ appear to be confined to non-marine sediments, such distributions in the Midland Valley can apparently be more specifically related to sediments containing abundant non-marine lamalginite rather than sediments containing abundant higher-plant matter.

Abundance of an unknown C_{29} *triterpane, peak 30*

M/z 191 mass fragmentograms of the lamosites and other non-marine lamalginite-rich shales referred to above all reveal the presence of an unidentified C_{29} triterpane (peak 30) which is seen as a shoulder on the $C_{29}\alpha\beta$ hopane. The compound is not confined to these particular types of deposit, but does appear to be closely associated with algal matter and, more specifically, lamellar alginite and *Botryococcus* (particularly the former). As the C_{29} unknown compound has its greatest abundance in extracts of lamosites and non-marine lamalginite-rich shales (see Table A.4), its presence in appreciable quantities, relative to the $C_{29}\alpha\beta$ and $C_{30}\alpha\beta$ hopanes, would appear to be a good marker for these deposits. The abundance of peak 30 in other liptinite-rich sediments in which algal matter is present is lower, relative to other hopanes, than in the non-marine, lamalginite-rich shales. The presence of alginite in sediments does not categorically imply the presence of peak 30, but the reverse is always true. The unknown C_{29} triterpane has not been found in extracts from coals and other terrestrial sediments in the Midland Valley unless there has been additional algal input.

The occurrence of an unidentified C_{29} triterpane with similar retention characteristics to peak 30 has been recorded in many sediments and oils of different ages and depositional environments. Philp *et al.* (1982) recognised a possible C_{29} triterpane, present as a shoulder on the $C_{29}\alpha\beta$ hopane, in Australian crudes, where it appears to be abundant in terrestrially-derived source rocks of Tertiary and Cretaceous age. A peak with an identical retention time is recorded in other terrestrially-sourced Australian oils (Philp *et al.* 1986b) although it is not labelled. A C_{29} triterpane eluting shortly after the norhopane has also been noted in Permian torbanites (Derenne *et al.* 1988) and in marine-sourced North Sea oils that have received varying amounts of terrestrial input from the Jurassic source rock (Hughes *et al.* 1985). The unknown compound also features prominently in the pentacyclic terpane distributions of Ordovician oils (Longman and Palmer 1987) and it can be recognised in the saturated gas chromatograms of the Guttenberg Oil Rock (Fowler 1984; Fowler and Douglas 1984), also of Ordovician age, and so precluding a contribution from vascular plants.

The widespread spatial and temporal occurrence of the unknown C_{29} triterpane in sediments and oils is indicative of an ubiquitous precursor, making a microbial derivation for this compound one possibility. The presence of the compound in Ordivician samples clearly indicates that the source is not exclusively associated with vascular plants or even the microbial reworking of vascular-plant material. The enigmatic *Gloeocapsomorpha prisca* is considered to be the most likely precursor for much of the organic matter in many marine Ordovician samples (Foster *et al.* 1986; Reed *et al.* 1986; Longman and Palmer 1987). A chlorophycean (eucaryotic) or cyanophycean (procaryotic) affinity for this organism has yet to be unequivocally established, although a recent detailed geochemical investigation (Hoffmann *et al.* 1987) favours a chlorophycean affinity, supporting earlier suggestions made on the basis of petrological evidence (Hutton *et al.* 1980).

It is apparent that the compound corresponding to peak 30 has a multiple source and could originate from blue-green or green algae, bacteria or higher-plant matter in a marine or non-marine environment. The restricted occurrence of peak 30 in samples from the Midland Valley which contain discrete lamalginite and telalginite points to a eucaryotic algal source for the precursor of the unknown triterpenoid in this province, although a contribution from the highly filamentous cyanophycean algae, thought to comprise part of the organic fraction in some lamosites and and sample Q, is also possible. In view of the complete absence of peak 30 from non-algal sediments in the Midland Valley, the possibility that its provenance may lie within a specific bacterial group which only metabolises algal lipids cannot be disregarded. The absence of the triterpane from many algal-containing sediments may indicate that the environmental conditions were not conducive to the microbial colonisation of the sediment by the specific group of microorganisms.

In Midland Valley sediments, the unknown C_{29} triterpane is accompanied by an unidentified C_{30} triterpane (peak 31). The latter varies in abundance relative to the former, but is usually subordinate to it. An unidentified C_{30} pentacyclic terpane with a similar retention time to peak 31 has been recognised as a widespread constituent in oils derived from terrigenous source rocks and has been referred to as "compound X" (Philp and Gilbert 1986a,b). The association of "X" with the unknown C_{29} triterpane is evident from inspection of the mass fragmentograms given in the papers of Philp *et al.* (1982), Philp and Gilbert (1986b) and Hughes *et al.* (1984) although their co-existence receives no comment. In view of the association of "compound X" with higher-plant source material, Philp and Gilbert (1986b) have suggested that it can be used as a characteristic terrigenous source marker, at least for Australian oils. The author's note the absence of "compound X" from other oils known to have been sourced from higher-plant matter (e.g. Handil oils from the Mahakam delta), which indicates that it is not an ubiquitous source indicator, but it may be associated with a specific type of vascular-plant input or an unusual bacterial contribution to the source rocks at the time of formation.

The current work supports the contention that "compound X" (peak 31) is not universally applicable as a higher-plant indicator by virtue of its co-existence with the unknown C_{29} triterpane (peak 30) which occurs solely in association with algal assemblages. Analogous to the occurrence of relatively low concentrations of extended hopanes, peaks 30 and 31 are most prominent in sediments containing abundant non-marine lamalginite. The presence of relatively large amounts of these compounds in oils and sediments could therefore be used as a source indicator for non-marine (more specifically, lacustrine) algal matter, the majority of which could be related to the modern-day form *Pediastrum*.

High Hopane/Moretane Ratios

High hopane/moretane ratios are a further feature characterising low-rank lamalginite-rich samples (apart from the lamosite from the section west of St.Monance, O/SBLA). If maturation-induced isomerisation reactions are the cause of increased hopane/moretane ratios , as is commonly assumed (Seifert and Moldowan 1980), then the values of 0.79-0.85 recorded in lamosites whose rank is not thought to exceed the equivalent of $\%R_o$av=0.70 are anomalously high. The majority of other low-rank sediments with similarly high hopane/moretane ratios ($\geq$0.75) contain abundant algal matter which may be of marine or non-marine origin (Fig.4.103). As mentioned in Section 4.3.3.4.2.1, the moretane content of algal-poor sediments is much higher than that in the algal-rich sediments of equivalent rank that occur in close proximity. These factors all point to a source control on moretane formation in sediments of the Midland Valley, which challenges the traditional and widely-accepted view that variations in hopane/ moretane ratios are rank-controlled.

(v) Steranes

Sterane distributions in which the $C_{27}\alpha\alpha\alpha$20R component comprises more than *c.*50% of the total C_{27}-$C_{29}\alpha\alpha\alpha$20R steranes are indicative of contributions from marine algae. Apart from this observation, steranes do not provide an effective means of defining algal-rich sediments. The utility of steranes as source indicators in the Midland Valley Carboniferous is discussed more fully in Section 4.4.1.4.5.

(vi) Aromatic Hydrocarbons

Lamalginite-rich sediments, regardless of provenance, are generally characterised by relatively simple distributions of aromatic hydrocarbons which are dominated by alkyltetralins and alkylated compounds based on the naphthalene skeleton. Homologous series of naphthalenes and phenanthrenes are are of relatively minor importance.

Alkyltetralins have been identified as prominent constituents in many coal extracts and pyrolysates, where they are thought to derive from carotenoid precursors present in the exines of higher-plant spores and pollens (Achari *et al.* 1973; Hayatsu *et al.* 1978; Wang and Simoneit 1990). The dominance of the aromatic hydrocarbon distributions in low-rank lamalginite-rich shales by alkyltetralins would therefore appear to be anomalous given the relatively small amounts of sporinite that can be discerned in the majority of samples studied.

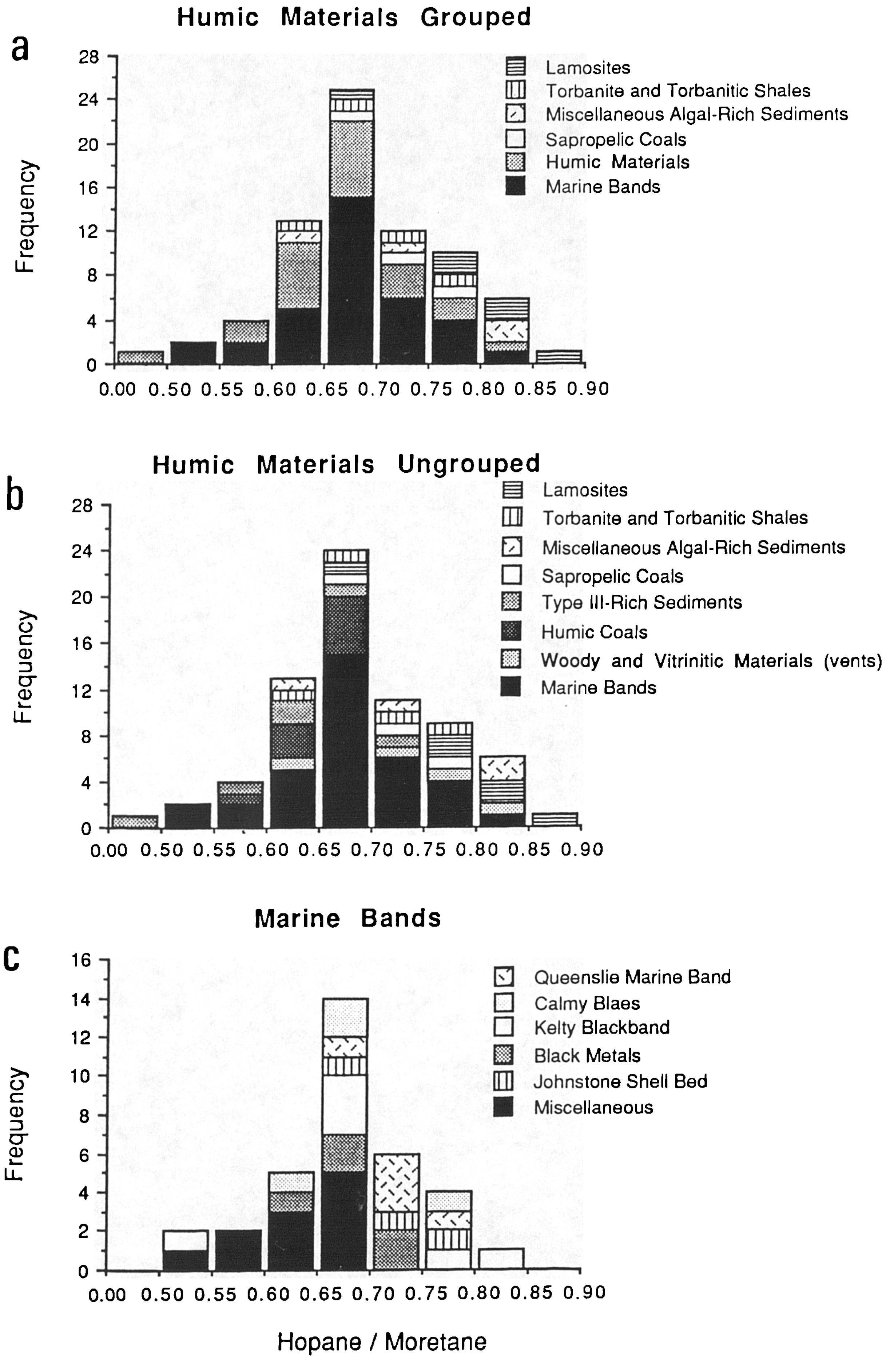


Fig.4.103 Histograms showing the distribution of hopane/moretane ratios.

The seemingly anomalous abundance of alkyltetralins in algal-rich shales from the Midland Valley may be resolved by considering some recent work on the distribution of aromatic components in coals and shales.

Püttmann and Villar (1987) and Villar *et al.* (1988) have observed that the distribution of aromatic hydrocarbons in many Tertiary and Cretaceous coals and shales is dominated by a relatively restricted range of components, many of which can be conceptually related to triterpenoid precursors based on the oleanane skeleton (Fig.4.104). These observations reinforce a long-establised view that β-amyrin is a likely precursor for many aromatic compounds in the geosphere (Spykerelle *et al.* 1977a,b; Laflamme and Hites 1979; Wakeham *et al.* 1980b; Chaffee *et al.*1984). Included in the suite of compounds described by Püttmann and Villar (1987) and Villar *et al.*(1988) are several alkylated naphthalenes and related compounds, *some of which are prominent* components in the aromatic fractions of the Midland Valley lamosites, e.g. alkyltetralins, *1,2,5,6-Tetramethylnaphthalene* and 1,2,5-Trimethylnaphthalene. In the majority of samples studied by the above authors, the alkylated naphthalenes are thought to form from the C-ring opening and rearrangement of aromatised oleanane skeletons (Fig.4.104). In extant plants, compounds based on the oleanane skeleton are restricted to angiosperms (Pant and Rastogi 1979), which did not evolve until Cretaceous times. The Carboniferous age of the sediments analysed in this thesis therefore precludes β-amyrin and the oleananes as being plausible precursors for the naphthalene derivatives seen dominating the aromatic distributions in sediments from the Midland Valley.

In addition to the occurrence of 1,2,5,6-Tetramethylnaphthalene, 1,2,5-Trimethylnaphthalene and the C_4 alkyltetralin (peak 10) in coals, these components have been reported in samples with no visible input of higher-plant matter (Püttman and Villar 1987). Instead of revealing the occurrence of tetracyclic triaromatic seco-triterpenoids of the amyrin type, which are thought to be intermediates in the formation of at least some alkylated naphthalenes (Fig.4.104), gc-ms analysis has shown the presence of monoaromatic tetracyclic seco-hopanoids of the type described by Hussler *et al.* (1984; Fig.4.105), which are thought to derive from the cleavage of the 8,14 bond in microbial hopanoid precursors. As Püttman and Villar (1987) have commented, "C-ring cleavage appears to be an omnipresent key reaction in the transformation process of pentacyclic triterpenoids to alkylnaphthalenes". These authors infer the generation of 1,1,5,6-Tetramethyl-1,2,3,4-tetrahydronaphthalene (peak 10) from the aromatisation and cleavage of seco-hopanoids which result, on further maturation, in the formation of 1,2,5-Trimethylnaphthalene or, after methyl rearrangement, in 1,2,5,6-Tetramethylnaphthalene (Fig.4.105). Thus, terpenoids based on both the amyrin and hopanoid

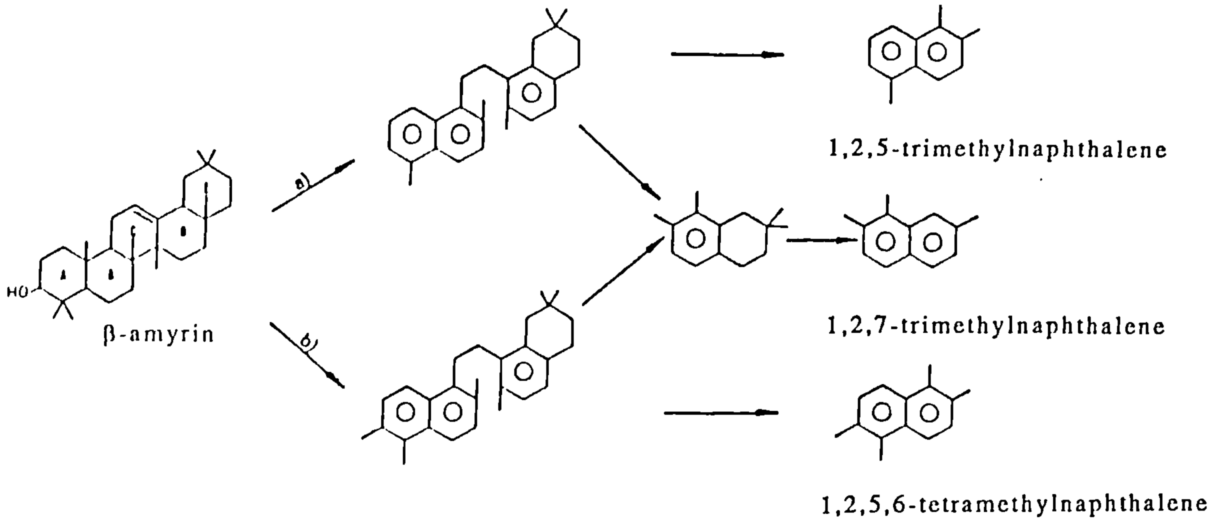


Fig.4.104 Postulated pathway for the formation of methylnaphthalenes from the degradation of β-amyrin (modified from Püttmann and Villar 1987).

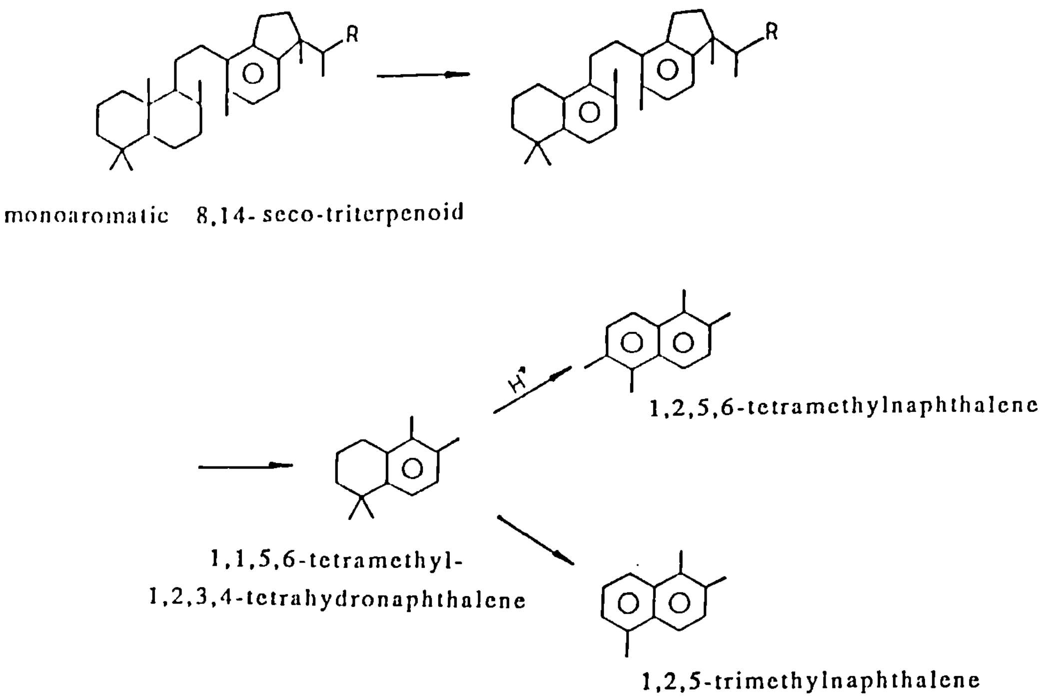


Fig.4.105 Postulated pathway for the degradation of monoaromatic seco-hopanoids to naphthalene derivatives (modified from Püttmann and Villar 1987).

skeletons can, after C-ring cleavage, result in products containing identical AB-ring carbon frameworks.

The prominence of peaks 10, 11f and 16 in the Carboniferous sediments of the Midland Valley, coupled with the presence of the monoaromatic 8,14-secohopane series in all the lamosites studied, points strongly towards a hopanoid origin for the former peaks. The high hopane/sterane ratios and pronounced contribution from benzohopanes in the samples is further supporting evidence that there was an abundant supply of hopanoid precursors available for conversion to alkyl-naphthalenes. Further evidence indicating that ring cleavage was instrumental in forming at least some of the aromatic components in the Carboniferous is the occurrence of peak 48. As mentioned in Section 4.3.3.1.2.2 , the compound corresponding to this peak is thought to be a monoaromatic tetracyclic terpenoid which formed from a fernane-related triterpenoid precursor via A-ring cleavage.

An additional source for the alkyltetralins observed in sediments from the Midland Valley may be carotenoids. As alluded to earlier, carotenoids present in sporopollenin have been regarded as a source for alkyltetralins observed in coal extracts and pyrolysates. Because of the relatively low abundance of terrigenous matter in the lamositic shales of the Midland Valley, a higher-plant origin for the carotenoids probably cannot account for the large quantities of alkyltetralins seen in these deposits. Carotenoids have been reported to be abundant in many extant algal groups (Schwendinger 1969; Goodwin 1971); therefore carotenoids derived from lamalginite and telalginite precursors (particularly the former) cannot be excluded as potential sources of alkyltetralins in the algal-rich sediments from the Midland Valley.

In addition to the alkyltetralins, the lamalginite-rich shales invariably contain relatively large concentrations of the compound 1,2,3,4-Tetrahydroretene (peak 33) and related diterpenoids. Diterpenoids are considered to originate predominantly from the resin acids of higher plants (Thomas 1970), and they are therefore often used as terrestrial marker compounds (e.g. Simoneit 1982; Simoneit and Mazurek 1982). The abundance of the 1,2,3,4-Tetrahydroretene, an intermediate in the formation of retene from abietic acid (Wakeham *et al.* 1980b), is anomalously high if a higher- plant source is invoked. Not only is there relatively little vitrinite or resinous matter in the lamalginite-rich shales in which it is most prominent, the presence of resinous material *per se* is relatively rare in Midland Valley sediments.

In the light of the postulated pathway for the degradation of hopanoids to alkylated naphthalenes, referred to earlier, it is possible that tetrahydroretene may have formed by a similar route. The hopanoid precursors could derive from bacteria or algae, both of which have made a significant contribution to the organic fractions of the sediments in which peak 33 is prominent. The possibility of an algal origin for tetrahydroretene, and therefore the related compounds simonellite (peak 32) and retene (peak 37) is supported by the known occurrence of diterpenoid skeletons in modern algae (Fenical 1978). Püttmann *et al.* (1986) have reported very high relative concentrations of phenanthrene in an algal-rich shale containing virtually no land-plant material and have also noted that phenanthrene abundance shows a positive correlation with algal content. These observations provide further evidence that aromatic compounds with phenanthrene skeletons might be derived from algal rather than the more commonly assumed higher-plant precursors. Notwithstanding the above suggestions, the possibility cannot be excluded that the aromatic hydrocarbon fractions of lamositic shales are revealing more of a contribution from terrigenous components than is evident from microscopical examination.

Akin to the occurrence of "terrestrial" phenanthrene derivatives discussed above, the prominence of cadalene in the aromatic fractions of several algal-rich samples might at first seem anomalous. Cadalene is prominent in the aromatic fractions of algal-rich samples from the Kelty Blackband, Queenslie Marine Band and the Eskmouth torbanite. Structurally-related precursors of cadalene (cadinenes and cadinols) are ubiquitous in the resins and essential oils of higher plants (Simonsen and Barton 1961). Cadalene overshadows the aromatic hydrocarbon distributions in the torbanite and the lamalginite-rich Kelty Blackband sample KBBI382, both of which contain relatively little higher-plant, let alone resinous, detritus. Other samples containing abundant higher-plant matter, including coals, contain very little, if any, cadalene. Cadalene has recently been reported as a major component in the aromatic fraction of the lacustrine Paraiba Valley oil shale (Loureiro and Cardoso 1990).

The above factors, coupled with reports of sesquiterpenes with the cadinane skeleton being a major constituent in some algal groups (Martin and Darias 1978; Scheuer 1978), suggest that, in addition to a higher-plant origin, cadalene could form from algal precursors.

The distributions of rearranged C-ring monoaromatic steroids were not investigated in detail because of their complexity, a lack of authentic standards with which to assign unequivocally their carbon numbers and isomeric configurations and also because of the coelution with non-rearranged C-ring monoaromatics and parent PAH observed under the gc-ms conditions employed. Nevertheless, the rearranged C-ring monoaromatic steroids were detected in all the samples in which the non-rearranged monoaromatics were detected. In samples rich in non-marine lamalginite (lamosites and lamalginite-rich samples from east

Fife), the rearranged C-ring monoaromatic steroids were greatly subordinate to the non-rearranged components.The relative concentrations of the rearranged components showed a marked variation in the remaining samples analysed (generally moderate/high in abundance), although very high concentrations were noted in all the samples from the Calmy Blaes and Queenslie Marine Band.

Rearranged C-ring monoaromatic steroids are thought to form under acid catalytic conditions similar to those necessary for the formation of rearranged steranes, as Moldowan and Fago (1986) have recorded a direct proportionality between the concentrations of diasteranes and rearranged C-ring monoaromatics present in a suite of marine sediments from West Germany. The depositional environment, based on the degree of anoxicity, is believed by the above authors to be the factor controlling the concentration of rearranged steroids since increases in Pr/Ph ratios are accompanied by increased concentrations of rearranged components.

Inspection of the histograms in Fig.4.106 (based on parameter O in Table A.5) reveals that high diasterane contents occur in the lamalginite-rich and cyst-bearing samples of the Calmy Blaes and Queenslie Marine Band and that low diasterane contents characterise samples rich in non-marine lamalginite. These abundances mirror those of the rearranged C-ring monoaromatic steroids and therefore parallel the observations of Moldowan and Fago (1986). The variations seen in the Pr/Ph ratios in sediments from the Midland Valley do not, however: the histograms in Fig.4.107 indicate that Pr/Ph ratios for the marine Calmy and Queenslie samples are similar to those for the non-marine lamalginite-rich shales. The data indicate that the concentrations of rearranged C-ring monoaromatic steroids in the Midland Valley are influenced more by source input than by the degree of environmental anoxicity. The nature of the depositional environment, *viz.* marine as against non-marine, is probably not a major control because, akin to the marine Calmy and Queenslie samples, rearranged C-ring monoaromatics are very abundant in humic coals and sediments rich in terrigenous debris. The factors leading to the formation of rearranged monoaromatics in sediments are probably more complex than previously supposed.

In addition to monoaromatic steroids, variations in the distribution of triaromatic steroids can be indicative of source control. Although the overall distribution of methyltriaromatics is remarkably consistent within all the coals and sediments analysed, samples rich in alginite (regardless of morphology or provenance) show enhanced concentrations of peak 4 (thought to be 4-methyl substituted) which accounts for *c.*70-80% of the height of peak 6 in the m/z 245 mass fragmentograms of these samples.

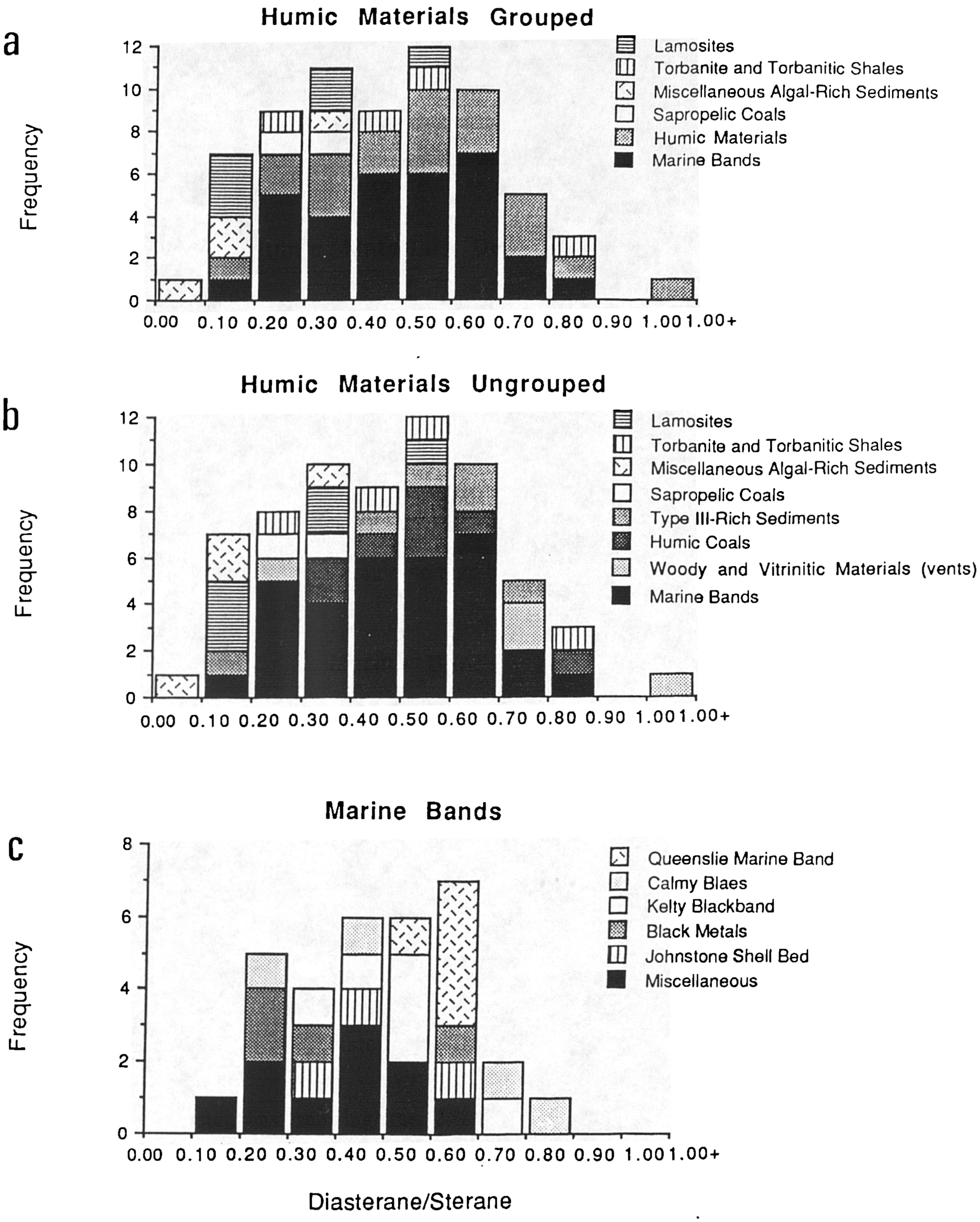


Fig.4.106 Histograms showing the distribution of diasterane/sterane ratios.

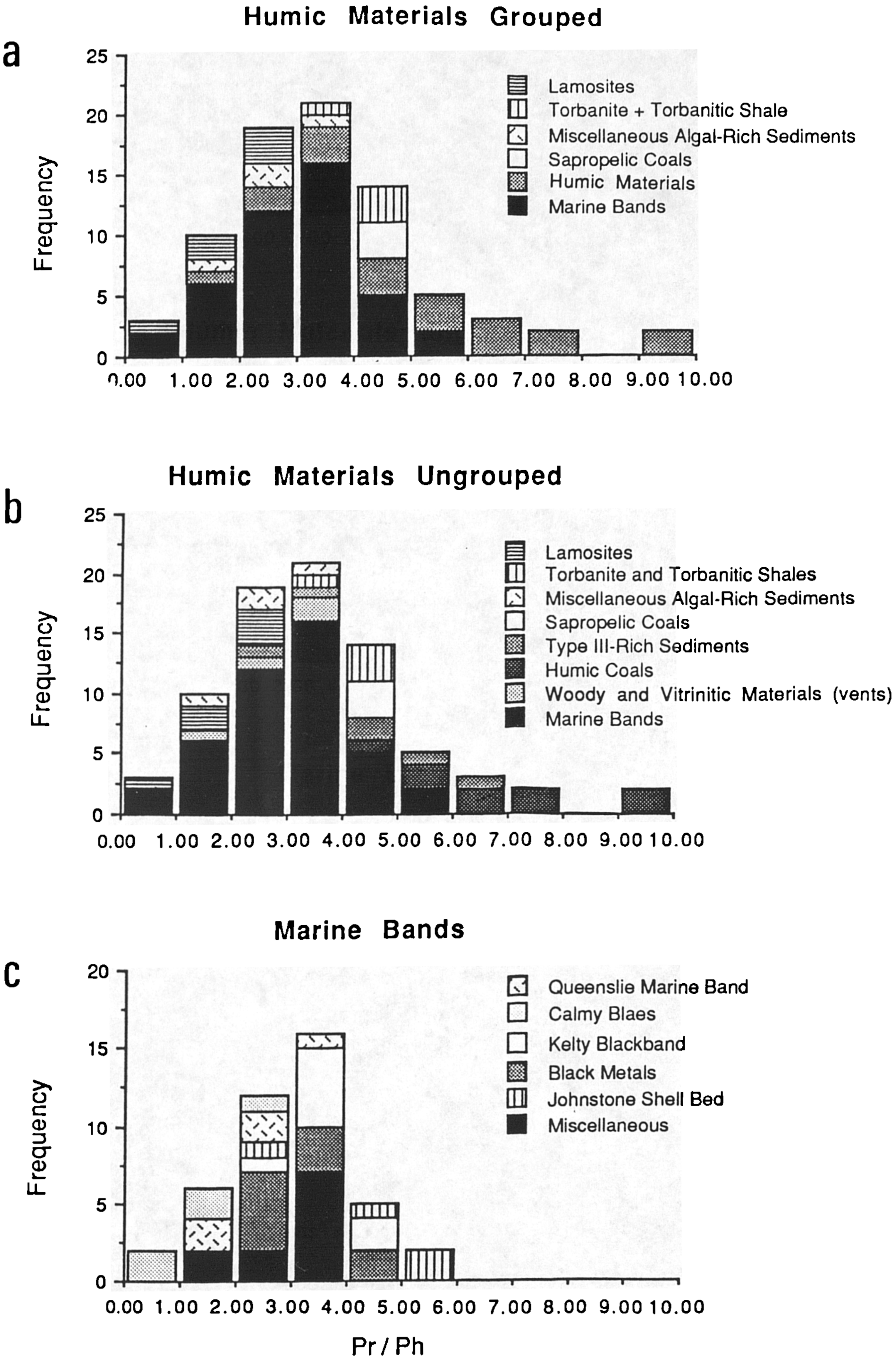


Fig.4.107 Histograms showing the distribution of Pr/Ph ratios.

The relative abundance of the triaromatic and nuclear-methylated triaromatic series (m/z 231/245) in low-maturity samples is a further feature which appears to be source controlled. The non-methylated triaromatics dominate over the methyl-substituted triaromatics in samples containing abundant alginite, whilst the reverse is true for the majority of sediments rich in terrigenous (particularly humic) debris (Fig.4.108). The preponderance of the desmethyl triaromatics is particularly pronounced in the majority of lamositic shales and also in other sediments rich in non-marine lamalginite.

4.4.1.4.2 Higher-Plant Markers

The presence of long-chain *n*-alkanes in which there is a marked OEP is a long-established indicator of terrigenous input although, as discussed in the last section, the potential of algae to produce such distributions in sediments from the Carboniferous of the Midland Valley should not be underestimated. Furthermore, from the analysis of the woody and vitrinitic materials from volcanic terrains (Section 4.2.2.3), it is evident that the absence of high molecular-weight *n*-alkanes can occur in organic materials of undisputed higher-plant origin. The biomarker distributions which appear to be highly characteristic of maceral assemblages dominated by vascular-plant input are based on polycyclic alkanes and aromatics, as discussed below.

(i) Predominance of Tetracyclic over Tricyclic Terpanes

As alluded to previously, the porportion of 3- *vs.* 4-ringed terpanes can give a guide to source input. Sediments with a marked higher-plant input, with or without additional algal matter, show the tetracyclic, 17,21-secohopanes (particularly the C_{24} member) to be present in much greater abundance than the tricyclic terpanes. Despite this difference, both the tricyclic and tetracyclic terpanes are generally of neglible abundance relative to the pentacyclics.

C_{24} tetracylic terpanes (not 17,21-secohopanes) have been reported to be significant terpane constituents in many terrestrially-sourced oils and they have consequently been regarded as markers for higher-plant debris (Richardson and Miller 1983; Philp and Gilbert 1982, 1986a,b; Czochanska *et al.* 1988; Weston *et al.* 1989). Notwithstanding the large amount of land-plant material present in sediments from the Midland Valley, high concentrations of C_{24} tetracyclics were only recorded in the samples from Orrock Quarry, where the compound represented by peak 12 was present in exceptionally high concentrations relative to the pentacyclic terpanes and could be readily discerned in gas chromatograms. The heightened concentration of peak 12 was accompanied by an increase in the

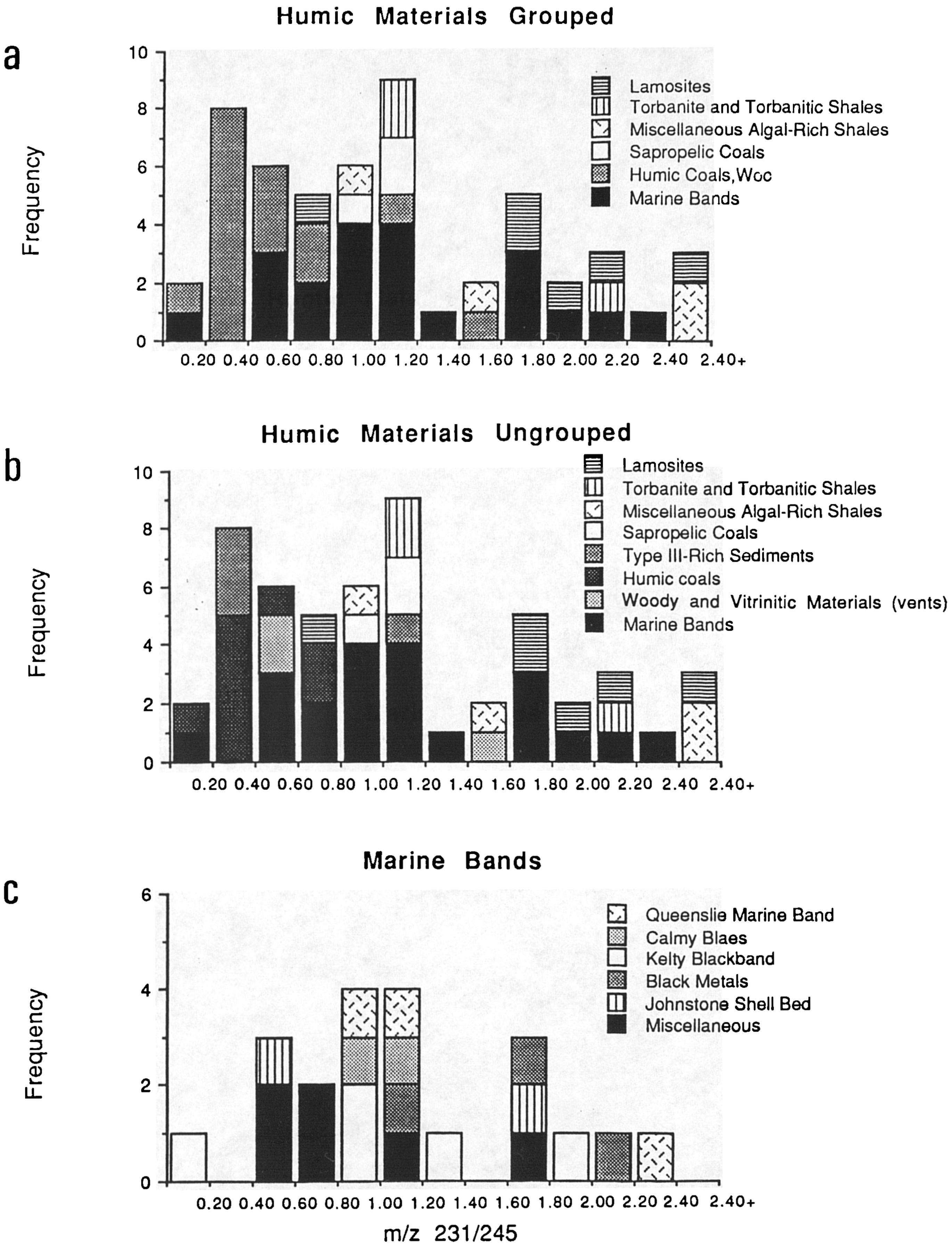


Fig.4.108 Histograms showing the distribution of triaromatics/methyltriaromatics..

number of C_{24} tetracyclic compounds present. Since peak 12 occurs in the majority of samples investigated in the Midland Valley, the restricted occurrence of very large amounts of the compound in the very low maturity Orrock samples could be related to sample rank rather than to organic-matter type. The work of Czochanska *et al.* (1988) and Weston *et al.* (1989) supports this view since these authors have shown that the abundance and distribution of tetracyclic terpanes in New Zealand oils are affected by maturity.

In addition to the possibility of rank control on the occurrence of C_{24} tetracyclic components, an evolutionary control is also conceivable. The terrestrially-sourced oils containing relatively high concentrations of C_{24} tetracyclic terpanes that have been documented from Indonesia (Richardson and Miller 1983), Australia (Philp and Gilbert 1982, 1986a,b) and New Zealand (Czochanska *et al.* 1988; Weston *et al.* 1989) are all derived from source rocks of Createaceous age or younger in which angiosperm floras contributed significantly to the organic matter that yielded the oils. The very low concentrations of tetracyclic components generally seen in organic matter from the Scottish Carboniferous may therefore reflect the lower evolutionary level of the flora, which may not have had the ability to synthesise large amounts of the precursors from which tetracyclic terpanes could form on maturation.

(ii) Abundance of C_{29} Triterpane, Peak 34

A measure of the prominence of this component was achieved by comparing its abundance with that of the $C_{30}\alpha\beta$ hopane (parameter f in Table A.4). Histograms of its abundance in all the low-rank samples analysed are shown in Fig.4.109. The greatest quantities of peak 34 (ratio $f<4$) occur in coals and sediments of marine or non-marine provenance in which the maceral assemblages are dominated by higher-plant matter. The highest abundance of the unknown compound was recorded in the woody sample from Orrock Quarry. Although the compound was identified in the majority of samples studied, suggesting a derivation from ubiquitous microbial precursors, the enhanced quantities seen in sediments containing abundant terrigenous debris (particularly vitrinite and inertinite) indicate that the precursor compound was synthesised in large amounts by higher plants. The presence of peak 34 in appreciable quantities in sediments would therefore seem to be a good marker for significant terrestrial input.

(iii) Enhanced Concentrations of $C_{29}\alpha\beta$ Hopane

Terpane fragmentograms for the majority of terrigenous-rich samples show enhanced concentrations of the $C_{29}\alpha\beta$ hopane (peak 29) relative to its C_{30} homologue (peak 33). Histograms showing the relative abundance of the two compounds

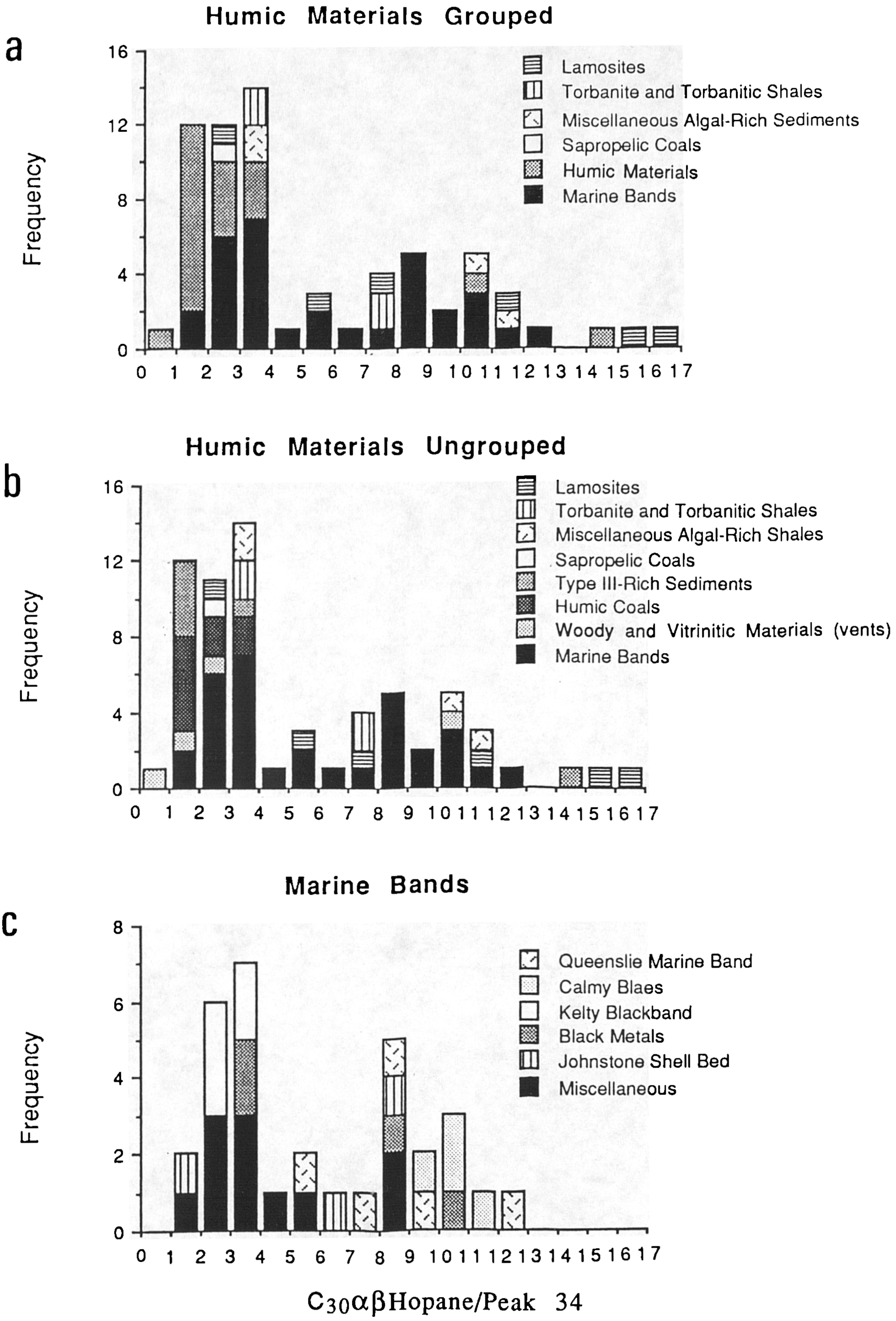


Fig.4.109 Histograms showing the distribution of $C_{30}\alpha\beta$ Hopane/Peak 34.

in the low-rank samples studied are shown in Fig.4.110. Samples in which the $C_{29}\alpha\beta$ and $C_{30}\alpha\beta$ hopanes are present in approximately equal amounts or in which the former dominates (i.e. ratios of ≥ 0.90 for parameter e in Table A.4) correspond to coaly materials and to marine and non-marine sediments which contain abundant vascular-plant debris in which, moreover, the dominant macerals are invariably vitrinite and inertinite. Most of the samples with $C_{29}\alpha\beta/C_{30}\alpha\beta$ hopane ratios <0.70 are marine or non-marine sediments containing abundant algal matter. Whilst enhanced concentrations of $C_{29}\alpha\beta$ hopanes are indicative of a major input of humic constituents to the organic matter, relatively low concentrations of this compound do not necessarily indicate the reverse, since several marine and non-marine samples with humic-rich maceral assemblages have values of the ratio $C_{29}/C_{30}\alpha\beta$ hopanes less than 0.90.

(iv) Very High Concentrations of $C_{29}\alpha\alpha\alpha 20R$ Steranes

Although there is a marked variation in the distribution of steranes in the materials analysed in the current project, a sterane distribution in which the $C_{27}\alpha\alpha\alpha 20R$ component comprises less than *c.*15% of the C_{27}-$C_{29}\alpha\alpha\alpha 20R$ steranes indicates, unequivocally, that the source material was a humic coal or a sediment (marine or non-marine) containing a high proportion of humic matter. Such samples have $C_{29}/C_{27}\alpha\alpha\alpha 20R$ ratios (parameter m in Table A.5) >3.50 (Fig.4.111). The utility of steranes in elucidating source input in samples from the Carboniferous of the Midland Valley is discussed more fully in Section 4.4.1.4.5.

(v) Aromatic Hydrocarbons

The extracts of sediments containing abundant terrigenous matter are characterised by complex distributions of aromatic hydrocarbons in which series of alkylated naphthalenes and phenanthrenes are significant components. Thus, the major source of these compounds in the Carboniferous of the Midland Valley would appear to be the diagenetic aromatisation of biogenic precursors present in higher plants. Alkylated naphthalenes are particularly prominent components, this observation according with those of other workers (e.g. White and Lee 1980; Radke *et al.* 1982b). These compounds could originate from sesquiterpenoid precursors (Murphy 1969; Bendoraitis 1974) or from the aromatisation of sporopollenin-derived carotenoids (Ikan *et al.* 1975).

Phenanthrene and alkyl phenanthrenes could originate from higher-plant steroidal and/or triterpenoidal precursors (Douglas and Mair 1965), but, unlike the transformations recorded in many recent sediments and coals (Wakeham *et al.*

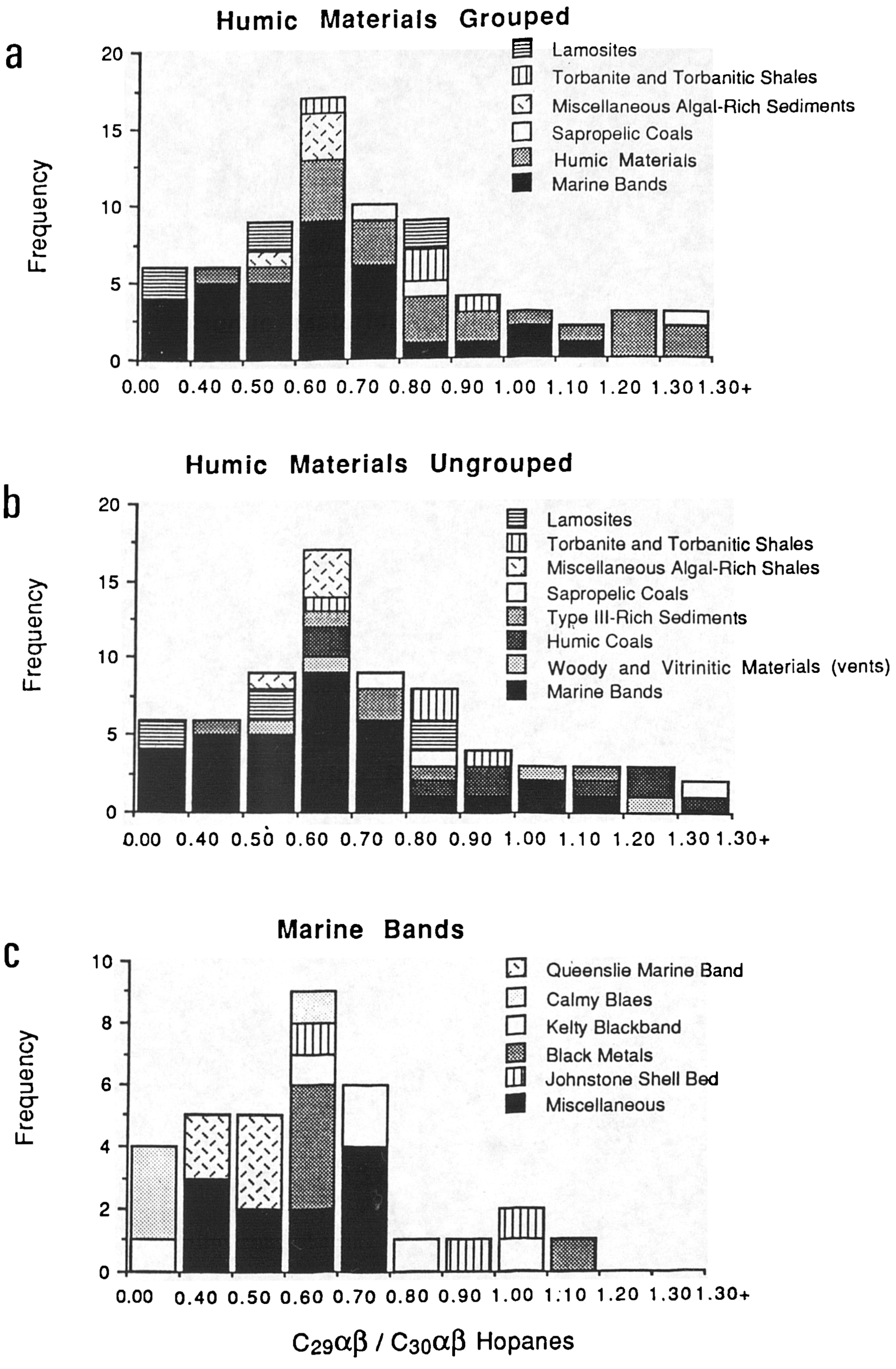


Fig.4.110 Histograms showing the distribution of $C_{29}\alpha\beta/C_{30}\alpha\beta$ hopanes.

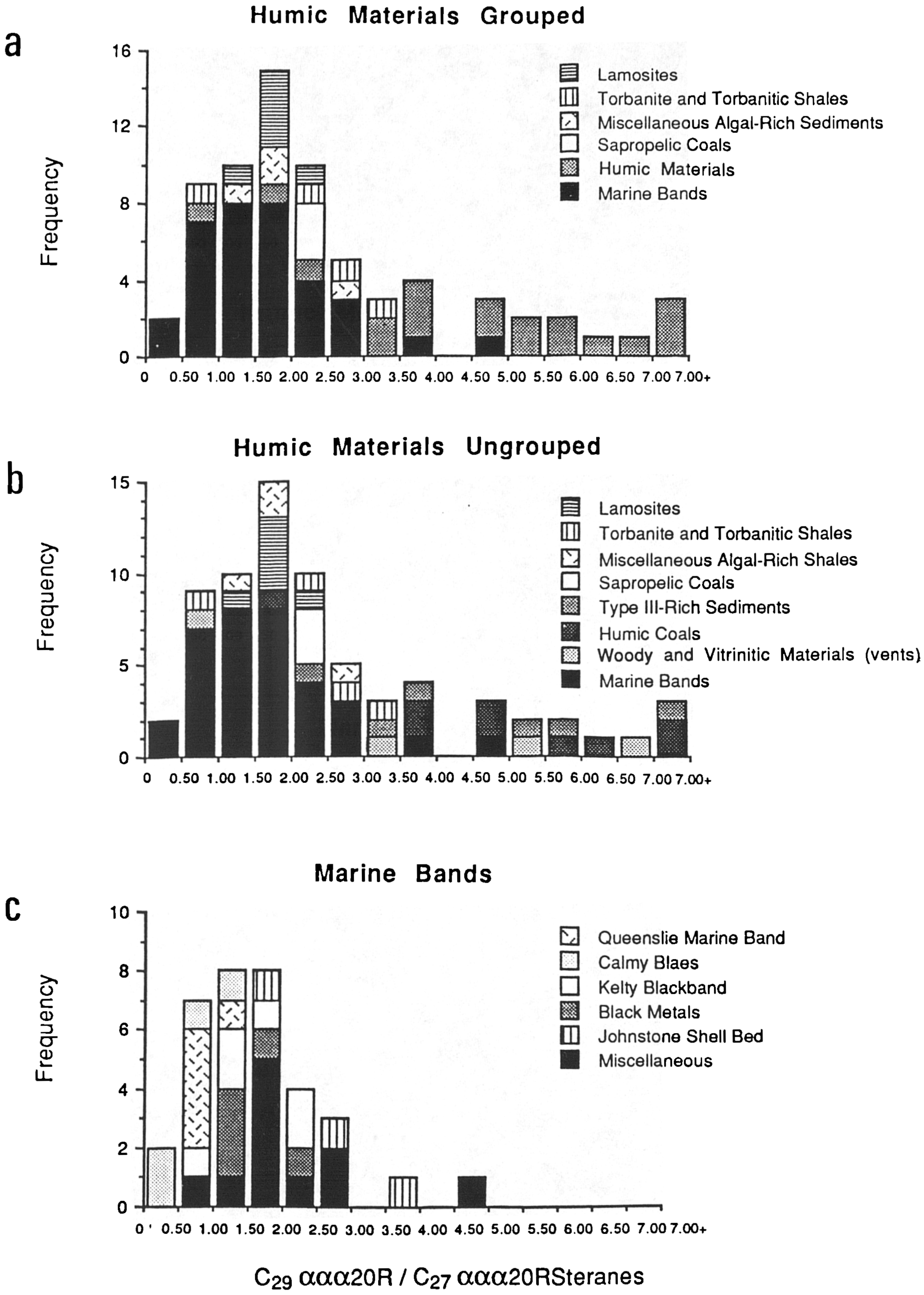


Fig.4.111 Histograms showing the distribution of $C_{29}\alpha\alpha\alpha20R/C_{27}\alpha\alpha\alpha20R$ steranes.

1980b), the Carboniferous age of the Midland Valley samples precludes derivation from triterpenoids based on the β-amyrin skeleton.

Retene and simonellite are often used as terrigenous markers (e.g. Simoneit 1977) because of the abundance of their diterpenoid precursors in conifer resins (Stonecipher and Turner 1970). The occurrence of these components in coals and sediments containing abundant terrigenous debris is indicative of a coniferous input, although in Carboniferous times these would have been primitive forms. The structurally-related compound 1,2,3,4-Tetrahydroretene has also been cited as a higher-plant marker (Simoneit and Mazurek 1982), but, in the Midland Valley, this component sees its greatest abundance in lamositic shales rather than in coals and terrestrial sediments. This factor is suggestive of a dual origin for this phenanthrene-related compound, as discussed in the last section.

Certain distributions of aromatic steroids are characteristic of humic coals and sediments rich in higher-plant matter. First, rearranged C-ring monoaromatics are abundant in such materials (particularly coals), but, as mentioned previously, increased concentrations of these components are not exclusively associated with abundant terrigenous debris. Second, the methyltriaromatic distributions differ in that peak 4 is only c.30% of the height of peak 6 in the m/z 245 fragmentograms (compare Figs 4.57b and 4.23c) and peak 9 is also enhanced. Third, a series of compounds with major ions of m/z=259 are prominent constituents and they are often sufficiently abundant to be recognised in TIC traces. These compounds, thought to be dimethyl- or ethyl-nuclear-substituted triaromatics, were barely detectable (if at all) in algal-rich sediments, suggesting that their precursors are derived from higher-plant sterols. Fourth, materials rich in higher-plant debris, particularly humic macerals, show a preponderance of methyltriaromatics (m/z 231/245 <1), as illustrated in Fig.4.108.

4.4.1.4.3 Microbial Markers

The detection of iso- and anteiso-alkanes, bicyclic alkanes and hopanes in all the samples studied is evidence for the ubiquity of microbial activity within the sedimentary environments prevailing during the Carboniferous in the Midland Valley, since the major source of these compounds is from the bacterial biomass as reviewed in Section 2.3.3.3. The degree of microbial reworking was assessed by using hopane/sterane ratios (Section 4.4.1.3). The strong predominance of hopanes over steranes in the majority of samples studied indicates that there has been significant reworking of organic matter by bacteria, regardless of the organic substrate or its depositional environment. Microbial activity was particularly intense in sapropelic environments.

4.4.1.4.4 The Occurrence of 28,30-Bisnorhopane

The elusive compound 28,30-bisnorhopane occurs in many of the samples analysed from the Midland Valley. Its occurrence cannot be correlated with any particular lithology or organic-matter type, although relatively high quantities of this compound are seen in samples from the Kelty Blackband horizon. The formation of bisnorhopane from higher carbon-numbered hopanoid precursors is not favoured on kinetic grounds (Kimble *et al.* 1974), and several possibilities have been advanced to explain its occurrence, sometimes in very large quantities, in sediments and petroleums. The original proposal of an origin from ferns (Seifert *et al.* 1978) was later disputed by Grantham *et al.* (1980) because the presence of bisnorhopane in North Sea oils was not accompanied by any evidence for terrestrial input in their source rocks. Grantham *et al.* (1980) suggested that the presence of bisnorhopane signified the accumulation of organic matter in a restricted and probably highly reducing environment or input from a specific, but unknown organism. More recently, Katz and Elrod (1983) suggest that the presence of bisnorhopane may be indicative of anaerobic bacteria growing in anoxic depositional environments. The widespread occurrence of bisnorhopane in coals, woody materials, marine and non-marine sediments, many rich in algal matter of various types, favours a bacterial origin, although the high Pr/Ph ratios observed in the vast majority of Midland Valley samples precludes microbial activity in the anoxic environmental milieux envisaged by Grantham *et al.* (1980) and Katz and Elrod (1983). In fact, the two samples with the lowest Pr/Ph values, Calmy Blaes sample C82 (Pr/Ph=0.80) and ANST F..from the Anstruther Borehole (Pr/Ph-0.79), contain no bisnorhopane. The occurrence of relatively large quantities of bisnorhopane in the Orrock wood, in which abundant microbial activity was detected from TEM analysis, lends further support to a bacterial origin for this compound. The exceptionally high bisnorhopane contents recorded in the Kelty Blackband, and to a lesser degree in the Black Metals, suggest that environmental conditions were particularly conducive to the development of the specific bacterial community(ies) which gave rise to bisnorhopane formation during the deposition of these sediments.

4.4.1.4.5 Steranes as Source Indicators

Ternary plots of the relative abundance of C_{27}, C_{28}, and $C_{29}\alpha\alpha\alpha20R$ steranes are much used in organic geochemistry as indices of the sources and depositional environments of organic matter. The rationale behind the use of these "Huang and Meinschein-type plots" was presented in Section 2.3.3.4.1. Calculation of the relative proportions of C_{27}-C_{29} steranes in the Midland Valley samples (see Table A.5) and their positions in the ternary plots show that the vast majority of the low-rank samples analysed, regardless of known provenance and type input, display a prevalence of C_{29} steranes.

In view of the dominance of C_{29} sterols in higher plants, a preponderance of C_{29} steranes in the extracts of recent and ancient sedimentary materials and in petroleums has often been cited as evidence of a terrigenous contribution to the organic matter (Huang and Meinschein 1976, 1979; Brassell *et al.* 1980; Hoffmann *et al.* 1984; Philp and Gilbert 1986a,b). Whilst this deduction undoubtedly holds for sediments and oils for which, on the basis of additional geochemical (and petrological) evidence, there is unequivocal confirmation of a substantial input of higher-plant material, it cannot account for the predominance of C_{29} steranes often reported in Lower Palaeozoic and Precambrian organic matter (Arefev *et al.* 1980; Fowler and Douglas 1987; Longman and Palmer 1987; Grantham 1986; Grantham and Wakefield 1988). The ages of these materials predate the evolution of continental plants, thus an alternative source for the precursor C_{29} sterols must be sought in other groups of organisms. C_{29} sterols have been found to be the dominant constituents in the sterol distributions of many living cyanobacteria and higher algae (De Sousa and Nes 1968; Reitz and Hamilton 1968; Paoletti *et al.* 1976b; Patterson 1971, 1974; Goodwin 1973; Boon *et al.* 1983). Since both of these algal types, but particularly the cyanobacteria, constituted a major part of the biomass during the Proterozoic and early Phanerozoic eons, an algal derivation has been invoked to account for the presence of C_{29} steranes in pre-Silurian organic matter (McKirdy and Hahn 1982; Moldowan *et al.* 1985; Grantham 1986; Fowler and Douglas 1987; Longman and Palmer 1987; Grantham and Wakefield 1988). Thus, although C_{29} sterols have traditionally been regarded as biomarkers for higher plants, important contributions from lower forms of plant life cannot be discounted. Furthermore, many C_{29} sterols once considered to be unambiguous markers for terrestrial input are now being detected in a variety of marine organisms (Brassell and Eglinton 1983; Volkman *et al.* 1981; Volkman 1986; Matsumoto *et al.* 1982), and, moreover, several "marine" sterols have also been discovered in lacustrine sediments (Wünsche *et al.* 1987). The vagaries of sterol occurrence in living organisms offer a clear warning that if any realistic assessment of source input is to be achieved on the basis of the distributions of their diagenetic products in ancient sediments, then the results of sterane analysis must be integrated with other geochemical, petrological and geological information.

From histograms showing the distribution of C_{29} against C_{27} steranes in the low-rank samples from the Midland Valley (Fig.4.111) and the triangular diagrams, it is apparent that the greatest predominance of C_{29} steranes is restricted to humic coals, vitrinites, woody materials and to other sediments containing a high proportion of vascular plant-derived matter of humic origin. Such samples have $C_{29}/C_{27}\alpha\alpha\alpha20R$ ratios >3.50 and show sterane distributions in which the C_{27} components comprise less than *c.*15% of the total C_{27}-C_{29} steranes, with the C_{29} steranes accounting for more than *c.*50%.

Whilst the position of most Midland Valley samples rich in terrigenous materials conforms to the location in the triangular diagrams predicted by Huang and Meinschein (1979), i.e. lying in the "terrestrial" and "higher-plant" fields, the majority of samples do not show the sterane distributions expected by the scheme of the above authors. The "fit" between the lacustrine and marine fields in the ternary plots of Huang and Meinschein and samples known to originate in lacustrine and marine environments in the Midland Valley is particularly poor. Although some of the lamositic shales do plot towards the lacustrine field, they clearly fall short of the lacustrine zone defined by Huang and Meinschein. There is also considerable overlap in the position of the lamosites with other non-marine, algal-rich samples and also with marine samples, the latter displaying great diversity in their maceral assemblages. The predominance of C_{29} steranes in the majority of marine and non-marine, algal-rich samples could either result from the swamping of any algal-derived C_{27} steranes by C_{29} steranes which originated from the vascular-plant matter that supplements the algal components to varying degrees, or could reflect an input of C_{29} steroids from the algae themselves. Given the known synthesis of C_{29} sterols by both procaryotic and eucaryotic algae, outlined above, and the very low abundance of terrestrial matter seen in several of the lamosites and marine samples, an algal origin seems entirely plausible. Because a vascular-plant contribution to the sediments cannot be precluded since the samples are Carboniferous in age, it is not presently possible to say how much, if any, of the observed sterane signatures in algal-rich sediments are due to interference from higher-plant input.

Sterols have only rarely been documented in bacteria where, moreover, they possess 4-methyl substituents and are present in concentrations that are greatly subordinate to those found in eucaryotic organisms (Schubert *et al.* 1968; Bird *et al.* 1971b; Bouvier *et al.* 1976; Kohl *et al.* 1983). Bacterial input can therefore be disregarded as a major influence on the sterane distributions recorded in organic materials from the Midland Valley.

Most of the samples in which the C_{27} steranes dominate over the C_{29} components are marine and are from the Calmy Blaes and Queenslie Marine Band. The highest proportion of C_{27} steranes correlates with the Calmy and Queenslie samples which contain the cyst-like algal bodies.

The proportion of C_{27} steranes recorded in the vitrinite from the coal ball-type structure from East Kirkton Quarry is anomalously high in view of its humic nature. The East Kirkton site is renowned for the abundance of rare (elsewhere), exceptionally well-preserved fauna which includes scorpions, arachnids and tetrapods (Wood *et al.* 1985). The high C_{27} sterane content of the sample may reflect the input of animal-derived sterols from the above fauna: thus, geochemical markers *may* be indicating an animal input that is not observed microscopically. The marked discrepancy between the sterane distribution of the Westfield Oil Shale and Westfield Canneloid Shale (Section 4.3.3.2.4.1) was attributed to an animal input, but again no microscopical evidence could corroborate this suggestion.

Steranes are obviously of limited use in discriminating between different types of algal input or even differentiating between marine and non-marine algal-rich sediments. Very high concentrations of C_{27} steranes may indicate a specific marine algal input or, as inferred for the Westfield Oil Shale and East Kirkton samples, a possible animal input. What is reasonably certain is that sterane distributions in which the C_{29} steranes comprise >50% of total C_{27}-C_{29} steranes are indicative of a marked input from terrestrial, humic-rich, maceral assemblages.

Regular steranes dominate over the diasteranes in all but one of the samples analysed. The diasterane/sterane ratios show a very broad distribution as illustrated by the histograms of Fig.4.106. Diasterane formation proceeds by the acid-catalysed backbone rearrangement of sterol precursors (Rubinstein *et al.* 1975). The acid sites of clay minerals are most commonly invoked as the catalytic agents (Rubinstein *et al.* 1975; Sieskind *et al.* 1979), although the presence of acidic pore waters during sediment deposition has also been suggested to explain diasterane formation in sediments (Moldowan *et al.* 1986).

Fig.4.106 shows that non-marine, algal-rich sediments (apart from the lamosite O/SBLA) have lower diasterane contents than the majority of other samples, whilst the algal-rich sediments from the Queenslie Marine Band and Calmy Blaes horizons are relatively high. Moldowan *et al.* (1986) have stated that variations in diasterane content are unlikely to be due to source-input variation because diasteranes and steranes are derived from common precursor sterols. As referred to in Section 4.4.1.4.1 in relation to the occurrence of rearranged monoaromatic steroids, Moldowan *et al.* (1986) highlighted the degree of environmental anoxicity, determined by Pr/Ph ratios, as an important factor governing diasterane abundance in sediments. A plot of Pr/Ph ratios against diasterane/sterane ratios for the Midland Valley samples shows a very broad scatter and no statistically significant correlation. That markedly different diasterane contents can occur in sediments at the same general level of oxicity and which contain different types of organic matter points to a source influence, but the influence of some other factor related to the differing depositional milieux cannot be discounted. Notwithstanding the latter possibility, large variations in diasterane content are apparent in sedimentary materials that accumulated in the same overall depositional regime at the same level of oxicity. Diasterane content is probably, therefore, the result of an interaction between a number of variables. The factors causing the transformation processes of sterols in the laboratory and in recent sediments clearly needs to be investigated in more detail before the variations in diasterane content can be satisfactorily interpreted in ancient sediments.

What is apparent, however, is that the nature of the enveloping matrix is important. As noted in Section 4.3.3.4.2.1, lower diasterane contents were recorded in carbonate-rich lithologies, which lack the acidic clay materials capable of inducing rearrangement. A further illustration of the importance of matrix effects in diasterane formation in Midland Valley sediments derives from the very high concentrations of diasteranes seen in the samples from Orrock and East Kirkton quarries, both of these lying in volcanic terrains. The great concentrations of active clay materials, resulting from the degradation of volcanic minerals in the enveloping matrices, were inferred to explain the high diasterane contents of the above samples (see Section 4.2.2.3).

4.4.1.4.6 Origin and Significance of Pyrolytic-Like PAH Distributions

The bulk of the aromatic components identified in the low-maturity samples studied originate, at least in part, from the progressive post-depositional, low-temperature aromatisation of non-aromatic biogenic precursors. The aromatic fractions of many of the coals and sediments studied do, however, contain significant contributions from components with more than three aromatic rings whose structures cannot be matched with the skeletal configurations of any known biogenic precursors. The most prominent of these compounds are the unsubstituted (parent) PAH pyrene, fluoranthene and benzofluorenes. Relatively minor quantities of their corresponding alkylated homologues are present. The types and distributions of these components observed in the Carboniferous samples resemble those seen in many recent sediments where their major source is attributed to the anthropogenic combustion and/or pyrolysis of fossil fuels (Hites *et al.* 1977; Lee *et al.* 1977; Laflamme and Hites 1978; Wakeham *et al.* 1980c). Natural combustion processes (fossil fires) have also been invoked as sources of parent PAH in recent sediments (Blumer and Youngblood 1975; Youngblood and Blumer 1975).

A characteristic feature of the pyrolytic-like distributions in recent sediments is their compositional similarity over a wide range of depositional environments (Blumer and Youngblood 1975; Hites *et al.* 1977). This consistency is also observed in the Carboniferous samples analysed, where it is maintained over a wide range of sediments containing different organic assemblages which were deposited in different environments. The constancy of the pyrolytic-like PAH distributions is also found in samples of different rank, for example the samples from Orrock Quarry (%$R_o$av-0.39), the algal-rich Q shale (%$R_o$av$\approx$0.63) and the shale above the Bush Coal (%$R_o$av-1.21). The marked similarities between the modern and ancient PAH distributions suggest a common mode of formation *viz.* the high-temperature alteration of organic matter. Temperature requirements for the formation of PAH mixtures dominated by parent PAH exceed 300°C; the optimum temperature range is 660°C-740°C (Lee *et al.* 1981). The occurrence of high-temperature combustion/pyrolysis products in Carboniferous samples which, on the basis of petrological and geochemical evidence, have experienced relatively mild thermal histories may initially appear anomalous.

The sorption of PAH on to particulate organic matter, notable soot, is a well-known phenomenon (Lunde and Bjørseth 1977; Gschwend and Hites 1981). The subsequent long-range transport of the PAH-laden particles, either as aerosols in the troposphere or by rivers or ocean currents, has been proposed to explain the occurrence of PAH in regions far removed from any apparent anthropogenic influence (Laflamme and Hites 1978; Windsor and Hites 1979; Wakeham *et al.* 1980c; Gschwend and Hites 1981; Tissier and Saliot 1983). A feasible explanation for the occurrence of pyrolytic-like PAH distributions in Carboniferous samples not exposed to severe heating may therefore be the sorption of combustion/ pyrolysis products on to organic moieties. The mode of occurrence of these PAH is suggestive of the "palaeocontamination" of organic matter which has not *per se* been exposed to temperatures sufficiently high to allow the synthesis of parent PAH.

Aromatics with up to three condensed rings are generally the most abundant constituents of the aromatic fractions of unburned fossil fuels whilst combustion-/ pyrolytically-derived PAH mixtures are dominated by compounds of three condensed rings and larger (Neff 1979). Although fossil and high-temperature PAH distributions have a compositional overlap, particularly with phenanthrenes (Wakeham *et al.* 1980b) and perylene (Louda and Baker 1984), the relative

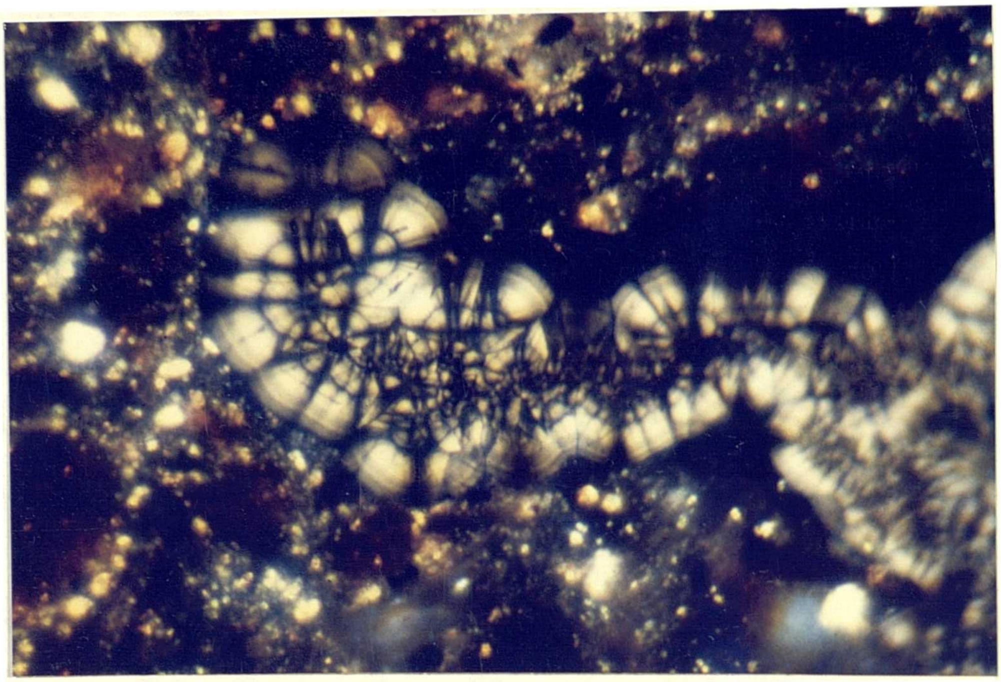


Plate 4.121 Spherulitic pyrolytic carbon showing extinction crosses in a low-rank sediment: reflected light, oil immersion, plane-polarised light.

Canneloid Shale, Westfield Basin; sample WDCS

x300

proportions of parent PAH and their homologues with greater and less than three condensed rings may give an indication of the amount of "palaeocontamination" of the diagenetic PAH distributions in the Carboniferous samples by combustion/ pyrolysis products.

In addition to the molecular characterisation of organic matter, the inclusion of high-temperature organic products in low-maturity sediments can be detected optically, in the form of pyrolytic carbon. In laboratory studies, this material forms from the cracking of coal-tar vapours at temperatures between 500-1000°C (Brown, Hesp and Taylor 1966). In the Midland Valley, pyrolytic carbon (usually lamellar in form) is most commonly seen in high-rank sediments near igneous intrusions, but it may also occur in low-rank samples. Finely-developed examples of the spherulitic variety, which rarely forms at temperatures below 700°C, were found in the *Botryococcus*-rich Canneloid Shale from the Westfield Basin (Plate 4.121). The occurrence of this high-temperature cracking product in this immature sample (discussed in Section 4.3.3.1.3) provides confirmation of the input of high-temperature combustion/pyrolytic artefacts which was evident from gc-ms analysis of aromatic hydrocarbon fractions.

Whilst gc-ms analyses detected the presence of components with more than three aromatic rings in almost all the samples analysed, the compounds were generally only present in significant concentrations (i.e. could be easily elucidated in TIC or gas chromatographic traces) in samples containing abundant terrestrial material, regardless of the depositional environment. Pyrolytic-like PAH distributions were particularly prominent in samples containing abundant vitrinite and inertinite. This point is illustrated by comparing the TIC traces of the woody and vitrinitic samples from volcanic terrains, the traces of humic coals and samples from the Black Metals, Johnstone Shell Bed and other marine horizons containing abundant higher-plant debris with those of algal-rich samples of marine or non-marine origin. Prahl and Carpenter (1983) have established the existence of relatively high concentrations of pyrolytically-derived PAH within the low-density fractions of many sediments in which vascular-plant debris has been identified as the major constituent of the low-density particulate material. Much of this plant debris was found to be lignaceous. Consideration of the occurrence of the PAH in recent sedimentary materials and the presence of compounds requiring high formation temperatures in the low-maturity Carboniferous samples indicates that, whilst the sorption of pyrolytic PAH to any organic component would appear to explain the near ubiquity of these components in the latter sample suite, there seems to be a preferential adherence to terrestrial matter, particularly the more porous vitrinitic and inertinitic components. Whether sorption was contemporaneous, i.e. occurred during subaerial exposure of the woody tissues to PAH-laden atmospheres, or whether impregnation of coalified materials occurred through percolating solutions containing waterborne PAH-bearing particulates is not known.

The Carboniferous age of the samples studied obviously precludes a source of their pyrolytic-like PAH distributions from anthropogenic activities. The origin of these PAH must lie in natural burning/pyrolytic processes. The widespread spatial and temporal occurrence of igneous activity in the Carboniferous of the Midland Valley (see Section 1.5) makes this the most likely mechanism for initiating the combustion/pyrolytic processes necessary for the production of high-temperature aromatic artefacts. The increased contributions from pyrolytic-like PAH which are seen in the aromatic fractions of samples known to be most closely associated with igneous activity lends very strong support to this suggestion. The following examples illustrate this association. The aromatic fractions of the low-rank samples from Orrock Quarry, enveloped in tuffaceous material, show significant contributions from typically pyrolytic PAH: any diagenetic aromatic distribution in the sample from the Coalyard Neck vent has been almost completely, if not entirely, overprinted by a characteristically simple, pyrolytic-like PAH distribution. It is possible that the warming of woody tissues occurred due to their intimate contact with hot ashy material during volcanic episodes. This heating may have been sufficient to activate the humic tissues, thereby enhancing their sorptive capacity and thus promoting the incorporation of PAH produced by the burning/pyrolysis of organic materials that presumably occurred during volcanic activity. Matrix activation could have occurred during atmospheric exposure or, in the case of the Coalyard and Orrock samples, after being enveloped in tuffaceous material. Heating is inferred to have been sufficient to catalyse PAH intake and mobilise resin and bituminous material (see Section 4.2.2.3), but was insufficient to have caused charring or burning of the organic matter with radical alteration of the fine cell structures. The increased exposure of the samples from the Coalyard and Orrock vents to PAH-laden atmospheres, coupled with the additional possibility of matrix activation through contact with hot ashes, may explain why the pyrolytic-like distributions in these samples are more prominent than in the humic coal samples investigated. There is the further likelihood that the comminuted nature of the vent samples enabled them to present a greater surface area over which PAH incorporation could have occurred.

The relatively lower concentrations of pyrolytic PAH in the sample from East Kirkton may, in part, be due to the protection afforded to the humic matter by the concretionary matrix. Since the exposure of organic matter to low temperatures over long periods of geological time favours the production of alkylated over non-alkylated PAH (Youngblood and Blumer 1975; Laflamme and Hites 1978), the lower relative contribution to the total aromatic fraction of the high-temperature PAH could also have arisen because of their dilution by the generation of diagenetically-derived, alkylated naphthalenes and phenanthrenes during the natural coalification of the sample.

A pyrolytic-like PAH distribution also dominates the aromatic fraction of the algal-rich sample Q. Although no exposures of igneous rocks are apparent in the Billow Ness coast section, from which Q was taken, the occurrence of a thin white-trap sill in the Anstruther Borehole indicates that igneous activity did occur in the vicinity during the accumulation of the Anstruther Beds, adding further support to the high-temperature genesis of the prominent aromatics in the sample.

Whilst it is feasible that the relatively high rank of the shale above the Bush Coal (BUSH SH; $\%R_oav=1.21$) at West Wemyss and the shale below the Third Abden Limestone (AB3; $\%R_oav=1.27$) from the Kinghorn-Kirkaldy section could be due to their proximity to unexposed igneous bodies, the highly brecciated nature of the vitrinite in these samples and the severity of the haematisation, which imparts a striking red colour to the hand specimens, are features which indicate that the elevated rank may, at least in part, have been accomplished by natural oxidation, since the petrographic features are highly characteristic of this phenomenon. These observations, coupled with the occurrence of aromatic hydrocarbon distributions that are probably entirely the result of pyrolytic/combustion processes, suggest that the oxidation occurred as a result of subaerial exposure of the organic matter to heavily PAH-laden atmospheres.

In the case of the shale above the Bush Coal, corroborating evidence stems from the discovery of thick sequences of volcanics c.5 miles north-east of West Wemyss, in the Firth of Forth (Ewing and Francis 1960; Francis and Ewing 1961). The volcanics encompass the same stratigraphic level as the Bush Coal (Middle Coal Measures) and they are thought to represent the remains of a major eruptive centre which was active during the deposition of the Middle and Lower Coal Measures sediments. Fall-out of volcanogenic airborne particulate matter probably constituted the predominant source of the high-temperature PAH found in the shale above the Bush Coal.

Major volcanism in the Kinghorn-Kirkaldy district had ceased by the time the shale below the Third Abden Limestone was accumulating in this area, but volcanic activity still persisted in the West Lothian district. Atmospheric transport of PAH from this area could account for the PAH fingerprint for the shale below the Third Abden Limestone (AB3), which is identical to that seen in the shale above the Bush Coal. An additional possibility is that PAH input has occurred due to erosion of the volcanic pile of the Burntisland Volcanic Formation, since AB3 lies on the flanks of the pile, which forms the core of the Burntisland Arch. PAH-laden hydrothermal solutions associated with the intrusion of an underlying teschenite sill could also have enhanced the pyrolytic fingerprint.

Whilst the presence of high molecular-weight parent PAH in Carboniferous samples is indicative of an input from burnt or pyrolysed organic matter, the occurrence of enhanced concentrations of some of the lower molecular-weight components *viz.* biphenyl and alkylbiphenyls seen in some samples yields information on the nature of the source material. The biphenyl skeleton is an important structural unit in lignins, particularly those of conifers, in which it is thought to account for *c.*25% of all units (cited in Radke 1987). Furthermore, the occurrence of biphenyl and alkylbiphenyls in a variety of geological materials shows that these units persist in the coalification process. Although biphenyl and alkylbiphenyls have been reported in coals, sediments and oils spanning a wide range of ages and geographic locations (Alexander *et al.* 1986a; Cumbers *et al.* 1987), these compounds are most commonly reported (and appear to be most abundant) in samples whose source material comprises higher-plant remains, for example coal extracts (White and Lee 1980; Püttmann *et al.* 1988), type III-rich sediments (Alexander *et al.* 1986a; Cumbers *et al.* 1987), coal tars (Mostecky *et al.* 1970) and vitrinite pyrolysates (Nip *et al.* 1988). Given that gymnosperms represent an important element of Lower Carboniferous floras (Scott *et al.* 1984), it is feasible that the high relative concentrations of components with biphenyl links (most commonly seen in samples containing abundant terrigenous debris and showing prominent pyrolytic-like PAH distributions) have arisen from the combustion/pyrolysis of gymnospermous vascular matter, at least some of which may have comprised the remains of primitive conifers such as *Cordaites*. The enhanced concentrations of biphenyl and alkylbiphenyls noted in a high-rank German coal (Püttmann *et al.* 1988) and in a Midland Valley meta-anthracite (see next chapter) lend further support to the suggestion that the occurrence of these components in Midland Valley samples resulted from exposure of vascular-plant tissues to elevated temperatures.

Although pyrolytic-like PAH distributions vary greatly in abundance, relative to the diagenetic PAH distributions in the samples investigated, gc-ms analyses detected pyrolytic-like PAH in nearly all the samples studied. These findings suggest that there is a background pyrolytic-like distribution of PAH in the Carboniferous succession in the Midland Valley, that exists as a consequence of pervasive igneous activity, which is analogous to that observed in recent sediments where the main source is anthropogenic combustion/pyrolysis. Since aeolian and aquatic currents are known to be highly efficient mechanisms for transporting particulate organic matter in recent environments (Laflamme and Hites 1978; Windsor and Hites 1979), it is likely that these were also important processes causing the widespread dispersal of pyrolytic/combustion-derived PAH in Carboniferous times.

4.4.2 Depositional Environments

4.4.2.1 Lamosites

It has long been recognised from palaeontological and sedimentological evidence that the algal-rich sediments of the Lothians Oil-Shale Group were deposited in a non-marine, shallow-water, lacustrine environment in a slowly subsiding basin termed Lake Cadell (Conacher 1917; MacGregor 1938; Moore 1968). The finely-laminated nature of the lamosites, their small grain size and the occurrence of articulated and exceptionally well preserved fish faunas (e.g. Dick 1981) are further indications of the tranquil conditions of sedimentation and the lack of sediment disturbance by burrowing or scavenging creatures.

The morphology of the progenitor algae, coupled with other geological information, can provide a more detailed insight into the algal mode of life and the depositional environments of the lamositic shales. The predominant lamalginite component in the Lothians lamosites is discrete lamalginite which resembles the extant freshwater genus *Pediastrum*, whose presence is indicative of open-water conditions (Sherwood *et al.* 1984). The occurrence of this alga is consistent with the known development of the laterally-extensive Lake Cadell, which is thought to have occupied an area of at least 2000km^2 during the accumulation of the Oil-Shale Group (Loftus and Greensmith 1988). The occurrence of the banded, cohesive, and highly filamentous algal fabrics in some lamosites points to algal accumulation in the form of benthonic, cyanophycean mats, indicating a relatively sheltered environment.

Two models can be invoked to explain the accumulation of algal matter in the Lothians-type lamosites, both of which differ widely in relation to the interpretations of organic-matter genesis. First, the high organic content and presence of relatively undisturbed laminations in the Lothians oil shales have been cited as evidence favouring accumulation in a perennial, thermally-stratified (meromictic) lacustrine environment in which the development of anoxic bottom conditions prevented bioturbation and resulted in a high degree of preservation of the organic matter (Greensmith 1962; Moore 1968; Loftus and Greensmith 1988; Parnell 1988). Algal accumulation in the meromictic regime is brought about by the blooming and subsequent settling of planktonic algae. Although this model may account for the accumulation of discrete lamalginite in the lamositic shales, the mat-like fabrics seen in several samples (particularly the Dunnet Shale), are not consistent with this mode of origin. The highly anastomosing and layered lamalginite bears more of a resemblance to that encountered in many of the oil shales within the Green River Formation (Hutton *et al.* 1980; Alpern 1981; Cook *et al.* 1981; Hutton 1987). Indeed, in a sedimentological assessment of the Lothians Oil-Shale Group, Greensmith (1962) remarked that "the lamination is too irregular to be seasonal" and that "in certain respects...the shales tend towards the composition of the Tertiary Green River shales of Colorado".

Intensive geological and geochemical studies of the Green River Formation have resulted in the formulation of two main depositional models which are distinguished on the basis of whether sediment deposition occurred within a permanently stratified lake (Bradley and Eugster 1969; Smith 1974; Desborough 1978), referred to above, or within a playa-lake complex (Eugster and Surdam 1973; Bradley 1973; Eugster and Hardie 1975; Surdam and Stanley 1979). The latter model is currently more favoured and implies that most of the Green River Formation was deposited in shallow, essentially unstratified, lakes fringed by extensive mud flats. Facies studies record the repeated transgression and regression of water across carbonate-rich mud flats which periodically dried out, as shown by the presence of polygonally-cracked surfaces, oolites and pebble conglomerates (Lundell and Surdam 1975). The episodic development of very low lake stands and high salinity is suggested by the repeated occurrence of evaporites in the succession. In contrast to the stratified lake model, algae within the playa-lake complex are considered to be largely of benthonic origin, having accumulated from a "flocculent ooze" derived from cyanophyceae (Bradley 1970, 1973; Eugster and Hardie 1975). Preservation is not thought to have occurred through the development of anoxic bottom conditions, as in the meromictic model, but through the desiccation and subsequent heat fixation of a "rubbery organic gel" which formed as a result of subaerial exposure (Bradley 1973). Although the planktonic green alga *Pediastrum* was reported in early studies of Green River shales (Bradley 1931), more recent detailed organic petrological analyses (Sherwood 1984) have failed to give a specific identification of any such lamalginite. The highly anastomosing, layered lamalginite observed through fluorescence microscopy is thought to represent the remains of benthonic, mat-forming, cyanophycean algae (Sherwood 1984; Sherwood *et al.* 1984). Planktonic algae are thus not thought to be major contributors to the organic matter in the Green River oil shales: furthermore, ultraviolet radiation would probably have prohibited their growth in shallow waters (Bradley 1973). The rhythmic alternations of organic-rich and organic-poor laminae in this deposit are attributed to fluctuations in the relative rates of algal accumulation and the seasonal and/or storm-controlled input of clastic material (Eugster and Hardie 1975).

The extensive studies of the Green River Shale can be applied to the depositional environment of the Midland Valley lamosites by considering the following lines of evidence. Evidence that sediments within the Oil-Shale Group have undergone periodic subaerial exposure has been recorded in the earliest studies of this succession (Carruther *et al.* 1912; Conacher 1917; Macgregor 1938). The presence of oolitic, limy cementstones and horizons which are sun-cracked and brecciated (particularly pronounced in marly strata), clearly attest to shallow-water deposition with subsequent emergence of the sediments to form carbonate-rich mud flats. These sedimentological features all invite comparison with the playa-lake model for deposition of the Green River Formation, but the general paucity of saline minerals within the Oil-Shale Group of the Midland Valley suggests that, unlike the Green River Formation, the climate did not become sufficiently arid to permit the widespread development of evaporites.

Although a flocculent, benthonic, cyanophycean ooze is considered to have been the source of algal matter in the Green River Shales (Bradley 1970, 1973), the cryptalgally-laminated fabric and the intimate association of the algal laminae with the mineral matrix seen in several Midland Valley lamosites indicate that the trapping and binding of sediment has been more important than might be expected from a purely flocculose mass which contains very little sediment (Golubic 1973). The alternating light (sediment-rich) and dark (organic-rich) laminae which are very pronounced in the Scottish lamosites containing abundant layered lamalginite may therefore reflect periodic fluctuations in the relative rates of mat growth and sediment deposition. Such an explanation is known to account for the development of similar microstructures in other laminated, organic-rich, ancient sediments, such as stromatolites, whose organic components are comprised mainly of the remains of benthonic, mat-forming, blue-green algae (Walter 1976). At least some derivation of algal matter from an ooze is possible, which could explain the presence of the bands of featureless organic material which are particularly prevalent in the Dunnet Shale and whose fluorescence intensity and colour are the same as those of the co-existing layered lamalginite. The close association of these "amorphous" bands with the lamalginite suggests that there may have been subtle, but rapid, variations in environmental conditions, determining whether the bottom-dwelling algae prevailed as sediment-stabilising mats or as flocculent "clouds" covering the sediment surface. In recent environments, benthonic algal masses are known to vary in their algal make-up, morphology and propensity to form mats. Transitions from one mat type to another have been documented, and these are governed by environmental factors including water depth (Golubic 1973; Krumbein and Cohen 1977). That similar environmental constraints influenced algal associations in Lake Cadell during deposition of the lamosites is not an unreasonable suggestion. Notwithstanding this possibility, it is also feasible that degradation of the original mat-forming algae has resulted in the formation of an algal "mush".

The occurrence of layered lamalginite in the lamositic shales of Fife and the Lothians is therefore ascribed to an origin from benthonic precursor algae in a playa-lake setting with affinities similar to those envisaged for the formation of the layered lamalginite-rich Green River shales. The presence of discrete, planktonic-looking lamalginite within the Scottish lamosites is, however, more suggestive of formation in a thermally-stratified lake. Thus, it seems that aspects of both models are represented within the lacustrine successions of the Midland Valley.

Consideration of sedimentological and geochemical evidence has already led to the suggestion that the two models invoked for the Green River Shale deposition should complement each other rather than be mutually exclusive (Boyer 1982), a view that has also been supported by the organic petrological observations of Sherwood (1984). Although algal accumulation in the Green River Shale is often cited as occurring mainly during high lake stands (Smith 1984; Eugster and Hardie 1975; Lundell and Surdam 1975; Surdam and Stanley 1979), the association of stromatolites, pisoliths, ooliths and oscillation ripples with oil shales are all indicative of a shallow-water depositional regime. The presence of mudcracks and pebble-conglomerates also indicate periods of desiccation (Lundell and Surdam 1975). That the variations in the water levels were far more rapid than had initially been postulated from earlier studies is inferred from the co-existence of lamellar and discrete lamalginite (frequently transitional) in Green River lamosites (Sherwood 1984). Since these algae are considered to have originated from benthonic and planktonic precursors, respectively, their presence within the oil shales is used to mark the development of, respectively, low- and high-water stands within the depositional basins. Fluctuating environmental conditions have also been invoked to account for the mixed lamalginite input in the lacustrine shales from the Mae Sot basin, Thailand (Sherwood *et al.* 1984).

Lothians lamosites are generally dominated by discrete or layered lamalginite, but alternations of these two algal types may occur, often over a distance of less than a few tens of microns. By analogy with the Green River oil shales

(Sherwood 1984), it seems likely that there were rapid and marked fluctuations in water levels during the deposition of the Lothians lamosites. Since Lake Cadell is considered to have been a large, shallow, low-lying feature with broad, gently sloping shores, only relatively minor changes in water level would have had a pronounced influence on the areal extent of the lake, resulting in major shifts between the thermally stratified and playa-lake environments. A refined model for lamosite formation in this lake, taking into account organic petrographic data, envisages the integration of the playa-lake and thermally stratified lake models in two possible ways. First, aspects of the playa-lake model are suggested by the formation of sediment-trapping benthonic mats in shallow water during low lake stands. Algae derived from flocculose masses may have contributed to the laminated mats, particularly in areas where there were exceptionally quiet waters (Golubic 1973). The deeper-water meromictic regime developed during expanded lake stands, where the deeper waters were more conducive to the blooming, settling and preservation of planktonic algae. Thus, the different types of lamalginite present in the Lothians lamosites may reflect the alternation of high and low lake stands resulting from the development of playa-lake and meromictic depositional environments respectively.

Second, rather than viewing these environmental changes as separate events occurring on a basin-wide scale, an alternative possibility is that both types of lamalginite formed concomitantly in different areas of the same basin. The benthonic mats could have occupied a niche in the shallow waters on the gently shelving periphery of the lake, while planktonic algae bloomed and settled in deeper waters to be preserved in undisturbed anoxic layers.

Mineralogically, some of the resulting layered, lamalginite-rich, lamosites are marls, and their formation is consistent with the binding, by filamentous algae, of carbonate-rich mud which also formed the adjacent mud flats that fringed Lake Cadell. Periodic emergence of the mats may have enhanced carbonate formation through evaporative processes, but excessive exposure of the algal-rich sediments during their formation is not thought to have occurred, due to the rarity of mudcracks and breccias within the resulting oil shales.

The presence of layered and discrete lamalginite in the Lothians lamosites is, then, evidence of deposition in a relatively large body of water. The occurrence of *Botryococcus*, on the other hand, suggests that there has been an input of organic matter from a more areally restricted freshwater environment. While *Botryococcus* may have flourished in small, ephemeral lakes that may have formed within depressions in the mud flats, the major provenance of this planktonic alga were the coal-forming, swamp environments which fringed the lake. Rivers traversing the peat bogs would have carried varying amounts of *Botryococcus* and other terrestrial debris into Lake Cadell through the numerous alluvial fan complexes which protruded into the lake (see Fig.1.6).

Whilst the above environmental interpretations relate to accumulation of algal matter in Lake Cadell, the occurrence of both layered and discrete lamalginite in shales from Fife indicates that similar depositional environments existed in the area to the northeast of Lake Cadell. In contrast to the generally quiescent depositional conditions which prevailed during the deposition of the Lothians Oil-Shale Group, sediments of equivalent age in Fife accumulated in a much higher-energy depositional regime in a large deltaic complex which, in part, separated Lake Cadell from the sea (Greensmith 1965; see also Fig.1.6). The presence of algal-rich shales in Fife is therefore evidence for the development of relatively open, freshwater lakes within the delta system, albeit of much restricted lateral extent. The thinness and sporadic occurrence of the algal-rich shales in Fife suggests that the lakes were probably ephemeral flood-plain lakes which may have shifted with changes in river courses. The occurrence of *Botryococcus* in the Fife shales again points to their close proximity to the more restricted aquatic environments associated with coal swamps.

The hydrocarbon distribution in the lamosite from the section west of St.Monance (O/SBLA) is anomalous compared with those of the other lamosites studied, including its lateral equivalent in the section east of St.Monance (SM7). Despite containing relatively little higher-plant matter, the former sample displays a hydrocarbon distribution more characteristic of a terrigenous sediment than a lamosite: its EOM shows an enhanced content of polar compounds, high Pr/Ph and Pr/n-C_{17} ratios, an increased content of extended hopanes relative to the $C_{30}\alpha\beta$ hopane, a low content of the unknown C_{29} triterpane peak 30 and an increased diasterane content. The distributions of aromatic components in the sample are also more similar to those seen in sediments rich in type-III kerogen, which contains relatively large contributions from series of alkylated naphthalenes and phenanthrenes and which shows large amounts of rearranged compared with non-rearranged C-ring monoaromatic steroids. The presence of terrigenous-type distributions in a lamosite may indicate that O/SBLA lies towards the edge of a lake in which algae accumulated, thus receiving increased exposure to a more restricted, terrigenous depositional regime rather than a "true" open-water aquatic regime in which the other lamosites accumulated. Some support for this interpretation is provided by the Pr/n-C_{17} ratio in O/SBLA, which is markedly higher than that recorded for the other lamositic shales (Fig.4.112). High ratios >1 are thought to be more indicative of organic-matter accumulation in a restricted,

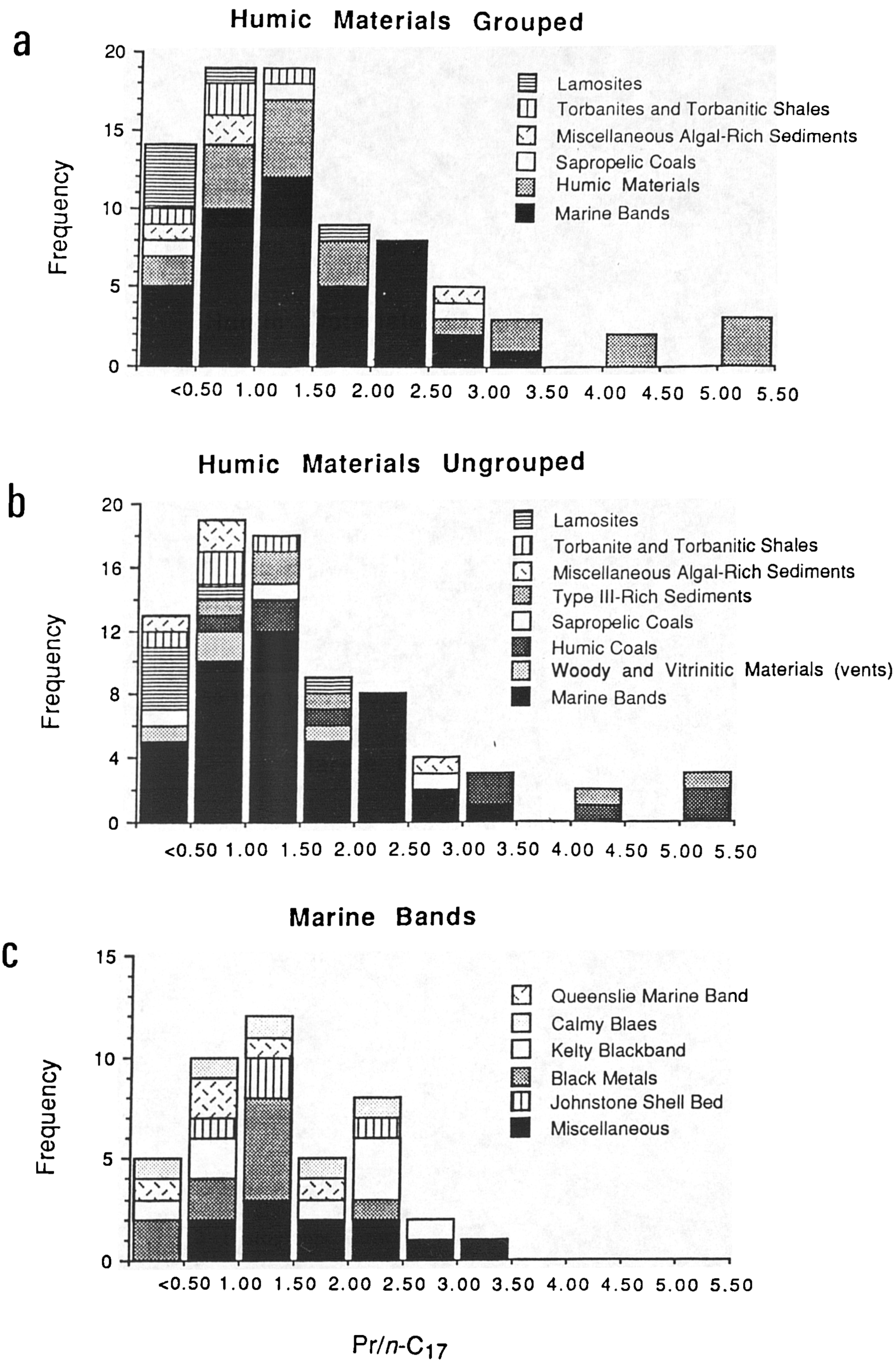


Fig.4.112 Histograms showing the distribution of Pr/n-C_{17} ratios.

peat-swamp facies (Lijmbach 1975; Didyk *et al.* 1978), whereas ratios <0.50 reflect more open-water conditions of sedimentation, as might be expected in a widespread lacustrine environment (Lijmbach 1975; Didyk *et al.* 1978).

The isoprenoid/*n*-alkane ratios of the lamosites (apart from the anomalous O/SBLA) are lower than those for the majority of humic and sapropelic coals, a phenomenon also noted by Powell (1986) when comparing Pr/*n*-C_{17} ratios for lacustrine-sourced oils with those sourced from rocks containing abundant terrigenous matter. Powell invoked the proposal of Lijmbach (1975) to explain the difference, namely that microbial activity was thought to be more severe in areally-extensive freshwater lakes than in the smaller peat-swamp pools. Greater bacterial removal of the phytol percursor in the larger lakes would therefore leave smaller amounts for conversion into isoprenoids. If such a scenario were applicable in the Midland Valley setting, the more extensive microbial reworking in the lamosites might be expected to be expressed by hopane/sterane ratios that are higher than those in humic and sapropelic coals. Fig.4.101 shows that the hopane/sterane distributions do not conform to those expected if Powell's and Lijmbach's explanation is valid for the Midland Valley, since the ratios for the lamosites are actually lower than those in most of the humic and sapropelic materials. It is possible that the reduced isoprenoid content of the lamosites was governed by some mechanism other than microbial activity or that there is a type control on phytol content.

4.4.2.2 Sapropelic Deposits

The depositional environment of the torbanite and torbanitic shales was very different from that of the lamosites. For over fifty years, torbanites have been recognised as localised, lenticular deposits which are closely associated with coal-bearing sequences (Conacher 1917; MacGregor 1938). The low vascular-plant input in these deposits was ascribed to the growth of algae in peat-swamp pools which were fringed by vegetation that filtered out all but the finest debris. In a study of the nature and depositional conditions of the cannels and boghead coals, Temperley (1935) recognised the transition between humic coals, spore cannels and algal cannels, but noted that the boundaries between these deposits and bogheads were sharp. This observation suggested that the algae existed as a discrete phase in the central, relatively deep-water parts of swamp pools whilst the transitional nature of the closely-associated sediments and their gradual increase in higher-plant components reflected increasing proximity to the pool flanks on which a variety of humic-coal components, eroded from adjacent swamp peats, accumulated as organic muds. That the accumulation of relatively "pure" masses of *Botryococcus* (or *Botryococcus*-related algae) was rare is indicated by the discovery of only one "true" torbanite throughout the course of the current study.

As stated earlier, the algal and humic materials that accumulated in sapropelic environments were supplemented by a major bacterial input, as witnessed by the very high hopane/sterane ratios in these deposits. The relatively low ratio (7) determined for the Canneloid Shale from Westfield suggests that microbial activity was probably not as intense in this sediment as it was in the other sapropelic deposits studied. This conclusion is borne out by the exceptional preservation of the algal colonies in the Canneloid Shale. This deposit is also notable for the very large sizes of its *Botryococcus* telalginite. From the current work it cannot be established that the environmental conditions during the formation of the Canneloid Shale were more equable and promoted a more luxuriant growth of *Botryococcus* (thus accounting for the large size of the colonies) than the environments operating during the formation of other deposits. It seems more likely that there was a sudden influx of sediment into the basin, causing disaggregation of the many algal colonies, followed by very rapid burial which restricted microbial attack of the cysts, an explanation which agrees with the known syn-sedimentary history of the basin.

The Pr/n-C_{17} and Pr/Ph ratios of the torbanitic and sapropelic deposits show a greater overlap with the humic-rich materials than do the lamosites which is not surprising since the former deposits are more closely associated with restricted, more oxidising peat-swamp environments. The distinction between the relatively restricted aquatic environment in which the sapropelic and humic coals accumulated and the more areally-extensive lakes, in which *Pediastrum*-related and benthonic algae existed, is well displayed by the differences in the Pr/Ph ratios of these deposits. The majority of sapropelic and humic-related materials have Pr/Ph ratios >4, whilst ratios <3 are characteristic of lamosites and the majority of other lamalginite-rich samples. The higher ratios in the humic and sapropelic coals are consistent with accumulation of the organic matter under a more oxidising depositional regime than that under which the lamalginite-rich deposits developed.

4.4.2.3 Sample Q

The depositional environments inferred for the Botryococcus-rich and lamalginite-rich shales presented above do not seem unreasonable since they are derived from comparisons with well-documented sequences in which algae with similar morphological characteristics to those in the Midland Valley have been identified and where there is abundant geological evidence from which to propose feasible models. The unusual petrological and geochemical characteristics of sample Q, from the east Fife coast, make the depositional history of the sample more speculative. The discrete lamalginite is much less filamentous than that in the lamositic shales, suggesting that it is probably not a *Pediastrum*-related form. The unique algal clasts in the sample are also a problem. There is no firm evidence that any of the algae in sample Q are of marine origin since positive identifications of marine acritarchs and marine phytoplankton have not been achieved. Indeed, only very rarely is the marine alga *Tasmanites* found in any of the marine shales examined from the Midland Valley. Despite these constraints, the morphology of the algae in sample Q and its known geological setting may shed some light on its depositional history. The following scenario is proposed.

The mode of association of the layered lamalginite with the mineral matrix in the calcareous clasts is so similar to that observed in lamosites containing layered lamalginite that the same algal-mat origin for the clasts is inferred. The occurrence of the lamalginite in the form of fairly smooth-edged clasts points to the break-up of the original mat fabric, with subsequent abrasion of the fragments. The small size of the clasts, and the lack of brecciation in the hand specimen, is suggestive of the sudden and forceful fragmentation of what may have originally been a very thin, benthonic algal accumulation. There may have been a weakening of the unlithified or semi-lithified mat fabric by desiccation cracks which could have been initiated by subaerial exposure, a phenomenon known to have brought about the development of polygonally-cracked and mud-chip laden surfaces on the lacustrine flats within the Green River Formation. The subsequent rapid transgression of lake or storm waters over the desiccated, mud-cracked surfaces resulted in the formation of pebble conglomerates and breccias within many of the Green River mudstones and oil shales (Eugster and Hardie 1975).

In contrast to the dominantly low-energy environmental conditions which prevailed during the accumulation of the Green River and Lothians lamositic shales, sedimentation in the east Fife area, as referred to above, was governed by a high-energy, deltaic regime. Given this palaeoenvironmental setting for sample Q, it is not unreasonable to suggest that there has been a deluge of water into a standing body of water causing the break-up of a benthonic mat which may have been accumulating in shallow water over the entire area of the basin bottom or which may have been present as a thin, desiccated crust at the margins. The sudden influx of water, and possibly sediment, could have been due to the breaching of the lake or lagoonal barriers (?levees) perhaps as a result of a shift in the river systems within the delta complex. There is the possibility of marine inundation, but, as mentioned earlier, there is no firm petrological (or geochemical) evidence of any contribution from marine organisms. Whilst the lamalginite enveloping the calcite grains is inferred to have had a benthonic mode of life, the discrete lamalginite was probably planktonic. It is unclear if the discrete lamalginite and *Botryococcus* telalginite in the sample co-existed with the benthonic type(s) or whether they are allochthonous, having been washed into the basin during the inferred depositional hiatus.

Sample Q therefore provides a rare example of a probable brecciated algal mat in which the resulting layered, lamalginite-rich, moieties may be envisaged as "rip-up" clasts. Although hand specimens of brecciated oil shales are only rarely reported within the Oil-Shale Group in the Midland Valley, it is apparent that brecciation can be discerned at the microscopic level without there being any evidence for this on the macroscopic scale.

4.4.2.4 Marine Horizons

Higher-plant material is widespread within the marine bands analysed and comprises at least 10% of the total organic fractions. Samples from the Kelty Blackband, Black Metals and Johnstone Shell Bed have an exceptionally high terrigenous content, with the organic assemblages of many samples consisting entirely of terrestrial matter. The ubiquity and abundance of higher-plant matter in the marine bands studied, and the predominantly non-marine nature of the successions in which they occur, suggest that they developed as the consequence of the transgression and regression of saline waters over the land surface and that the terrigenous source was never far away. Conditions may therefore have been quasi-marine rather than truly marine. The marine inundation of the low-lying swamps and other non-marine environments led to the mixing of non-marine organic components with marine algal matter. The very high terrestrial content of the marine bands in the Limestone Coal Group suggests that the horizons reflect little more than the ingress of marine waters over peat-swamp terrains. In the case of the Kelty Blackband, the finely-laminated and canneloid nature of many samples points to the accumulation of organic matter in a restricted environment. Marine incursions probably occurred into a predominantly sapropelic environment.

The abundance of algal cysts and flecks in the Calmy Blaes and Queenslie Marine Band and the generally lower terrestrial content of these horizons suggests that they are the most "marine" of the marine bands studied. The reduced terrigenous input could reflect the accumulation of the deposits in relatively deep waters, distal to any land masses, or it could indicate that terrestrial run-off was minor. The frequent occurrence of highly calcareous samples in the Queenslie Marine Band suggests that clastic input was low in many parts of the basin.

A structural control on the depositional environments of marine bands is inferred from the differences in the types of algal matter occurring in samples of the Queenslie Marine Band and Calmy Blaes taken from basins lying to the east and west of the structural high defined by the Burntisland Arch and Bo'ness Line (see Fig.1.4). The structural high probably acted as a barrier by allowing the development of differing environmental conditions in the adjacent basins in which different algal communities flourished. Variation in the Pr/*n*-C_{17} ratios within the Black Metals and differences in the amount and type of organic matter in the Kelty Blackband can also be related to the proximity of the samples to structural highs (discussed in the relevant section). Palaeontological investigations have shown that structural highs (particularly the Burntisland Arch) acted as barriers to the migration of macrofauna (Wilson 1967; 1974). Thus, there is no reason why this control should not have influenced the distribution of organic components which can only be detected on a microscopical or molecular level.

Pr/Ph ratios suggest that the depositional environments of the marine bands were generally oxidising. On the basis of the sample suite studied, anoxic environments are restricted to the Upper Limestone Group in west Fife, as shown by Pr/Ph ratios <1 in two samples of the Calmy Blaes and one sample of the marine shale above the Plean No. 1 Limestone.

4.4.2.5 Steranes as Environmental Indicators

The exclusive use of ternary plots of sterane distributions for defining the depositional environments of samples in the Midland Valley could lead to erroneous conclusions since many known marine samples plot in the "terrestrial" field of Huang and Meinschein (1979). There is also much overlap between the sterane distributions of marine bands and those of non-marine, algal-rich, lacustrine samples. That the majority of marine bands straddle the "terrestrial" and "estuarine/bay" fields supports the inference, made from petrological observations, that the marine and terrestrial environments lay in close proximity and that the former received a marked input of higher-plant matter from the latter. Increased proximity to the "terrestrial" field correlates with an increase in the vascular-plant content of the organic assemblages. The location of samples from the Calmy Blaes and Queenslie horizons in the "open marine" and upper part of the "estuarine/bay" fields accords with the abundance of marine algae, which contribute large quantities of C_{27} sterols, and supports the suggestion made previously that the samples are more marine in character than the marine bands in the Limestone Coal Group.

Despite the large spread of sterane distributions seen in Midland Valley sediments and the frequent lack of correspondence between the predicted and actual locations of samples in the Huang and Meinschein-type plots , information about depositional environments of organic matter in the Midland Valley can still be gleaned from this type of ternary diagram. The following generalisations can be made: sterane distributions in which the C_{27} component comprises less than *c.*15% of the C_{27}-C_{29} steranes are confined to coals, vitrinites and sediments in which the organic matter is comprised almost entirely of higher-plant material which accumulated in non-marine environments. Sterane distributions in which the C_{27} component accounts for over *c.*40% of the C_{27}-C_{29} steranes are found in marine samples containing abundant algal matter. Intermediate sterane distributions are not diagnostic of a particular depositional environment or organic input because there is much overlap in the distributions of the various types of non-marine, algal-rich samples and the marine samples which contain widely differing organic assemblages.

Few of the sterols found in living organisms are sufficiently restricted in distribution to be source specific (Volkman 1986). Furthermore, similar sterane distributions are seen in Midland Valley sediments that accumulated in different environments, whilst dissimilar sterane distributions are also recorded in sediments that were deposited in the same environment (see also Volkman 1986, 1988 on recent sedimentary regimes). It is therefore apparent that, akin to the use of steranes as source indicators, steranes should only be used as indicators of depositional environments when complemented by other geochemical and geological data.

4.3.3 Source Potential

Optical analyses show that the Carboniferous succession in the Midland Valley is exceptionally rich in organic matter. Although pyrolysis data were available for only a small fraction of the samples studied optically, these were derived from sediments containing different types and amounts of organic matter and should indicate the hydrocarbon potential and organic richness of other sediments with similar petrographic characteristics.

The Rock-Eval data corroborate the microscopical observations. All TOC determinations exceed 0.5%, the value cited as the minimum required for a sediment to be a viable source rock (Ronov 1958). All but two of the samples analysed have TOCs >1%. The average value for sediments throughout the succession in east Fife is 11.8%. The Carboniferous succession in the Midland Valley therefore satisfies at least one criterion for the generation of commercial quantities of hydrocarbons *viz.* an adequate amount of organic matter.

The further requirement of organic matter being of a type appropriate for the generation of hydrocarbons is also met in the Midland Valley Carboniferous. Several types of organic matter and organic assemblages have the potential to source commercial quantities of hydrocarbons. Sediments with the greatest potential for generating liquid hydrocarbons are the alganite-rich torbanites, torbanitic shales and lamosites, as indicated by hydrogen indices exceeding 600. The rarity, thinness and limited areal extent of the torbanite and torbanitic shales precludes these deposits *per se* from being major contributors to the petroleum potential of the Midland Valley, although the widespread occurrence of *Botryococcus* telalginite in the Carboniferous is likely to confer at least some oil-bearing potential on the sediments in which the telalginite occurs.

Of much greater economic i portance are the laterally-extensive lamosites of the Lothians Oil-Shale Group. The limited analyses available for lamosites in this study, coupled with the pyrolysis results of similar deposits in other parts of the world (Hutton *et al.* 1980; Cook *et al.* 1981; Sherwood 1984), suggest that the lamosites rich in layered, algal mat-derived lamalginite have a greater potential than the deposits richer in discrete lamalginite.

Algal-rich shales lying at the same stratigraphic level as the Lothians lamosites, albeit within a different facies, occur in east Fife and are also highly oil-prone. On the basis of the available data, the part of this sequence with the greatest oil potential lies in the Anstruther Beds (hydrogen indices are in the range of 343-689).

Algal-rich samples also occur within marine bands, but their occurrence is sporadic. The majority of marine samples analysed contain abundant vitrinite and inertinite, thus marine bands *per se* are not likely to contribute significantly to the liquid hydrocarbon potential of the Carboniferous, but may contribute to the generation of gas.

Although the non-marine, algal-rich sediments provide the greatest single potential source of liquid hydrocarbons in the Midland Valley, sediments rich in humic components, including coals, should not be discounted as potential contributors to the oil potential of the province. Most sediments rich in humic components have at least a fair potential to generate hydrocarbons (i.e. S_2 yields >2mgHC/g rock). The varying oil proneness of the kerogens in the sediments can be explained in terms of the relative proportions of hydrogen-rich and hydrogen-poor macerals present, irrespective of whether the former derive from vascular plants or algae or whether these accumulated in marine or non-marine environments.

The H/C ratio of sporinite places it on the type II coalification track, and it is sufficiently high for this maceral to yield liquid hydrocarbons on maturation. Notwithstanding this, humic-rich sediments in the Midland Valley containing large quantities of sporinite do not show a significant oil potential because of the "diluting" effect of the much lower H/C ratios of the accompanying vitrinite and inertinite. The hydrocarbon potential of the spore-rich sediments, often with good/ excellent source potential from S_2 yields, would be realised by gas generation or, at most, mixed oil and gas generation. Oil proneness of the above types of kerogen are only achieved when the sporinite and humic components are supplemented by relatively large amounts of algal matter (*c.*20% of total organic matter). Mixed algal and vascular-plant assemblages with high oil-yielding potentials are most likely to be found in the cannel coals and canneloid shales which formed in restricted, sapropelic environments.

It should be borne in mind that many canneloid and algal-rich sediments contain large amounts of highly dispersed or adsorbed hydrogen-prone matter within the mineral groundmass which gives rise to matrix fluorescence. This material may contribute towards oil yield upon thermal maturation of the sediments.

The liquid-generative potential of the terrestrial sediments is commonly attributed to the input of hydrogen-prone, cuticular components from spores, pollens and leaves and also to resins (Snowdon 1980; Thomas 1982; Powell and Snowdon 1983; Shanmugam 1985), whilst the vascular, cellulosic tissues from which vitrinite and inertinite are derived are widely considered to be solely gas prone. The results of liquefaction (Youtcheff *et al.* 1983) and pyrolysis experiments (Durand and Paratte 1982; Monthioux and Landais 1987) on humic coals and vitrinites show that vitrinites contain varying amounts of liquid hydrocarbons which are trapped within the micropore system that vitrinites have long been known to possess (van Krevelen 1961). The very high absorptive capacity of vitrinite is usually prohibitive to coals and coaly sediments acting as source rocks for liquid hydrocarbons since the quantities of hydrocarbons generated are rarely sufficient to accomplish the saturation of the pore space that must first occur to enable excess hydrocarbons to migrate from the vitrinite matrix (Powell 1978; McAuliff 1979).

Evidence that many vitrinites in the Midland Valley contain hydrocarbons is given by the widespread occurrence of "scruffy" vitrinites, often with scratched surfaces. Such textural features are known to be characteristic of perhydrous vitrinites (Teichmüller 1974a). That some vitrinites in the Midland Valley may be at or near their threshhold for hydrocarbon expulsion is assumed from the exudation of oil from cracks, although this phenomenon has, so far, only been recorded in coals from the Westfield Basin. Further evidence suggestive of hydrocarbon expulsion from vitrinites in the Midland Valley is provided by the occurrence of brown material around vitrinites stringers, which presumably exuded from them. The hydrogen indices for such samples are invariably higher than for samples with similar maceral assemblages, but which contain no exudates. This observation suggests that some vitrinites are more oil-prone than others.

Although the yield of hydrocarbons per unit mass from liptinitic macerals greatly outweighs that from vitrinite, the tremendous abundance of vitrinite in the carboniferous succession might compensate to some degree for its relatively low oil potential. The abundance of alginite and sporinite in the Midland Valley succession *diminishes the importance of vitrinite as a source for liquid hydro-*carbons, although it should not entirely be dismissed as a contributor to the petroleum potential of the area.

Rather more controversial is the issue of hydrocarbon generation from inertinite. As mentioned on p.53, the observed reactivity of inertinite during hydrogenetion and coalification is not consistent with its name, leading Smith and Cook (1980) to conclude that "inertinite may contribute more to hydrocarbon generation than was previously believed". Evidence in support of this suggestion lies in the occurrence of oil in some inertinite-rich and liptinite-poor successions in the Cooper Basin, Australia (Smyth 1983).

Akin to the possibility of oil generation from vitrinite, alluded to above, the great abundance of inertinite in the Carboniferous of the Midland Valley *might* be sufficient to offset its low H/C ratio and *might* make it a viable source for hydrocarbon material on a basin-wide scale. Notwithstanding this possibility, the generation of liquid or gaseous hydrocarbons from inertinite in the Midland Valley is likely to be miniscule in comparison with the amounts that could be generated from liptinitic and vitrinitic components.

The foregoing discussion has shown that the Carboniferous succession in the Midland Valley has a considerable potential for the generation of both liquid and gaseous hydrocarbons. The potential will only have been realised if the sediments have attained an appropriate maturity. The areas in the Midland Valley where the sediments have reached maturity conducive to hydrocarbon generation can be defined from the rank evaluation presented in the next chapter.

CHAPTER 5

VARIATION IN RANK

5.1 INTRODUCTION

This chapter presents the results of an investigation of rank variation within the Carboniferous of the eastern and central Midland Valley. Vertical and lateral variations in the maturity levels attained through regional coalification are discussed initially, with consideration also given to factors which can affect the determination of the true level of organic metamorphism as recorded by vitrinite reflectance.

An assessment of the extent to which both intrusive and extrusive igneous activity has modified the background geothermal gradient is then given, followed by the presentation of rank-map data (based on vitrinite reflectance) which illustrate the degree to which igneous activity has perturbed regional patterns of heat flow at different horizons in the Carboniferous.

The final part of the rank study investigates the effect that geologically rapid heating has had on the geochemical properties of organic matter, particularly on the variations observed in commonly-used maturation indices based on saturated and aromatic hydrocarbons.

5.2 REGIONAL COALIFICATION

5.2.1 Vertical and Lateral Maturity Variations

The series of coalfield rank maps published by the National Coal Board (NCB 1960), based on a combination of volatile-matter and coking data, suggests that there is a gradual rank increase in moving westwards across the Midland Valley from the Fife Coalfield to the Central Coalfield. There is no indication of how much of the present-day rank distribution (particularly in the Stirling-Clackmannan-Central Coalfield basins) was caused by proximity to igneous materials.

The pattern of rising rank westwards is confirmed by the reflectance study undertaken in the present project. Evaluation of the vertical and lateral variations of regional maturity levels was achieved through the construction of maturation profiles, based on vitrinite reflectances, for nearly forty borehole and field sections. Those profiles presented in the main text have been included to illustrate specific points: the remainder are included in Appendix III. The localities of the boreholes studied are shown in Fig.5.1, although not all of these are suitable for the determination of background reflectance values because of significant interference from igneous intrusives.

Rank maps were constructed to illustrate the level of organic metamorphism (at different geographical locations at the same stratigraphic level) which has

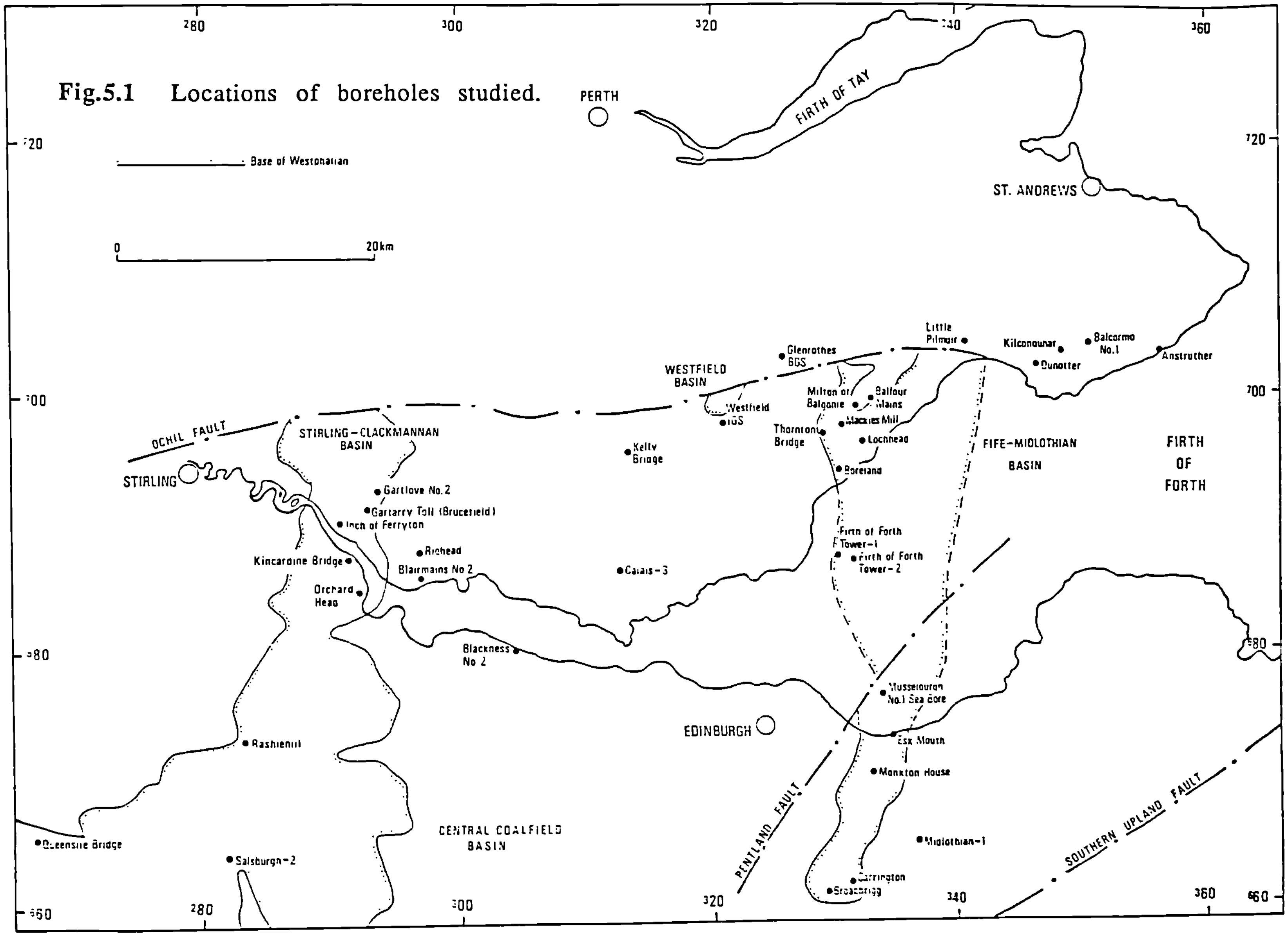


Fig.5.1 Locations of boreholes studied.

been achieved, *in all probability*, solely through exposure to the background geothermal gradient. Given the pervasive nature of intrusive and extrusive igneous activity in the Carboniferous succession, it is impossible to be absolutely certain that a given maturity has been derived entirely through regional coalification. From consulting lithological logs provided by oil companies and the Geological Survey and from considering the reflectance profiles, the samples plotted on the "background" rank maps are not thought to have suffered rapid heating associated with igneous activity unless otherwise indicated.

Reflectance values were measured directly on vitrinites in samples at a specific stratigraphic level or were determined at the level at which the horizon occurred in a borehole or field section through interpolation. Both types of determination comprise the "measured reflectances" in the map keys. "Projected reflectances" denote estimates of ranks at levels below total depth (TD) in the boreholes. An estimate of the maturity at such a horizon was made by projecting the background vitrinite-reflectance trend line beyond TD through the amount of section required to reach the stratigraphic level of interest. Stratal thicknesses were estimated from the published isopach data of Browne *et al.* (1987). These predicted values probably give no more than a general indication of maturity levels since structural complexities, poor exposure and rapid lateral thickness variation mean that much uncertainty surrounds many of the published isopach thicknesses (M.A.E.Browne *personal communication*).

Rank maps showing the variation in the regional level of coalification at different stratigraphic horizons are given in Figs 5.2a-k. Because the Midland Valley Sill is the main agent responsible for modifying background geothermal gradients (see next section) and because this intrusion probably represents the last major thermal event to affect organic matter in the eastern and central Midland Valley, the regional reflectance values on the maps represent the maximum levels of maturation attained prior to the intrusion of the Midland Valley Sill complex in early Permian times.

The maps of the Calmy Blaes (Figs 5.2a,b) and Passage Group (Figs 5.2c,d) horizons show the determinations obtained for all available samples at these stratigraphic levels. Because so few samples are thought to have been heat-affected, it was not considered worthwhile drawing separate post- and pre-sill maps for these horizons. The reflectance values exceeding $\%R_o av=1.00$ that occur in the Calmy Blaes in the Rashiehill and East Carron bores (Central Coalfield) are known, or suspected, respectively, to be heat-affected. No background reflectance profiles could be constructed for the East Carron bore,but the profile of the Rashiehill borehole indicates that pre-sill rank levels were $\%R_o av \approx 0.70$ at

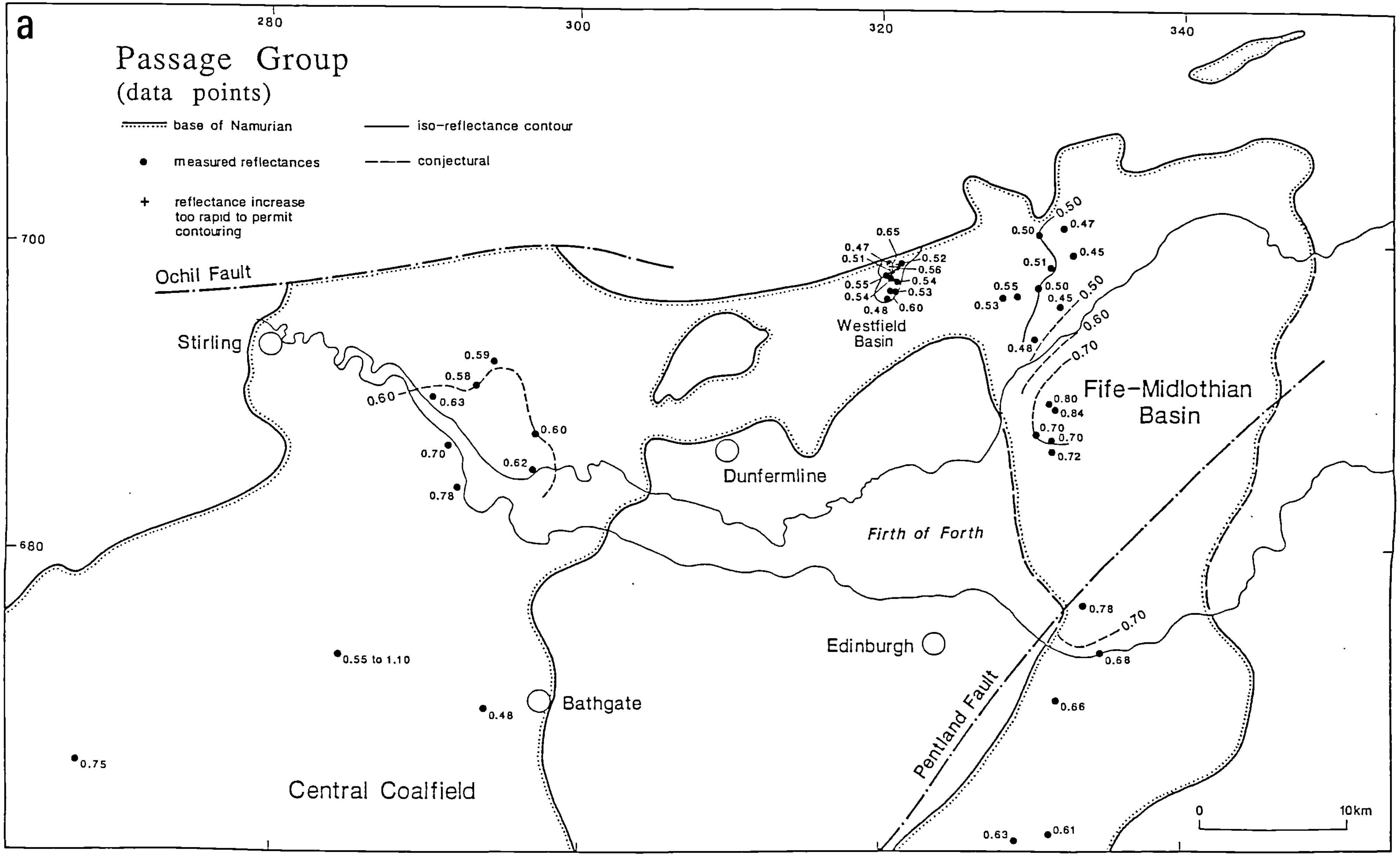
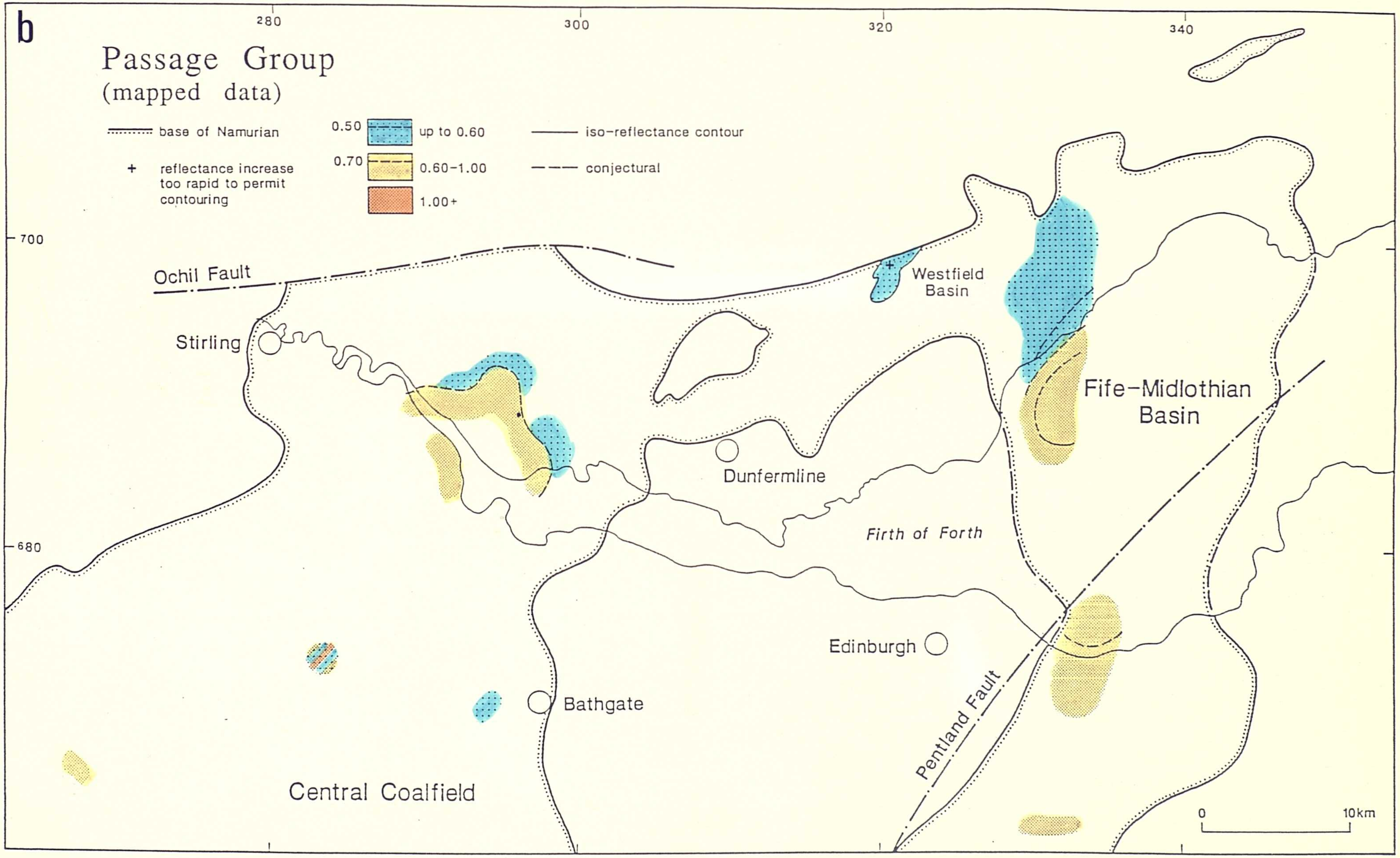
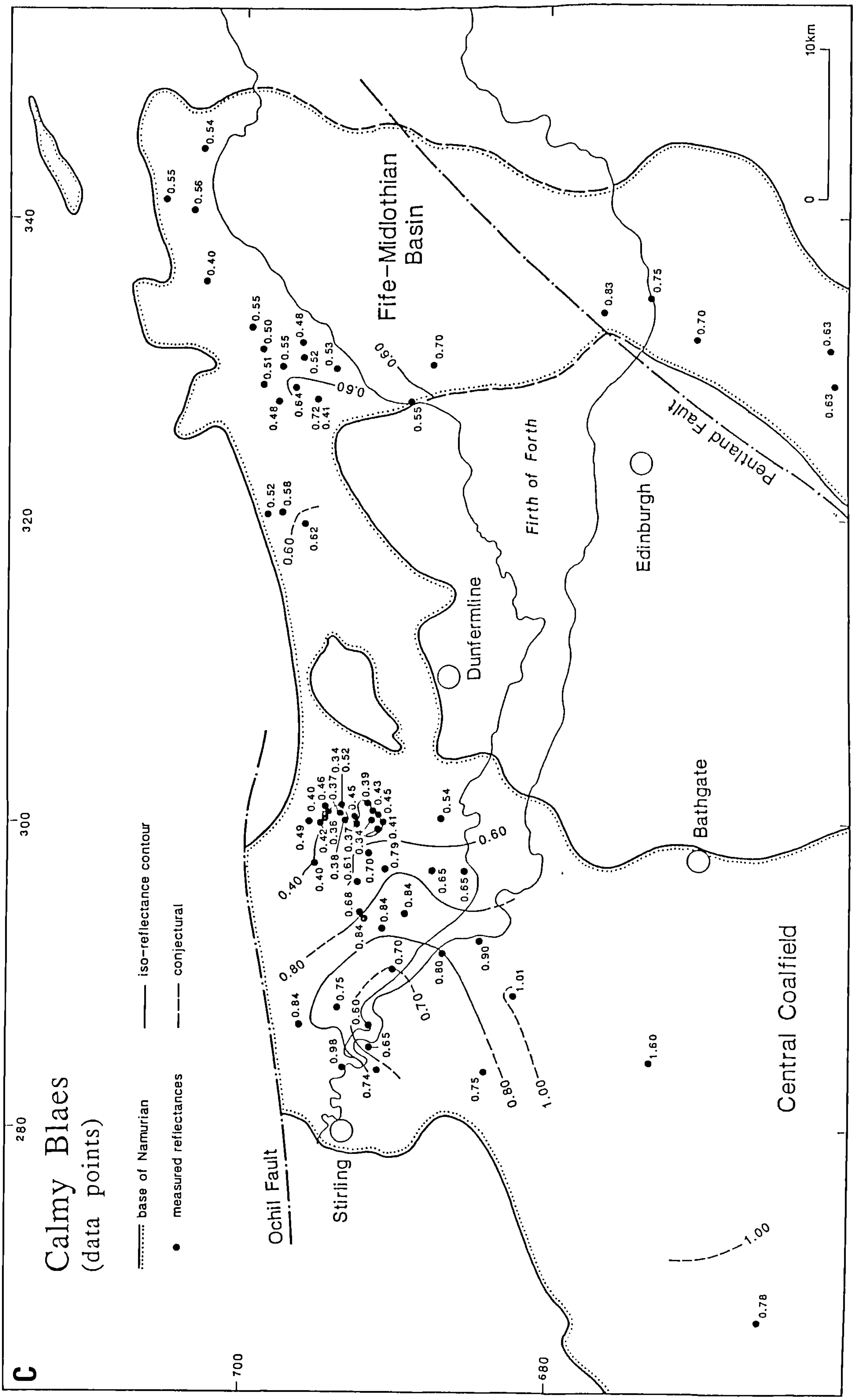
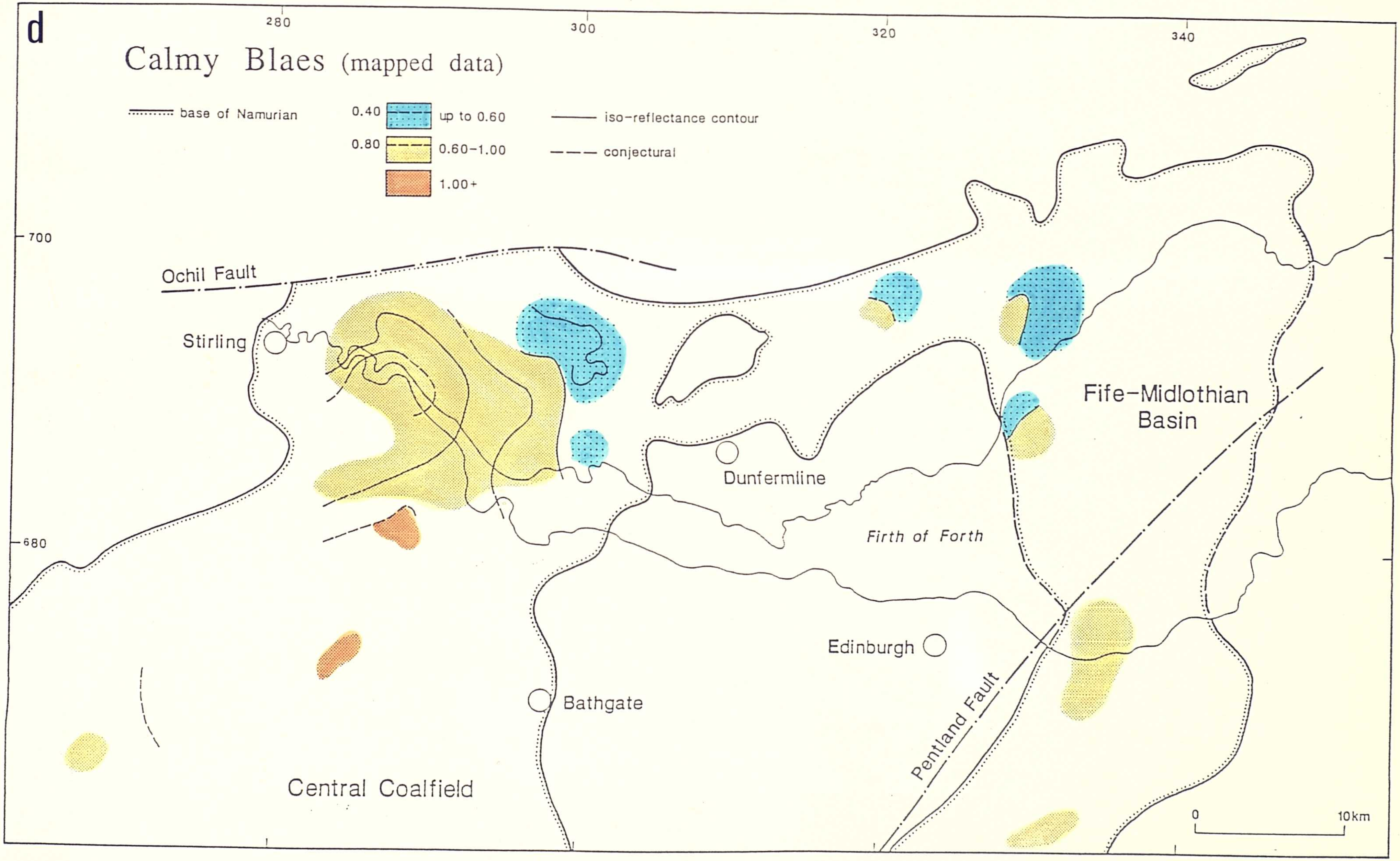
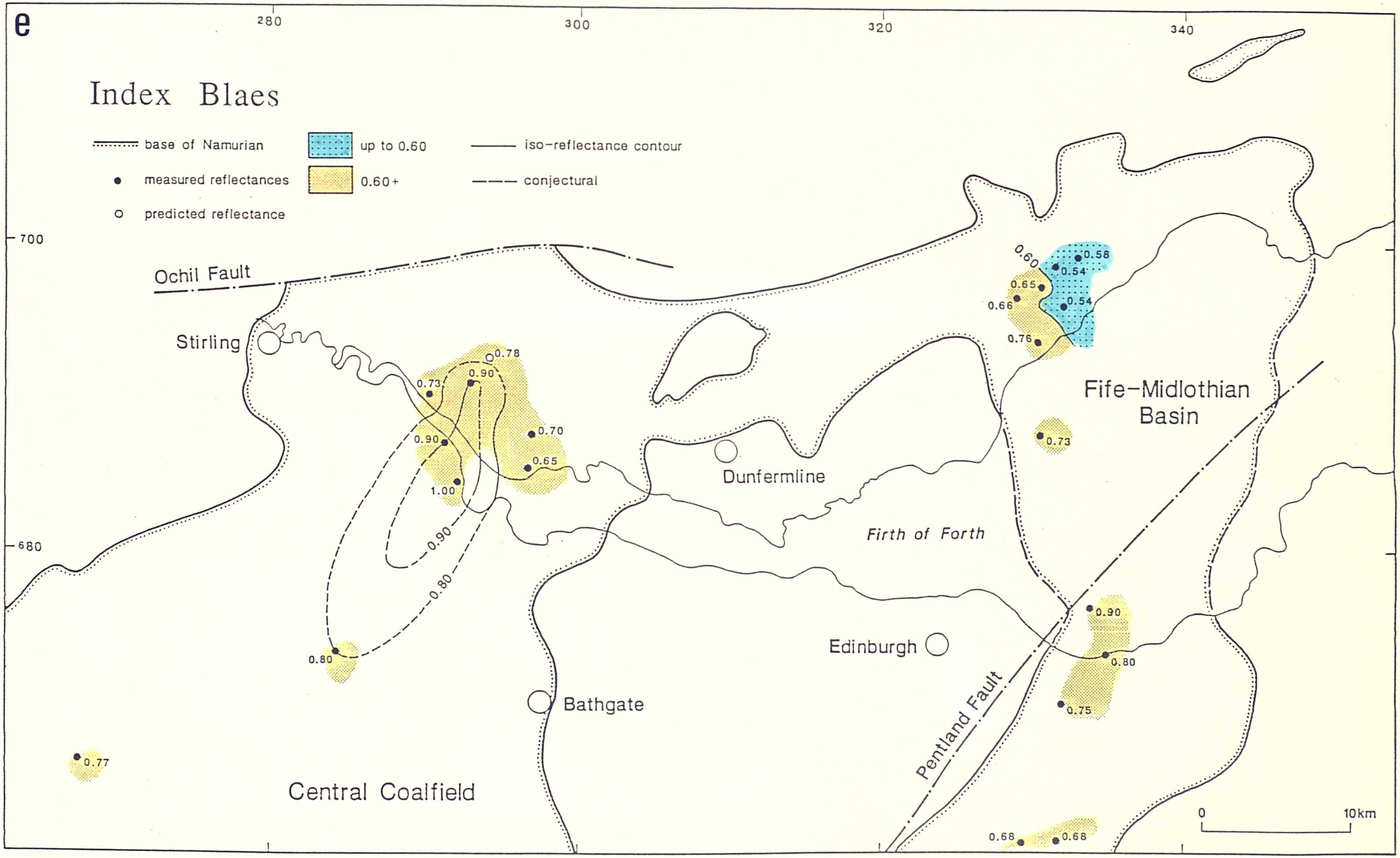


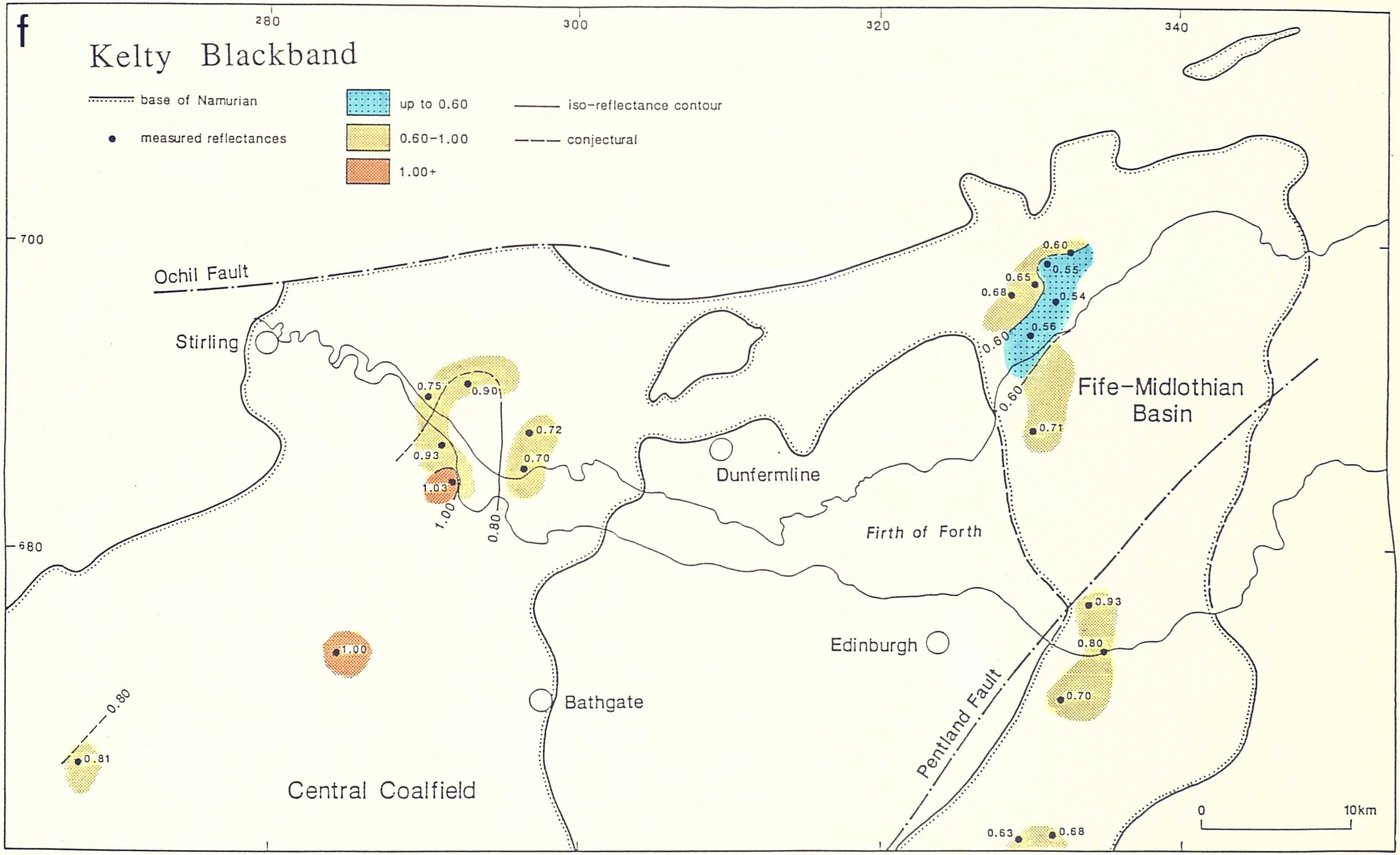
Fig.5.2 Rank maps showing regional coalification patterns at different stratigraphic levels in the Carboniferous.

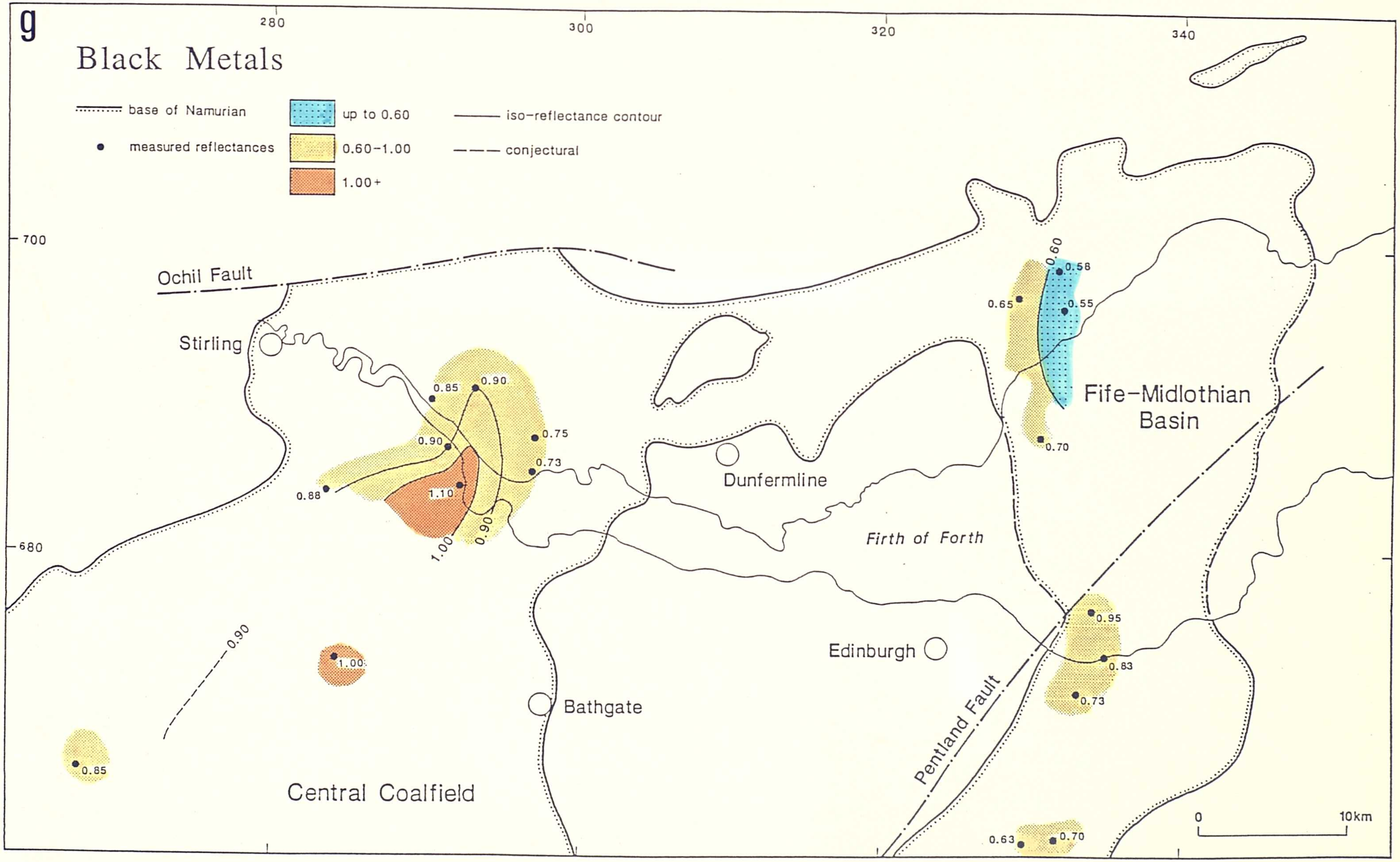

b
Passage Group
(mapped data)
base of Namurian
+ reflectance increase too rapid to permit contouring
0.50
up to 0.60
0.70
0.60-1.00
1.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Westfield Basin
Fife-Midlothian Basin
Dunfermline
Firth of Forth
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km

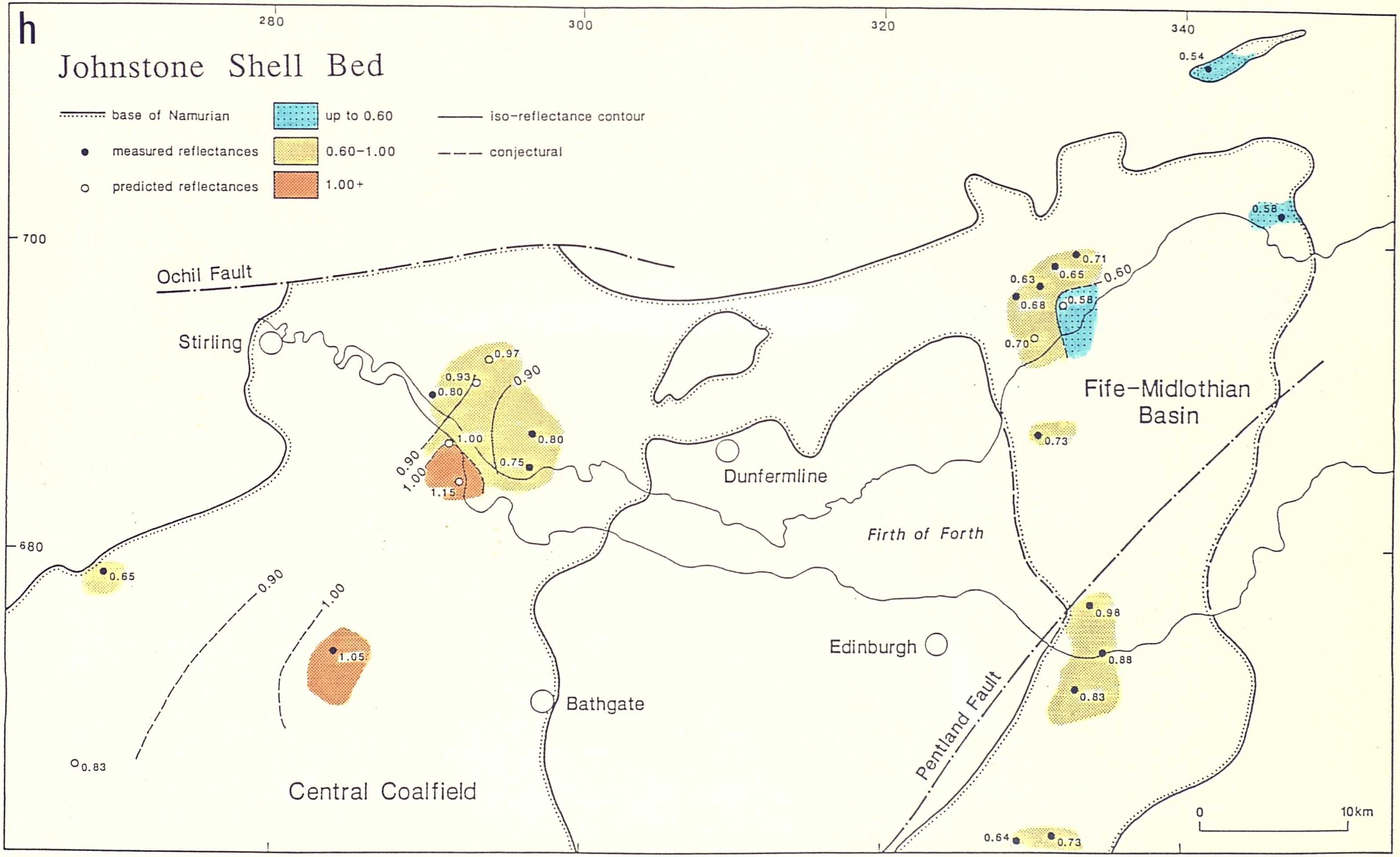

C
Calmy Blaes
(data points)
base of Namurian
measured reflectances
iso-reflectance contour
conjectural
Ochil Fault
Stirling
Dunfermline
Edinburgh
Bathgate
Firth of Forth
Fife-Midlothian Basin
Pentland Fault
Central Coalfield
0
10km
280
300
320
340
700
680
0.40
0.60
0.70
0.80
1.00
0.84
0.98
0.74
0.65
0.75
0.60
0.70
0.84
0.68
0.40
0.38
0.61
0.70
0.79
0.49
0.42
0.36
0.37
0.34
0.41
0.40
0.46
0.37
0.45
0.34
0.52
0.39
0.43
0.45
0.65
0.54
0.80
0.90
1.01
1.60
0.78
0.52
0.58
0.62
0.48
0.64
0.72
0.41
0.51
0.55
0.50
0.53
0.48
0.55
0.70
0.83
0.75
0.63
0.40
0.55
0.56
0.54

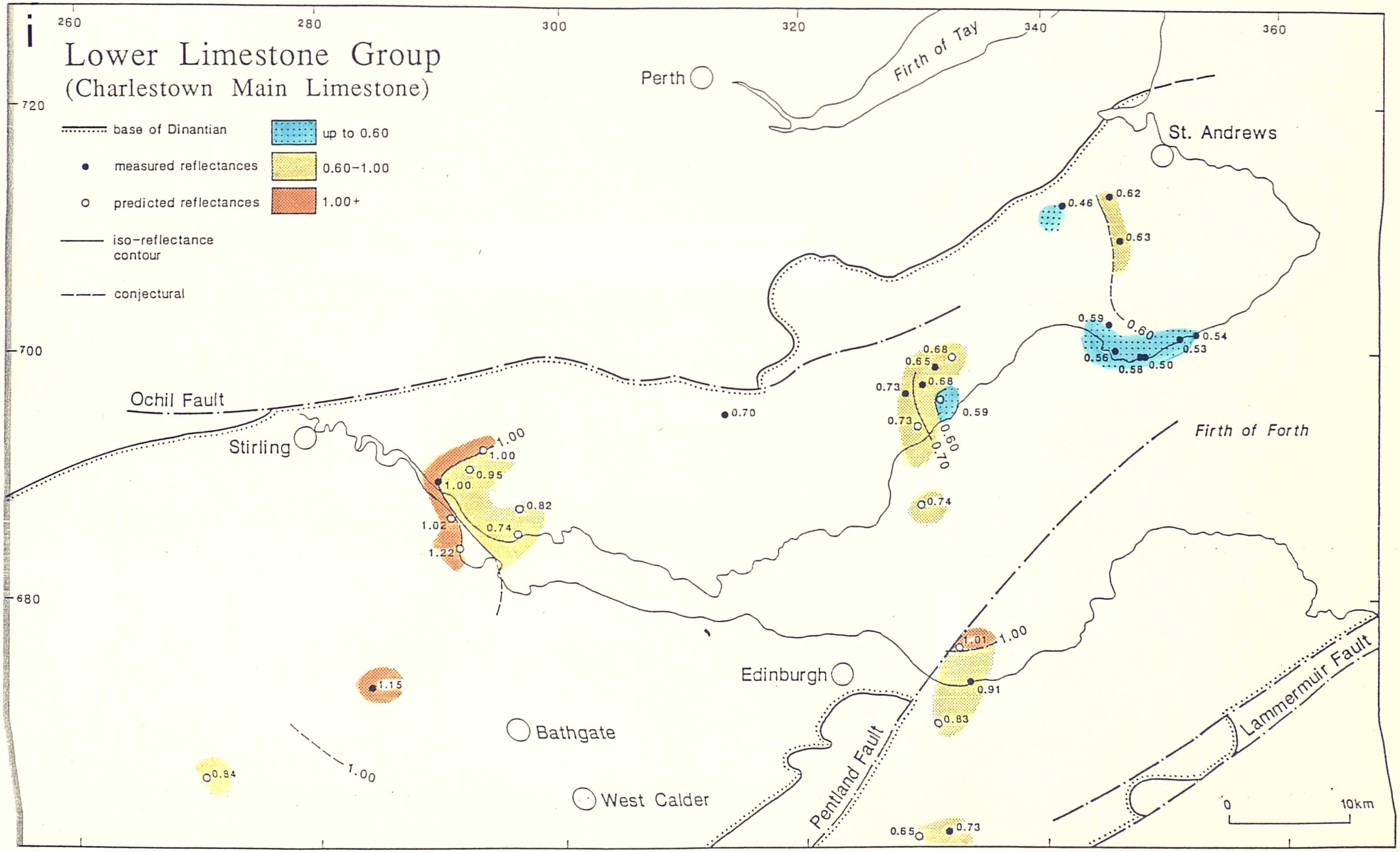

d
Calmy Blaes (mapped data)
base of Namurian
0.40
up to 0.60
0.80
0.60–1.00
1.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife–Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km

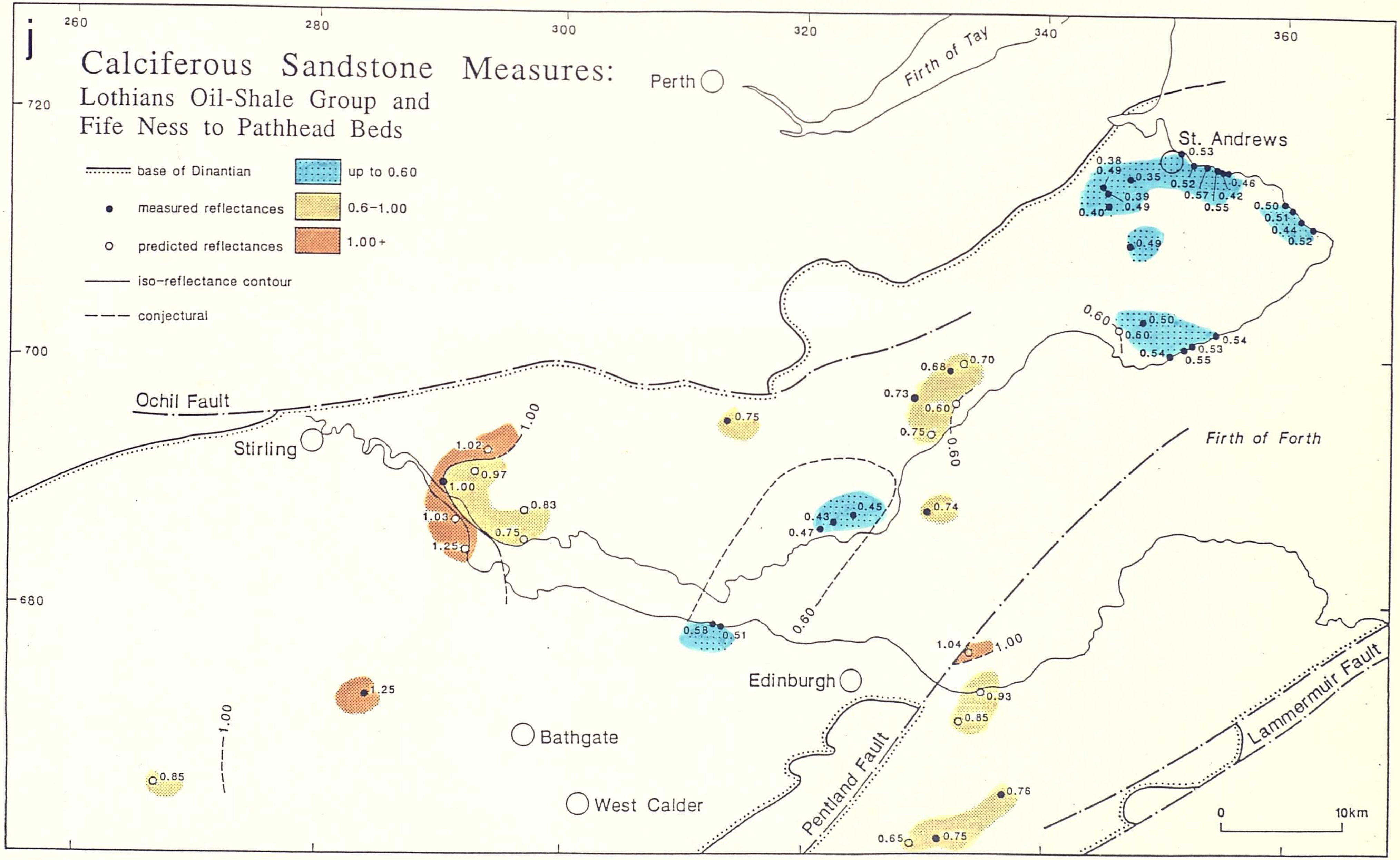

e
Index Blaes
base of Namurian
measured reflectances
predicted reflectance
up to 0.60
0.60+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Fife-Midlothian Basin
Firth of Forth
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0.60
0.58
0.54
0.65
0.54
0.66
0.76
0.73
0.78
0.90
0.73
0.70
0.90
0.65
1.00
0.90
0.80
0.80
0.90
0.80
0.75
0.77
0.68
0.68
0
10km


f
Kelty Blackband
base of Namurian
measured reflectances
up to 0.60
0.60-1.00
1.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Edinburgh
Bathgate
Central Coalfield
Fife-Midlothian
Basin
Pentland Fault
0.60
0.55
0.65
0.68
0.54
0.56
0.60
0.60
0.71
0.75
0.90
0.93
1.03
0.72
0.70
1.00
0.80
1.00
0.80
0.81
0.93
0.80
0.70
0.63
0.68
0
10km


g
Black Metals
base of Namurian
measured reflectances
up to 0.60
0.60–1.00
1.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Edinburgh
Bathgate
Central Coalfield
Fife–Midlothian Basin
Pentland Fault
0.85
0.90
0.75
0.90
0.73
0.88
1.10
1.00
0.90
0.90
1.00
0.85
0.60
0.58
0.65
0.55
0.70
0.95
0.83
0.73
0.63
0.70
0
10km

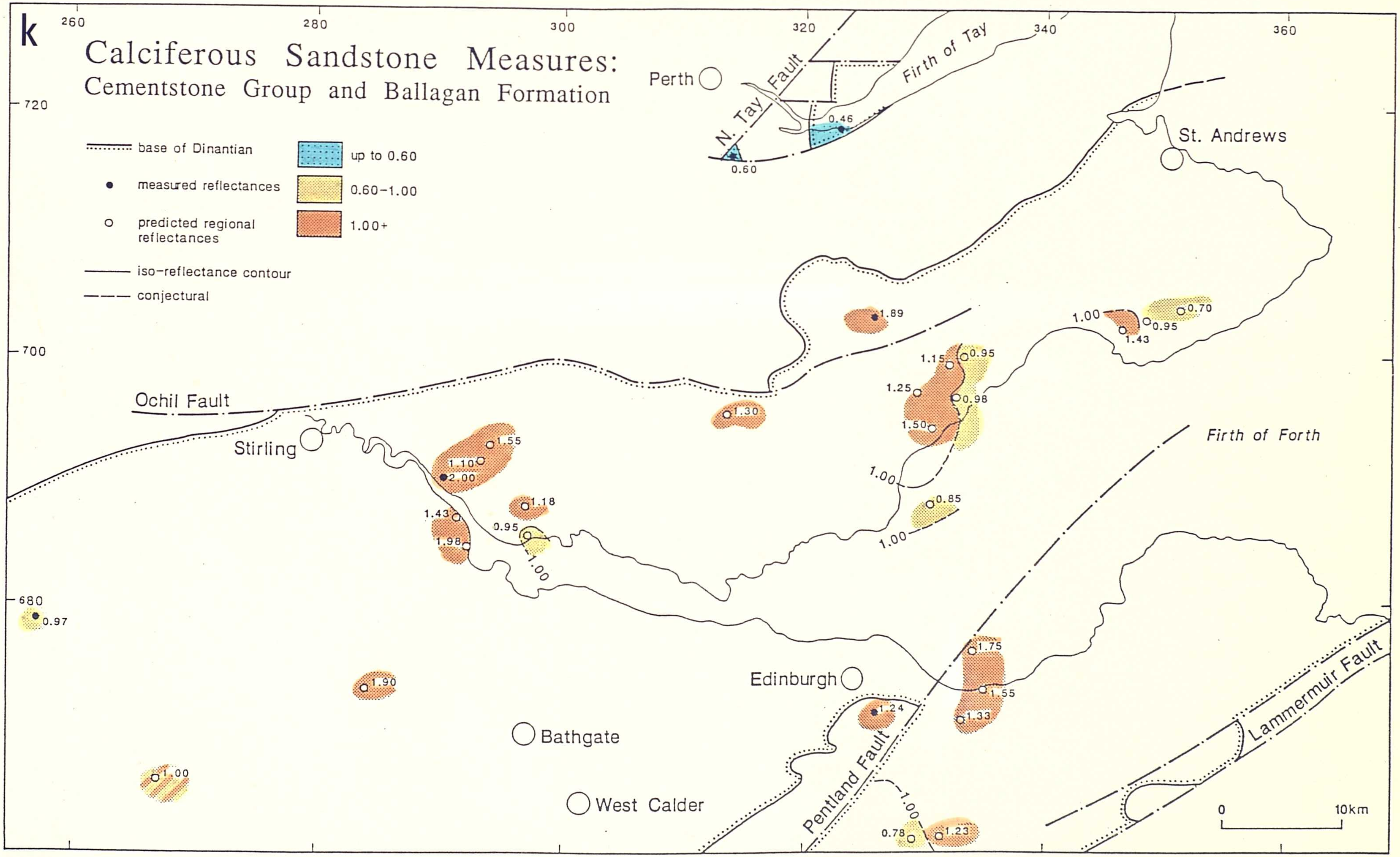

h
Johnstone Shell Bed
base of Namurian
measured reflectances
predicted reflectances
up to 0.60
0.60-1.00
1.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife-Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km
0.54
0.58
0.71
0.65
0.63
0.60
0.68
0.58
0.70
0.73
0.97
0.93
0.90
0.80
1.00
0.80
0.75
0.90
1.00
1.15
0.65
0.90
1.00
1.05
0.83
0.98
0.88
0.83
0.64
0.73


i
Lower Limestone Group
(Charlestown Main Limestone)
base of Dinantian
measured reflectances
predicted reflectances
iso-reflectance contour
conjectural
up to 0.60
0.60–1.00
1.00+
260
280
300
320
340
360
720
700
680
Perth
Firth of Tay
St. Andrews
Ochil Fault
Stirling
Firth of Forth
Edinburgh
Bathgate
West Calder
Pentland Fault
Lammermuir Fault
0
10km
0.46
0.62
0.63
0.59
0.60
0.54
0.53
0.56
0.58
0.50
0.68
0.65
0.68
0.73
0.73
0.59
0.60
0.70
0.70
0.74
1.00
1.00
0.95
1.00
0.82
1.02
0.74
1.22
1.01
1.00
0.91
0.83
1.15
0.84
1.00
0.65
0.73



j

Calciferous Sandstone Measures: Lothians Oil-Shale Group and Fife Ness to Pathhead Beds



k

Calciferous Sandstone Measures:
Cementstone Group and Ballagan Formation

the Calmy horizon. Because the Calmy Blaes lie well above the level of the Midland Valley Sill at the remaining localities, the reflectance values are thought to represent the regional rank levels. The preceding argument also applies to the map of the Passage Group: the only evidence for igneous-affected organic matter at this level originates from the Rashiehill borehole where the maturity of Passage Group strata encompasses the range $\%R_oav \approx 0.55-1.10$. The background rank for this level is $\%R_oav \approx 0.60$. It is not known whether the two measured vitrinite reflectances for samples in the basal Carboniferous (Cementstone Group/ Ballagan Formation) within the Fife-Midlothian Basin are fully representative of background heating: borehole data indicate that the remaining measured values on this map are due to regional coalification. Although the distribution of reflectance data that can be confidently assigned to "background" is patchy, the measurements represent the only available data and do, nevertheless, enable general trends to be established.

Inspection of the maps indicates that, for a given stratigraphic level, the rank is higher in the Stirling-Clackmannan-Central Coalfield basins than it is further to the east in the Fife-Midlothian Basin and its immediate surroundings. This general pattern is maintained throughout the Carboniferous. The higher maturities recorded moving offshore in the Fife-Midlothian Basin and moving westwards towards the depocentre of the Stirling-Clackmannan Basin (near Kincardine) probably reflect increased depth of burial, but the general pattern of rank increase moving westwards is probably not solely attributable to differences in burial history. This deduction stems from the depth contours of Browne *et al.* (1985) which indicate that at least 4km of Carboniferous sediments are present in the centre of the Fife-Midlothian Basin, with less than half this thickness apparent in the Kincardine district. In contrast to the palaeotemperature trends, as indicated by vitrinite reflectance, present-day temperature trends appear to be related to depth of burial since temperatures are higher at the base of the Carboniferous in the Fife-Midlothian Basin than in the basins further to the west (Browne *et al.* 1987).

A factor more likely to have influenced the background rank levels is heat flow associated with extrusive igneous activity. Although the trend towards increasing rank moving westwards contradicts the known trend in sediment thickness, an increase in the thickness of volcanic rocks is evident progressing westwards from Fife (Fig.1.14). There are mainly pyroclastic deposits in the east, but in the central and western parts of the Midland Valley, there are extensive sequences (several hundred metres thick in places) of basaltic lavas in the Lower Carboniferous. With this disposition of volcanic activity, the "heat sink" during the Carboniferous in the central and western parts of the Midland Valley would probably have been greater than in the east and, consequently, the level of organic maturation of equivalent stratigraphic horizons would be expected to be generally higher towards the west.

Although inferred higher thermal activity towards the west may account for the higher background rank levels observed there, the vitrinite reflectance gradients do not show a corresponding increase, as might be expected (Fig.5.3).

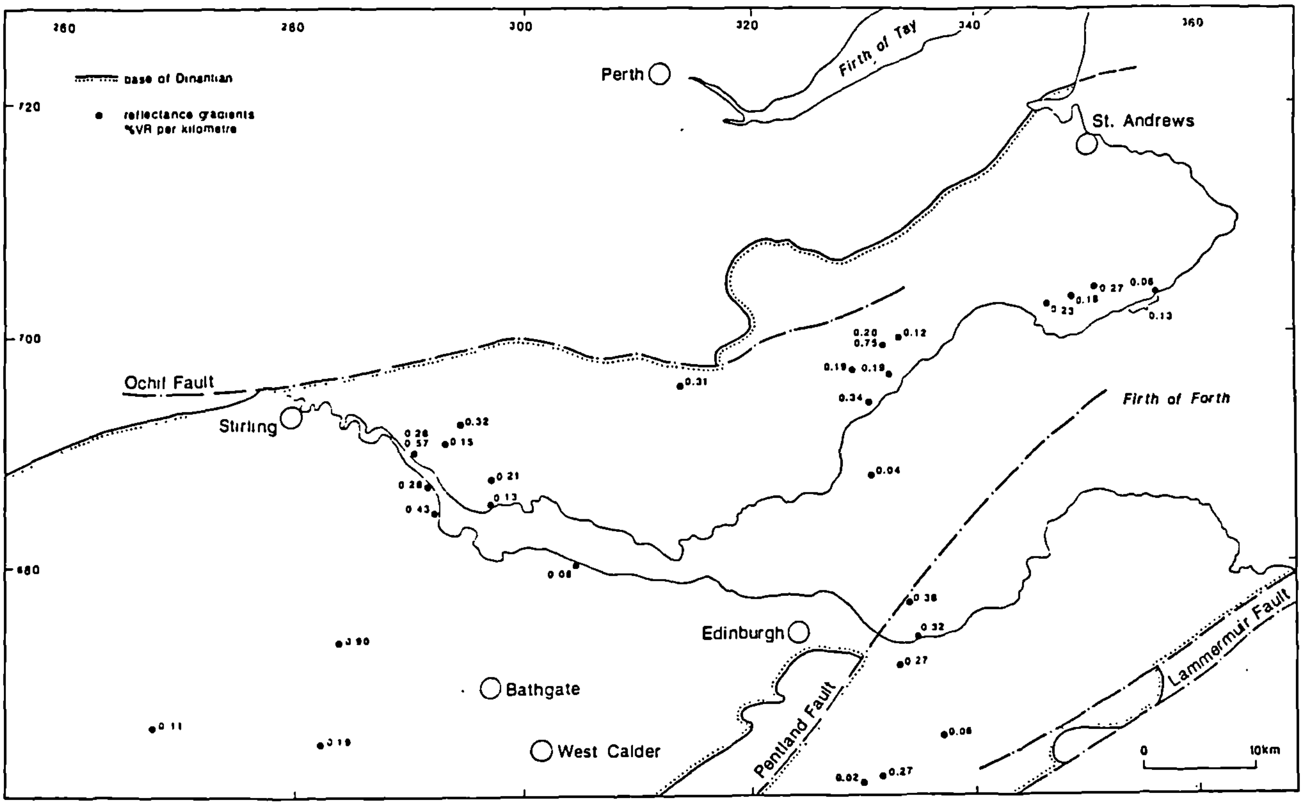


Fig.5.3 Map showing distribution of vitrinite reflectance gradients.

While reflectance gradients in the east are low (%R_o=0.06-0.38/km), similarly small reflectance increases with depth are found much further to the west. Contrasting reflectance gradients are also encountered in successions within relatively short distances in the same sedimentary basin, suggesting that geothermal gradients varied considerably from place to place.

Nothwithstanding the lack of correlation between vitrinite reflectance gradients and palaeotemperature patterns, as indicated by the rank map data, there is a broad correspondence between trends of vitrinite reflectance patterns and present-day temperature gradients. Fig.5.4a shows the distribution of temperature gradients tabulated by Browne *et al.* (1987) lying in the present study area. Contoured data are shown in Fig.5.4b. The limited data available are

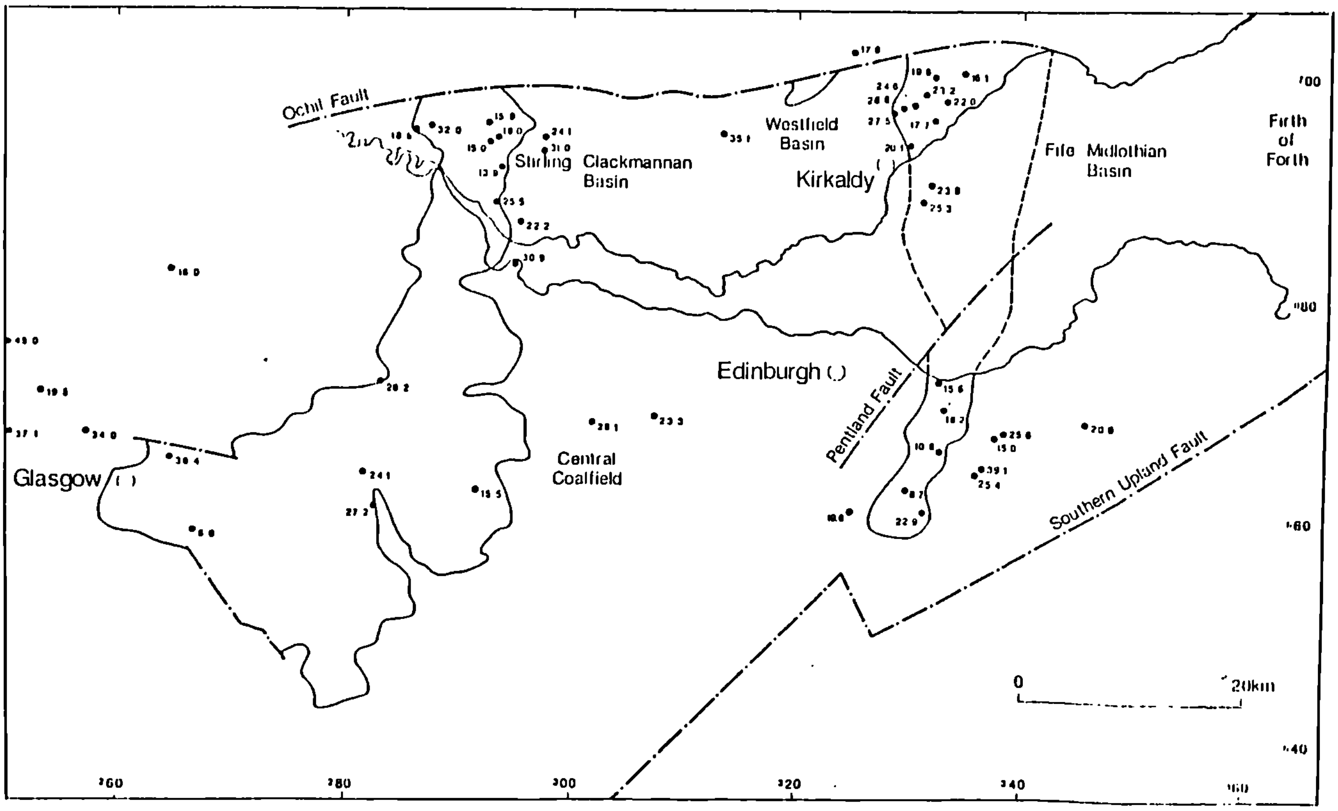


Fig.5.4a Distribution of present-day temperature gradients (°C/KM) in the eastern and central Midland Valley (data from Browne *et al.* 1987).

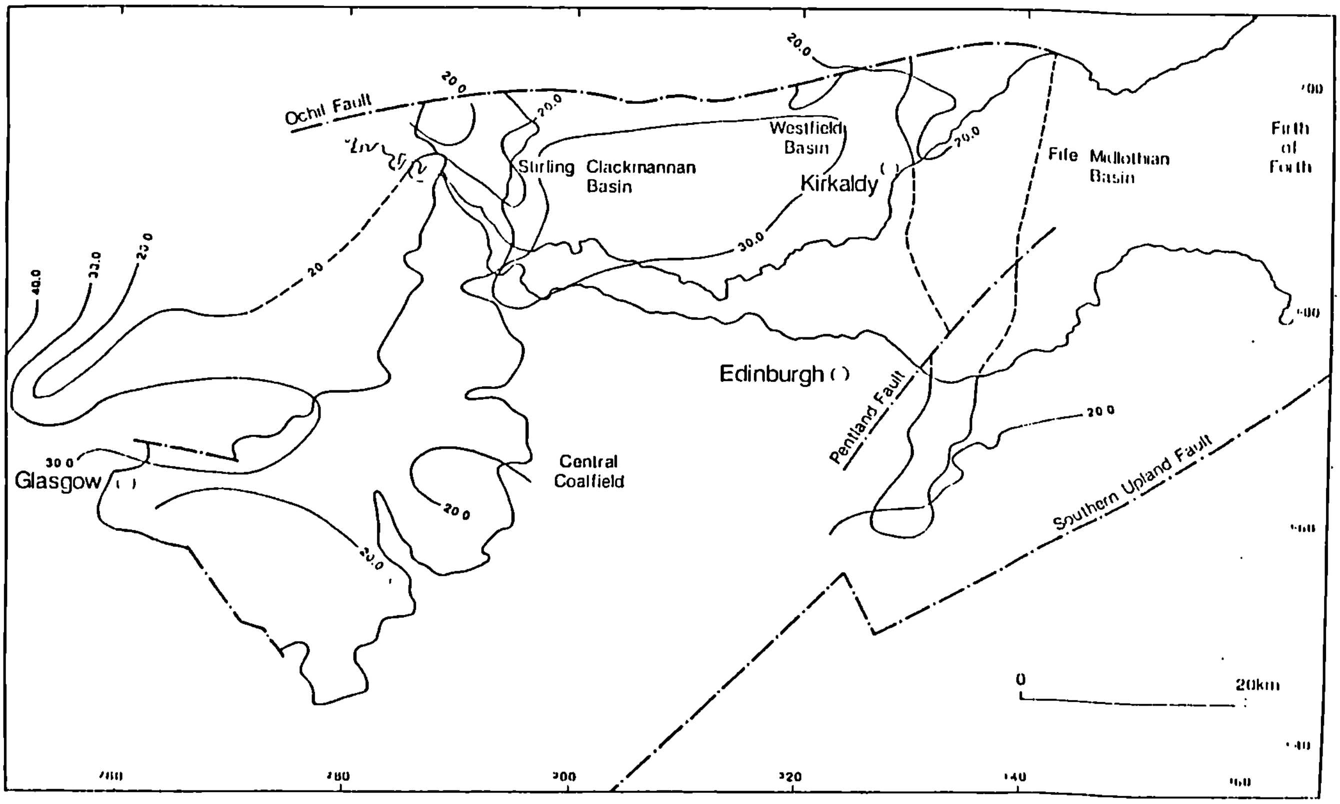
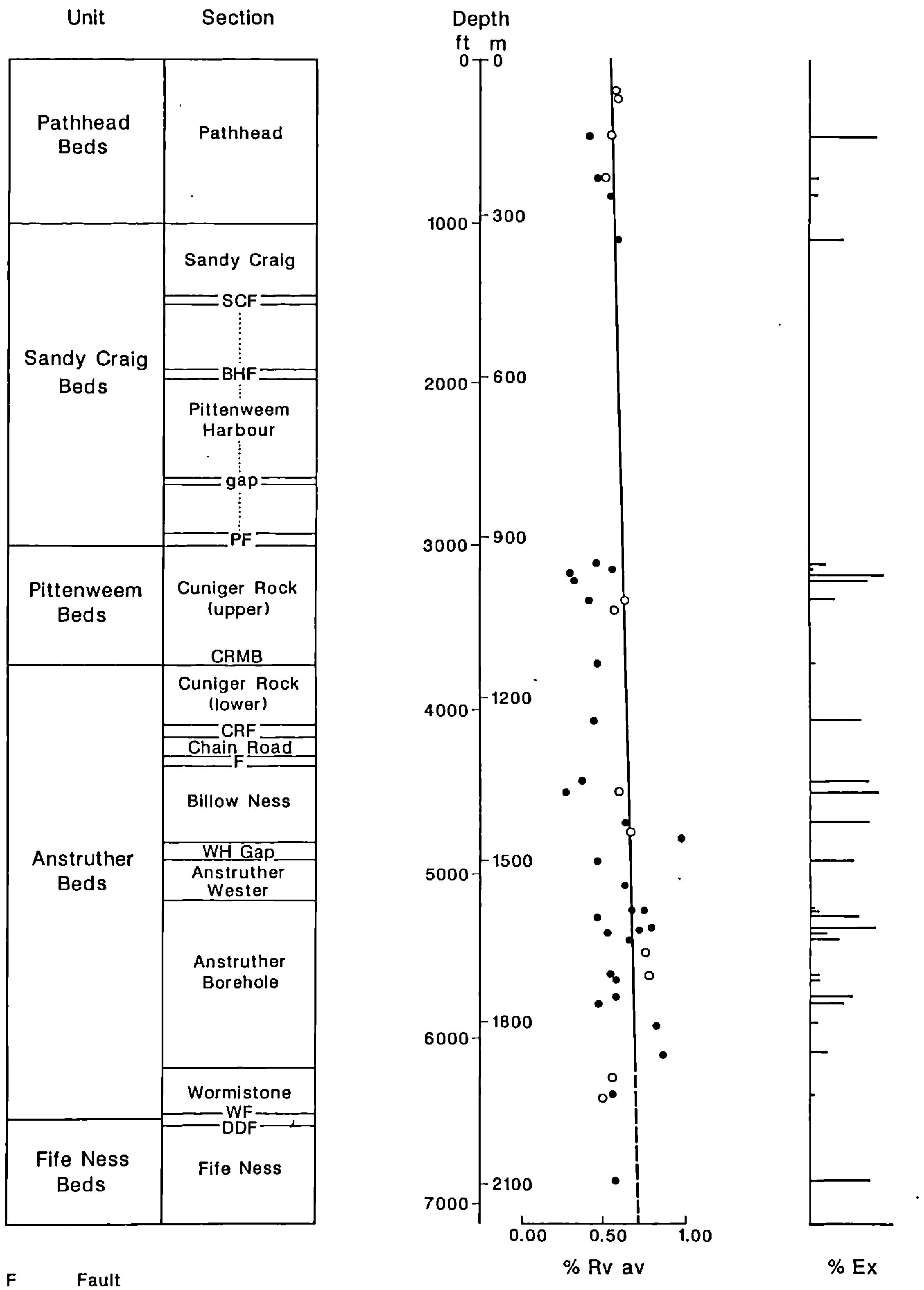


Fig.5.4b Contoured map of present-day temperature gradients (°C/KM).

unevenly distributed and temperature gradients in individual basins are very variable, but the gradients in the western holes are, overall, higher than those in the east. The mean value of the temperature gradients in the deepest western holes in the Midland Valley is 26.2±4.3°C/km whereas that of the deepest eastern holes is 20.5±3.4°C/km (Browne *et al.* 1987). The differences in the temperature gradients are paralleled by those in present-day heat-flow data. There is a marked variation in the range of heat-flow values determined from boreholes in the Midland Valley (36-77mW/m^2), but the average value for boreholes in the western part of the province is 59.1±4mW/m^2 compared with 47.1±9mW/m^2 for the easternmost values (Brown *et al.* 1987). The east to west increase in heat-flow and temperature data observed in the Midland Valley lends support to the suggestion made previously that enhanced thermal activity in the western part of the study area was responsible for the higher regional maturity levels in Carboniferous strata. Whether the present-day thermal effects are vestiges of a thermal regime established during or before Carboniferous times or, as Browne *et al.* (1987) have speculated, the remnants of overprinting by Tertiary igneous activity which is still providing heat in the western parts of the Midland Valley is not known. Given the lack of Tertiary igneous materials in the current study area, the former situation seems more likely. Additional factors which may have heightened heat flow to the west include E-W changes in crustal thickness, a more radioactive crust to the west and an upward movement of groundwater in the Glasgow district (Browne *et al.* 1987).

Perturbations in the general pattern of E-W rank increase are most pronounced in the upper part of the Calciferous Sandstone Measures (Strathclyde Group). Fig.5.2j (and the corresponding post-sill map shown later) reveals a NE-SW-trending tract of low-maturity strata intervening between areas which later developed into the Fife-Midlothian and Stirling-Clackmannan-Central Coalfield basins. This tract corresponds to the Burntisland Arch, and the low maturity of the overlying strata is consistent with the geological evidence that this major structure persisted as a structural high after the Dinantian. Additional evidence corroborating minimal sediment accumulation over the arch is the occurrence of very low-rank woody material in Orrock Quarry, Burntisland (see Section 4.2.2.3).

That much of the Calciferous Sandstone Measures sequence in east Fife has also experienced little burial is evident from the low maturities recorded in the available samples. A composite stratigraphic section has been compiled from individual coast sections (Fig.4.3). Despite the relatively smooth maturity profile (Fig.5.5) which encompasses most of the composite section, such "section stacking" may not provide a true representation of the maturation gradient in the lower



F	Fault
SCF	Sandy Craig Fault
BHF	Boat Harbour Fault
PF	Pittenweem Fault
CRMB	Cuniger Rock Marine Band
CRF	Cuniger Rock Fault
WH	West Haven
WF	Wormistone Fault
DDF	Danes Dike Fault

Fig.5.5 Composite maturation profile (based on coal reflectances) for east Fife coastal sections and Anstruther Borehole (%Ex = percent exinite; see Section 5.2.2).

Carboniferous sequence as a whole, because thermal gradients may have varied considerably throughout the east Fife area. The regional gradient encompassing most of the Anstruther Beds interval was established from samples in the Anstruther Borehole and the Billow Ness field section, which together represent an areally restricted part of the Anstruther Beds sequence. The elevated "background" rank levels (*c.*$\%R_oav>0.60$) in this part of the succession may reflect the presence of a local "hot spot" in the vicinity of Anstruther since the high reflectance value for the unoxidised sample S ($\%R_oav=0.97$; see Fig.4.3 for sample horizons), the presence of a small sill in the Anstruther Borehole and the occurrence of large quantities of pyrolytic PAH in sample Q (see Section 4.3.3.1.4.2) are all factors suggesting that igneous activity occurred in the Anstruther Beds in the Anstruther district. The relatively low reflectance values measured within the Wormistone and Fife Ness field sections are believed to be truly representative of sample maturity. The reflectance of samples in the lower part of the Anstruther Beds in the Wormistone section are lower than those of strata lying only a short distance above (in the same stratigraphic unit) which means that the former samples do not "fit" the projected maturity trend established from the overlying strata. (Fig.5.5). This observation, coupled with the lower reflectance values in the Fife Ness Beds, indicate that the separate field sections represent individual "blocks" of the Carboniferous succession which have experienced different thermal histories and thus emphasises the need for caution in using stacked sections for interpreting the thermal history of the Carboniferous in east Fife.

Further evidence for different depths of burial for strata within the Calciferous Sandstone Measures (Strathclyde Group) in east Fife comes from biomarker data. The sequence of Sandy Craig and Pittenweem Beds, which is well exposed around Pittenweem, is known to be attenuated in the St.Andrews district (Forsyth and Chisholm 1977). Although vitrinite reflectance data for samples at comparable stratigraphic levels are variable (Fig.5.6), comparison of biomarker data for samples from the north coast of east Fife (StA6,8,9) with those for samples from the south coast at a similar stratigraphic level (SM14,15,17,18) indicates that the former samples are much more immature. Not only do the northern samples show a greater predominance of biomarkers with biological stereochemistries (see Tables A.4 and A.5 and Fig.4.95), the two samples comprising part of the St.Andrews Castle Marine Band (StA8,9) proved to be the only samples analysed in this project in which hopenes were detected (see Fig.4.90c), bearing further testimony to their low rank. The biomarker distributions within these suites of samples indicate that the Calciferous Sandstone Measures succession in the region

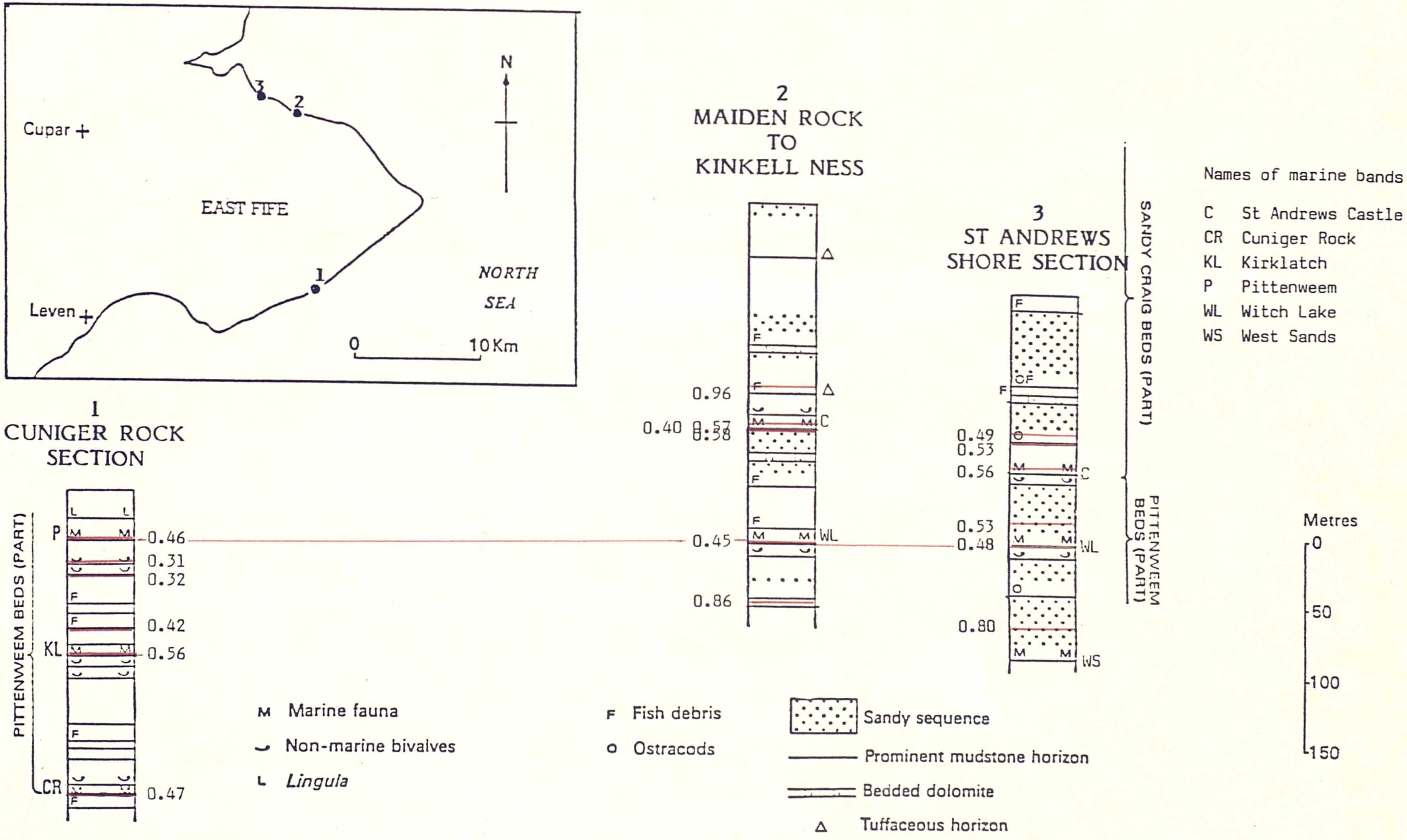


Fig.5.6 Maturity levels (vitrinite reflectance) in east Fife coastal sections (modified from Forsyth and Chisholm 1977).

of St.Andrews was not buried as deeply as the strata at the same stratigraphic level on the south coast of east Fife. Akin to the Burntisland Arch, the thinning of strata in the northern part of east Fife may be a consequence of the draping of sediment over a structural high.

No explanation is readily apparent for the relatively high (>$\%R_o$av=0.80) reflectance values recorded in the upper parts of the Pittenweem Beds in the sections near St.Andrews (Fig.5.6). There appears to be no association with igneous material, and the samples are not oxidised. The high reflectance value of StA10 (see Fig.4.4 for sample locations) is possibly a result of the proximity of the sample to an igneous plug near Kinkell Cave, from which the sample was taken (section shown in Appendix III p.360). Much of the variation in vitrinite reflectance values shown in Figs 5.5 and 5.6 is attributable to differences in the liptinite content of the samples (see below).

5.2.2 Influence of Liptinitic Macerals on Vitrinite Reflectance

5.2.2.1 Evidence for Vitrinite-Reflectance Suppression

From the construction of borehole maturation profiles, based on vitrinite reflectance, it is apparent that many sediments show reflectance values which are considerably lower than those derived from coals at the same stratigraphic level and which have been subjected to the same level of regional coalification. This phenomenon occurs throughout the eastern and central Midland Valley, as illustrated by the borehole plots shown in Fig.5.7 (see also Fig.5.5). Also included in the figures are vertical profiles showing the exinite content of the sediments. The results are semi-quantitative estimates of exinite content derived from combined reflected-light and fluorescence microscopy. This approach only yields a total for discrete exinitic entities: some samples displayed a general background fluorescence which probably originated in highly disseminated organic matter which could not be quantified, but which was almost certainly of lipoid affinity. The exinite values quoted refer to the percentage of the total organic matter contained in the sediments, which was generally high. The coals analysed were "normal" in that they contained the expected type and amount of exinite (almost exclusively sporinite which comprised <15% of the total organic matter) for autochthonous Carboniferous coals. As discussed in Chapter 4, sporinite was the dominant exinitic component in most sediments, although algal-rich horizons were frequently encountered.

Fig.5.7 shows that there is a greater spread of vitrinite reflectance data from sediments, with the reflectances of coal vitrinites showing little dispersion. Regression lines have been fitted, where possible, to the reflectance data from

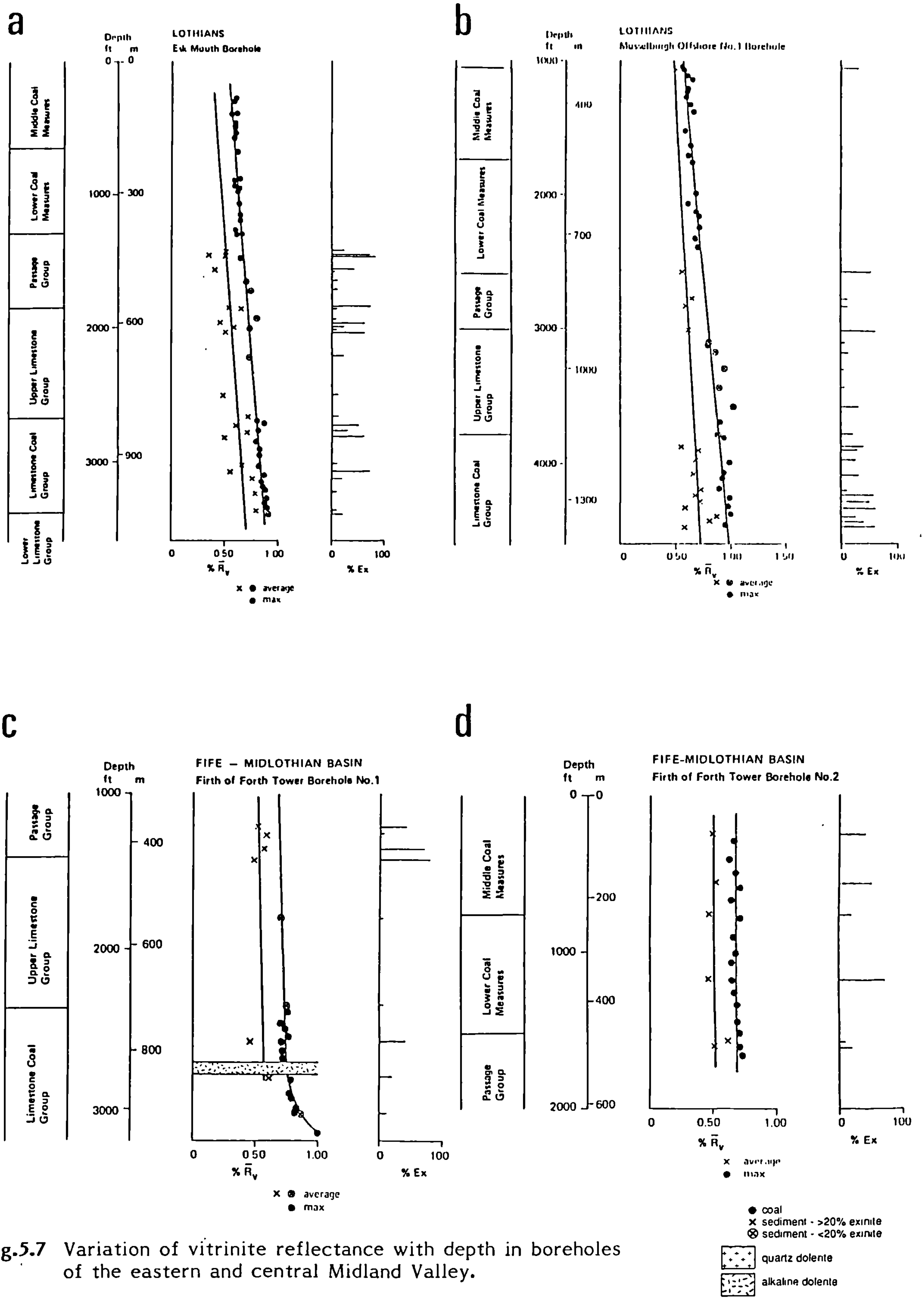


Fig.5.7 Variation of vitrinite reflectance with depth in boreholes of the eastern and central Midland Valley.

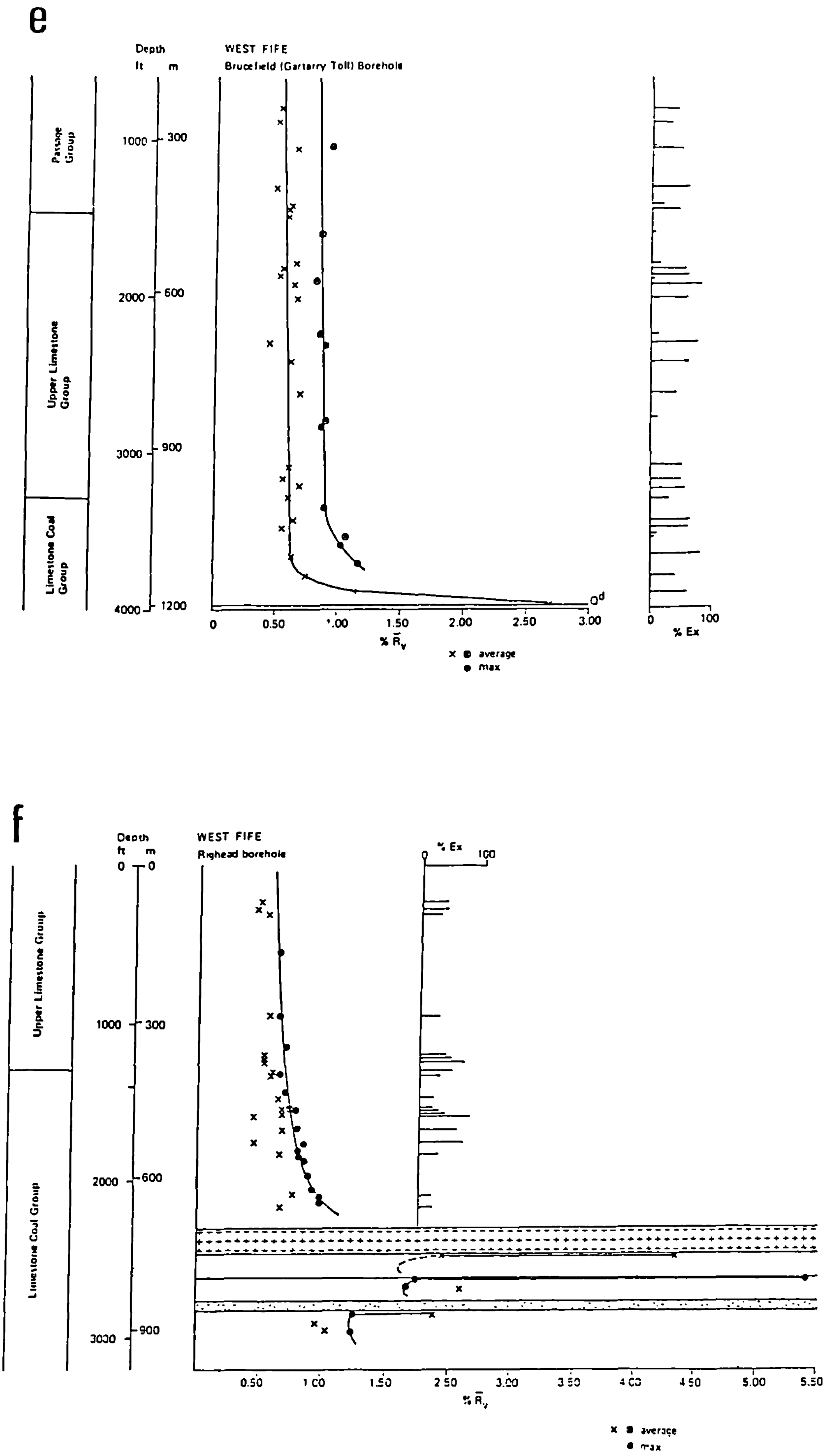

e
Depth
ft m
WEST FIFE
Brucefield (Gartarry Toll) Borehole
Passage Group
Upper Limestone Group
Limestone Coal Group
1000
2000
3000
4000
300
600
900
1200
0
0.50
1.00
1.50
2.00
2.50
3.00
% R̄v
x ● average
● max
0
100
% Ex
f
Depth
ft m
0
0
WEST FIFE
Righead borehole
% Ex
0
100
Upper Limestone Group
Limestone Coal Group
1000
2000
3000
300
600
900
0.50
1.00
1.50
2.50
3.00
3.50
4.00
4.50
5.00
5.50
% R̄v
x ● average
● max

Fig.5.7 (cont.).

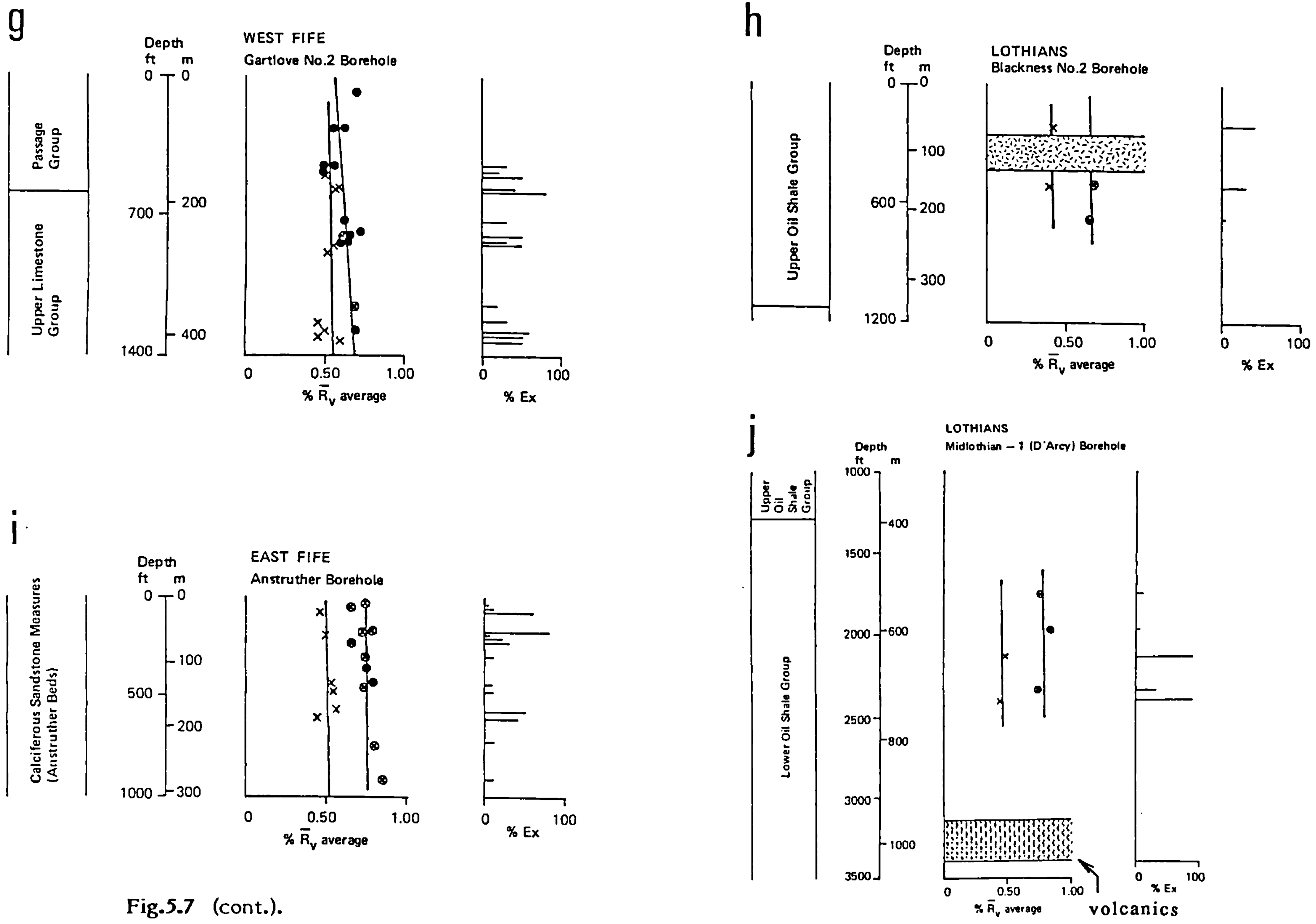

g
Passage Group
Upper Limestone Group
Depth
ft m
0 0
700 200
1400 400
WEST FIFE
Gartlove No.2 Borehole
0 0.50 1.00
% $\bar{R}_v$ average
0 100
% Ex
h
Upper Oil Shale Group
Depth
ft m
0 0
100
600 200
300
1200
LOTHIANS
Blackness No.2 Borehole
0 0.50 1.00
% $\bar{R}_v$ average
0 100
% Ex
i
Calciferous Sandstone Measures (Anstruther Beds)
Depth
ft m
0 0
100
500 200
1000 300
EAST FIFE
Anstruther Borehole
0 0.50 1.00
% $\bar{R}_v$ average
0 100
% Ex
j
Upper Oil Shale Group
Lower Oil Shale Group
Depth
ft m
1000
400
1500
2000 600
2500 800
3000
1000
3500
LOTHIANS
Midlothian – 1 (D'Arcy) Borehole
0 0.50 1.00
% $\bar{R}_v$ average
0 100
% Ex
volcanics

Fig.5.7 (cont.).

the two groups of samples (coals and sediments), with the exception of those vitrinites from sediments which apparently lie within the coal-reflectance plots. Inspection of the exinite log shows that most of these samples contain very little exinite. In most of the plots, there is a distinct separation between the two regression lines which usually lies in the range $\%R_o$=0.20-0.30(absolute). Any suggestion that this separation is due to the measurement of maximum reflectance on some coal vitrinites and average reflectances in the vitrinite clasts in the argillaceous sediments can be dispelled. Because of the relatively low levels of regional coalification encountered in the Midland Valley, there are no detectable differences between measured maximum and average vitrinite reflectances, apart from those samples lying in the thermal aureoles of sills. Corroborating evidence is found in Figs 5.7g-j where two distinct reflectance populations are apparent in sequences in which average reflectances were determined for all samples.

Comparison of the percentage exinite in sediments with vitrinite reflectance values indicates that a broad correlation exists between the amount of exinite present and the distance from the regression line based on coal vitrinites. Thus, the presence of relatively high amounts of exinite apparently has the effect of suppressing the measured vitrinite-reflectance values. A "rough and ready" threshold figure for the point at which suppression of vitrinite reflectance becomes noticeable is 20%. The suppression effect observed in Midland Valley sediments is not dependent on the presence of any particular type of liptinitic organic matter. Examination of the petrographic data relevant to each of the boreholes shown in Fig.5.7 indicates that deviations from the trend line for coal vitrinites can be brought about by an association with any hydrogen-prone organic matter such as spores, wispy or flecky liptodetrinite, telalginite or even amorphous fluorescing organic matter.

Some samples containing less than the "prerequisite" amount of exinite also show reflectance suppression. The vitrinites in these samples are invariably associated with brown bituminous/humic material which exudes from the vitrinite and stains the surrounding matrix (see Plate 4.99). Although this material does not fluoresce, Rock-Eval data (Section 4.3.2) indicate that the samples in which these vitrinites occur have slightly enhanced hydrocarbon potentials.

The regression lines drawn for the two distinct vitrinite populations are either parallel or show a divergence with increasing depth. The divergence is probably not related to the increase in the level of regional coalification with increasing depth because the sediments at the base of the boreholes in which the phenomenon is noted (Figs 5.7b and g) are also characterised by high liptinite contents.

The limited data available for high-rank sediments in which liptinite can still be discerned indicate that, at ranks approaching $\%R_o$=1.00, the optical properties of the suppressed and "normal" vitrinites begin to converge. Whether this is specifically related to the rapid heating associated with the igneous intrusions in the sequences in which the observations were made (Figs 5.7c,e,f) is not known because the appropriate data were not available for boreholes in which the ranks exceeded $\%R_o$=1.00 through regional coalification.

5.2.2.2 Causes of Vitrinite-Reflectance Suppression

The data presented in the last section confirm an effect on vitrinite reflectance through association with liptinitic materials that has already been recognised (see Section 2.2.4.1.2.3 and Price and Barker 1985 for a review). Whilst previous workers have illustrated suppression effects related to the presence of exinite in isolated localities or samples (Taylor 1966; Hutton *et al.* 1980; Cook *et al.* 1981; Kalkreuth 1982), the current work amplifies these studies by showing that vitrinite-reflectance suppression is not a localised event, but can occur through considerable thicknesses of strata over wide areas.

The expulsion of aliphatic-rich fluids from exinitic macerals and its subsequent incorporation within the vitrinite matrix is the mechanism commonly invoked to explain suppression phenomena (Hutton *et al.* 1980; Cook *et al.* 1981; Kalkreuth 1982; Price and Barker 1985) and one which seems applicable to the suppression effects observed in sediments from the Midland Valley. The reflectances of coal vitrinites and those in sediments with $\leq$20% exinite are not depressed because the volume of exinite present is not high compared with the amount of vitrinite (or inertinite) available to absorb expulsions from the exinitic material.

An additional factor likely to affect suppression is particle size. In fine-grained sediments, vitrinite is usually present as small clasts and stringers which present larger surface areas to any expelled fluids than do vitrinites of coals. The small vitrinite entities are also capable of absorbing aliphatic-bearing fluids from the sediments to a greater degree than are the vitrinites of coals. Similarly, it is possible that smaller volumes of finely-divided liptinitic matter (e.g. liptodetrinite, tiny wispy lamellar algal matter) could bring about the same absolute amount of suppression as a higher volume of exinite comprising larger-bodied entities such as spores and telalginite. The increased surface area over which hydrocarbons could be expelled into the sediment matrix in the former case could compensate for the lower volume of material present. Some evidence (albeit very limited) in support of this suggestion is forthcoming from the Blackness and

Anstruther boreholes where *c*.40% of the exinitic matter (of which at least half is finely divided) produces the same degree of suppression as much larger volumes of sporinite in other boreholes within parts of the succession at similar regional coalification levels. The evidence from Midland Valley samples must be regarded as slightly tenuous in view of the absence of firm quantitative data and also the difficulties inherent in accurately assessing volumes of freely-dispersed organic matter in sediments.

While variation in exinite content seems to be the overriding factor controlling pronounced vitrinite-reflectance variation in the Carboniferous of the Midland Valley, other factors have been proposed to explain major reflectance discrepancies. The most important of these relates to variation in the redox conditions prevailing in the depositional environment. Wenger and Baker (1987) have postulated that the relatively high reflectances measured in organically-lean, calcareous shales are a consequence of the sediments having experienced a more oxic diagenesis than low-reflecting, organic-rich, black shales in the same sequence, which are thought to have accumulated in anoxic environments. Despite the latter shales being rich in liptinite, the authors dismiss the possibility that this has induced vitrinite-reflectance suppression because solvent extraction of the shales failed to produce any increase in vitrinite reflectance, which they thought would have occurred if absorption of hydrogen-rich materials by vitrinite were the cause of suppression. Akin to the results of the above authors, reflectance values determined on Midland Valley sediments known to contain suppressed vitrinites showed no change after solvent extraction. Because the evidence presented in the last section leans strongly towards an exinitic influence on vitrinite reflectances in the Midland Valley, the failure of commonly-used extraction procedures to cause changes in the optical properties of vitrinites may indicate that aliphatic matter is very tightly bound within the vitrinite matrix. Much stronger solvents (e.g. pyridine) may be required to ensure the swelling of vitrinite and the release of hydrocarbons from the matrix.

Further evidence linking the occurrence of low-reflecting vitrinites with environmental anoxia is provided by Newman and Newman (1982) who found that vitrinites with suppressed reflectances occurred in coals thought to have formed during anaerobic peatification. Not only would the preservation potential of hydrogen-prone components, and the likelihood of their impregnating vitrinite, be enhanced, the hydrogen content of the vitrinite could be supplemented through the "working-over" of organic matter by anaerobic bacteria (Price and Barker 1985).

A conflicting palaeoenvironmental scenario envisages anoxic conditions as being conducive to the formation of relatively high-reflecting vitrinites through the maintenance of high oxygen contents due to the covering of peats by a stagnant watermass which prevented the degradation of humic materials (Fermont 1988). Low-reflecting vitrinites are thought to be associated with oxygen depletion which occurred during periods of intense microbial activity which were promoted by the influx of oxygenated, nutrient-rich waters into the swamps.

Opinions obviously vary in relation to the environmental milieux causing deviations in reflectance values, but the common and long-established association between perhydrous vitrinites and sapropelic environments (Kröger 1968; Kunstner 1974; Teichmüller 1974a,b), in conjunction with the studies outlined above, points strongly towards the requirement of anaerobic environmental conditions as a prerequisite for the formation of the majority of low-reflecting vitrinites in coals or sediments in which the influence of exinite can be disregarded.

In summary, although processes operating at the time of sediment accumulation could modify the chemistry of humic tissues and so lead to variations in the reflectances of the resulting vitrinites, the weight of evidence suggests that it is the association with exinitic macerals which is the most influential factor governing major deviations in vitrinite reflectance values in the Carboniferous sequence of the Midland Valley. The degree of suppression will be additionally controlled by factors such as the amount, type and size of the exinitic moieties present and also the physical state of the vitrinite, particularly the accessibility to its fine structure, which will vary as the porosity changes with increasing coalification.

It is worth noting that, although major deviations in vitrinite-reflectance profiles in boreholes have been attributed to suppression effects, there is no published literature which considers whether such perturbations are mirrored in maturity profiles based on molecular parameters. Data from the east Fife coastal sections indicate that the pronounced scatter in vitrinite-reflectance values which occurs within the Viséan sequence (Fig.5.5), which is related to liptinite content, is not paralleled by the scatter of data seen in the maturity profiles based on molecular parameters (Fig.5.8).

If the unsuppressed and suppressed vitrinite-reflectance data are considered together (Fig.5.8), little increase in maturity with increasing depth can be inferred from this parameter. A definite trend towards increased maturity with increased depth is only apparent when considering coals or sediments containing $\leq$20% liptinite. The trend defined by "unsuppressed vitrinites" is shown in Fig.5.8 (+). Only one of these samples was extracted. The remaining reflectance data on the

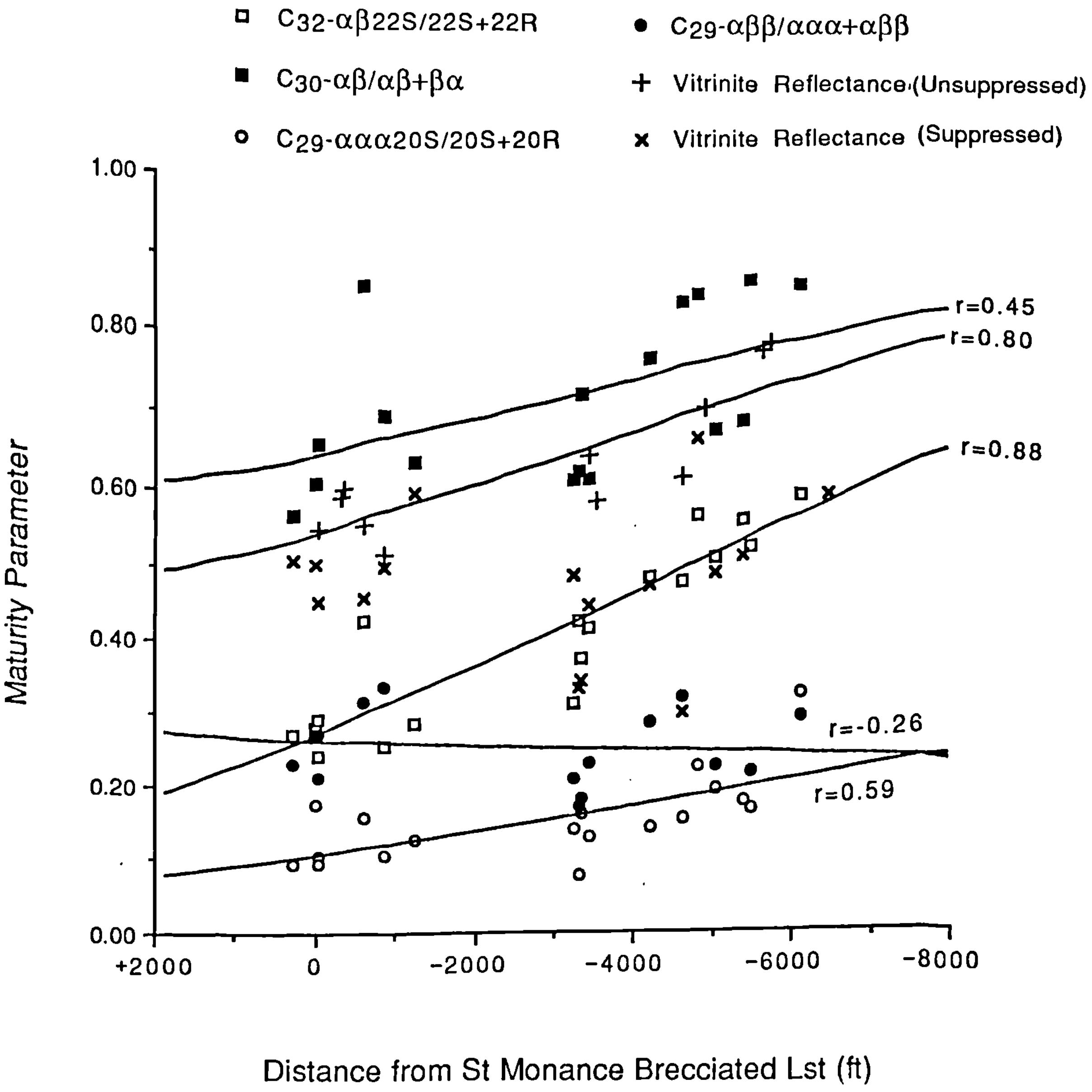


Fig.5.8 Variation in different maturity parameters with increasing depth in the Viséan sequence in east Fife (coastal sections and Anstruther Borehole).

diagram (x) are for suppressed vitrinites in samples that were extracted. In contrast to the suppressed reflectance data, maturity data based on biomarkers show a much reduced scatter and, apart from the αββ sterane data, display an overall increase over the section studied. Contrary to conventional expectations, the αββ steranes show an overall trend towards decreasing values throughout the section. An explanation for this anomaly is forthcoming following closer inspection of the data plot. While an apparent net decrease in αββ/αββ+ααα ratios is apparent over the entire section shown in Fig.5.8, general trends towards increased values occur within individual "blocks" of the succession. For example, a general increase in αββ steranes is evident over the stratigraphic interval incorporating samples SM1-SM14 which corresponds to the conformable Lower Limestone Group to

Sandy Craig Beds sequence exposed on the coast northeast of St.Monance (+408' to -1112' in Figs 4.3 and 5.8). An overall increase in αββ sterane content was recorded over the interval encompassing the Pittenweem Beds to the middle of the Anstruther Beds (Cuniger Rock to Billow Ness field sections; -3117' to -4485' in Figs 4.3 and 5.8) and also within the lower part of the Anstruther Beds sequence (Anstruther Wester and Anstruther Borehole sections; -4920' to 5985' in Figs 4.3 and 5.8). Despite the increase in the αββ steranes in the latter interval, the average value for the αββ ratio is less than that determined in sediments in the Lower Limestone Group to Pathhead Beds interval.

The "stepping" evident within the maturity profile based on αββ steranes (not apparent in other parameters) provides a further illustration of the need for caution when utilising composite sections, constructed from individual field sections designed to show the stratigraphic sequence, for interpreting maturity trends.

5.3 IGNEOUS ACTIVITY

5.3.1 Effects of Extrusive Igneous Activity

5.3.1.1 General

The presence of over one hundred volcanic necks penetrating the Carboniferous rocks of east Fife testifies to the extensive eruptive activity which occurred in the area during this period. Associated with the necks are pyroclastic rocks which are exceptionally well preserved along coastal sections around east Fife. The best-exposed areas cover a section extending over approximately 12km, southwest of St.Monance (Fig.5.9).

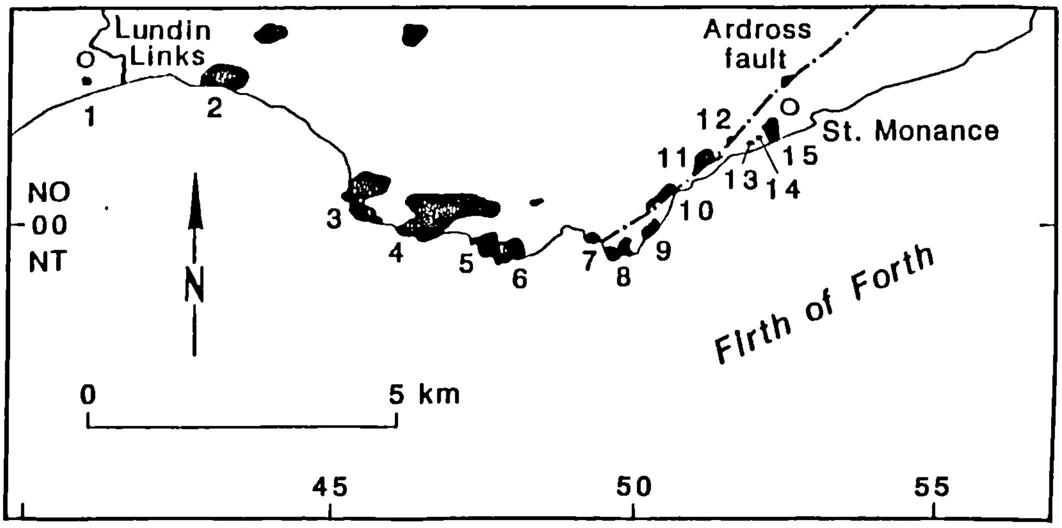


Fig.5.9 Location map for east Fife volcanic necks.
1 Lundin Links; 2 Viewforth; 3 Ruddons Point; 4 Kincraig; 5 Craigforth; 6 Chapel Ness; 7 Elie Harbour; 8 Elie Ness; 9 Wadeslea; 10 Ardross; 11 Coalyard Hill; 12 Newark; 13 Dovecot; 14 Davies; 15 St.Monance.

The vent deposits comprise principally tuffs and agglomerates, either bedded or unbedded, which may be associated with basaltic and/or pyroclastic intrusions. Fragments of various types of sedimentary rocks have long been known to occur in the tuffaceous/agglomeratic deposits, including organic-bearing lithologies such as oil shales, coals and, more rarely, woods (Geikie 1879, 1900, 1902; Balsillie 1920). No systematic organic-related studies have been undertaken on the vent debris.

In the current project, the organic-bearing clasts were chipped from the enveloping igneous matrix with the aim of assessing any possible effects that extrusive igneous activity might have had on organic metamorphism. Reflectances were measured on vitrinites in coaly and argillaceous vent clasts. The maturities of the clasts were compared with those attained by the surrounding country rocks. The nature of the clasts and of the organic matter within them is first considered.

5.3.1.2 Clasts in the Volcanic Necks

The sizes of the organic-containing clasts found in the necks varied from boulders to material of dust-like character. The typical appearance of pyroclastic matter containing assorted organic-bearing rock fragments is shown in Plate 5.1. Shale clasts (including oil shales) were most commonly observed, coal clasts less so, but when the latter were found they were sometimes rimmed by calcite and/or displayed an intricate permeation by calcite-filled cracks (Plate 5.2). Some of the coaly fragments had a fibrous structure reminiscent of wood grain: these clasts were always heavily calcitised. Although low-rank wood fragments of the type found in Orrock Quarry were not found in the present study, Geikie (1879) has documented the occurrence of wood in the east Fife vents which is "frequently encrusted with calcite". Fragments of wood encased in calcite which are of similar overall appearance to the fibrous clasts found in the east Fife vents have also been reported in tuffaceous deposits near Linlithgow. The calcite-rimmed woody clast shown in Fig.23 of Cadell (1925; p.160), which is encased in ash, closely resembles that of the clast referred to previously as the "Coalyard wood" (Section 4.2.2.3).

Despite the failure to find exceptionally well-preserved hand specimens of Orrock-type wood in the east Fife vents, microscopical examination revealed a marked similarity between the cell structure of the Orrock wood and those of the heavily-calcitised, fibrous-looking samples. The best example of the latter sample type is the Coalyard wood (sample A43; discussed in Section 4.2.2.3), although similar observations were made on samples KIN16, KIN20 and C from the Kincraig and Elie Harbour necks. Although of higher rank (%R_o=0.59) than the Orrock wood (%R_o=0.39), the Coalyard-wood sample contains cavities of the type

Plate 5.1 Typical appearance of pyroclastic vent deposits in east Fife necks containing carbonaceous clasts.

Plate 5.2 Coal fragment in a volcanic tuff showing permeation by calcite.

Elie Neck; sample C.

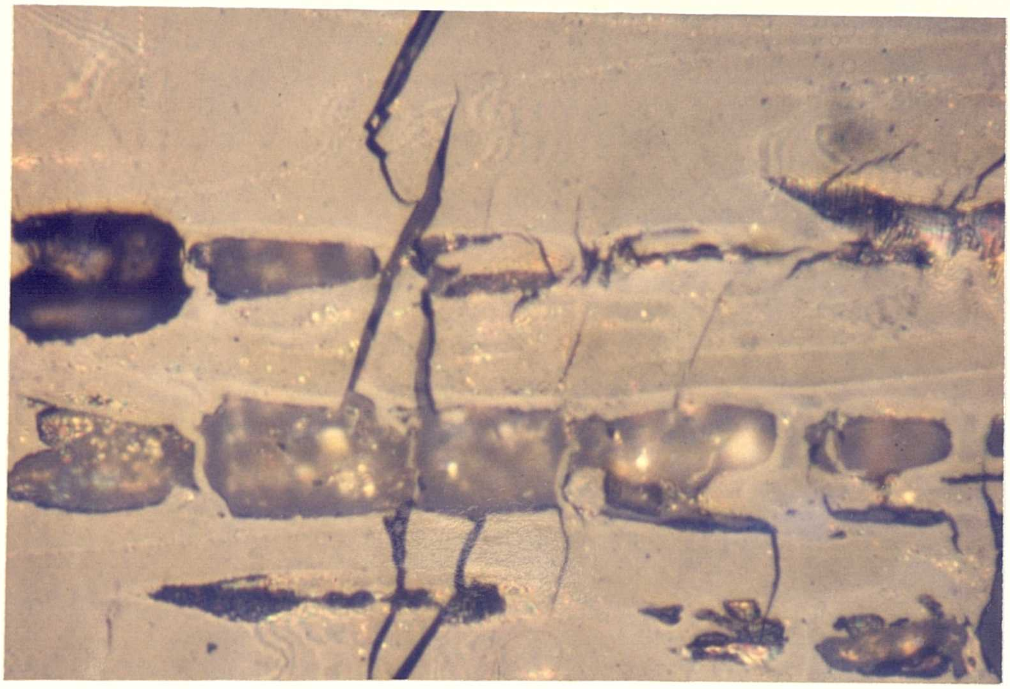


Plate 5.3 Calcitised vitrinite clast showing fine preservation of cellular detail: reflected light, oil immersion, plane-polarised light.

Coalyard Hill neck; sample A43.

x750

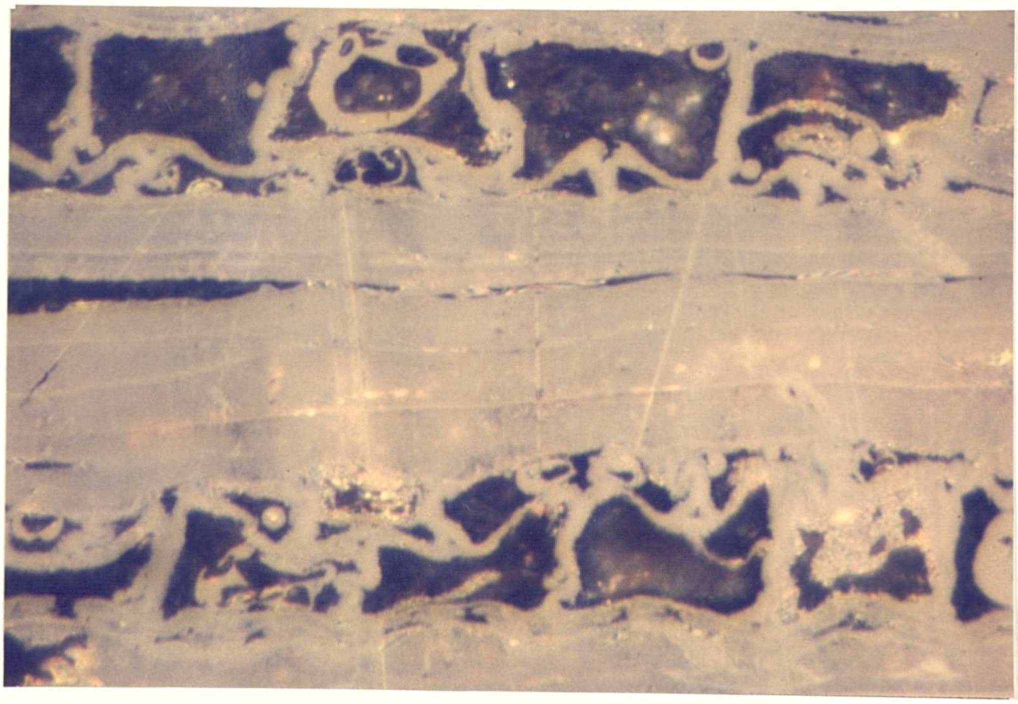


Plate 5.4 Orrock wood (for comparison with Plate 5.3): reflected light, oil immersion, plane-polarised light.

x750

shown in Plate 5.3 which probably correspond to the "disturbed zones" of the Orrock wood in which were contained various types of microorganisms (*cf.* Plate 5.4 and refer to Section 4.2.2.3). Much of the very fine detail of the cellular contents has been obscured in the east Fife vent samples, but darker bands corresponding to fungal hyphae can still be recognised, as can higher-reflecting bands corresponding to cell-wall lamellae.

The close correspondence between the petrographic characteristics of the fibrous, calcitised samples in the east Fife vents and the Orrock wood sample (also heavily calcitised) points to similarities in their geological histories. From Section 4.2.2.3 it was concluded that the woody appearance of the Orrock sample and its fine state of preservation were indications that the sample was not coalified. The retention of similar petrographic features in the clasts from east Fife vents suggests that these too have not been coalified *sensu stricto*, i.e. they have not passed through a gelification stage which would have resulted in the obscuring of much of the cellular structure. The ranks of the fibrous clasts are within the range of bituminous coals although they have seemingly bypassed the "conventional" coalification process. Much of their present-day rank must have been achieved through contact with hot igneous materials. The implication, therefore, is that fibrous vent clasts have been incorporated in the vents *as woods*. Such an inference accords entirely with the mode of emplacement of the east Fife necks (see next section).

In addition to the high-rank woods, microscopical examination of the vent clasts revealed the presence of a diverse array of organic components analogous to that described in Chapter 4. Lamalginite-rich and *Botryococcus*-rich samples were found, as were clasts containing assorted terrigenous debris. Marine organic components could not be specifically identified, although there is no reason why these components should not be present. Flecks of free hydrocarbons were seen, but these were rare.

One petrographic peculiarity noted in only two vent clasts (Elie Ness neck; samples GG and KK) was the occurrence of organic matter bearing a striking resemblance to suberinite (Plates 5.5 and 5.6). This liptinitic maceral originates in suberised higher-plant tissues which occur in corkified cell walls. Since primitive plants did not form cork, the occurrence of suberinite is considered to be confined predominantly to Tertiary coals, although it has been documented in a few Mesozoic coals (Stach *et al.* 1982). The occurrence of suberinite in east Fife is unusual not only because of its rarity in the Midland Valley *per se*, but because it represents only the second documented report of suberinite in samples of Carboniferous age. An earlier reference to suberinite in Carboniferous (Westphalian B)

Plate 5.5 Suberinite in carbonaceous vent clast: reflected light, oil immersion, plane-polarised light.

Elie Ness neck; sample KK.

x750

Plate 5.6 Suberinite clast in ?fluidised coal (see text): reflected light, oil immersion, plane-polarised light.

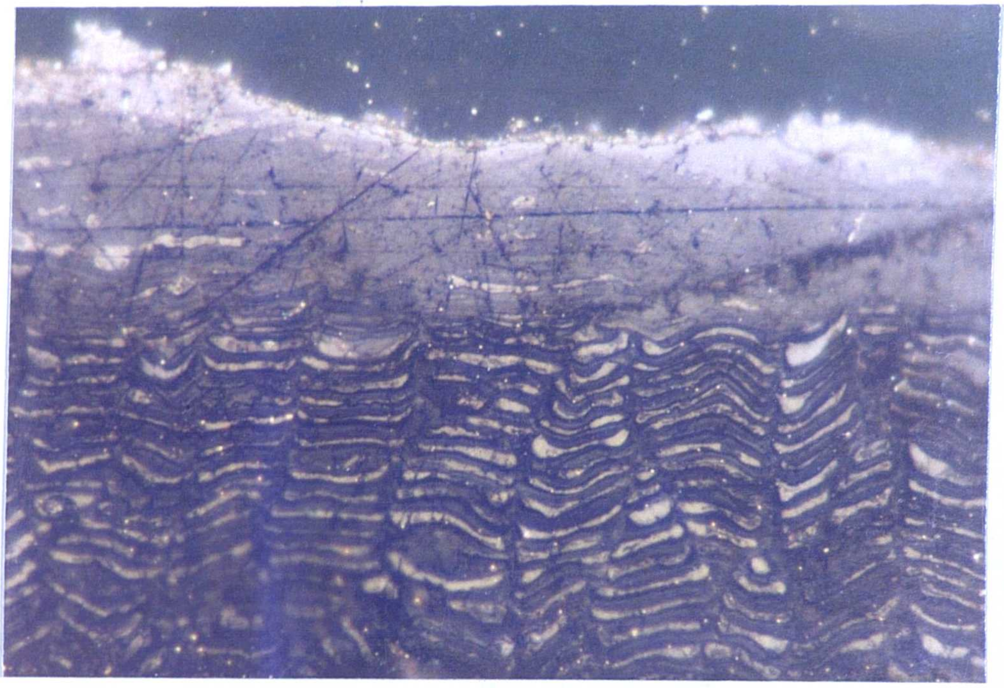
Elie Ness neck; sample GG.

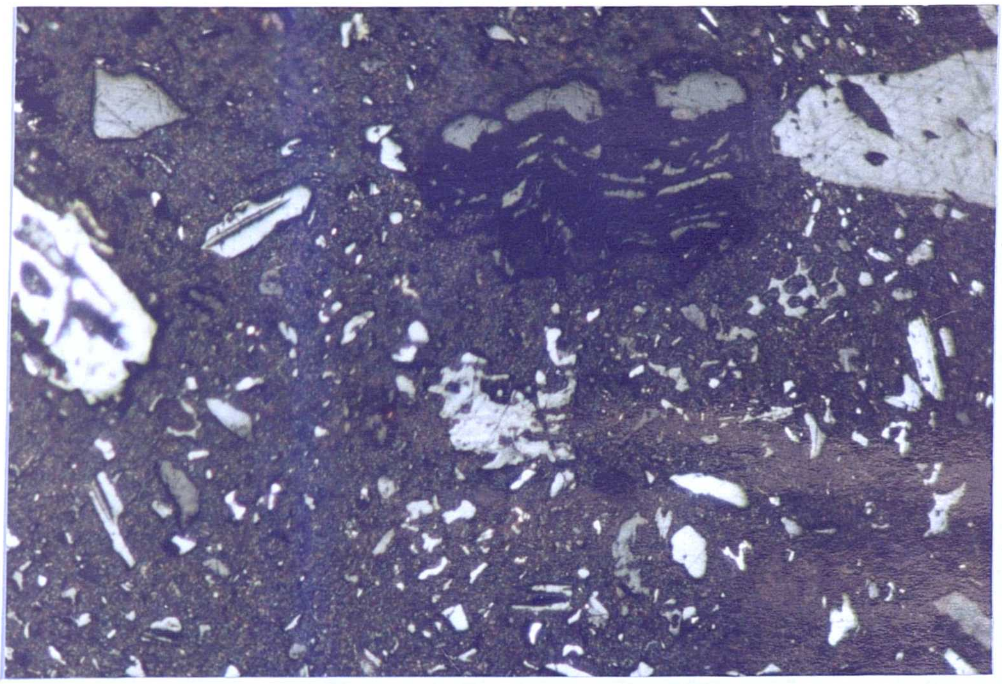
x300

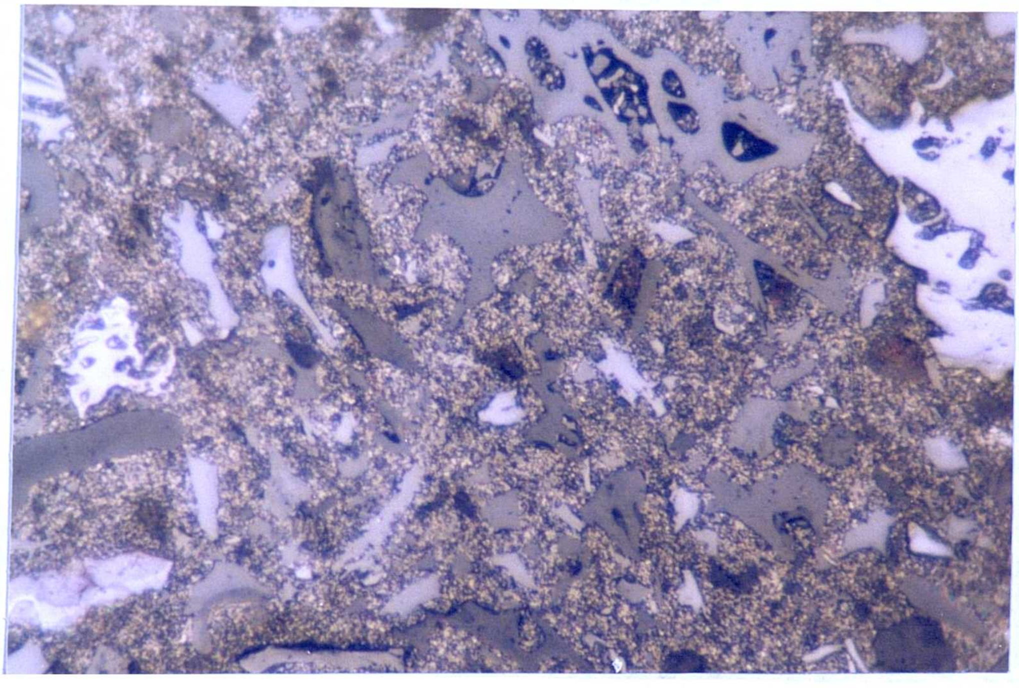
Plate 5.7 Detail of matrix of a possible fluidised coal showing randomly-oriented fragments set in a granular-mosaiced matrix: reflected light, oil immersion, plane-polarised light.

Elie Ness neck; sample GG.

x750







samples was made by Calder and Mukhopadhyay (1989). Clearly, either some Carboniferous/early Permian plants did have the capacity to produce suberin, or the material in the vents is of Mesozoic age or later. The possibility that organic matter of Mesozoic/Tertiary age has been incorporated in the vents can be discounted because there is absolutely no evidence for any post-Permian igneous activity in east Fife. Radiometric age determinations indicate that the vents are *at least* of early Permian age (Forsyth and Chisholm 1977; Forsyth and Rundle 1978). It is therefore possible that the occurrence of suberinite in vent clasts is recording the onset of the development of a suberin-bearing flora in late Carboniferous/early Permian times in Scotland.

The petrography of one of the suberinite-bearing clasts deserves comment. From Plate 5.6, randomly-oriented maceral fragments can be seen set within a high-reflecting granular-looking groundmass. Closer inspection of the matrix (Plate 5.7) reveals that it comprises numerous fine, rounded inclusions of anisotropic material which are interpreted as being the bodies of a mesophase texture. Such textures are known to form in the vitrinites of heat-affected coals of medium/low-volatile bituminous rank (see Section 2.2.5.2). Although granular-mosaic textures were recorded in vitrinites in other clasts from east Fife vents, the texture of the type shown in Plate 5.7 was unique to a clast from the Elie Ness neck (sample GG). The petrography of the sample corresponds very closely with those reported in samples from coal dykes occurring in a Coal Measures sequence in New South Wales (Britten and Taylor 1979). These dykes are thought to have formed following the interaction of igneous intrusives with coal seams which led to the production of a reservoir of hot, fluidised coal which was subsequently injected into pre-existing joints to form a dyke-like body on solidification. It is thus possible that the organic matter in sample GG is a coal-fluidisation product. Because the characteristic texture is confined to only one sample, coal fluidisation was apparently rare in the Scottish Carboniferous.

5.3.1.2.1 Reflectance Data

The general geology of the areas neighbouring the necks from which the clasts were removed and plots showing the distribution of vitrinite reflectance data from the vent clasts and country rocks are shown in Fig.5.10. Although not included in Fig.5.9, data from the Rock and Spindle neck, near St.Andrews, are presented (Fig.5.10k).

Reflectance values for vitrinites in the country rocks are low, but variable, and do not attain reflectances higher than *c.*$\%R_o av=0.60$. There are some instances where anomalously high reflectances do occur, for example near the

St. Monance neck to Newark neck

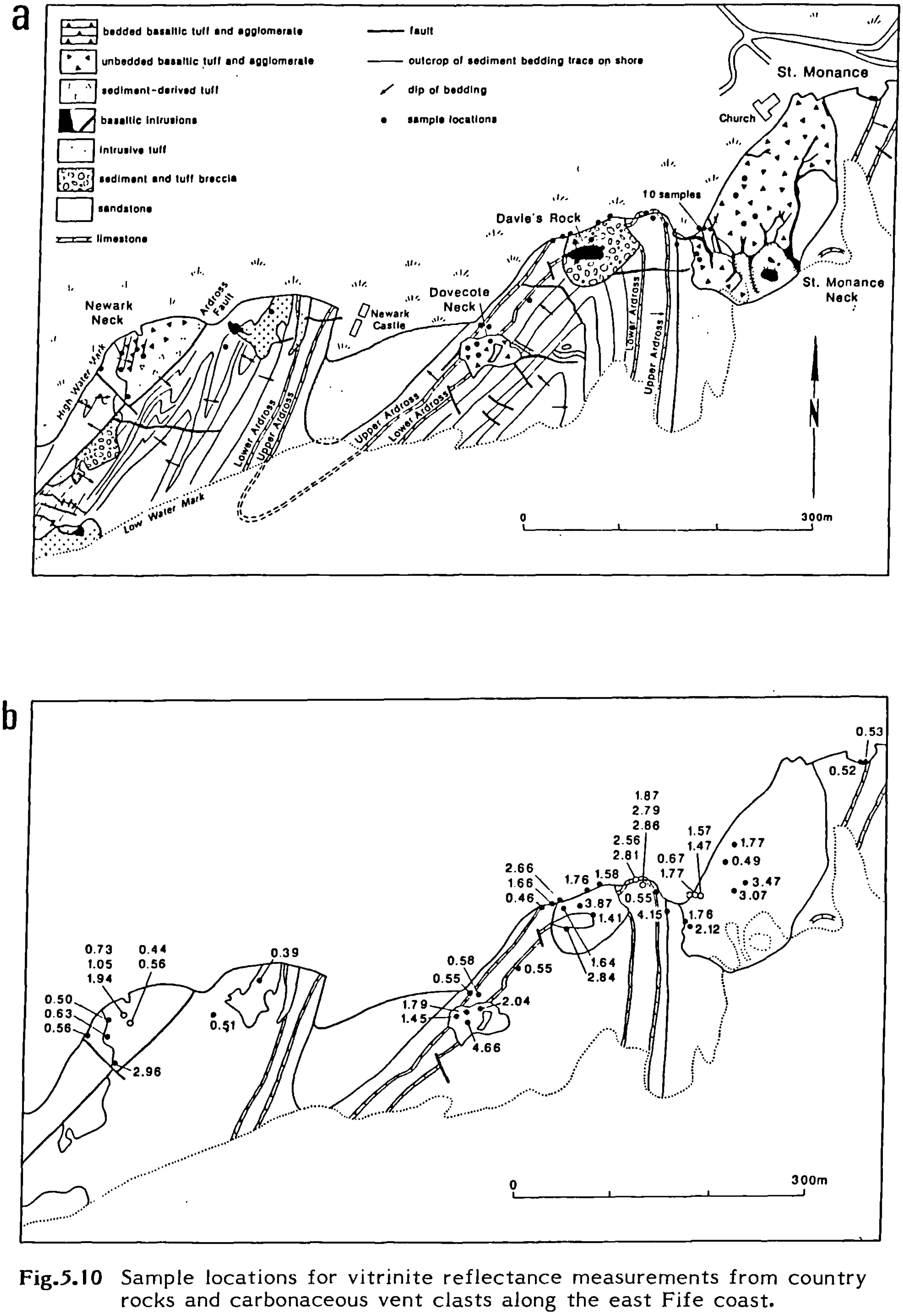
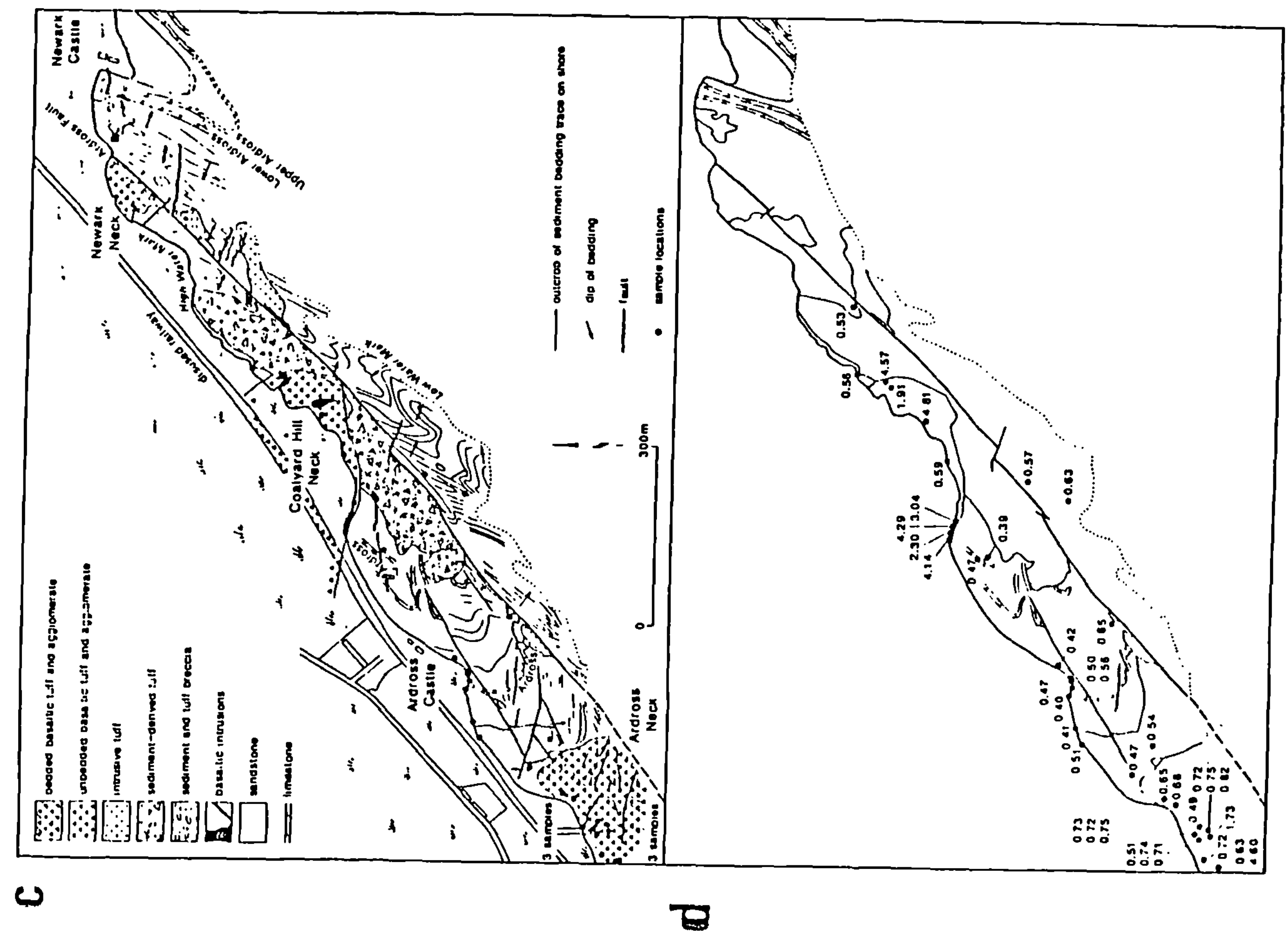


Fig.5.10 Sample locations for vitrinite reflectance measurements from country rocks and carbonaceous vent clasts along the east Fife coast.

Fig.5.10 (cont.).

Newark neck to Ardross neck



Ardross neck to Elie Ness neck

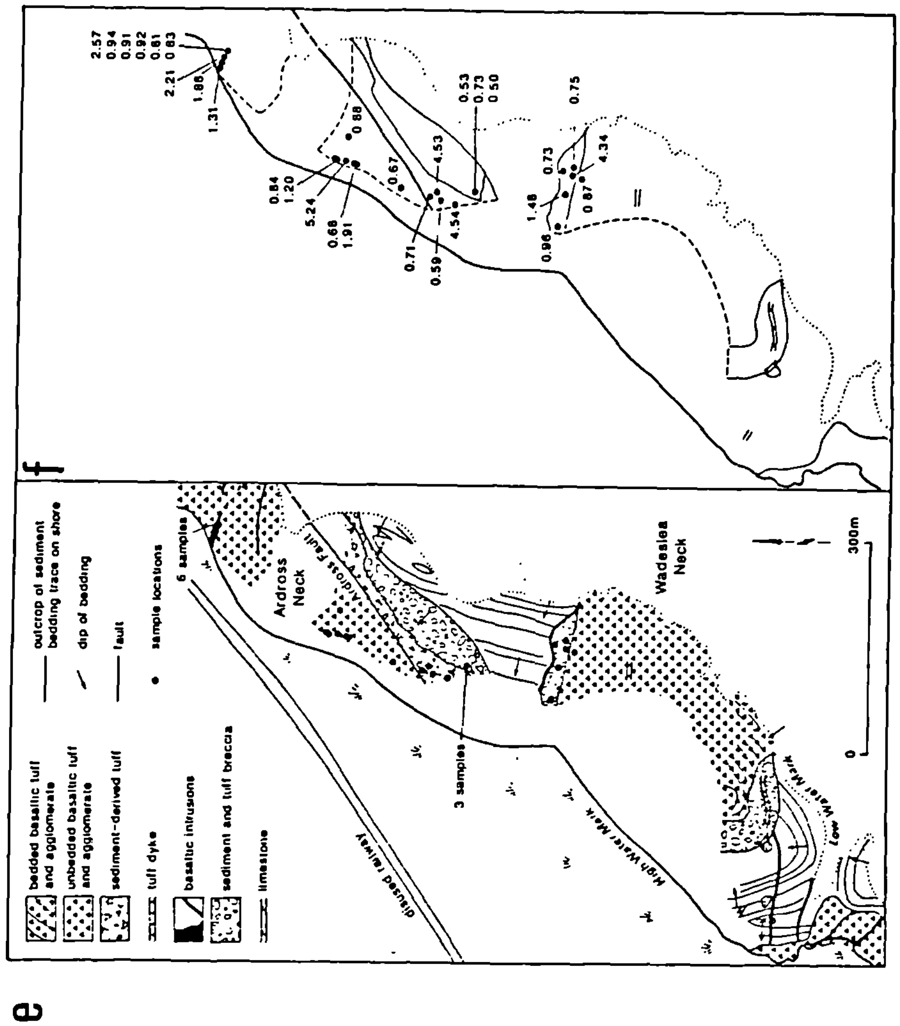
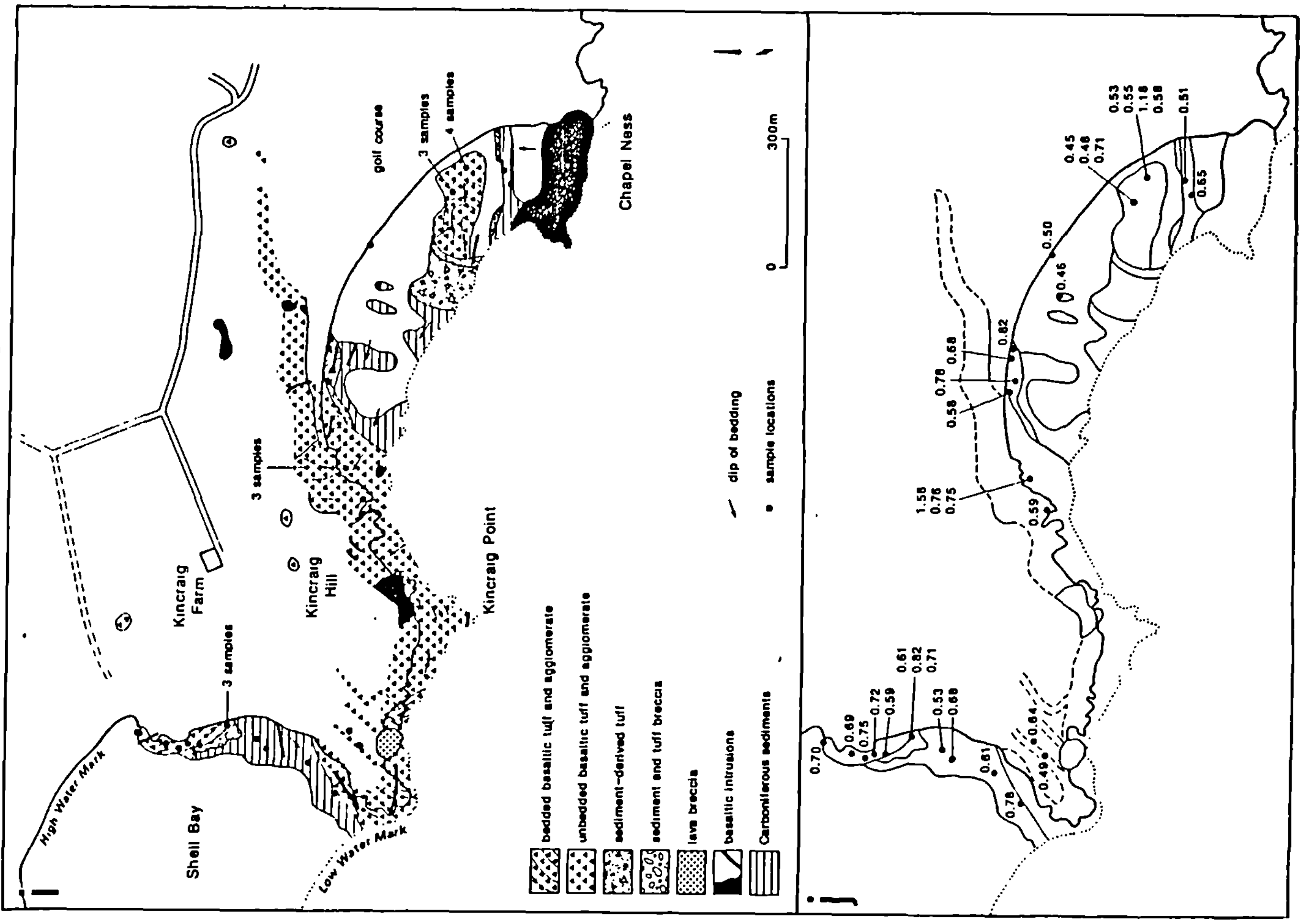
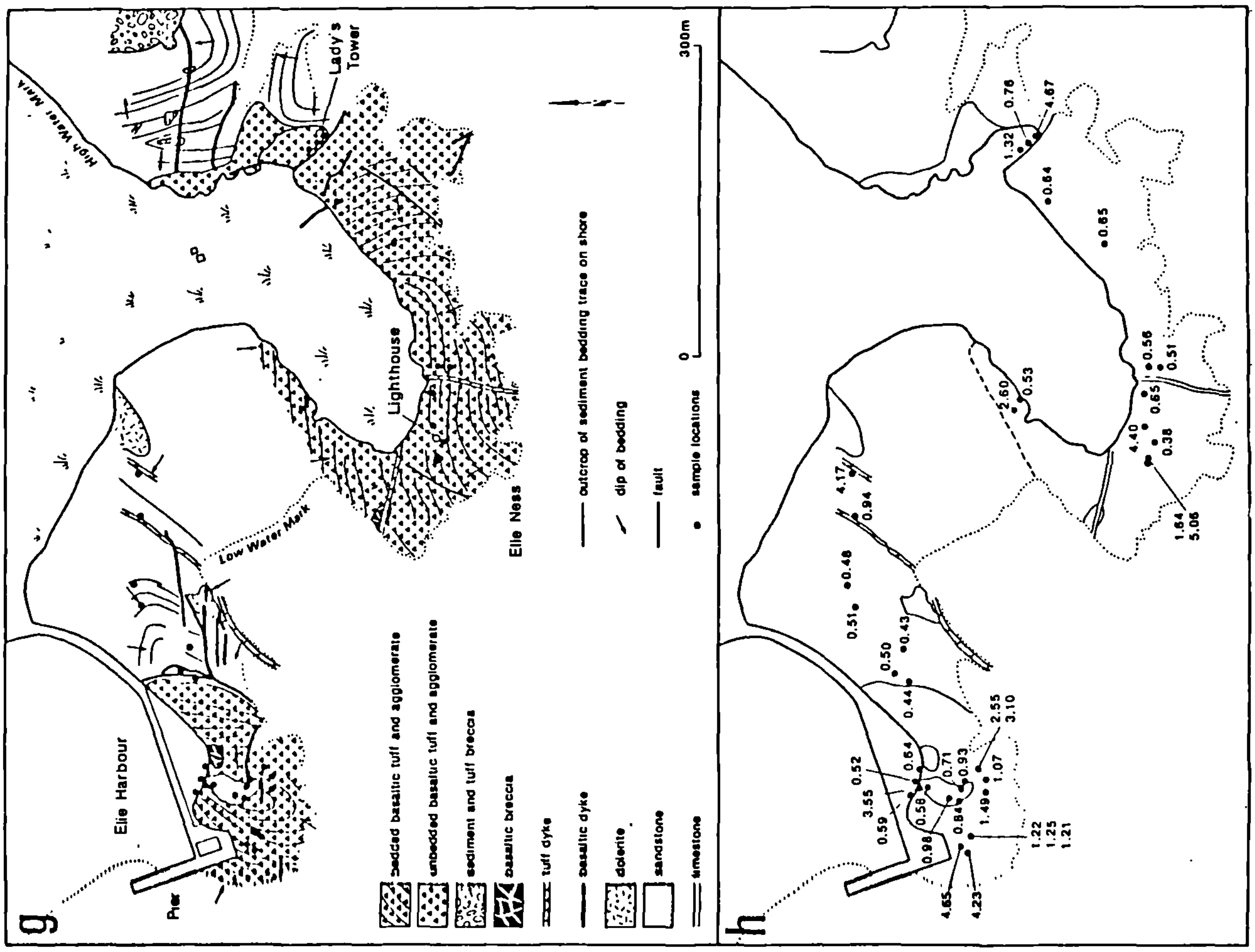


Fig.5.10 (cont.).

Chapel Ness neck to Kincraig neck



Elie Ness neck to Elie Harbour neck



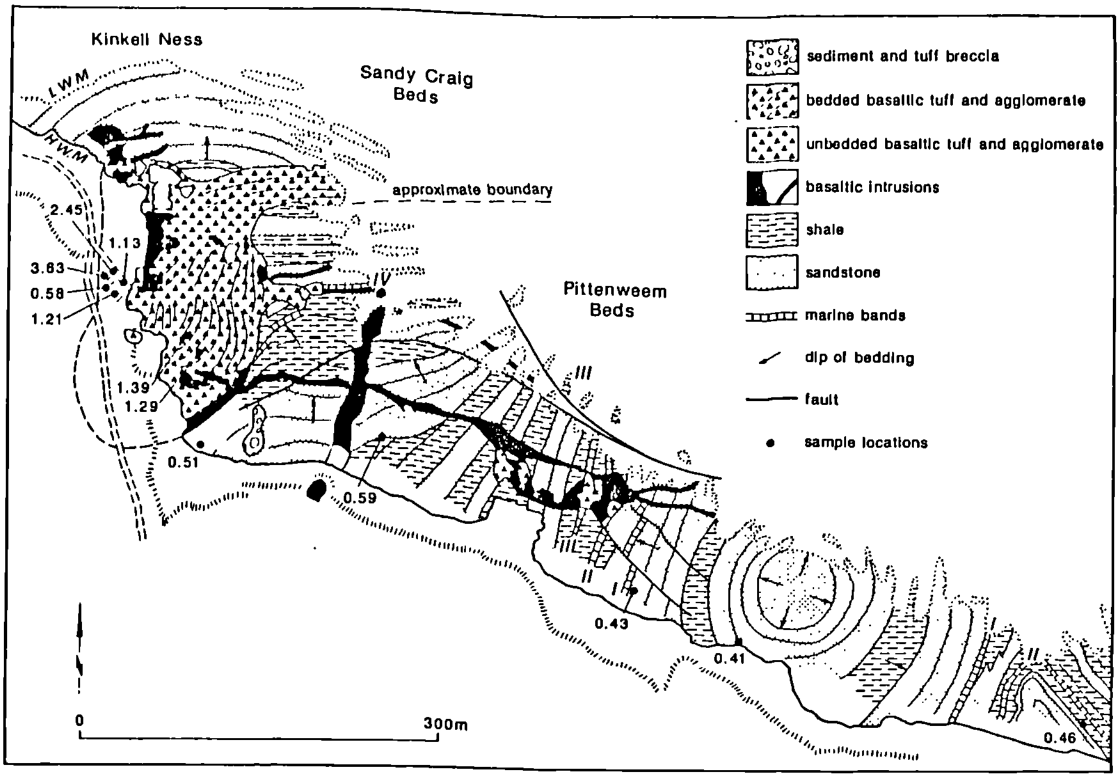


Fig.5.10 (cont.).

Davie's Rock and St.Monance necks (Fig.5.10b) and in the intervening tract between the Elie Ness and Elie Harbour necks (Fig.5.10h). Such high values (up to %R$_0$av=4.17) above the average reflectance for the country rocks are unusual. Where they do occur, they are probably related to unexposed igneous bodies. Numerous small plugs and dykes are associated with the necks (Forsyth and Chisholm 1977), which have provided localised sources of high temperatures to raise the vitrinite reflectance of the country rocks.

A histogram showing the reflectance distribution for the country-rock vitrinites is shown in Fig.5.11a. The anomalously high values that were occasionally recorded and are thought to relate to the proximity of igneous bodies have been excluded. The modal-class interval for this distribution lies between %R$_0$av=0.50-0.60.

Over most of the coastal section from St.Monance to Elie Ness there is little change in stratigraphic horizon, as confirmed by the intermittent exposure of the Ardross Limestones(Pathhead Beds). Strata surrounding the Rock and Spindle to the north lie lightly lower in the Calciferous Sandstone Measures succession (Pittenweem Beds). The Elie Harbour neck is juxtaposed with strata of the lower Limestone Group while the sediments surrounding the Chapel Ness-Kincraig necks lie in the Limestone Coal Group. Despite the change in country-rock horizons, the reflectance distribution is not felt to be unduly influenced by any background reflectance adjustment that might have been caused by parts of the section having been under substantially greater or lesser amounts in sedimentary cover.

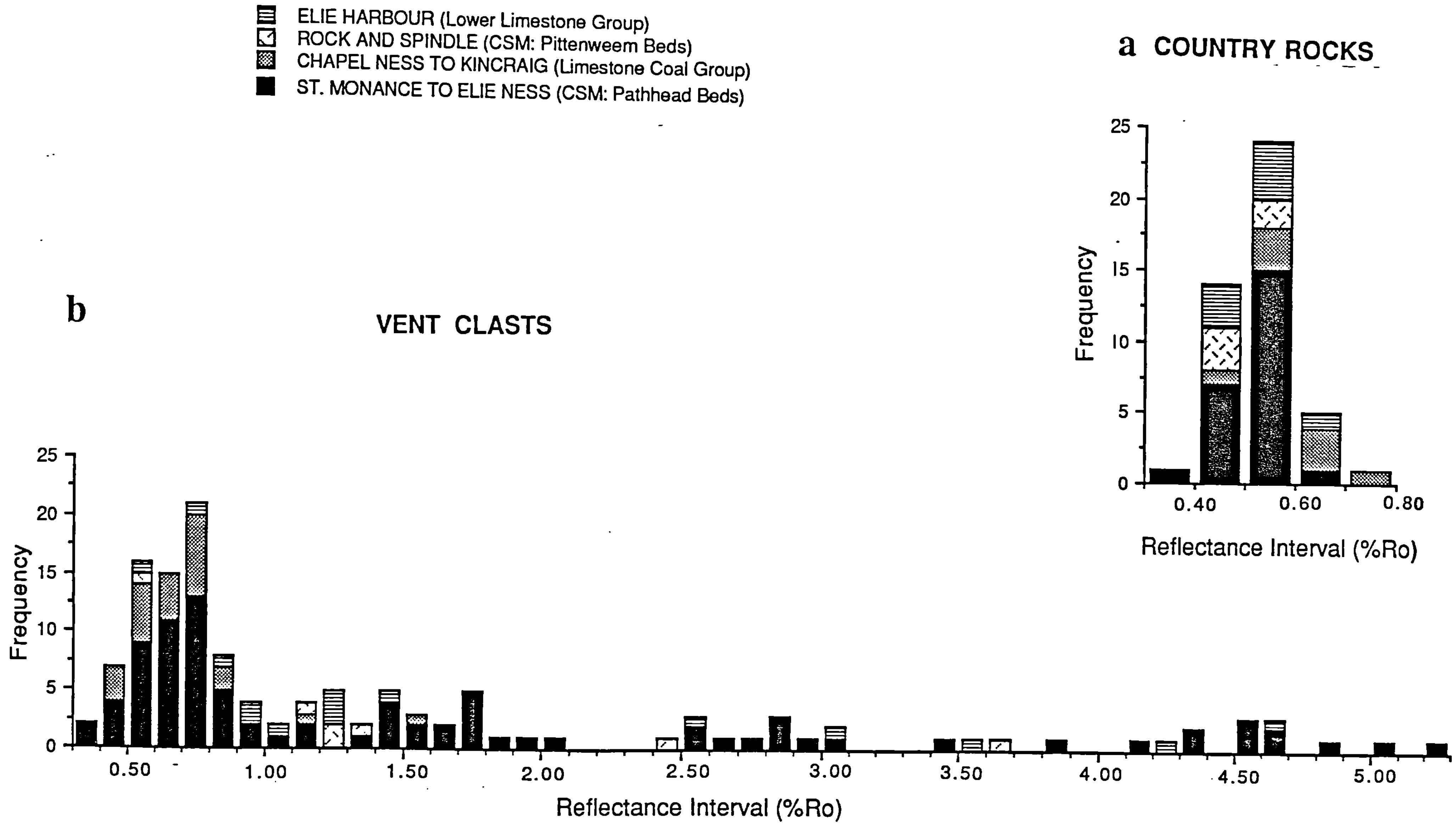


Fig.5.11 Histograms showing reflectance distributions of vitrinites in country rocks (a) and in carbonaceous vent clasts (b) from east Fife coast sections.

The reflectance histogram for the vitrinites of the country rocks over the Chapel Ness to Kincraig section does show a light skew towards higher values, but this asymmetry may reflect insufficient sampling. The skew probably does not relate simply to depth of burial because the Limestone Coal Group lies higher in the succession than the other country-rock successions. Furthermore, background reflectance levels and reflectance gradients are low in east Fife and so major variations of background reflectance levels would not be expected over the sections studied.

The distribution of vitrinite-reflectance values from organic clasts in the pyroclastic vent deposits shows a pronounced skew, with the modal-class interval lying between $\%R_0av=0.70-0.80$ (Fig.5.11b). While values of $\%R_0av<1.00$ are found for clasts from all shore sections examined, the majority of values from the Chapel Ness to Kincraig section are low. Most of the reflectance values lying beyond the range $\%R_0av=1.00-5.30$ are confined to the St.Monance to Elie Harbour and Rock and Spindle sections. No specific low or high ranges of reflectance appear to be associated with particular types of tuff or agglomerate.

5.3.1.2.2 Maturity Evaluation

Despite extensive volcanic activity throughout the east Fife succession, it is apparent that much of the organic matter in the country rocks and pyroclastic vent deposits shows little sign of having been exposed to more than modest temperatures. This feature was first remarked upon by Geikie (1879) and Balsillie (1920) who both noted the apparent lack of alteration of sediment clasts enclosed in the east Fife necks. Fig.5.11 illustrates the point well: the modal-class interval for the vent clasts is only two intervals higher than that for the country rocks. Of the remaining samples in the distribution of Fig.5.11b, a substantial number lie in the range $\%R_0av=1.00-2.00$, beyond which there are discontinuous reflectance intervals up to reflectances greater than 5%. Although difficult to prove, due to the lack of adequate exposure, it is possible that several of the samples with reflectance values higher than $\%R_0av=2.00$ in the St.Monance and Kinkell Ness (Rock and Spindle) sections are the result of contact metamorphism with crypto-volcanic plugs (probably basaltic) in the cliff faces (Francis and Hopgood 1970; Forsyth and Chisholm 1977). The reflectances of some vent clasts are lower than the mean value for the country rocks and can be explained by absorption, by the vitrinites,of hydrocarbons expelled from liptinite macerals (see Section 5.2.2).

To explain the distribution of reflectances, it is important to gain some understanding of the emplacement mechanism of the volcanic necks, an aspect first considered by Geikie (1879, 1902). Since then, the age, structure and petrography of the east Fife necks have commanded the attention of many geologists, and recent summaries of current knowledge are given by Forsyth and Chisholm (1977) and Francis (1983b). These authors suggest that the pyroclastic rocks of Fife display all the characteristics of deposits arising from Surtseyan-type volcanism which is initiated by the interaction between rising magma and water (Walker and Croasdale 1972). Sea and lagoons provided the major sources of water, with a lesser contribution from water contained within the unconsolidated sediment pile on which the volcanoes grew (Kokelaar 1983). The explosive interaction between magma and water (phreatomagmatism) resulted in the generation of high pressure gas and ash streams which drilled through the sediment column, reducing both the unconsolidated surface sediments and lithified country rock to a mixture of debris of varying grades which also contained fragments of parent magma. The presence of surface waters resulted in the build-up of wide-diameter, low-altitude tuff rings which were frequently breached, causing further explosive activity.

The vent structures cannot entirely be explained by phreatomagmatic activity: subsidence was also instrumental. This factor was first recognised by Geikie (1902) on the evidence that bedded tuffs and agglomerates (originally surficial deposits) now occupy lower positions in the necks and have therefore become juxtaposed with older country rocks which are themselves dragged down against the neck margins. The timing of the subsidence is controversial, but the model of Lorenz (1973) is considered to fit the field relations observed in east Fife most satisfactorily. He suggests that subsidence continues throughout the volcanic episode, beginning initially with ring-fracturing, when cylindrical conduits form above fissures, and continuing after each eruptive pulse. The net result is the progressive movement of pyroclastics down the neck. The relationships between the different processes involved in neck emplacement are shown in Fig.5.12 while the age relationships between the necks and the strata that now surround them are shown in Fig.5.13.

Given the mode of emplacement outlined above, it is not surprising that there is a wide range in the vitrinite-reflectance values recorded from the clasts entrained in the vent deposits. The clasts may originate from the present outcrop level, from above or from below it. Within the same neck, it is also possible to find fragments of low-reflecting, wood-like, material of the type referred to earlier and vitrinites of anthracitic to meta-anthracitic rank. The origin of the woody clasts is entirely consistent with the interpretation, based on stratigraphic and structural evidence, that east Fife Carboniferous volcanism occurred in a Surtseyan regime. Tree trunks and other terrigenous debris could have been

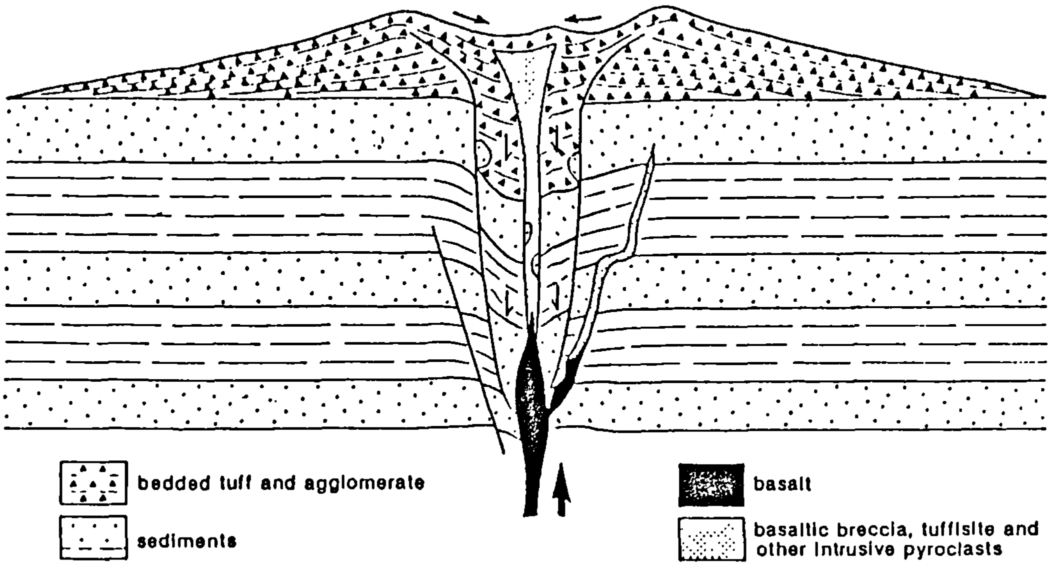


Fig.5.12 Illustration of processes involved in the emplacement of volcanic necks in a sedimentary succession (from Forsyth and Chisholm 1977).

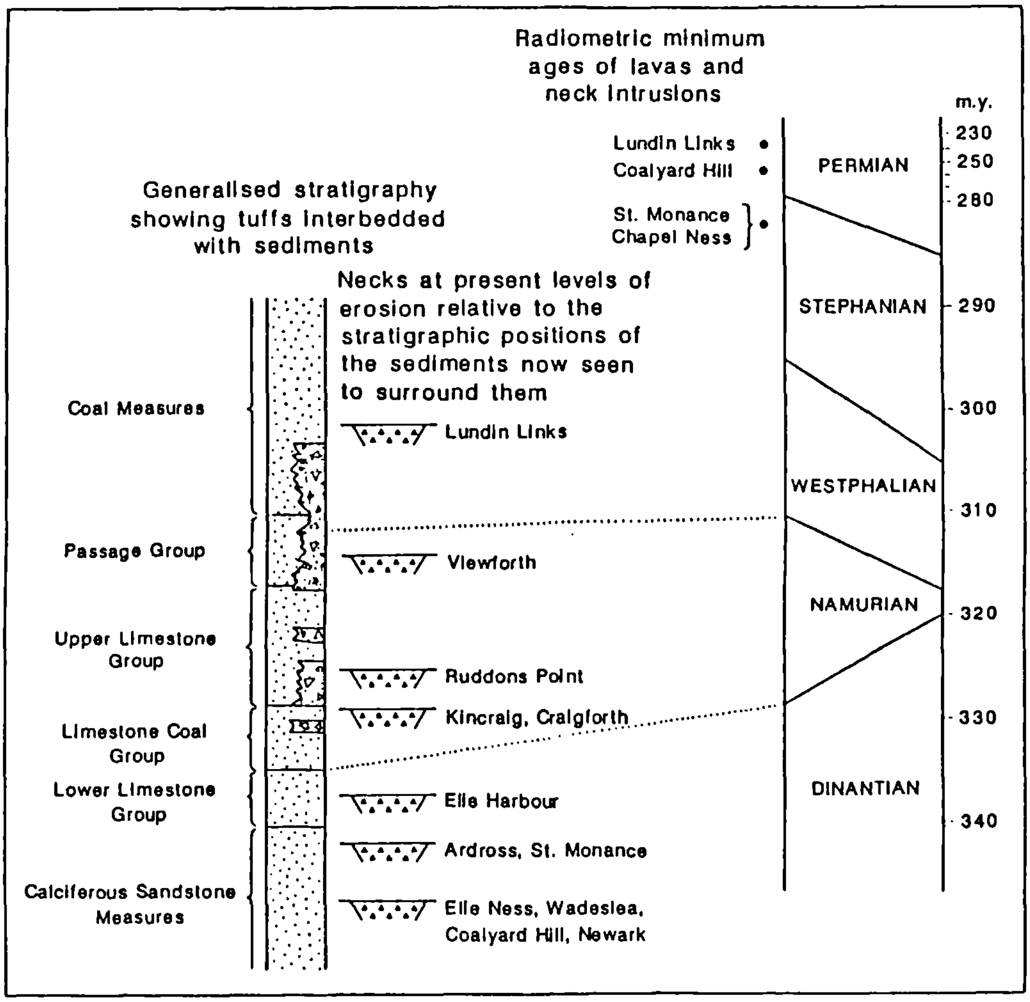


Fig.5.13 Stratigraphic position of volcanic necks, at present level of erosion, exposed between Lundin Links and St.Monance.

incorporated in the pyroclastics, having been torn from the subaerially-exposed flanks of the volcanoes which are thought to have been conducive to colonisation by a wood-bearing flora (Geikie 1879; Cadell 1925). Geikie (1879) found that specimens of wood extracted from the vents were always coniferous and inferred that the subaerial emergence of the volcanoes resulted in the volcanic cones persisting as "dry insular spots" on which the vegetation (coniferous) differed from that of the reeds and club-mosses of the surrounding swamps. It is interesting to note that the Orrock wood was inferred to be a primitive conifer on the basis of the geochemical data presented in Section 4.3.3.2.4.1.

The origin of the anthracitic and meta-anthracitic vitrinites is less easy to decide. One possibility is that coals and vitrinite-bearing clasts may have achieved substantially higher ranks by the increased temperatures experienced through incorporation in the hot gas and ash streams. Alternatively, and perhaps more likely, very high-rank clasts could have reached their present condition through exposure to thermal metamorphism caused by intrusions associated with the volcanic activity, or even by intrusions of an earlier thermal event, after which the affected sediments were comminuted by the later volcanic activity. The first view is enforced by observations of very high-rank vitrinites occurring in both country rocks and vent clasts which lie near, or are thought to lie near, igneous plugs or cryptovolcanic igneous masses. Furthermore, at one locality (Ardross neck; Appendix p.229), a thermal aureole was detected in tuffs adjacent to a basalt dyke (locality d in Francis and Hopgood 1970) by measuring vitrinite reflectances in clasts sampled with increasing proximity to the intrusion (shown diagrammatically in Section 5.3.2.1.1). Thus, rank imposition in some of the vent clasts occurred after incorporation in pyroclastic material.

The occasional occurrence of vitrinites displaying mosaic structures in the tuffs indicates that at least some of the organic matter had attained a caking- or coking-coal rank prior to further exposure to high temperatures. Given the relatively low background rank of strata within the Calciferous Sandstone Measures sequence in east Fife (Section 5.2.1), it seems likely that rank enhancement prior to incorporation in the vents was achieved during an earler igneous cycle. Mosaic occurrence lends support to the geochronological model of vent emplacement proposed by Macintyre *et al.* (1981) from the study of numerous crystalline clasts in the east Fife necks. Isotopic data point to two phases of thermal activity associated with neck formation. An earlier phase, involving sub-surface crystallisation, probably occurred during the Namurian, but was not related to vent development at the surface. Surficial vents only formed during a final explosive magmatic phase in late Carboniferous/early Permian times. In the light of this evidence, the attainment of caking- and coking-coal rank vitrinites could have occurred in the earlier, Namurian, magmatic phase of Macintyre *et al.* (1981). It is also possible that many of the high-rank vitrinites now seen in the vents could have been raised to this level of maturity during the earlier phase: their rank may have lain beyond the reflectance range which would allow mosaic development on further heating during the later volcanic episode (i.e. *c.*$\%R_o>1.50$).

Of the main mass of vent clasts studied, most do not appear to have been exposed to temperatures much greater than those that affected the organic matter of the country rocks, despite having been caught up in hot gas and ash streams. Minimal alteration of organic matter, if any, has previously been noted in carbonaceous sediments entrained within, or closely associated with, volcanic deposits (Geikie 1879, 1902; Cadell 1892, 1898, 1901, 1925; Balsillie 1920), although no explanations have been offered. Implicit in the concept of Surtseyan volcanism, from which the east Fife necks are believed to result, is the presence of large volumes of water (Walker and Croasdale 1972; Kokelaar 1983). It is probable that the large quantities of water present, either in the free state (lagoon/sea water) or as sediment pore water, would have acted as a pervasive and very efficient coolant in the Surtseyan system. Not only would the water have exerted a direct cooling effect on the hot igneous materials, heat absorption by the vapourisation of pore waters in sediments would have prevented the efficient transfer of heat to the organic matter. Pore-water vapourisation would have been particularly important within and directly below the volcanic cones, where sediments would have been of low density and unconsolidated.

An additional influential factor would have been the maturities of the clasts at the time of incorporation in the vents. Much of the organic matter stripped from the country rocks would have been of relatively low rank or, in the case of woods, very immature. The increased porosity and/or water content of low-rank organic matter would have been more inimical to effective heat transfer. Thus, a combination of high water content in the volcanic province and the low maturity of the organic matter at the time of volcanism meant that the alteration of organic components would generally have been prevented or minimised.

The structures and field relationships observed in diatremes (volcanic necks) in the Sydney Basin are so similar to those seen in the east Fife vents that similar emplacement mechanisms can be invoked. In a discussion of the relationship between the reflectances of vitrinites of clasts within volcanic breccias of the diatremes of the Sydney Basin and vitrinites in the associated country rocks, Crawford *et al.* (1980) argued that, because of the similarity of reflectances, the final rank of the clast vitrinites was imposed by temperature increase due to depth of burial. In support of this view, they have cited that the extensive calcitisation observed in coal clasts (Plate 5.2) is evidence of the shrinkage of the coal with later burial, after inclusion in the volcanic breccias. The carbonate is thought to have originated from circulating groundwater. This explanation does not seem to hold for the Fife volcanic necks. Although there is an overlap between the reflectances of the country rocks and those from the vent clasts, there is a distinct difference between the modal-class intervals of the reflectance distributions from the volcanic rocks and country rocks (Fig.5.11). Burial metamorphism cannot therefore be adduced for the final reflectance levels of the clasts in the volcanic rocks. Although an unknown quantity of organic matter would have risen in the ash streams from below the present stratigraphic level, much organic matter must also have been derived from higher in the sedimentary succession (possibly as much as 2km above the present position in some cases according to Forsyth and Rundle 1978) due to the subsidence of pyroclastic and sedimentary materials down the neck. The latter type of organic matter would have been of lower rank than the vitrinites in the country rocks at the present level of erosion. The presence of clast vitrinites with mosaics confirms that higher-rank material was present: some of this could have come from stratigraphic levels lower than those at which the necks currently lie or could have been derived from the stoping of higher-rank vitrinites, thermally altered elsewhere.

It therefore seems that the present rank of many of the vitrinites in the pyroclastic-vent deposits has been imposed through their association with volcanic activity and not depth of burial. In the case of the east Fife vents, the calcitisation seen in several clasts is probably related to a combination of shrinkage in response to increased temperature, and also to hydrothermal activity. Evidence in support of these suggestions stems from the extensive calcite veining of igneous rocks that is often noted in contemporaneous hydrothermal regimes, for example, the Guaymas Basin (Curray *et al.* 1982), in which shallow-level basaltic bodies are being intruded into an unconsolidated sediment pile in which the organic matter is immature. High calcite contents are also characteristic of white-traps. These rocks most commonly form at the margins of intrusive igneous bodies in the Midland Valley (Stecher 1888; Day 1928), but they have also been recorded in fragmentary form in east Fife volcanic vents (Balsillie 1920). The importance of water in the formation of white trap has long been recognised (Day 1928): the traps are believed to form as the result of the interaction of the hydrothermal fluids with carbonaceous matter.

Shrinkage is likely to be more pronounced in immature, and therefore relatively more porous, organic matter than in material of higher rank which is of lower porosity due to increased compaction and infilling of cell cavities by humic gels during coalification. It can be no coincidence, therefore, that the clasts found to be encrusted in calcite in the present study (e.g. Plate 5.2) and those calcite-rimmed clasts reported by Geikie (1879) and Cadell (1925) are *all* either wood fragments or clasts of higher rank which are inferred to have been incorporated in the vents *as woods*. The heavy calcitisation of carbonaceous matter in vent clasts and in other geological environments may therefore provide a good indication that the organic matter was immature at the time of its interaction with igneous materials.

5.3.1.2.3 Geochemical Characteristics of some Carbonaceous Vent Clasts

Geochemical analyses were performed on selected carbonaceous clasts removed from the neck deposits. The geochemistry of some low-rank woody and vitrinitic materials from the Orrock and Coalyard Hill vents has been discussed in Section 4.3.3.2.4. Other clasts examined geochemically were Elie sample L (coal lying in a sandstone raft in the Elie Harbour neck; $\%R_o av=0.71$), sample BB (Davie's Rock neck; $\%R_o av=1.64$) and sample 5B (raft of carbonaceous matter near the edge of the St.Monance neck; $\%R_o av=2.36$). Although not a vent clast, sample 5D, lying close to the margin of the St.Monance neck, in the contact zone of a dyke intruding the country rock and the neck, is included because of its proximity to the vent. The average reflectance of vitrinite in the contact zone was $\%R_o av=2.26$. The 10-sample locality indicated in Fig.5.10a represents the dyke locality, a picture of which is included in Raymond and Murchison (1988).

The high-rank sample SMW13 (probably a lamosite) is also included in this sample suite because, although it is located in the cliff face, its high maturity has probably been achieved through proximity to tuffaceous deposits associated with cryptovolcanic bodies which are thought to exist in this part of the coast section (Francis and Hopgood 1970). Details of these and other vent and intrusion-related samples are given in the appropriate sections of the Appendix and in the "additional samples near igneous intrusions" sections of Tables A.1-A.6.

Aliphatic Hydrocarbons

Representative gas chromatograms of the saturated hydrocarbon fractions of the vent-clast samples not previously discussed are shown in Fig.5.14. The trace of 5D closely resembles that of BB (Fig.5.14b). The relative abundance of medium molecular-weight *n*-alkanes in Figs 5.14b-d is probably due to the cracking of higher molecular-weight homologues. Such distributions are to be expected in high-rank organic materials. The occurrence of relatively large concentrations

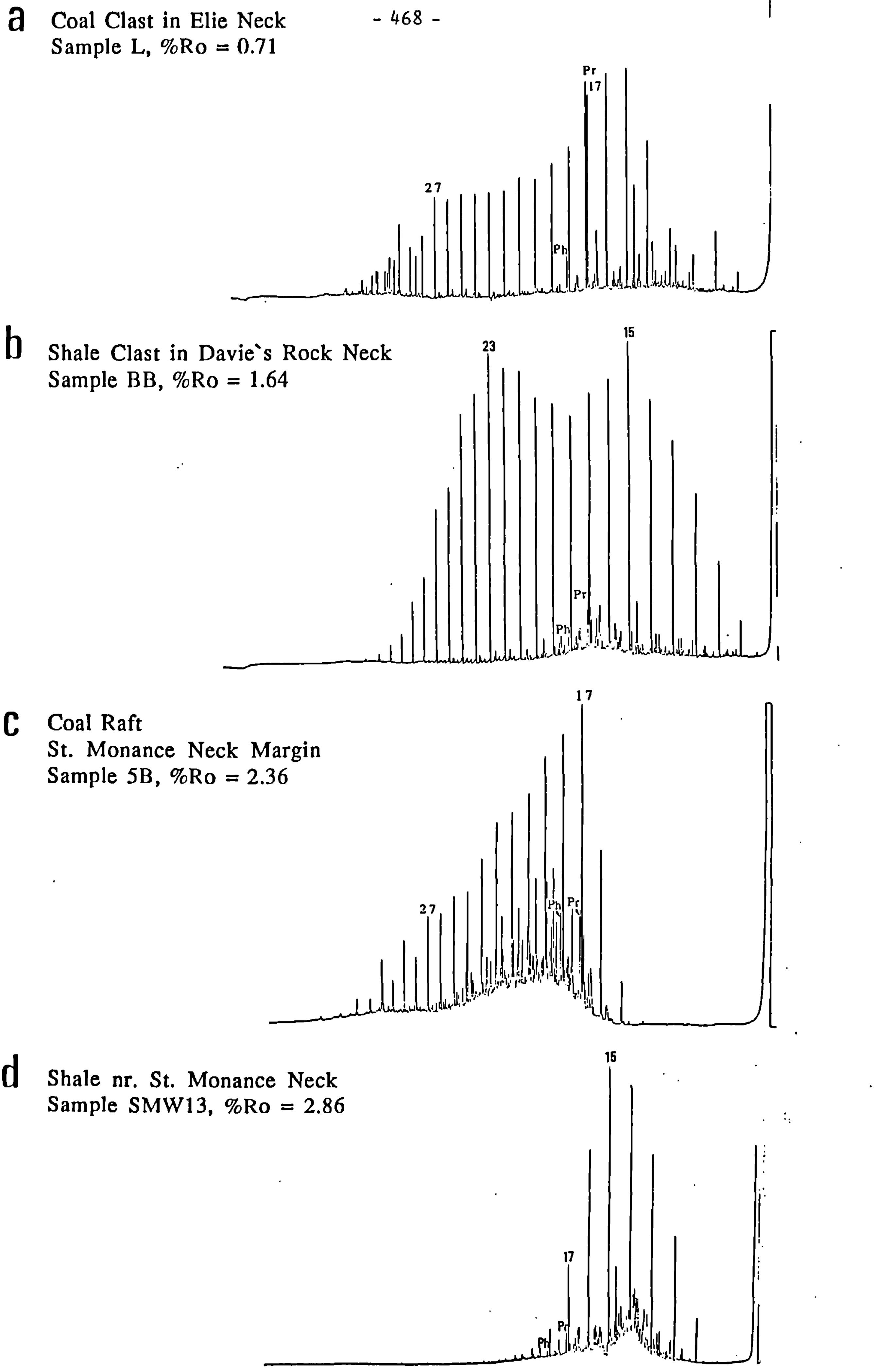


Fig.5.14 Gas chromatograms of the saturated hydrocarbon fractions of carbonaceous samples associated with volcanic vents.

of medium-length *n*-alkanes in the relatively low-rank Elie L sample (Fig.5.14a) is therefore surprising. This distribution may represent the palaeocontamination of the indigenous *n*-alkane fingerprint which could have occurred by the absorption of high-rank particulate matter from the atmosphere and/or from hydrothermal fluids. Alternatively, the enhancement in medium molecular-weight *n*-alkanes in Elie sample L could reflect an input of bacterially-derived *n*-alkanes, as discussed in Section 4.3.3.2. Support for a major microbial input stems from the very high hopane/sterane ratio (88). A significant unresolved component was present in 5B (Fig.5.14c) as well as numerous branched compounds which could not be identified.

The most distinctive feature of the samples associated with the east Fife vents is the presence of bimodal *n*-alkane distributions in the high-rank samples BB (Fig.5.14b) and 5D (similar to BB) in which relatively smooth *n*-alkane profiles skewed towards the low/medium molecular-weight members might be expected as illustrated in Figs 5.14c and d. The occurrence of *n*-alkane envelopes in which there is a prominent high molecular-weight component has been documented in the *n*-alkane profiles of petroliferous exudates in recent sediments from the Guaymas Basin (Simoneit 1984; Kawka and Simoneit 1987). These substances (hydrothermal petroleums) are believed to result from the action of hydrothermal processes on immature organic matter. Such high molecular-weight *n*-alkane "humps" are thought to be the artefacts of complex fractionation processes that operated during the geologically instantaneous generation, expulsion and migration of hydrocarbons in the dynamic hydrothermal regime. Although the tectonic environment in which hydrothermal activity in the Guaymas Basin occurred (a sea-floor spreading ridge) is not comparable with the environment in which volcanism occurred in east Fife, there are aspects of the former environment which have their analogues in the Carboniferous of east Fife. First, the presence of water was an important factor and governed the course of Surtseyan volcanism as described earlier; second, the sediments juxtaposed with the upper reaches of the volcanic necks would have been highly unconsolidated, akin to those found in basins in which ocean-floor spreading processes are active; and third, the organic matter in the unconsolidated, water-laden sediments would have been immature.

Although no exceptionally well-preserved cell structures are evident in the vitrinites of samples 5D and BB, which would suggest that the organic matter was at the wood or peat stage of coalification at the time of the igneous activity, the presence of a high molecular-weight hump in the *n*-alkane trace (giving rise to a bimodal envelope) suggests that the organic matter was of low rank and that, like the Guaymas Basin example, hydrothermal fluid movement exerted an important control on the distribution of molecular components present. A more detailed consideration of the occurrence of high molecular-weight *n*-alkane distributions covering a relatively narrow carbon-number range is given in Chapter 6 in relation to the occurrence of such distributions in some of the bitumens studied.

Biomarker profiles of the vent samples are unusual because vitrinite reflectance data indicate that samples BB, 5B and 5D have experienced temperatures in excess of those for samples lying at the end of the oil window, yet the biomarker maturation indices have not attained their equilibrium values. The highest biomarker values obtained were found in the sample of lowest rank (Elie sample L). The extent of the occurrence of this phenomenon in heat-affected organic matter, and possible explanations for the discrepancies between rank as defined by optical and geochemical parameters are only best appreciated following the consideration of many more heat-affected samples, which is undertaken in Section 5.3.2.2.

Aromatic Hydrocarbons

As with the TIC traces of the Orrock and Coalyard samples shown in Fig.4.68, those of the other vent samples are characterised by the prominence of PAH with pyrolytic-like distributions (Fig.5.15). The trace of sample 5D is very similar to that of 5B (Fig.5.15c). As discussed in Section 4.4.1.4.6, the occurrence of relatively large amounts of high-temperature combustion/pyrolysis products in volcanic terrains is a clear indication that igneous activity constitutes an important source of these compounds in geological environments. The presence of the high-temperature PAH in the relatively low-rank coal Elie L (Fig.5.15a), as in the Orrock and Coalyard samples, consolidates the view expressed earlier that sorption of PAH by relatively porous humic/vitrinitic materials is an important means for "concentrating" pyrolytic-like PAH in geological samples.

Particularly prominent in the east Fife vent samples are the 4H-cyclopenta-[def]phenanthrenes (methylenephenanthrenes; peaks 22, 24, 31). These components attest to the high-temperature origin of PAH with ≥ 3 rings in the samples studied, since they have been identified as significant components in combustion/pyrolysis products (Lee *et al.* 1977). The sterically-strained 4,5 position in the molecule is not a thermodynamically favoured structure in "normal" geological environments, in which the exposure of this high-temperature artefact to relatively low temperatures over long periods of time results in its transformation to a more

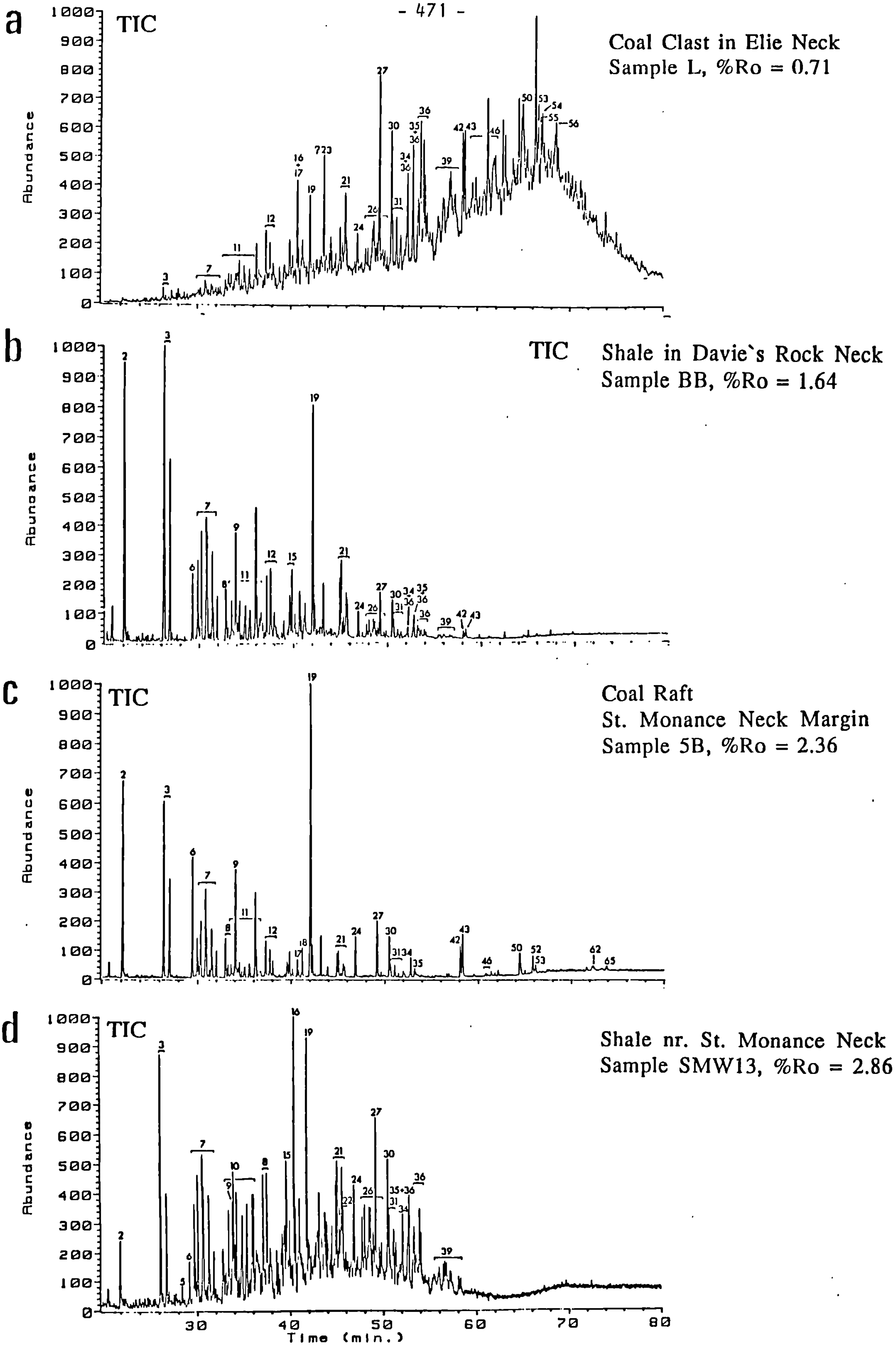


Fig.5.15 Total ion chromatograms showing the distributions of aromatic compounds in carbonaceous samples associated with volcanic vents (peak assignments in Table 4.7).

stable configuration. The relative abundance of components with this configuration in the east Fife samples is a further indication that the samples have not suffered deep post-Carboniferous burial. Had significant burial occurred, the partial or complete removal of the strained 4,5 configuration would be predicted on the basis of the negligible amounts or absence of methylenephenanthrenes recorded in fossil fuels (Youngblood and Blumer 1975).

An additional feature worth noting is the prominence of components with a biphenyl link in the high-rank, coaly samples. This observation offers further support to the previous inference (Section 4.4.1.4.6) that the combustion/pyrolysis of lignaceous cellular tissues is an important source of biphenyl-based compounds in the Midland Valley Carboniferous. Although the high reflectance of sample BB precluded the petrographic characterisation of the organic matter, the presence of high-reflecting phytoclasts with morphologies suggestive of vitrinite and inertinite, and the presence of relatively large contributions of biphenyl-related components, is indicative of the organic precursors being vascular-plant tissues.

5.3.2 Effects of Intrusive Igneous Activity

5.3.2.1 Petrological Aspects

The effect of igneous intrusives on organic maturation in the Midland Valley was first assessed by examining vitrinite-reflectance profiles of borehole and field successions penetrated by alkaline-dolerite (usually teschenite) sills and/or by the tholeiitic (quartz-dolerite) "Midland Valley Sill". Both types of succession may additionally contain volcanic material (lavas and tuffs). Patterns of reflectance variation in the Carboniferous of the eastern and central Midland Valley have also been compared with those from other heat-affected sequences in the British Isles and the world. The reflectance profiles contained in the text are those which best illustrate the points under discussion: the remaining plots are included in Appendix III.

5.3.2.1.1 Effects of Quartz Dolerites and Alkaline Dolerites

Reflectance variation in boreholes penetrated by quartz-dolerite sills are shown in Fig.5.16. Despite relatively few points for the Mackies Mill and Balfour Mains boreholes (Figs 5.16e,f), gradient curves could still be fitted. Encircled points refer to samples whose reflectances are anomalously low due to the suspected absorption of expelled hydrocarbons from liptinitic macerals (see Section5.2.2). Both samples affected in this way were taken from the Kelty Blackband which is characterised by an exceptionally high overall content

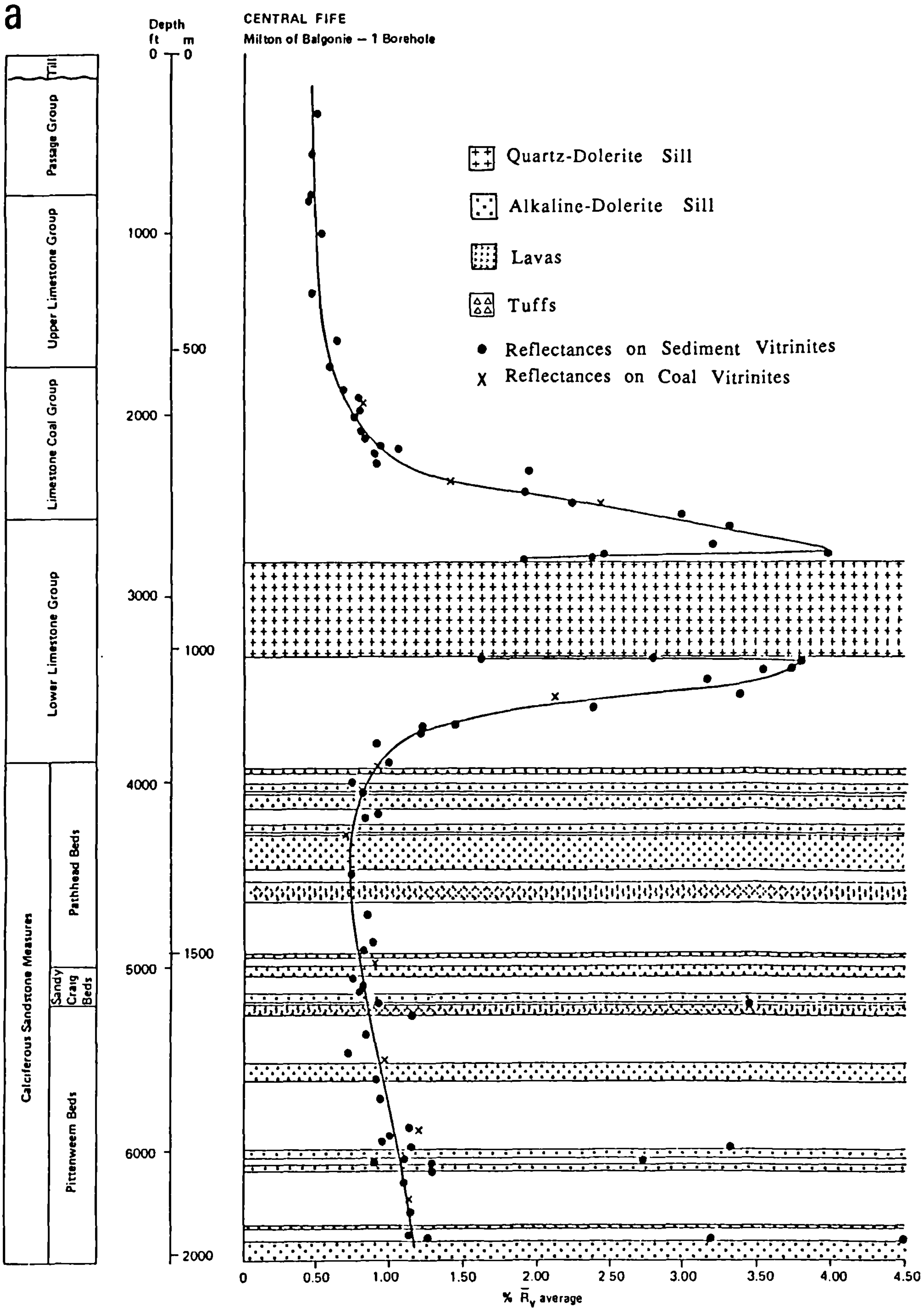


Fig.5.16 Vitrinite-reflectance variation in boreholes penetrated by quartz-dolerite sills.

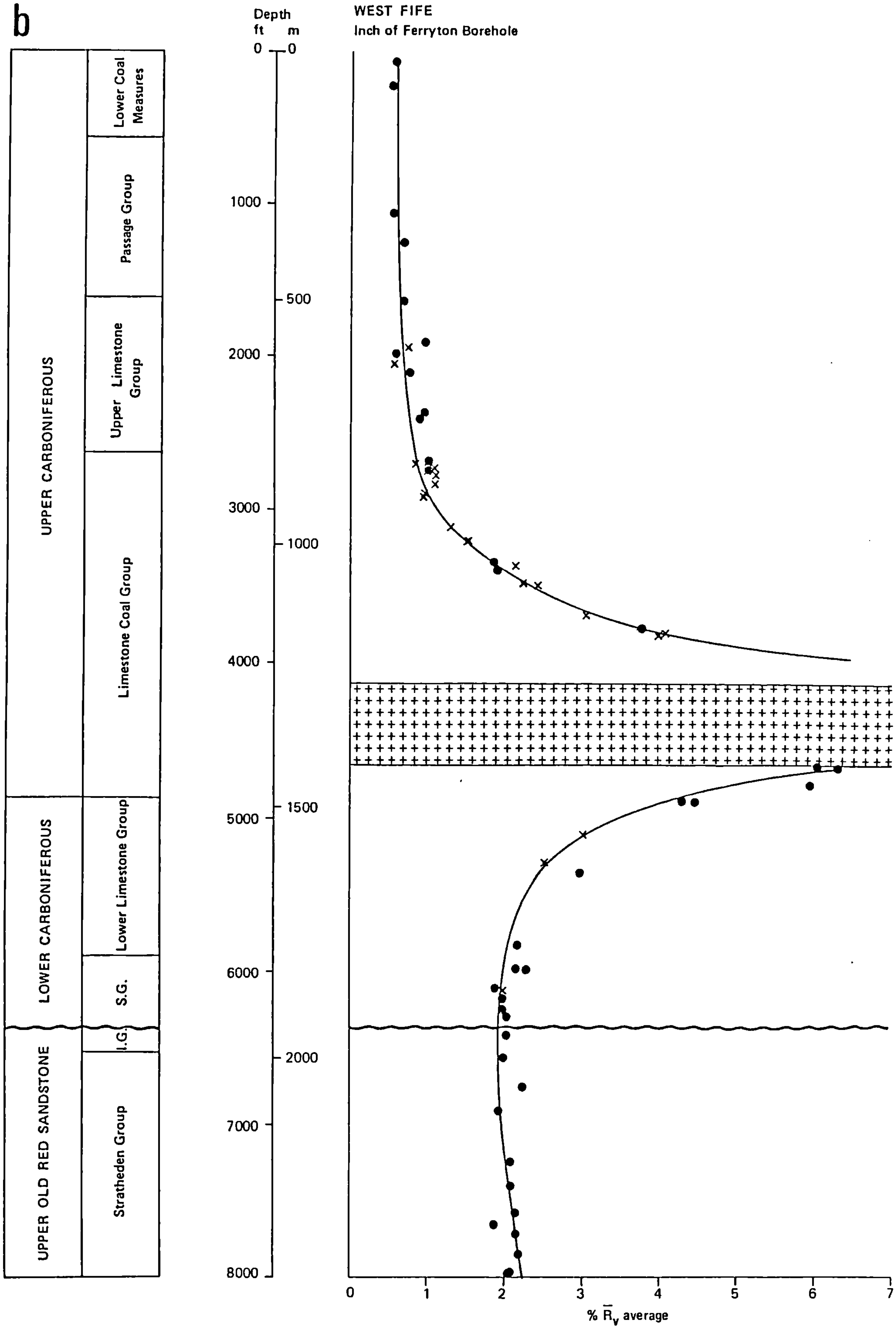

b
UPPER CARBONIFEROUS
LOWER CARBONIFEROUS
UPPER OLD RED SANDSTONE
Lower Coal Measures
Passage Group
Upper Limestone Group
Limestone Coal Group
Lower Limestone Group
S.G.
I.G.
Stratheden Group
Depth
ft m
0 0
1000
500
2000
3000
1000
4000
5000
1500
6000
2000
7000
8000
WEST FIFE
Inch of Ferryton Borehole
0
1
2
3
4
5
6
7
% $\bar{R}_v$ average

Fig.5.16 (cont.).

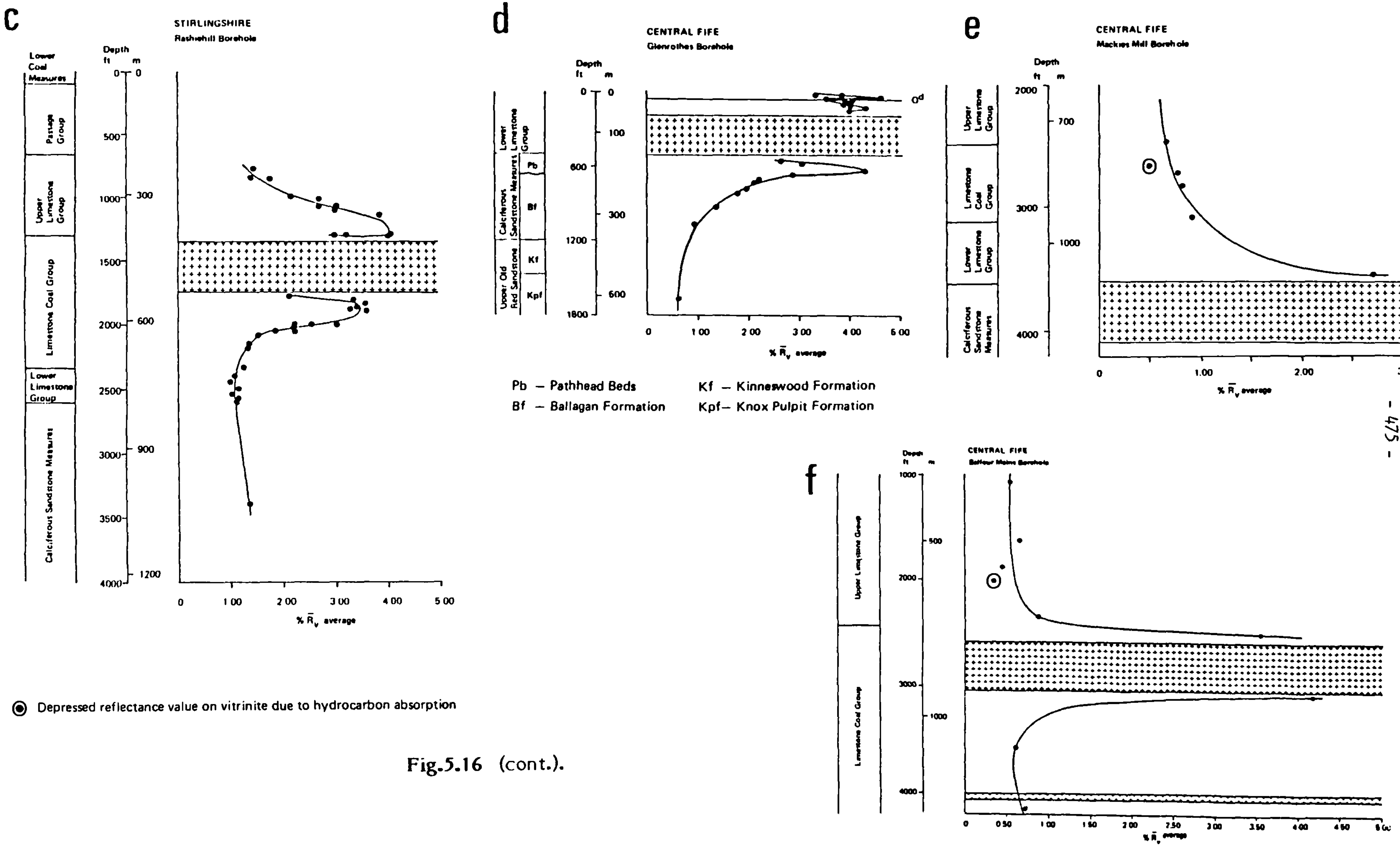

c
STIRLINGSHIRE
Rashiehill Borehole
Lower Coal Measures
Passage Group
Upper Limestone Group
Limestone Coal Group
Lower Limestone Group
Calciferous Sandstone Measures
Depth ft m
0
500
1000
1500
2000
2500
3000
3500
4000
300
600
900
1200
0 1.00 2.00 3.00 4.00 5.00
% R̄v average
d
CENTRAL FIFE
Glenrothes Borehole
Lower Limestone Group
Calciferous Sandstone Measures
Upper Old Red Sandstone
Pb
Bf
Kf
Kpf
Depth ft m
0
600
1200
1800
100
300
600
Od
0 1.00 2.00 3.00 4.00 6.00
% R̄v average
Pb — Pathhead Beds
Bf — Ballagan Formation
Kf — Kinneswood Formation
Kpf— Knox Pulpit Formation
e
CENTRAL FIFE
Mackies Mill Borehole
Upper Limestone Group
Limestone Coal Group
Lower Limestone Group
Calciferous Sandstone Measures
Depth ft m
2000
3000
4000
700
1000
0 1.00 2.00 3.00
% R̄v average
f
CENTRAL FIFE
Balfour Mains Borehole
Upper Limestone Group
Limestone Coal Group
Depth ft m
1000
2000
3000
4000
500
1000
0 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00
% R̄v average
Depressed reflectance value on vitrinite due to hydrocarbon absorption

Fig.5.16 (cont.).

of liptinitic macerals (see Section 4.2.3.4). The maturity profile of the Balfour Mains borehole (Fig.5.16f) may be oversimplified because stratigraphic data indicate the presence of a fault in the sequence and also that the sill may be transgressive at this locality (Knox 1954).

A detailed petrological study of the response of organic matter in the Rashiehill borehole to igneous activity has been reported (Raymond 1983; Raymond and Murchison 1989). Many of the observations described in sediments in the last study correspond to those made (on coals) by Jones and Creaney (1977; see p.64 for review), and also apply to other heat-affected successions in the Midland Valley.

The salient feature evident from Fig.5.16 is the development of thermal aureoles which extend at least several tens of metres above and/or below the tholeiitic intrusions. An assessment of aureole size was made by measuring the distance from the intrusion-sediment contact to the point at which the inflection in the background reflectance gradient commences (termed D) and dividing this value by the intrusion thickness (T). Values of D/T for all intrusions studied in this project (including those from other provinces) are given in Table 5.1. Variation in the aureoles produced by non-multiple tholeiitic intrusions in the eastern and central Midland Valley lies in the range D/T=1.20-3.91. Thus, in no quartz dolerite examined was aureole thickness above or below the sill less than the intrusion thickness.

The gradient curves for the Glenrothes (Fig.5.16d), Rashiehill (Fig.5.16c) and Milton of Balgonie (Fig.5.16a) holes are complicated by the occurrence of a pronounced reflectance inversion close to the sediment-intrusion contact. Additional complications in the reflectance profile of the Glenrothes bore arise through interference from a thin quartz-dolerite intrusion some 40m above the main sill. Inspection of Fig.5.16, and other profiles in which the phenomenon is recorded, shows that the reversals commence between approximately $\%R_o$=4.00-5.00. Reversals near intrusions have also been recorded in XRD data (Khorasani *et al.* 1990) and these have been interpreted as reflecting the interruption of the overall progressive increase in molecular ordering which occurs in vitrinites at high temperatures. An additional factor may relate to polishing difficulties: vitrinite surfaces of a sufficiently high quality for accurate reflectance determination are difficult to produce in vitrinites of anthracitic rank and higher.

The reflectance variation downhole in boreholes and in field localities which are intruded by alkaline-dolerite sills (teschenites) and a dyke are shown in Fig.5.17. The Blackness No.2 bore also contains a teschenite sill, and this was shown in Fig.5.7h. The total thickness of the teschenite sill at Colinswell

Table 5.1 Parameters calculated from vitrinite reflectance profiles (boreholes and field sections).

Locality	Intrusion Type	Intrusion Thickness T (ft)	Aureole Thickness D (ft)	Distance to 1%VR D1%VR (ft)	$\frac{D}{T}$	$\frac{D1\%VR}{T}$	Log T	Log D	Log D1% VR	Estimated Background Rank	Age of Intrusion	Age of Intruded Strata[a]	Source of Data[b]
SCOTLAND Eastern and Central Midland Valley													
Rashiehill (A)	quartz-dolerite sill	389	1200	700	3.08	1.80	2.59	3.08	2.85	0.80	Stephanian	LCG	1
Rashiehill (B)	quartz-dolerite sill	389	657	657	1.69	1.69	2.59	2.82	2.82	0.80	Stephanian	LCG	1
Inch of Ferryton (A)	quartz-dolerite sill	511	2000	1250	3.91	2.45	2.71	3.30	3.10	0.85	Stephanian	LCG	2
Inch of Ferryton(B)	quartz-dolerite sill	511	1500	NDP	2.93	NDP	2.71	3.18	NDP	0.90	Stephanian	LCG	2
Righead (A)	quartz-dolerite sill	159	860	180	5.41	1.13	2.20	2.93	2.26	0.75	Stephanian	LCG	2
Righead (B)	quartz-dolerite sill	159	400	NDP	2.52	NDP	2.20	2.60	NDP	0.75	Stephanian	LCG	2
Thornton Bridge	quartz-dolerite sill	445	800	360	1.80	0.81	2.65	2.90	2.56	0.70	Stephanian	CSM	2
Mackies Mill	quartz-dolerite sill	503	1240	520	2.47	1.03	2.70	3.09	2.72	0.65	Stephanian	CSM	2
Milton of Balgonie (A)	quartz-dolerite sill	510	1400	600	2.74	1.18	2.71	3.15	2.78	0.65	Stephanian	LCG	2
Milton of Balgonie (B)	quartz-dolerite sill	510	840	500	1.65	0.98	2.71	2.92	2.70	0.65	Stephanian	LCG	2
Balfour Mains (A)	quartz-dolerite sill	468	1000	200	2.14	0.43	2.67	3.00	2.30	0.60	Stephanian	LCG	2
Balfour Mains (B)	quartz-dolerite sill	468	560	180	1.20	0.38	2.67	2.75	2.26	0.60	Stephanian	LCG	2
Righead	teschenite sill	55	19*	NDP	0.35	NDP	1.74	1.28	NDP	0.75	Namurian	LCG	2
Blackness No.2	teschenite sill	174	68*	NDP	0.39	NDP	2.24	1.83	NDP	0.67	?Visean	CSM	2
Firth of Forth Tower-1	teschenite sill	59	23*	NDP	0.39	NDP	1.77	1.36	NDP	0.73	Namurian	LCG	2
Westfield IGS	teschenite sill	186	20*	NDP	0.11	NDP	2.27	1.30	NDP	0.59	Namurian	ULG	2
Colinswell Section	teschenite sill	66	8	6	0.12	0.09	1.82	0.90	0.78	0.55	?Visean	CSM	2
Lochhead	teschenite sill	84	18*	NDP	0.21	NDP	1.92	1.26	NDP	0.48	Namurian	ULG	2

Table 5.1 (cont.).

Locality	Intrusion Type	Intrusion Thickness T (ft)	Aureole Thickness D (ft)	Distance to 1%VR D1%VR (ft)	$\frac{D}{T}$	$\frac{D1\%VR}{T}$	Log T	Log D	Log D1% VR	Estimated Background Rank	Age of Intrusion	Age of Intruded Strata[a]	Source of Data[b]
Boreland	teschenite sill	186	64*	NDP	0.34	NDP	2.27	1.81	NDP	0.65	Namurian	LCG	2
Ardross Inclusions	olivine-dolerite dyke	6.56	0.98	NDP	0.15	NDP	0.82	-0.008	NDP	0.95	Namurian	CSM	2
<u>Ayreshire</u>													
Saltcoats	quartz-dolerite dyke	5.4	19.7	16.4	3.65	3.04	0.73	1.29	1.21	0.79	Tertiary	LCM	3
<u>Morvern</u>													
Loch Aline A	quartz-dolerite dyke	5.4	13.1	10.0	2.43	1.85	0.73	1.11	1.00	0.92	Tertiary	Jurassic	4
Loch Aline B	quartz-dolerite dyke	4.7	13.1	6.9	2.78	1.47	0.67	1.11	0.84	0.81	Tertiary	Jurassic	4
Loch Aline C	quartz-dolerite dyke	1.6	2.3	1.5	1.44	0.94	0.20	0.36	0.18	0.90	Tertiary	Jurassic	4
Loch Aline D	quartz-dolerite dyke	5.4	6.6	4.0	1.22	0.74	0.73	0.82	0.60	0.89	Tertiary	Jurassic	4
Loch Aline E	quartz-dolerite dyke	2.9	1.3	1.2	0.45	0.41	0.47	0.11	0.08	0.92	Tertiary	Jurassic	4
N.E. ENGLAND													
Allenheads	quartz-dolerite sill	233	810	NDP	3.48	NDP	2.37	2.91	NDP	2.30	Stephanian	Visean	5,6
Harton (U)	quartz-dolerite sill	200	1630	920	8.15	4.60	2.30	3.21	2.96	1.10	Stephanian	Visean	7
Harton (L)	quartz-dolerite sill	104	900	NDP	8.65	NDP	2.02	2.95	NDP	2.48	Stephanian	Visean	7
Whitley Bay (U)	quartz-dolerite sill	213	1370	671	6.43	3.15	2.33	3.14	2.83	0.90	Stephanian	Visean	8
Whitley Bay (L)	quartz-dolerite sill	120	570	NDP	4.75	NDP	2.08	2.76	NDP	2.20	Stephanian	Visean	8
Throckley	quartz-dolerite sill	126	508	278	4.02	2.21	2.10	2.71	2.44	1.10	Stephanian	Namurian	1
Longhorsley	quartz-dolerite sill	240	1510	800	6.29	3.33	2.38	3.18	2.90	1.00	Stephanian	Visean	3
Boulmer	quartz-dolerite dyke	98.1	839	787	8.56	8.02	1.99	2.92	2.90	0.85	Stephanian	Namurian	4
Elsdon	quartz-dolerite dyke	88.6	141	66	1.59	0.74	1.95	2.15	1.82	0.75	Stephanian	Visean	4
Burnmouth	quartz-dolerite	7.4	35.0	20.5	4.73	2.77	0.87	1.54	1.31	0.61	Stephanian	Tournaisian	3

Table 5.1 (cont.).

Locality	Intrusion Type	Intrusion Thickness T (ft)	Aureole Thickness D (ft)	Distance to 1%VR D1%VR (ft)	$\frac{D}{T}$	$\frac{D1\%VR}{T}$	Log T	Log D	Log D1% VR	Estimated Background Rank	Age of Intrusion	Age of Intruded Strata^{a}	Source of Data^{b}
Kielder	quartz-dolerite dyke	98.8	328	197	3.32	1.99	1.99	2.52	2.29	0.71	Stephanian	Tournaisian	3
Seal Sands	quartz-dolerite sill	49.9	80.1	80.1	1.61	1.61	1.70	1.90	1.90	1.00	Stephanian	Namurian	3
Beadnell	quartz-dolerite dyke	30	70	40	2.33	1.33	1.48	1.85	1.60	0.57	Stephanian	Visean	9
Hett	quartz-dolerite dyke	24	22	15	0.92	0.63	1.38	1.34	1.18	0.91	Stephanian	Westphalian	9
Ludworth	quartz-dolerite dyke	32.8	46.5	NDP	1.42	NDP	1.52	1.67	NDP	1.03	Stephanian	Westphalian	10
Collywell Bay	tholeiite dyke	0.98	1.31	1.15	1.34	1.17	-0.009	0.12	0.06	0.76	Tertiary	Westphalian	4
Collywell Bay	tholeiite dyke	3.28	5.25	4.10	1.60	1.25	0.52	0.72	0.61	0.69	Tertiary	Westphalian	4
Collywell Bay	tholeiite dyke	0.33	0.33	0.20	1.00	0.61	-0.48	-0.48	-0.70	0.67	Tertiary	Westphalian	9
River Irthing	tholeiite dyke	12.1	13.1	3.3	1.08	0.27	1.08	1.11	0.52	0.68	Tertiary	Visean	4
Saughtree	tholeiite dyke	9.2	NDP	78.7	NDP	8.55	0.96	NDP	1.90	NDP	Tertiary	Tournaisian	4
Netherton	tholeiite dyke	14	35	25	2.50	1.79	1.15	1.54	1.40	0.77	Tertiary	Westphalian	9
Bedlington	tholeiite dyke	10	5	5	0.50	0.50	1.00	0.70	0.70	0.83	Tertiary	Westphalian	9
USA													
Colorado	lamprophyre dyke	8	7.3	7.3	0.91	0.91	0.90	0.86	0.86	1.00	Tertiary	Cretaceous	11
Colorado	lamprophyre dyke (S. Side)	12.1	17.7	9.9	1.46	0.82	1.08	1.25	1.00	0.40	Tertiary	Cretaceous	12
Colorado	minette dyke	34	52	34	1.53	1.00	1.53	1.72	1.53	0.64	Tertiary	Cretaceous	12
Colorado	dyke	4.27	3.12	1.94	0.73	0.45	0.63	0.49	0.29	0.46	Tertiary	Cretaceous	13
California	dyke	12.14	26.4	7.55	2.17	0.62	1.08	1.42	0.88	0.33	-	-	14
Montana	dyke	30.18	15.09	7.03	0.50	0.23	1.48	1.18	0.85	0.55	-	-	14
Texas	sill	673	2464	NDP	3.66	NDP	2.83	3.39	NDP	1.50	-	-	15
USSR Tungusk Basin													
#1	dyke	8.86	9.83	9.83	1.11	1.11	0.95	0.99	0.99	0.66	-	-	14
#2	dyke	8.86	10.63	7.68	1.20	0.87	0.95	1.03	0.89	0.66	-	-	14
#4	dyke	5.91	9.26	NDP	1.57	NDP	0.77	0.97	NDP	1.61	-	-	14
#5	dyke	5.91	8.07	NDP	1.37	NDP	0.77	0.91	NDP	1.50	-	-	14
#6	dyke	21.33	13.25	NDP	0.62	NDP	1.33	1.12	NDP	1.88	-	-	14

Table 5.1 (cont.).

Locality	Intrusion Type	Intrusion Thickness T (ft)	Aureole Thickness D (ft)	Distance to 1%VR D1%VR (ft)	$\frac{D}{T}$	$\frac{D1\%VR}{T}$	Log T	Log D	Log D1% VR	Estimated Background Rank	Age of Intrusion	Age of Intruded Strata[a]	Source of Data[b]
AUSTRALIA													
Queensland	andesitic basalt dyke	8.9	6.8	NDP	0.76	NDP	0.95	0.83	NDP	1.35	Tertiary	Permian	16
Queensland	alkaline-dolerite dyke	282	197	157	0.70	0.56	2.45	2.29	2.20	0.30	Tertiary	Tertiary	17
INDIA													
Ranigunj	peridotite dyke	4.5	3	2.5	0.67	0.56	0.65	0.48	0.40	0.86	Triassic-Jurassic	Permian	18
Ranigunj	peridotite dyke	4.5	4	NDP	0.89	NDP	0.65	0.60	NDP	1.25	Triassic-Jurassic	Permian	19
CAPE VERDE	dolerite sill	49.2	30	7	0.61	0.14	1.69	1.48	0.85	0.35	Miocene	Cretaceous	20,21
GREENLAND	basalt dyke	14.8	19.7	8.20	1.33	0.55	1.17	1.29	0.91	0.39	-	Jurassic	22
GERMANY	dyke	2.46	1.42	NDP	0.58	NDP	0.39	0.15	NDP	1.50	-	-	14
IRELAND													
W. Approaches Basin (B)	olivine-gabbro sill	131	738	656	5.63	5.01	2.12	2.87	2.82	0.96	Jurassic	Jurassic	23

* Maximum possible aureole thickness

a LCM - Lower Coal Measures, ULG - Upper Limestone Group, LCG - Limestone Coal Group, CSM - Calciferous Sandstone Measures.

b 1. Raymond, 1983; 2. Raymond this thesis; 3. Buxton, 1987 4. Margoudis, 1985; 5. Creaney, 1975; 6. Creaney, 1980; 7. Ridd *et al.*, 1970; 8. Jones and Creaney, 1977; 9. Aganoglu, 1972; 10. Pearson, 1988; 11. Crelling and Dutcher, 1968; 12. Bostick and Pawlewicz, 1984; 13. Clayton and Bostick, 1986; 14. Bostick, 1979; 15. Dow, 1977; 16. Khorasani *et al.*, 1989; 17. Hutton and Henstridge, 1985; 18. Chatterjee *et al.*, 1964; 19. Ghosh, 1967; 20. Peters *et al.*, 1978; 21. Simoneit *et al.*, 1981; 22. Perregaard and Schiener, 1979; 23. Jones, J.M. unpublished data.

(U) = Upper Leaf (L) = Lower Leaf

(A) = Above Sill (B) = Below Sill

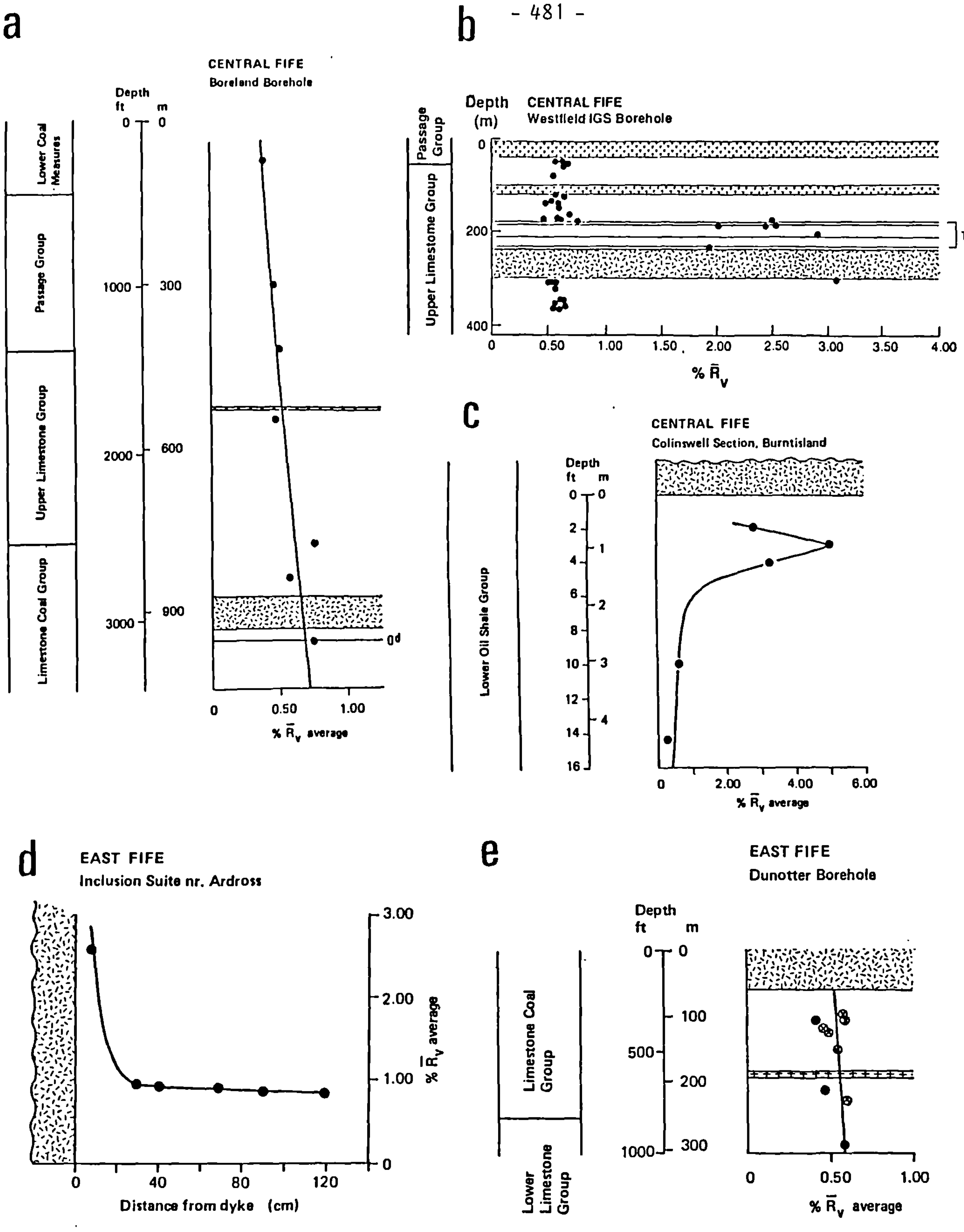


Fig.5.17 Vitrinite-reflectance variation in boreholes and field sections penetrated by alkaline-dolerite intrusions.

● Reflectances on vitrinites

⊗ Reflectances from carbon contents

▨ Teschenite sill

⊞ Quartz-dolerite sill (Dalmahoy type)

⁘ Olivine-dolerite sill

O^d Olivine-dolerite sill

⁙ Lavas

is believed to be *c.*20m (M.A.E.Browne *personal communication*) whilst the olivine-dolerite dyke cutting the Ardross neck is *c.*2m thick (locality d of Francis and Hopgood 1970). The aureole around the latter intrusion was established from reflectance measurements performed on clasts lying within tuffisite which had been emplaced up the dyke wall. The encircled crosses in the Dunotter borehole plot represent reflectance values which have been calculated from published volatile-matter yields of the coals (Forsyth and Chisholm 1968). The considerable scatter of regional reflectance values in the Westfield borehole (Fig.5.17b) is probably due to the incorporation of liptinitic matter in the vitrinites of the sediments, giving them an inherent heterogeneity, an effect particularly pronounced in the vitrinites of the Westfield Basin (see Section 4.2.2.1).

Although sills of considerable thickness are present in the Boreland (Fig.5.17a), Dunotter (Fig.5.17e) and Westfield (Fig.5.17b) boreholes, there is no indication that the heat from these intrusions has affected the optical properties of vitrinites (or other macerals) even relatively close to the intrusions. Only near to the sediment-intrusion contacts is the reflectance of vitrinites raised to a level well above the background reflectance trend. In the Dunotter borehole, a feature to note, which will be referred to later, is the presence of a thin tholeiitic sill in the succession around which no distinct thermal aureole has apparently developed.

Estimating the size of aureoles associated with alkaline dolerites is less easy than for quartz dolerites. This is because the narrowness of the former aureoles means that it is rare in borehole samples to find a sufficient number of closely spaced samples sufficiently close to the intrusions to allow precise definition of an aureole width. The aureoles have therefore been estimated from the intrusion margins to the nearest reflectance measurement above or below the intrusion depending upon sample availability. This procedure yields a maximum possible aureole width around alkaline intrusions. Despite this exaggeration, the relationships examined have not been invalidated. From Table 5.1 it is apparent that the aureole width associated with the alkaline-dolerite intrusions in the eastern and central Midland Valley is always less than the intrusion width (<40% of the intrusion width for the sample suites studied).

In seeking an explanation for the marked contrast in the extent of aureole development around alkaline dolerites and quartz dolerites in the Midland Valley, it is necessary to evaluate the different factors that are likely to influence the properties of organic matter when exposed to igneous activity.

Intrusion Temperatures

Although the temperature differences between acid and basic magmas are of the order *c.*400°-500°C, and as such might be expected to produce different aureole sizes in the sediment sequences into which they intrude, temperature variation within the magmas giving rise to the different intrusion types in the Midland Valley are not likely to account for the marked contrast between the aureoles seen in Figs 5.16 and 5.17. Both sill types (and the dyke near Ardross) originate from basic magmas. Despite the compositional differences between tholeiitic and alkaline intrusions, the latter including olivine dolerites, teschenites, essexites and picrites, these differences are hardly likely to be significant in terms of intrusion temperature. All the basic magmas were almost certainly intruded into the sediments at *c.*1000°C or higher (eg. Delaney, 1988). Any temperature differences that might have existed are unlikely to be sufficient to explain the degree of contrast between the sizes of aureoles of tholeiitic and alkaline-dolerite intrusions. Furthermore, if minor temperature variations were important, the higher temperatures associated with the more basic alkaline-dolerite intrusions would be expected to produce larger aureoles than the tholeiitic magmas which is clearly not the case.

Emplacement Time

The time taken for the emplacement of the magmas also seems to be an improbable explanation for the contrasting aureole behaviour. Because of their similar intrusion temperatures, the fluidities of the two magma types were also probably similar. Inorganic geochemical data indicate that the tholeiitic intrusions were emplaced relatively quickly and in substantial volume (Macdonald *et al.*1981). The alkaline intrusions might have been emplaced more rapidly, were the magma of higher fluidity (at a higher temperature), but if so, this would not have led to the observed gradient patterns. Although there may have been variations in the flow time of the magmas and in their rates of cooling, these influences are more likely to have produced differences of degree rather than the radical contrasts observed in the thermal aureoles.

Magma Volume

Magma volumes, represented by sill thicknesses and their areal extents, offer no help in finding an explanation: there is virtually no aureole surrounding relatively thick alkaline intrusions while thin tholeiites can display significant aureoles (Ridd *et al.* 1970).

Physical Condition of Coals and Sediments at the Time of Intrusion

Based on the known compositions and characteristics of the magmas, the prediction would be that intrusions of similar scale, forming from these broadly similar magma types, would produce reflectance aureoles of virtually the same extent when they invaded sedimentary successions of comparable degrees of lithification and organic maturity. That this expectation is not satisfied suggests that it is variation in the last-named parameters *viz.* differing physical conditions of the coals and sediments at the time of intrusion which is the most likely cause of the contrasting reflectances patterns. Justifying this suggestion requires consideration of both the timing and mechanism of sill emplacement.

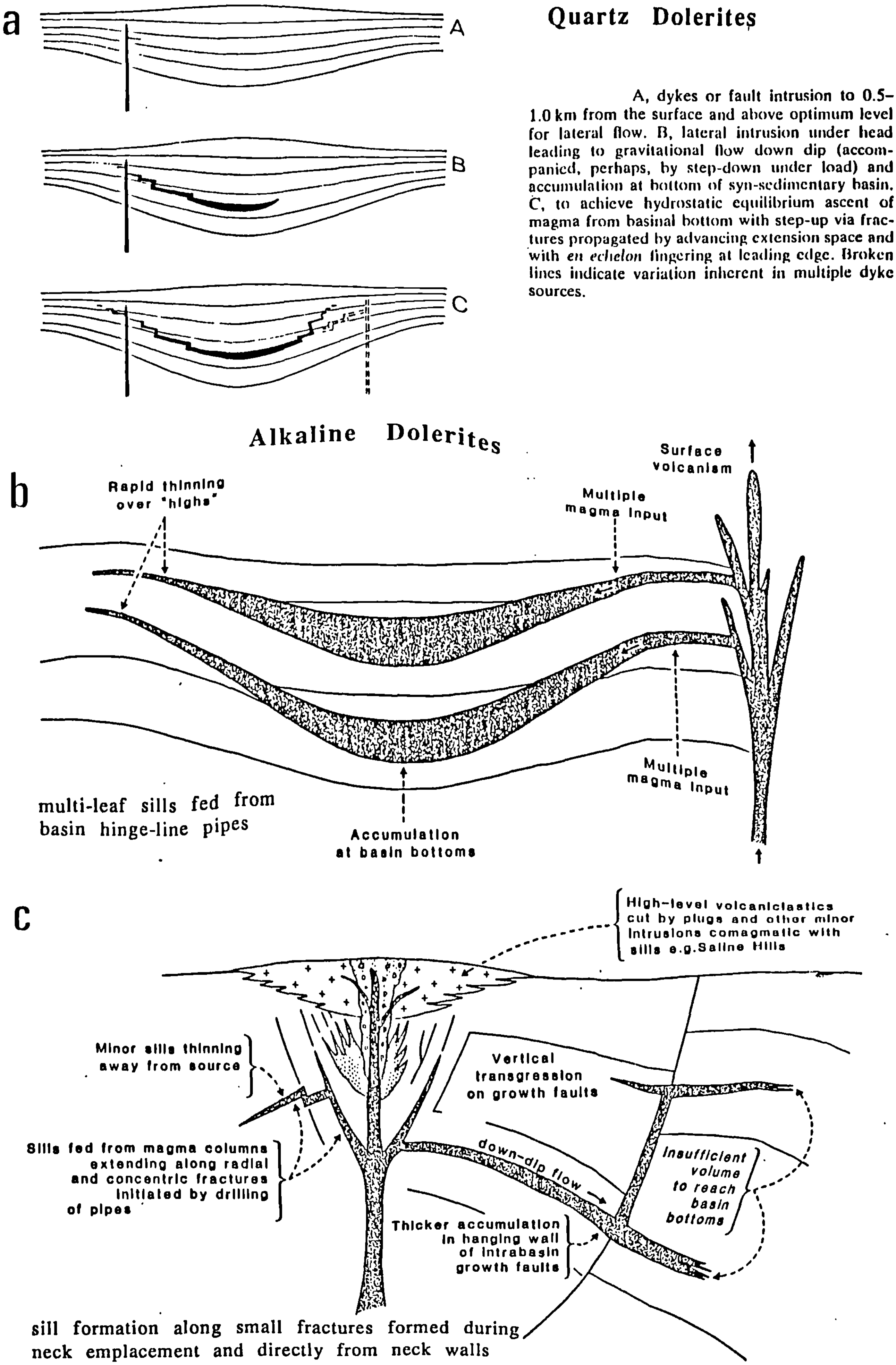
Evidence is strong that the tholeiitic and alkaline intrusions belong to separate magmatic events. Radiometric age determinations on tholeiitic intrusions comprising the Midland Valley Sill yield ages of *c.*295Ma (Fitch *et al.* 1970), i.e. an early Permian age on the revised time-scale of Lippolt *et al.* (1984). In contrast, the alkaline intrusions of the eastern and central Midland Valley gave a range of radiometric dates, based on the potassium-argon method. Many of these dates are regarded as artificially low due to argon loss. Thus, the age of the olivine-dolerite sill complex in east Fife probably lies (at least) at the older end (316Ma) of the 304±12Ma range cited by Forsyth and Rundle (1978). Such an age is indicative of emplacement during Namurian times. The alkaline dolerites of central and west Fife are not fresh enough to lend themselves to radiometric age-dating, but the petrochemical and volcanic stratigraphical considerations of Francis and Walker (1987) indicate that intrusion of the dolerites (mainly teschenites in this area) was related to eruptive episodes spanning upper Viséan to mid-Carboniferous time, but probably no later than Namurian time (Upper Limestone Group). Most of the west Fife alkaline dolerites have been emplaced in Namurian strata. Some of the alkaline dolerites of Fife and the Lothians lie within the Calciferous Sandstone Measures and are thought to belong to a much earlier intrusive phase, but, like those of Fife, are thought to be related to contemporaneous volcanism (de Souza 1979).

A mechanism for the emplacement of tholeiitic sills, particularly those of the Midland Valley of Scotland and northern England, has been proposed by Francis (1982). Dykes and/or fault intrusions are believed to have penetrated to within *c.*0.5-1.0km of the sediment surface, below which lateral intrusion from the dyke feeders occurred under a head of pressure causing the lateral spread of magma down-dip along bedding planes under gravitational flow into synsedimentary basins. After accumulating at the basin bottoms, the magma would have been driven up-dip until it reached levels corresponding to those of the feeders. That the dykes did not pierce surface sediments is indicated by the absence of any known association of the quartz-dolerite intrusions with extrusive igneous activity. The pressure of the overlying sediment column would have prevented magma from water in sill

reaching the surface. To meet the requirement of having sufficient water in the sediments for steam to form before the advancing magma front, to create space and so reduce resistance to intrusion, Francis has advocated that sill emplacement occurs in unlithified sediments. A diagrammatic representation of the model for tholeiite emplacement is shown in Fig.5.18a.

Optical studies on organic matter in boreholes sequences from the areas discussed by Francis (1982) indicate that some modification of his proposed mechanism is required to explain the fact that at least some of the vitrinites in the coals and sediments were of medium-volatile bituminous rank before sill emplacement in early Permian times (Ridd *et al.* 1970; Jones and Creaney 1977; Raymond 1983). The attainment of this level of regional coalification is implied by the occurrence of granular mosaic textures in vitrinites lying within the thermal auroles of many of the tholeiitic sills. To develop such textures, the molecular structure of the vitrinite must first have been altered to that corresponding to a relatively high level of coalification (caking/coking rank, with reflectances encompassing the range $\%R_o \approx 0.8$-1.5) by the regional geothermal gradient *prior* to sill emplacement. When the instrusions were emplaced, the vitrinites essentially underwent carbonisation (see Section 2.2.5.2). In previous studies, granular mosaics have been identified in the Rashiehill borehole (Raymond 1983; Raymond and Murchison 1989) and in the Salsburgh borehole (Padley 1988), both in the Central Coalfield, whilst the present study has revealed the presence of mosaiced vitrinite in the Inch of Ferryton, Righead and Gartarry Toll boreholes (west Fife), as well as in the Limestone Coal Group sediments of the Castlerankine Burn field section.

Where possible, projection of the background reflectance gradients to the level of the tholeiite intrusion in the above sequences gives an indication of the background rank at the time of emplacement. The reflectance values so derived are consistent with the achievement of at least a caking-coal rank prior to intrusion. The immediate implication of the above observations is that the sediments in the successions were lithified before invasion of the magma. Although mosaics were not detected within the aureoles of the Midland Valley Sill in the Fife-Midlothian Basin, the invaded sediments are still inferred to have been lithified by Permian times. This likelihood derives from the calculated background rank being of the order $\%R_o \approx 0.60$-0.70 in the intruded sequences, a level of coalification not typically regarded as being conducive to mosaic development. The attainment of even this relatively low level of organic metamorphism implies sediment compaction, with a concomitant reduction in porosity and removal of substantial quantities of water from the sediments and organic matter. One of the



Quartz Dolerites

A, dykes or fault intrusion to 0.5–1.0 km from the surface and above optimum level for lateral flow. B, lateral intrusion under head leading to gravitational flow down dip (accompanied, perhaps, by step-down under load) and accumulation at bottom of syn-sedimentary basin. C, to achieve hydrostatic equilibrium ascent of magma from basinal bottom with step-up via fractures propagated by advancing extension space and with *en echelon* fingering at leading edge. Broken lines indicate variation inherent in multiple dyke sources.

Fig.5.18 Models for the emplacement of quartz-dolerite and alkaline-dolerite sills. a from Francis 1982; b from Francis and Walker 1987.

features widely recognised in the early stages of maturation of peats and coals is the loss of large amounts of moisture through compaction processes. Further evidence of sediment compaction prior to tholeiitic sill emplacement comes from the sharp contacts observed between the sills and their associated sediments, both in the north of England and in the Midland Valley.

More recently, the mechanism proposed by Francis (1982) has been modified to account for the emplacement of the alkaline-dolerite sills of Fife (Francis and Walker 1987). Again, the down-dip flow of magma is an integral part of the model, but instead of the magma reaching sill-intrusion level through dyke feeders, it is suggested as being intruded through volcanic pipes which were drilled into wet, unconsolidated basinal Namurian sediments. Two possible scenarios for such a model are shown in Figs 5.18b and c. Walker and Francis (1987) describe an instance of just such an emplacement of an olivine-dolerite sill in Fife, in which the explosive interaction between magma and heavily water-laden coal-bearing sediments is invoked to explain the formation of coal-bearing tuffisites and heavily fragmented coal near to the sill margins. Palinspastic reconstructions indicate that sill intrusion occurred under a thin (<500m) sedimentary cover which, in conjunction with the presence of well-preserved botanical structures in the coals, suggests that the coals were at the lignite stage at the time of magma invasion and would therefore have had a high water content.

The complex nature of the sill-sediment boundary is illustrated by the obscuring of original sedimentary structures and the occurrence of veins of reconstituted sediment cutting non-reconstituted sediment, both factors indicative of partial mixing and homogenisation. Microfolding and crumpling of sediments is suggestive of soft-sediment deformation. The induration of invaded sediments, the incorporation of sediment blebs into igneous material, the occurrence of igneous clasts in surrounding sediment and the fingering or lobing of igneous material into the invaded sediment provide further evidence for the complex boundary relationships associated with teschenitic intrusions in Fife, but are also observations that have been made in much earlier field studies of alkaline-dolerite intrusions (Howell and Geikie 1860; Geikie 1879; Peach *et al.* 1910; Bailey 1923). The intimate textural relationships between the alkaline dolerites and the invaded sediments clearly contrast with the sharp junctions observed in the tholeiites.

The protrusion "in tongues and irregular projections" of country rocks into volcanic necks and the frequently ill-defined boundaries between the neck and the surrounding rocks have been noted in the east Fife necks (Geikie 1879) whose emplacement, akin to the alkaline-dolerite intrusions, relied heavily on the presence of abundant water. The occurrence of shale clasts was noted in two

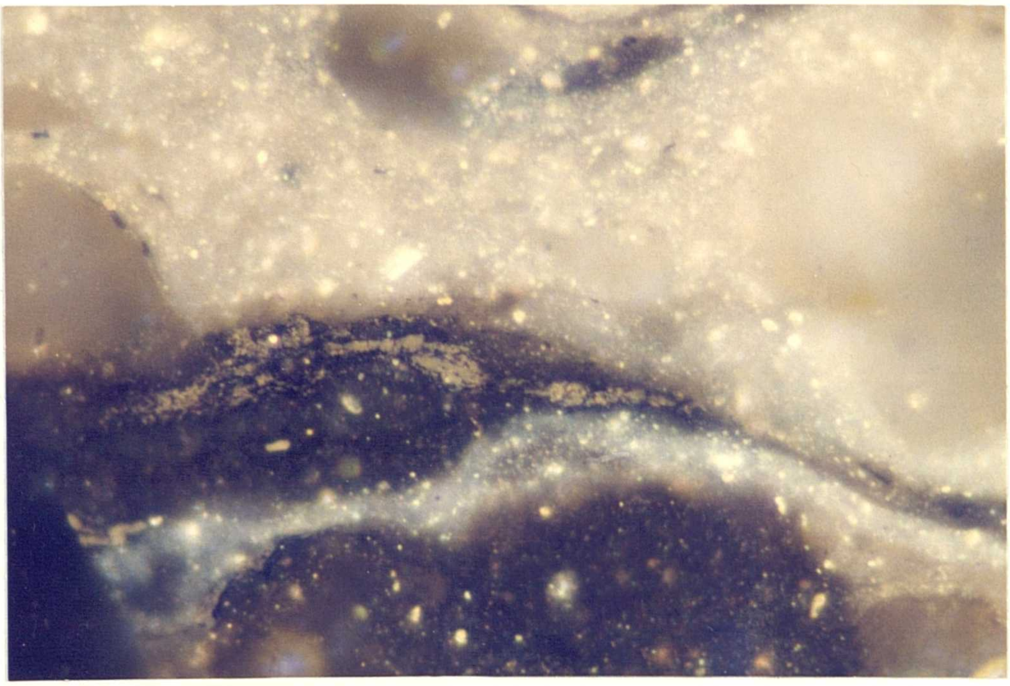


Plate 5.8 Slivers of high-rank sediment (dark brown matrix) incorporated in lower-rank sediment (white matrix, low-reflecting phytoclast at top centre): reflected light, oil immersion, plane-polarised light.

Westfield IGS borehole; sample W36.

x750

of the teschenite sills in the Westfield borehole examined in the current project, and the intimate mixing of slivers and clasts of high-rank carbonaceous sediments with low-rank sediments was noted on a microscopical level in some shales (e.g. Plate 5.8). This observation, and also the identification in this study of igneous fragments in some of the east Fife sedimentary vent clasts, further strengthens the view that the Namurian sediments in the Westfield Basin at the time of teschenite intrusion were in the same state as many of those in east Fife at the time of extrusive igneous activity *viz.* unlithified and water-laden.

Two other features which are apparent in successions invaded by alkaline-dolerite sills, and which were also recorded in association with the east Fife volcanic necks, are the marked induration of the intruded sediments and organic matter by calcite (Geikie 1879; Bailey 1923 ; Day 1923; Walker and Francis 1987) and the apparent absence of country-rock baking (Peach *et al.* 1910; Carruthers *et al.* 1912; Day 1928). The latter point stems from field observations and clearly corroborates the very limited aureole development around alkaline-dolerite intrusions that has been established microscopically from the present study. As referred to previously, calcitisation is particularly prevalent in vent clasts which are thought to have been immature at the time of incorporation. Abundant calcitisation associated with the alkaline dolerites is therefore consistent with the low degree of maturation and high water content of the sediments at the time of intrusion.

An additional relevant point relates to the formation of white trap which itself is rich in calcite (Day 1923), This material forms at the contact zones of igneous bodies where it effectively represents a reaction rim formed by the interaction of hydrothermal fluids, carbonaceous matter and igneous rock. Although white traps occur at the margins of both alkaline dolerites and quartz dolerites, consideration of the available Midland Valley literature indicates that white trapping is most commonly associated with, and appears to be most extensively developed in, alkaline-dolerite intrusions. Indeed, Day (1923) has remarked that in the Linlithgow district "where quartz-dolerite intrusions came into contact with carbonaceous shales, the conversion of the dolerite into white trap is hardly perceptible". Inspection of numerous borehole lithology logs held within the BGS in Edinburgh also indicates that extensive white-trap formation, induration and the occurrence of irregular contacts has been most frequently recorded at sill margins which have, either at the time of drilling, or later, been identified as alkaline dolerites. Water is instrumental in the formation of white trap (Day 1923). The more extensive formation of this material around alkaline dolerites is therefore consistent with the inference that there was more water available for reaction in the sediments into which alkaline dolerites were intruded than was present in sediments invaded by tholeiitic magmas.

The important difference then, between the emplacement of the alkaline-dolerite sills and the tholeiitic sills is the condition of the sediments at the time of intrusion: during alkaline-dolerite magmatism, the sediments possessed (presumably) a higher porosity and almost certainly contained much greater volumes of water. Although the alkaline-dolerite sills in the current work all probably relate to an episode of mid-Carboniferous (Namurian) volcanism, the close spatial and petrochemical relationship between some of the olivine dolerites of the Lothians succession and volcanics thought to be contemporaneous with sedimentation suggests that these sills were also not much younger than the sediments into which they were intruded, i.e. they were unlithified and water laden. The small aureole around the dyke cutting the Ardross neck is probably a consequence of the intrusion being emplaced only a short time after neck emplacement in early Permian times. It seems feasible, therefore, that all alkaline-dolerite intrusions of the eastern and central Midland Valley, regardless of age, were intruded into sequences in which there was an abundant supply of water and in which the organic matter was of low rank.

In the case of the alkaline intrusions investigated, it seems that magma at a temperature of *c.*1000°C has been close to organic matter, yet has had relatively little effect upon it, indicating a pronounced temperature differential between the magma and wet sediment over a short vertical/lateral distance. Such rapid temperature drops at igneous-sediment contacts have previously been predicted in the heat-flow calculations of Lovering (1935) and Jaeger (1959, 1964). The temperature fall from the intrusion margins would have been very rapid, largely due to heat being absorbed by the vapourisation of pore water. With the large volumes of water in the unconsolidated sediments there would in any case be poor heat conduction from the magma, leaving the immature, dispersed organic matter and/or low-rank coals little affected or entirely unaltered.

The emplacement of magma into water-filled, unconsolidated sediments would seem to explain satisfactorily the reduced thermal aureoles in sequences invaded by alkaline dolerites, but does not readily account for the development of much wider aureoles around the tholeiitic sills. In the case of the tholeiites, the environment at the time of magma invasion was different. Not only had compaction of the sediment pile occurred, with the concomitant loss of water, but the organic matter of the coals and sediments had been exposed to a background thermal gradient for several million years (up to *c.*20my after the Namurian intrusions), so raising the rank of the vitrinites to at least high-volatile bituminous rank before intrusion occurred. Consequently, the general rank increase imposed by regional heat flow made the contained organic matter susceptible to further alteration by the rise of temperature due to tholeiitic intrusions. The transfer of heat through the sediments was therefore much more efficient in early Permian times, with the alteration of organic matter above and below the tholeiitic sills extending over much greater distances. Experimental results corroborate this explanation: thermal conductivity increases with decreasing sediment porosity and, furthermore, the conductivities of unconsolidated materials are lower than those of their consolidated counterparts (Woodside and Messmer 1961a,b).

In the light of the above interpretations, the lack of an extensive aureole around the tholeiitic sill in the Dunotter borehole (Fig.5.17e) would appear to be anomalous. Consideration of the radiometric age of the sill provides a solution. The rock was identified as a tholeiitic dolerite by Forsyth and Chisholm (1968), and to be similar in composition to the tholeiitic sills of the Dalmahoy type. These sills are unusual petrographically and chemically, and an early suggestion that they represent the intrusive equivalents of Lower Carboniferous volcanism in the Dalmahoy area (Campbell and Lunn 1927) has been substantiated by a radiometric date of 320±7Ma (de Souza 1979). The tholeiitic magma therefore invaded sediments that were similar to those intruded by the alkaline sills and thus were probably in an unconsolidated, water-saturated state, containing very low-rank organic matter that was hardly affected by the intrusion.

In the eastern and central Midland Valley, on the basis of the present data, it seems safe to predict that wherever an extensive reflectance aureole is observed, the succession will have been invaded by an early Permian tholeiitic sill, whether this is seen or not. Thus, in the successions of the Orchard Head, Kincardine Bridge and Blairmains boreholes (Fig.5.19) and the Gartarry Toll borehole (Fig.5.7e), in which no major sill is recorded, there must have been an invasion beyond total depth by an early Permian tholeiitic intrusion. Mining records indicate that the Midland Valley Sill underlies much of the Stirling-Clackmannan Basin, in which its transgressive nature is best displayed (e.g. Dinham and Haldane 1932). The sill mainly lies at the base of the Limestone Coal Group and in the Lower Limestone Group in this district. The marked thermal effects that the sill has had on organic matter in these strata is evident from the Inch of Ferryton borehole (Fig.5.16b) and the rank maps discussed later in Section 5.3.2.1.3.

Reflectance gradients for the Firth of Forth Tower No.1 (Fig.5.7c) and the Lochhead boreholes (Fig.5.19c) also suggest the influence of tholeiitic invasion at depths greater than total borehole depth. The patterns of reflectance have not been influenced by the earlier alkaline sills in these successions.

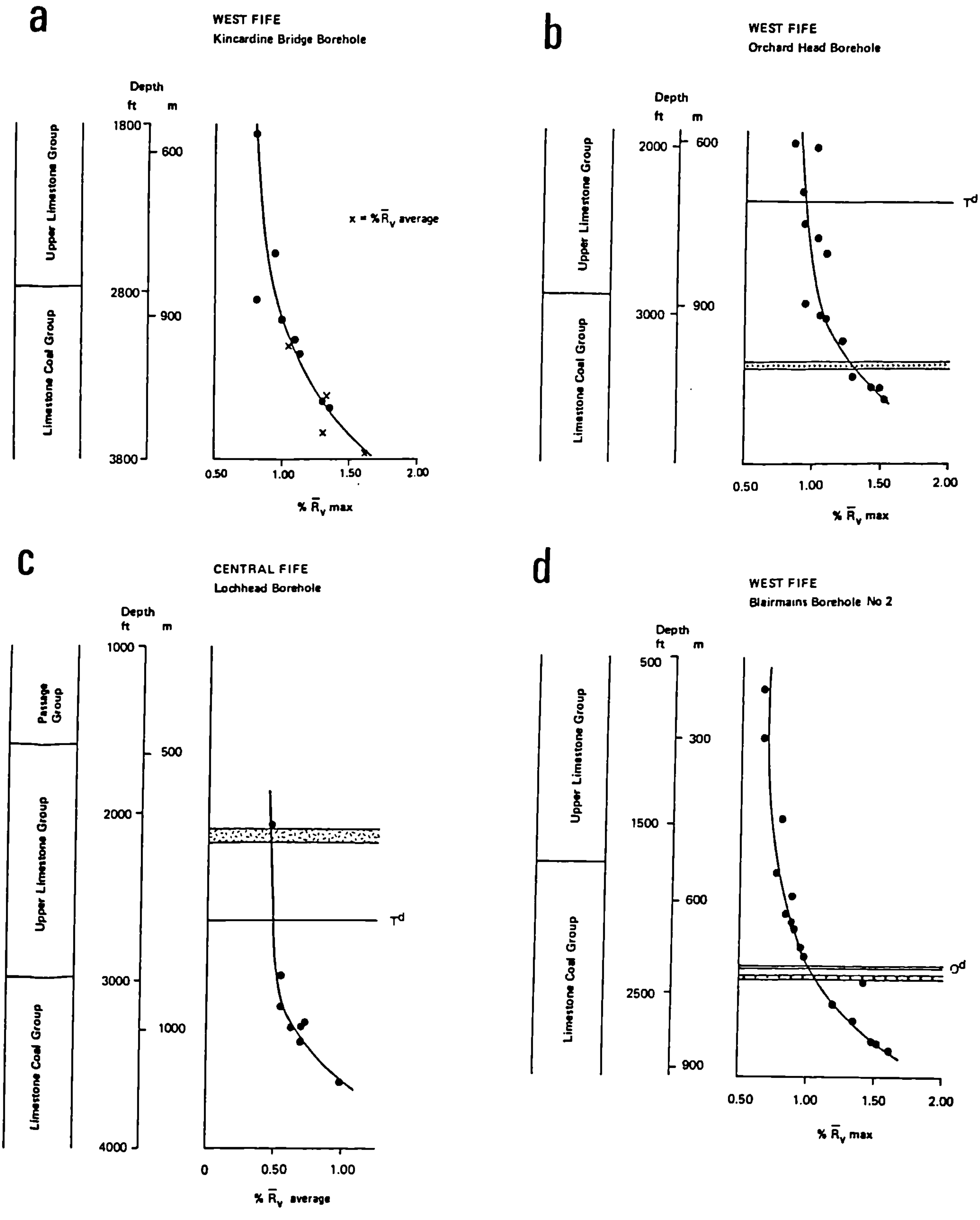


Fig.5.19 Vitrinite-reflectance variation in boreholes in which the quartz-dolerite Midland Valley Sill probably occurs beyond total borehole depth.

Observations by other workers support the view expressed above. The presence of immature and unaltered lipids close to a dolerite sill (*c.*30m thick) is reported in the protokerogen of unconsolidated sediments of the Guaymas Basin, but no acceptable explanation for the lack of organic alteration was proposed (Simoneit and Philp 1982; Simoneit *et al.* 1984). Petrographic analyses on samples forming part of the same DSDP study also reveal that, despite an exceptionally high background heat flow and close proximity to intrusives, the average huminite reflectance is only $\%R_o$=0.40 (Rullkötter *et al.* 1982). Einsele *et al.* (1980) also refer to "minor thermal decomposition of organic carbon" near sills in the same basin. The dolerites in the Guaymas Basin (*c.*3.5Ma) would appear to represent recent analogues of the Carboniferous alkaline-dolerite sills of the eastern and central Midland Valley. The large volume of water present in both the organic matter and the unconsolidated sediments must have been crucial in increasing the rate of cooling and impeding organic metamorphism.

Besides the deductions of the current project, there has only been one other instance of the variation in the pattern of reflectance aureoles being attributed to the water content of the sediments. Thus, Snyman and Barclay (1989) have compared the extensive alteration to a Colorado coal intruded by a thin lamprophyric sill with the narrow thermal aureoles surrounding many South African lignites intruded by thick dolerites. Their explanation agrees with the deductions drawn in the current work. They suggest that the wide aureoles caused by the lamprophyre was due to its intrusion into an essentially dry environment, but that much of the heat from the dolerites was absorbed in the heating and evaporation of large volumes of water in the lignites and associated sediments, so producing only thin aureoles.

For the situations discussed in this section, the pronounced contrast appears to be between invasion, by magmas of similar character, of unconsolidated wet sediments containing immature organic matter and of lithified sediments containing mature organic matter which is of bituminous rank. Gradations between these contrasting situations undoubtedly exist. Dow (1978) and Baker *et al.* (1978), for example, cite an instance of immature Upper Cretaceous shales intruded by a dolerite sill in which the extent of the reflectance aureole is approximately the same as the sill thickness. A more extended series of results confirming these observations is given by Simoneit *et al.* (1978, 1981). This case seems to represent an intermediate situation in which the sill intrudes sediments that are more consolidated than those in the recent Guaymas Basin, but are not sufficiently lithified to allow the rapid transfer of heat to develop more extensive aureoles in the contained organic matter, which presumably had also begun to mature due to the regional geothermal gradient.

5.3.2.1.2 Relationship between Intrusion Thickness, Aureole Thickness and Level of Organic Maturation.

The data presented above show that the extent of aureole development is strongly influenced by the levels of consolidation and water saturation of the invaded sediments and organic materials, both of which probably strongly influenced the rank level of the organic matter prior to intrusion. This section extends the above study by examining more closely the reflectance profiles on either side of intrusions to determine if there is any general relationship between intrusion thickness and aureole thickness on the one hand and the level of organic maturation and sediment compaction on the other at the time of magma emplacement. The study is initially confined to the analysis of tholeiitic and alkaline-dolerite intrusions in the eastern and central Midland Valley and is then expanded by adding comparable data from other provinces derived from available literature (see Table 5.1 for sources).

5.3.2.1.2.1 Eastern and Central Midland Valley

The simplest relationship to examine is that between intrusion thickness and aureole thickness. Before the relationship is discussed in detail, two points are worth mentioning. First, from Table 5.1, it is apparent that the reflectance aureoles extend to greater distances above sills than below. While sediment compaction and porosity were identified as important factors influencing aureole development, these parameters could not account for differential aureole formation. If they did, the increased compaction and presumably the decrease in porosity which would be expected with increasing depth would, on the basis of the arguments put forward above, lead to greater aureole development below the sills. What seems more reasonable is that larger aureoles above sills are a reflection of the better transfer of heat upward from the intrusions by volatiles emitted from the magma during solidification and/or by the heated pore waters of the intruded sediments. Such an explanation has previously been invoked to explain the wider aureoles above sills (Briggs 1935; Anderson 1963; Peters *et al.* 1978).

Second, differences in the background reflectance gradients are also apparent in some borehole sequences. Inspection of the profiles for the Milton of Balgonie and Inch of Ferryton holes (Figs 5.16a and b respectively) reveals that the joining of the regional reflectance gradients above and below the sills leads to a "kink" at the level of the sill. This phenomenon has also been observed in deep boreholes in northeast England (Ridd *et al.* 1970), although no explanation for its occurrence has been advanced. One possibility is that the sills may have acted as physical barriers to the upward migration of heated pore waters and/or volatiles that were present below the sill. Although somewhat speculative, the "trapping" and subsequent increase in a liquid/vapour envelope could have resulted in an increase in the background reflectance gradient below the sills. Slow lateral diffusion of the volatiles and hydrothermal fluids might also have resulted in the development of an overpressured zone, in which the regional geothermal gradient would have been enhanced, thus leading to a gradual increase in the background reflectance gradient. "Kinks" towards higher reflectance values have previously been reported in overpressured zones (e.g. Law *et al.* 1989; Cooper 1990), thus the development of overpressured zones in association with igneous activity may be a feasible explanation for the dog-leg gradients observed in some intruded sequences. That the kinks are not noted in all intruded sequences in the Midland Valley may reflect sampling deficiencies or vagaries in the physical characteristics of sediments at different localities. The trapping of fluids and volatiles by intrusive sheets and/or the formation of overpressured zones might also account for the failure of background reflectance profiles between the leaves of multiple intrusions to return to the levels predicted by the regional coalification level above the sills (see, for example, Righead; Fig.5.7f and the Harton borehole; Ridd *et al.* 1970). The "banking up" of conductively-transferred heat is not likely to have enhanced the background reflectance gradients between leaves or below sills because thermal-conductivity data (e.g. Lovering 1935) show that the thermal conductivities of igneous rocks are greater than those of sediments.

Plots of the thicknesses of intrusions and the aureoles associated with them are shown in Fig.5.20. Data relating to aureoles developed both above and below the sills are included. The alkaline dolerites are all teschenitic sills apart from one, the olivine-dolerite dyke cutting the Ardross neck. The conditions at the time of emplacement of this dyke are thought to have been similar to those envisaged for the teschenite sills, thus justifying its inclusion in the alkaline-dolerite data set.

Although there is a considerable scatter of points, a broad relationship of increasing aureole thickness with increasing intrusion thickness is observed for both the quartz dolerites and the alkaline dolerites (Fig.5.20a). The correlation coefficient (r) for the quartz-dolerites (Pearson product-moment coefficient) is not quite significant, but the coefficient for the alkaline dolerites is. The correlation becomes statistically significant within the quartz-dolerite set if the intrusions in the Fife-Midlothian Basin and Stirling-Clackmannan-Central Coalfield Basin are considered individually (Fig.5.20b). The highest degree of "fit" is achieved through considering the upper leaves of intrusions only (Fig.5.20c).

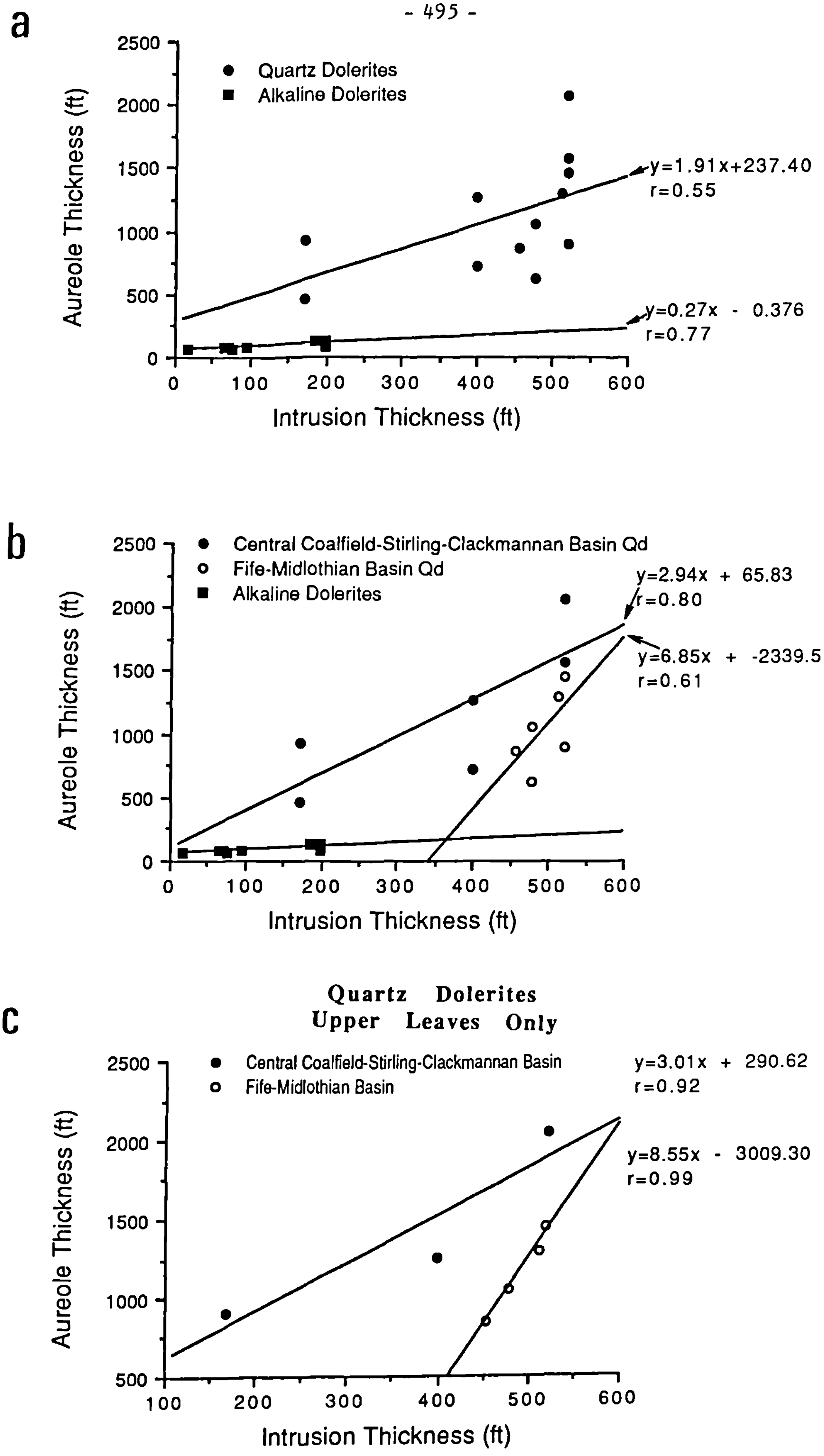


Fig.5.20 Plots showing the relationship between aureole thickness and intrusion thickness for intrusions in the eastern and central Midland Valley.

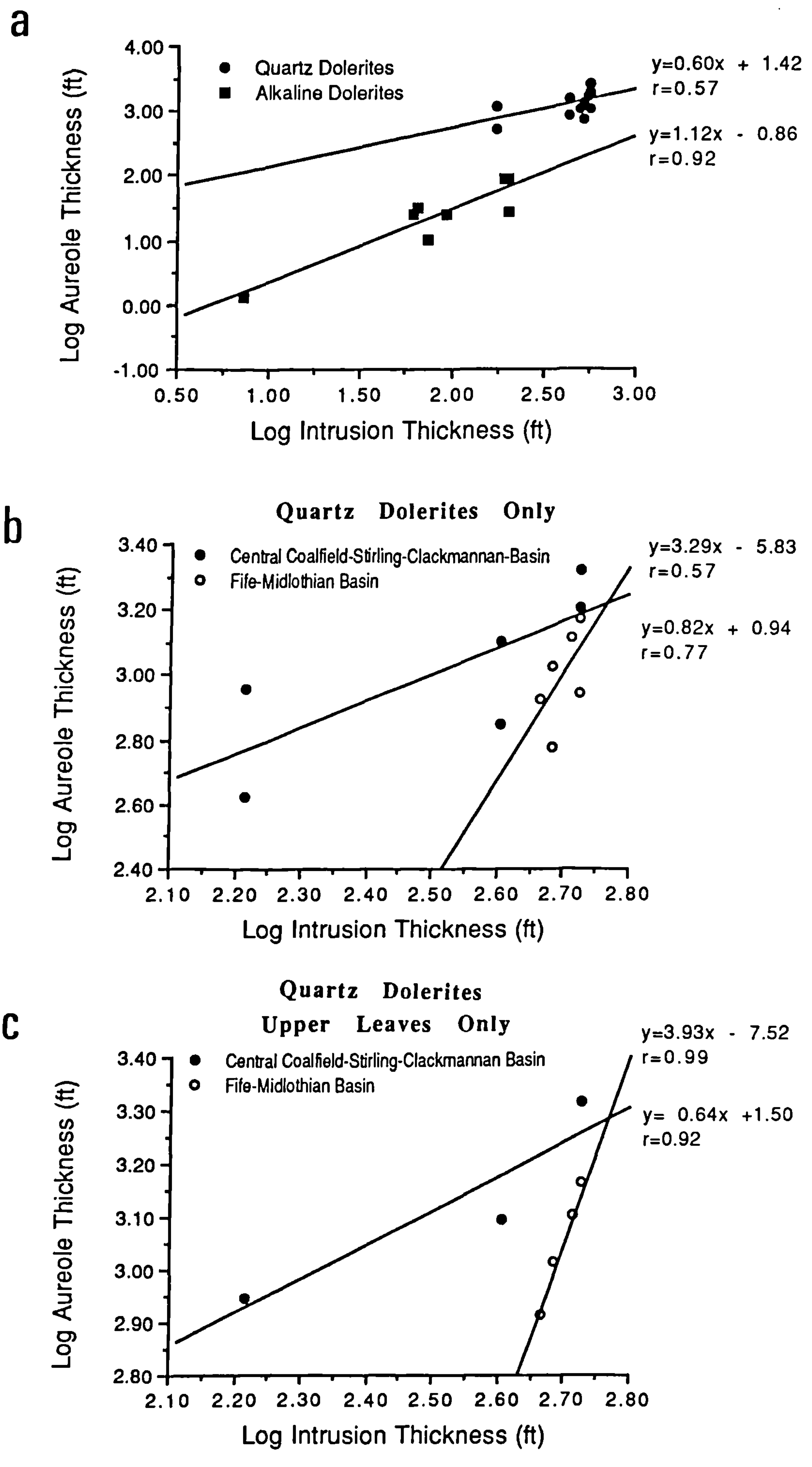


Fig.5.21 Log/log plots showing the relationship between aureole thickness and intrusion thickness for intrusions in the eastern and central Midland Valley.

The construction of log/log plots for the different sample suites (Fig.5.21) not only emphasises the difference in the degree of separation between the alkaline dolerites and quartz dolerites (Fig.5.21a; the former lie more than one standard error from the regression line based on tholeiites and an improved correlation is observed in both intrusion suites), but also accentuates the different trends which exist for quartz dolerites in different basins (Figs 5.21b,c). Although the data sets are individually small, the populations are nevertheless discrete.

From the foregoing section, the most obvious factor to examine when attempting an explanation for the different trends between aureole thickness and intrusion thickness for different groups of dolerites is the pre-existing level of maturity produced by the regional geothermal gradient that existed before the intrusions were emplaced. To relate these three parameters, the aureole width (D) and intrusion thickness (T) have been combined to give D/T, which has then been plotted against background maturity, represented by vitrinite reflectance (Fig.5.22). The method for calculating the background maturities was explained in the last section. Although rough and ready, it is the only method to obtain a representative pre-existing reflectance value. Implicit in the use of the parameter as a background maturity indicator is the assumption that the background rank increase has not occurred as a result of post-Carboniferous burial or igneous activity. Given that the Midland Valley Sill was, in all probability, the last thermal event to affect organic matter in the Carboniferous sequence in the eastern and central Midland Valley, the assumption seems reasonable.

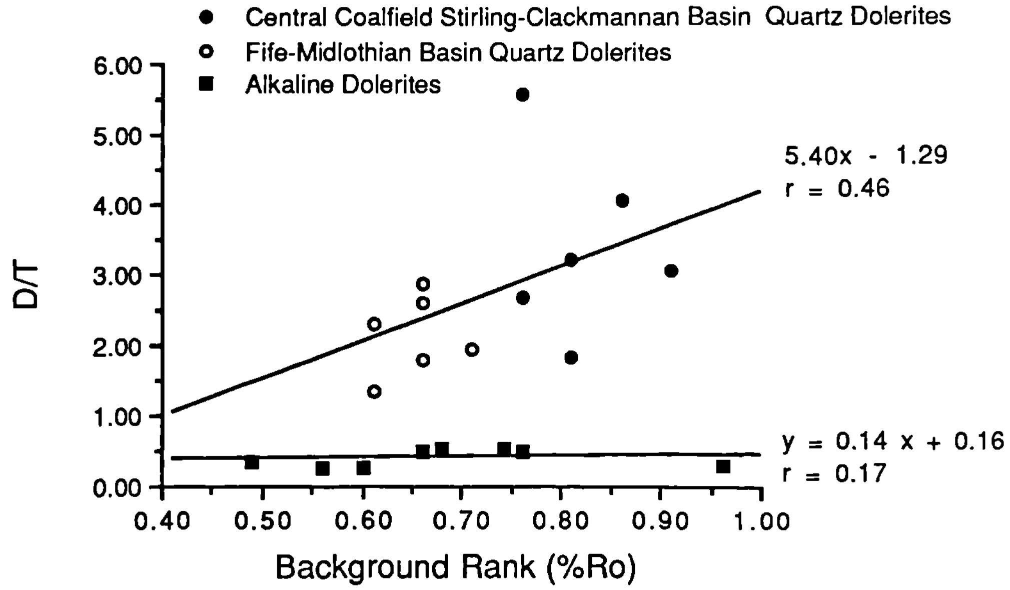


Fig.5.22 Relationship between background rank and the number of times aureole thickness exceeds intrusion thickness (D/T) for intrusions in the eastern and central Midland Valley.

There is a very poor correlation (r=0.17) between background rank related to the alkaline dolerites and the ratio D/T. The correlation between background rank for the quartz dolerites is substantially higher (r=0.46; statistically significant), and the value would be even higher (r=0.63) were it not for the single point lying far from the regression line which corresponds to the upper leaf of the Righead quartz-dolerite sill. The development of an aureole more than five times the thickness of a sill is anomalous in the Midland Valley, but is known from northern England, where D/T values exceeding this have been recorded from the upper leaves of multiple Whin Sill intrusions (Table 5.1; Ridd *et al.* 1970; Jones and Creaney 1977). Since the Midland Valley Sill is commonly >400ft thick in the Stirling-Clackmannan Basin, the anomalously thin (155ft) quartz dolerite in the Righead bore is suspected as being one leaf of a multiple intrusion (Francis *et al.* 1970). The petrological data therefore corroborate the geological evidence. Despite the anomalous point in Fig.5.22, the interesting feature is that there are again two distinct populations identifiable within the quartz dolerites (*cf.* Figs 5.20 and 5.21), one relating to the Fife-Midlothian Basin and immediately surrounding areas, the other to the Stirling-Clackmannan-Central Coalfield Basin.

The most plausible explanation for the differences brought out by Fig.5.22 lies in the background rank levels immediately before emplacement of the intrusions. The lack of correlation between D/T and background rank for the alkaline-dolerite plots indicates that any assumption that the background vitrinite-reflectance values currently associated with this group of alkaline-dolerite sills were approximately representative of sediment maturities at the time of sill emplacement is categorically incorrect. Vitrinite reflectances at the time of intrusion would be low, probably less than $\%R_o=0.30$, the value accepted as characteristic of humic matter at the peat stage of coalification. The imposition of the greater part of the background rank of the sediments and coals occurred after the emplacement of the alkaline-dolerite sills, i.e. from mid-Carboniferous times up to the end of the Carboniferous. By the time the early Permian quartz dolerites were intruded, organic matter in the Carboniferous succession had generally increased in maturity, but to a lesser degree in the Fife-Midlothian Basin than in the Stirling-Clackmannan-Central Coalfield Basin, so resulting in thinner thermal aureoles in the former area. The higher regional rank levels (for a given stratigraphic horizon) recorded in the latter basin complex were evident from the regional rank maps shown in Fig.5.2. As explained earlier (Section 5.2.1), the overall rank increase to the west is not thought to relate to depth of burial. Thus, the overriding factor governing the contrasting nature of the aureoles within the quartz-dolerite suite, as it was between the quartz dolerites and teschenites, was the maturity of the organic matter at the time of intrusion emplacement which, in turn, was controlled by the degree of compaction and water content of the sediments.

5.3.2.1.2.2 Other Provinces

The data presented above obviously constitute a relatively restricted data set. This section examines if the relationships established above can be applied to intrusions in other geological provinces from the UK and abroad. The Midland Valley samples are included for comparison in a data set comprising 67 determinations.

A plot of intrusion thickness *vs.* aureole thickness (Fig.5.23a) again shows an obvious correlation which is statistically significant ($r=0.83$). Fig.5.23b is an enlargement of the bottom left corner of Fig.5.23a. Greater degrees of fit are achieved through the log/normal (Fig.5.23c) and log/log (Fig.5.23d) relationships. The points for the north of England dolerites apparently follow different trends from those of the Midland Valley. The separation between the alkaline-dolerite intrusions of the Midland Valley and the majority of the remaining samples is obvious from all three plots. One of the "worldwide" intrusions follows the same trend as that of the Midland Valley alkaline dolerites, suggesting that, if the conclusions of the last section are valid, the nature of the intruded sediments and their contained organic matter at this locality (Stuart Oil Shale, Queensland) were similar to those of the Midland Valley alkaline dolerites. Examination of Table 5.1 does indeed suggest that similar intrusion conditions existed since the oil shales into which the geologically young dyke is intruded are immature ($\%R_o \approx 0.30$). Other "worldwide" samples lying just within the standard error envelope close to the Midland Valley alkaline dolerites are also inferred to have been intruded into immature sediments.

The relationship between background rank and the extent of aureole development (Fig.5.24) indicates that up to about $\%R_o=1.00$, there is a general increase in the D/T ratio after which a decrease is apparent (Fig.5.24a). The course of the envelope after *c.* $\%R_o=1.00$ is uncertain due to sampling deficiencies: a tail-off is suspected because the aureole widths associated with the upper leaves of the Harton and Whitley Bay boreholes are probably anomalously high because of the multiple nature of the intrusions. An additional possible source of error in Fig.5.24a is that the geothermal histories of the "worldwide" intrusions are not known to the writer. Thus the "background" reflectance values (Figs 5.24a,b) could have been imposed after igneous activity, as for the teschenite sills of the Midland Valley.

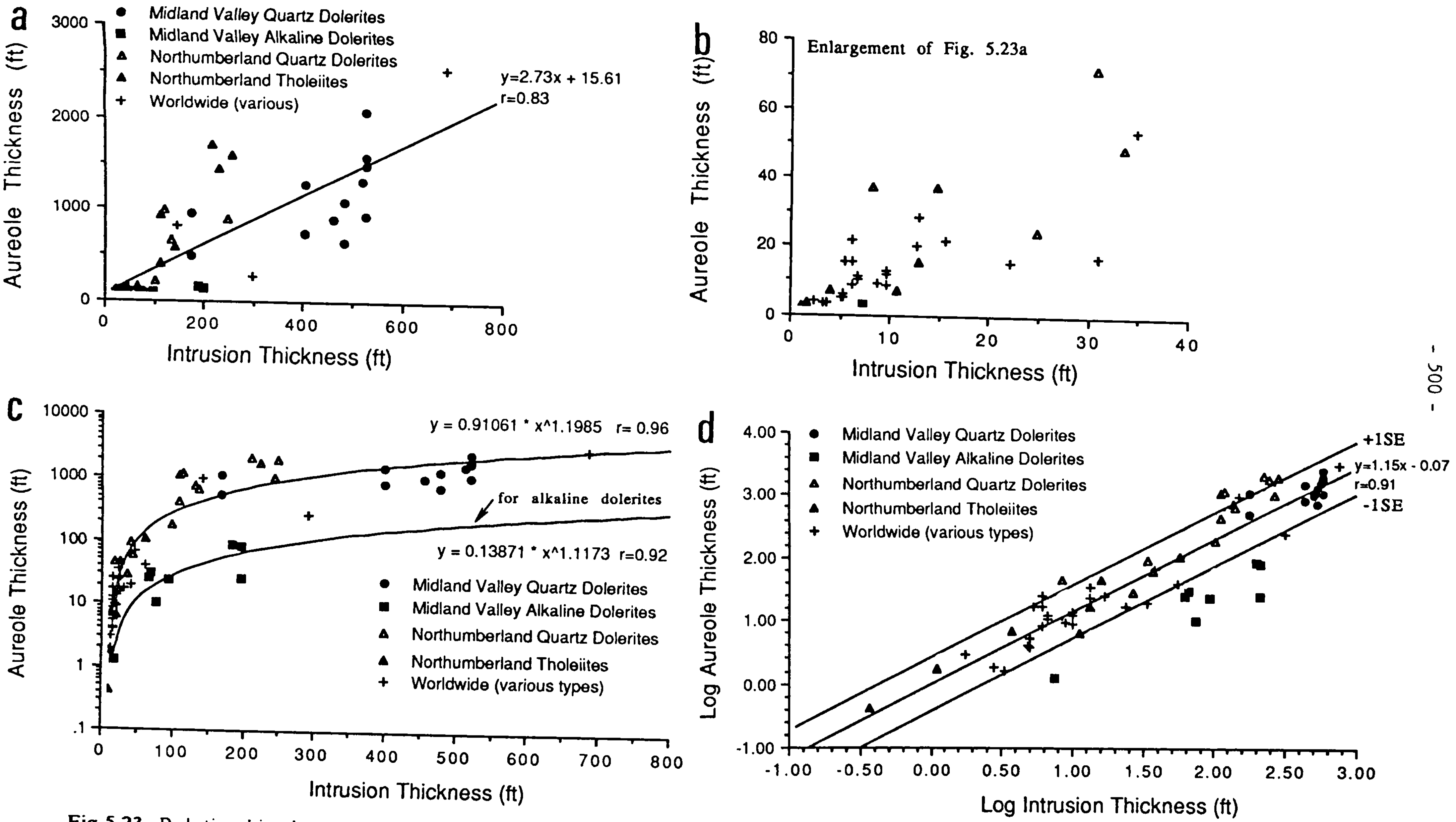


Fig.5.23 Relationships between aureole thickness and intrusion thickness for intrusions in the Midland Valley and worldwide.

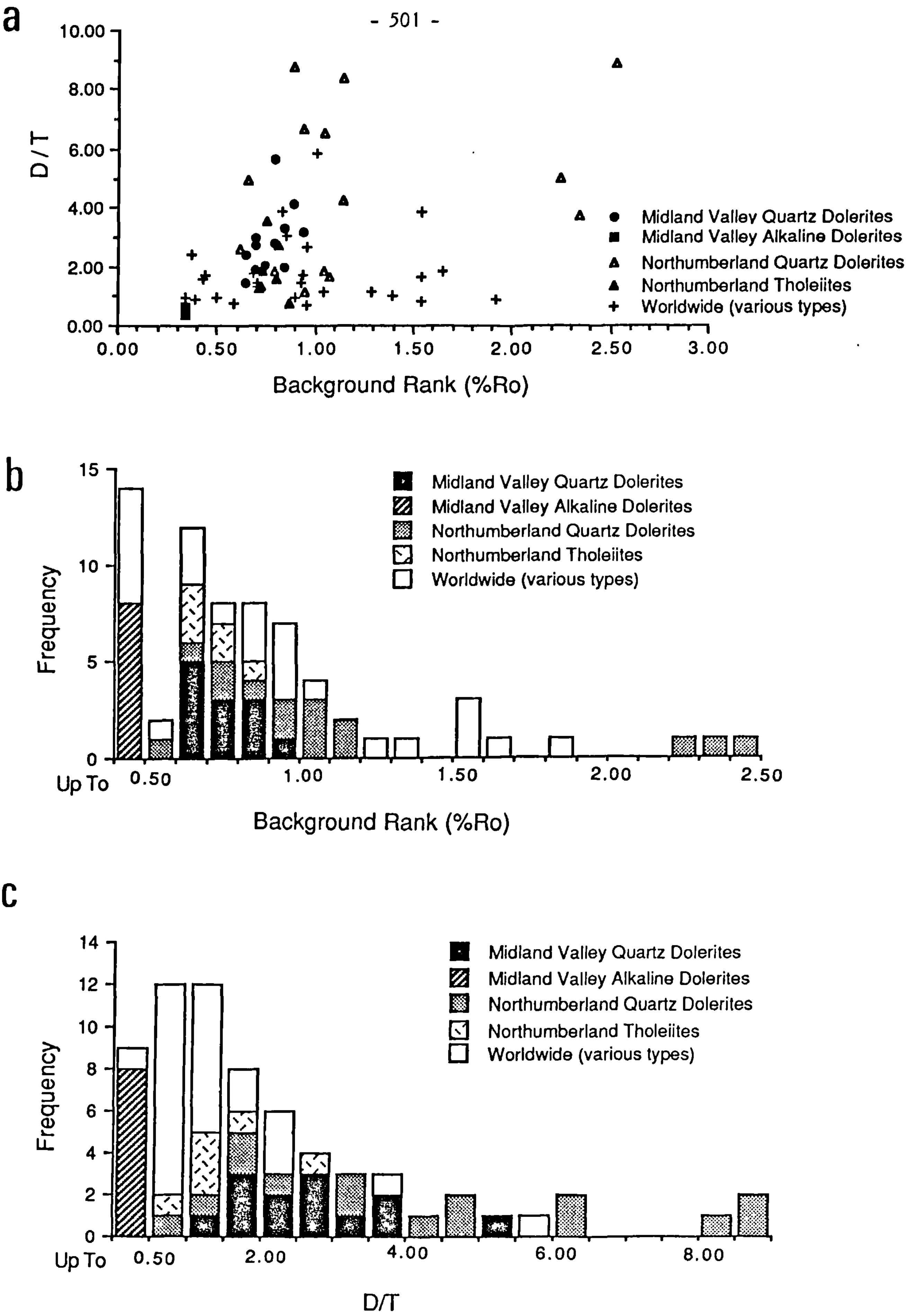


Fig.5.24 Relationships between background rank and the number of times aureole thickness exceeds intrusion thickness (D/T).

The long-standing recognition that igneous intrusions alter organic matter in proportion to the intrusion thickness has led to the formulation of several empirical "rules". These variously state that the distance over which the metamorphic effect of an intrusion is felt is equal to half of its thickness (Williams 1810; cited in Briggs 1935), is approximately equal to (cited in Blignaut 1952) or is roughly twice the intrusion thickness (Dow 1977). It is obvious from the Midland Valley data set and from the data of other provinces (Figs 5.24a,c) that the extent of aureole development is very variable, supporting the contention of Briggs (1935) that any given rule of thumb is likely to be "as unreliable as it is venerable". Despite the variations, analysis of the available data indicates that most aureoles extend from approximately half to twice the intrusion thickness, thus lying within the range of the "rules" established by earlier authors. The conclusion from Figs 5.24a-c is that large aureoles (more than one intrusion width) form in sediments whose ranks lie in or beyond the oil window (mainly the former), by which time the sediments are presumably sufficiently well compacted and dewatered to allow efficient heat transfer through the sediments either by the background geothermal gradient or by igneous intrusions.

The investigation of the relationship between intrusion thickness and aureole thickness can be extended to sequences in which neither the entire intrusion thickness nor the entire aureole thickness are visible. The relationships established above also hold if the aureole width is measured to where the vitrinite reflectance is %R_o=1.00, rather than to the point of inflection of the background reflectance gradient. The use of Fig.5.25 in conjunction with Fig.5.23d permits an assessment

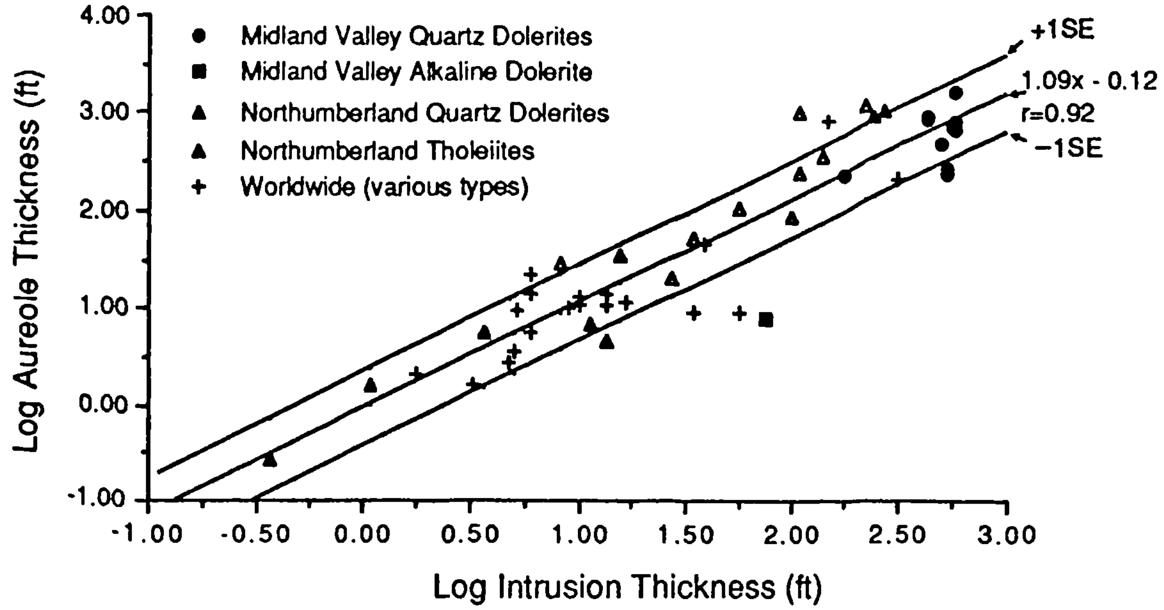


Fig.5.25 Relationship between intrusion thickness and aureole thickness, where aureole thickness is calculated as the distance to %R_o=1.00 (D1%VR in Table 5.1).

of intrusion thicknesses or aureole thicknesses in sequences where these may only be partially exposed because of erosion and/or lack of drill penetration. Similar plots could be constructed for different aureole-reflectance values. Given the different trends noted in different sets of data, the greatest accuracy is likely to be achieved if data calibration is performed on samples from the province under consideration.

5.3.2.1.3 Lateral Rank Variation throughout the Carboniferous

The preceding sections have revealed that the quartz-dolerite intrusions of the Midland Valley are the igneous materials that are most likely to result in the widespread alteration of organic matter in the province, although significant levels of organic metamorphism would also be expected in close proximity to alkaline dolerites and hot extrusive materials. Because of the pervasive nature of igneous activity in the Midland Valley Carboniferous (see Chapter 1), the effects that igneous materials have had on the organic maturation of the sediments in which they occur might be expected to be variable and widespread. This expectation is confirmed from inspection of the rank maps constructed for different stratigraphic levels in the Carboniferous. The maps are presented as pairs comprising raw reflectance data points and coloured, mapped data. Maps for the Passage Group and Calmy Blaes were shown in Fig.5.2, and some measured data for samples in the lowermost Calciferous Sandstone Measures (Inverclyde Group) were included in Fig.5.2. Petrological details of all the samples used to construct the rank maps are given in Appendix II.

The reflectance data of Fig.5.26 record the net level of organic maturation attained by rapid heating due to close contact with igneous materials and by slower heating induced by exposure to the background geothermal gradient. The main features of each rank-map pair are outlined below.

Queenslie Marine Band

Rank variation in the Queenslie Marine Band (Fig.5.26a,b) is very pronounced and is probably largely due to the occurrence of widespread igneous activity in Coal Measures times. Volcanic activity was particularly intense in the region offshore of central Fife. The development of a major eruptive centre in the Firth of Forth has been postulated on the basis of the discovery of thick lavas and tuffs in the Firth of Forth No.3 Tower Bore and also from the offshore thinning of coal seams (Ewing and Francis 1960; Francis and Ewing 1961). The Midland Valley Sill intersects Coal Measures strata offshore (Francis, Michael and Wellesley

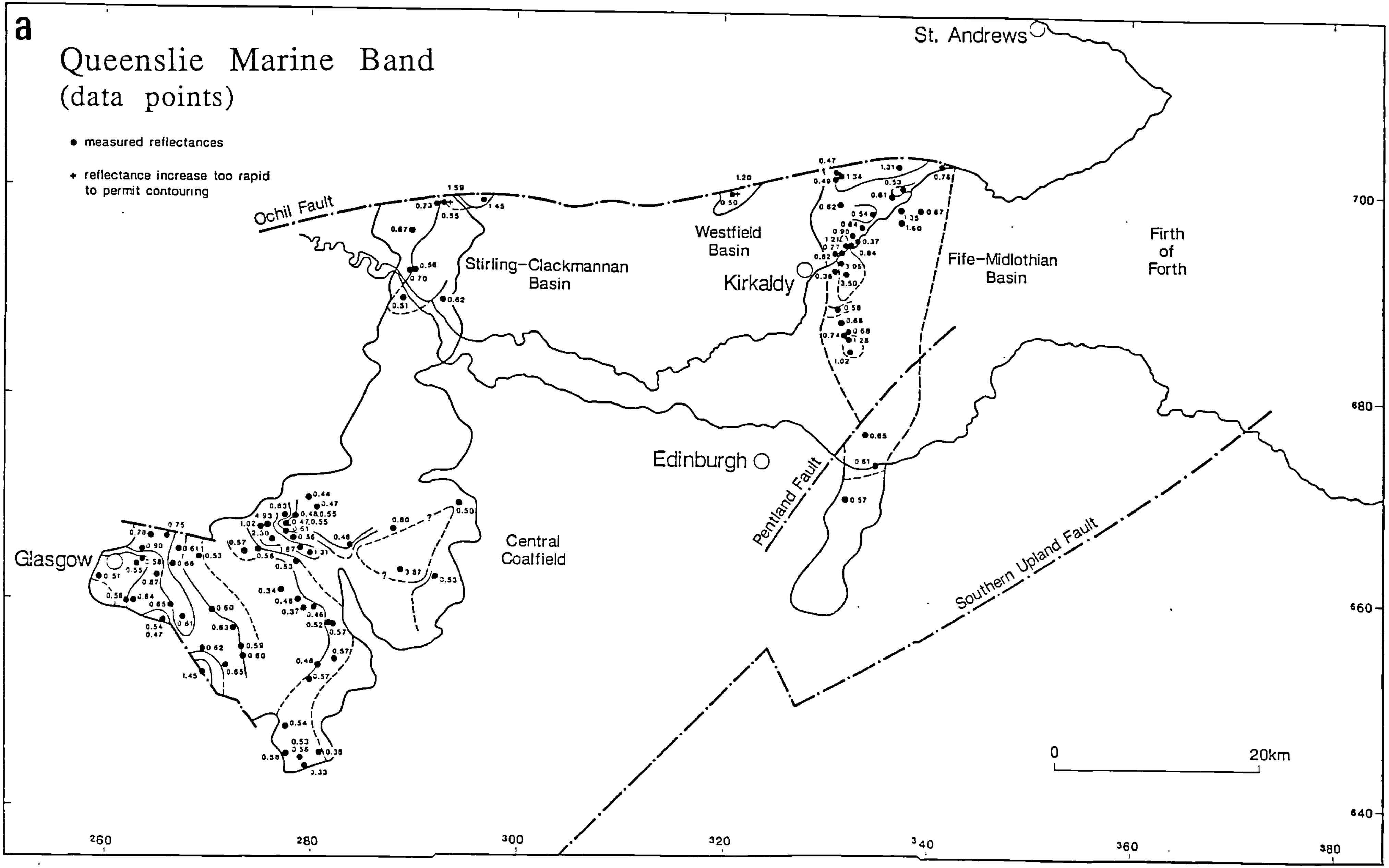
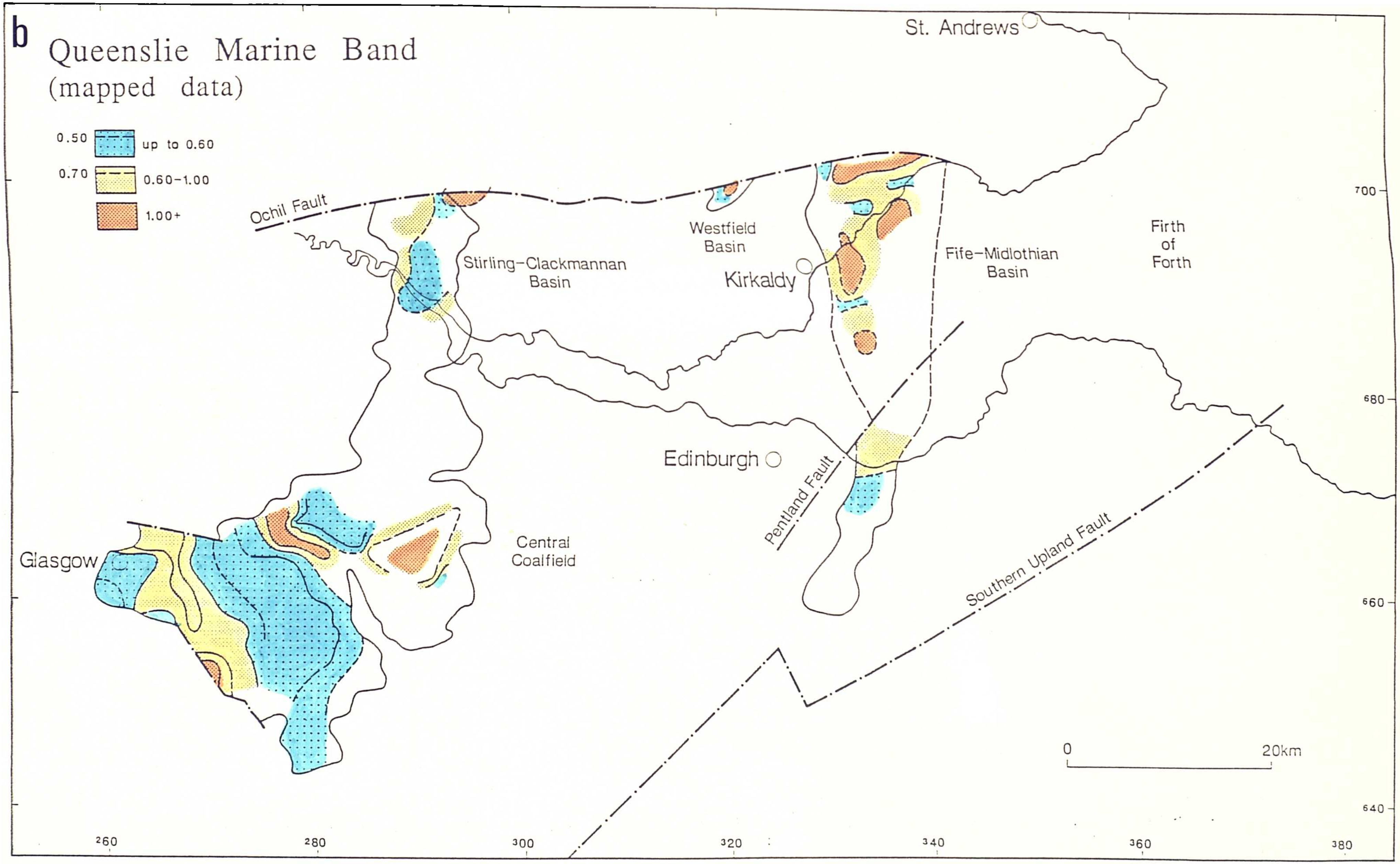
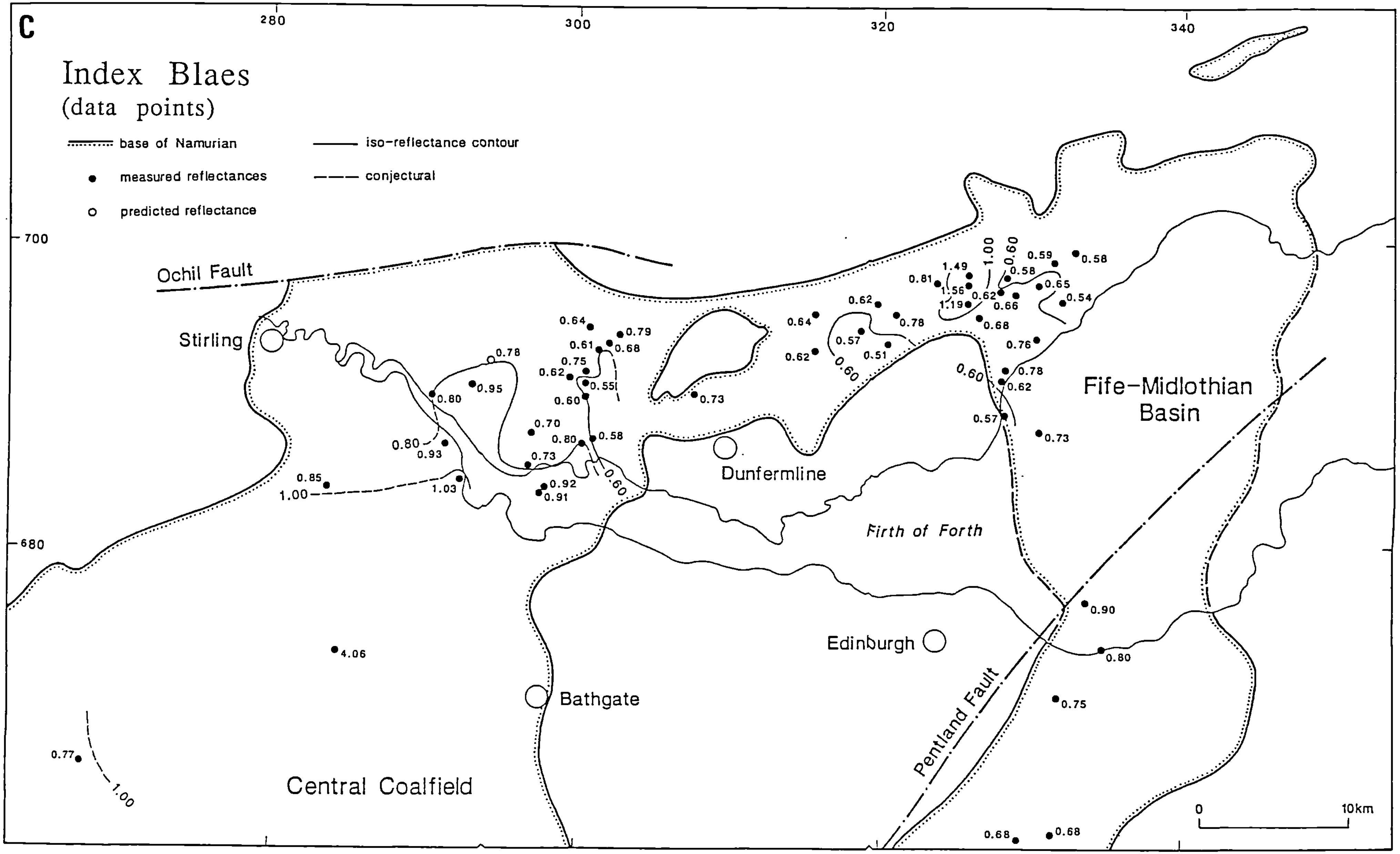


Fig. 5.26 Rank maps showing present-day (post Midland Valley Sill) maturity levels at different stratigraphic levels in the Carboniferous.



b Queenslie Marine Band
(mapped data)


C
Index Blaes
(data points)
base of Namurian
iso-reflectance contour
measured reflectances
conjectural
predicted reflectance
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife-Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km
0.64
0.79
0.61
0.68
0.78
0.75
0.62
0.55
0.80
0.95
0.60
0.70
0.80
0.58
0.80
0.93
0.73
0.85
1.00
1.03
0.92
0.91
0.60
0.73
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0.64
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0.62
0.60
0.78
1.49
0.81
1.56
1.19
1.00
0.60
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0.68
0.76
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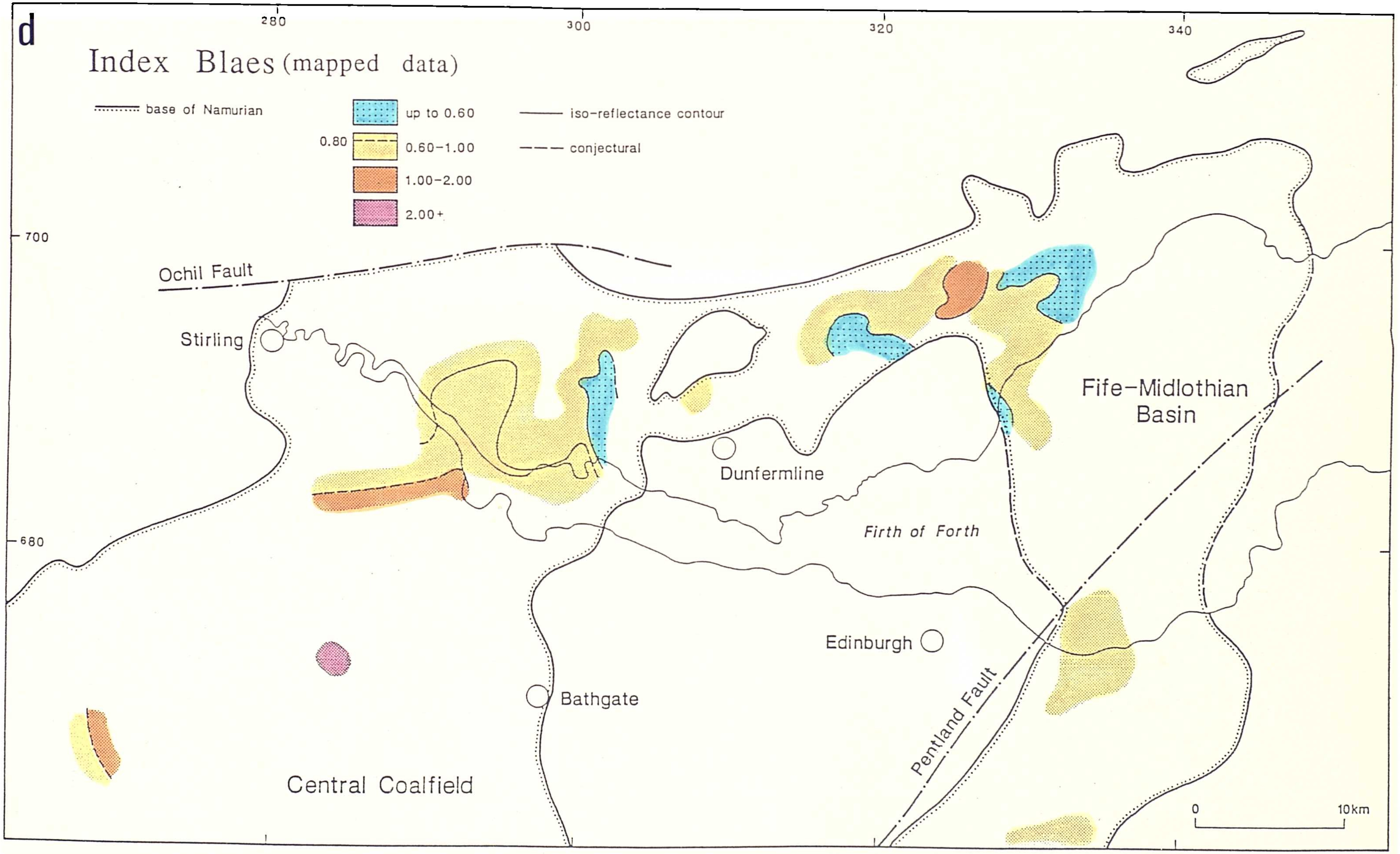
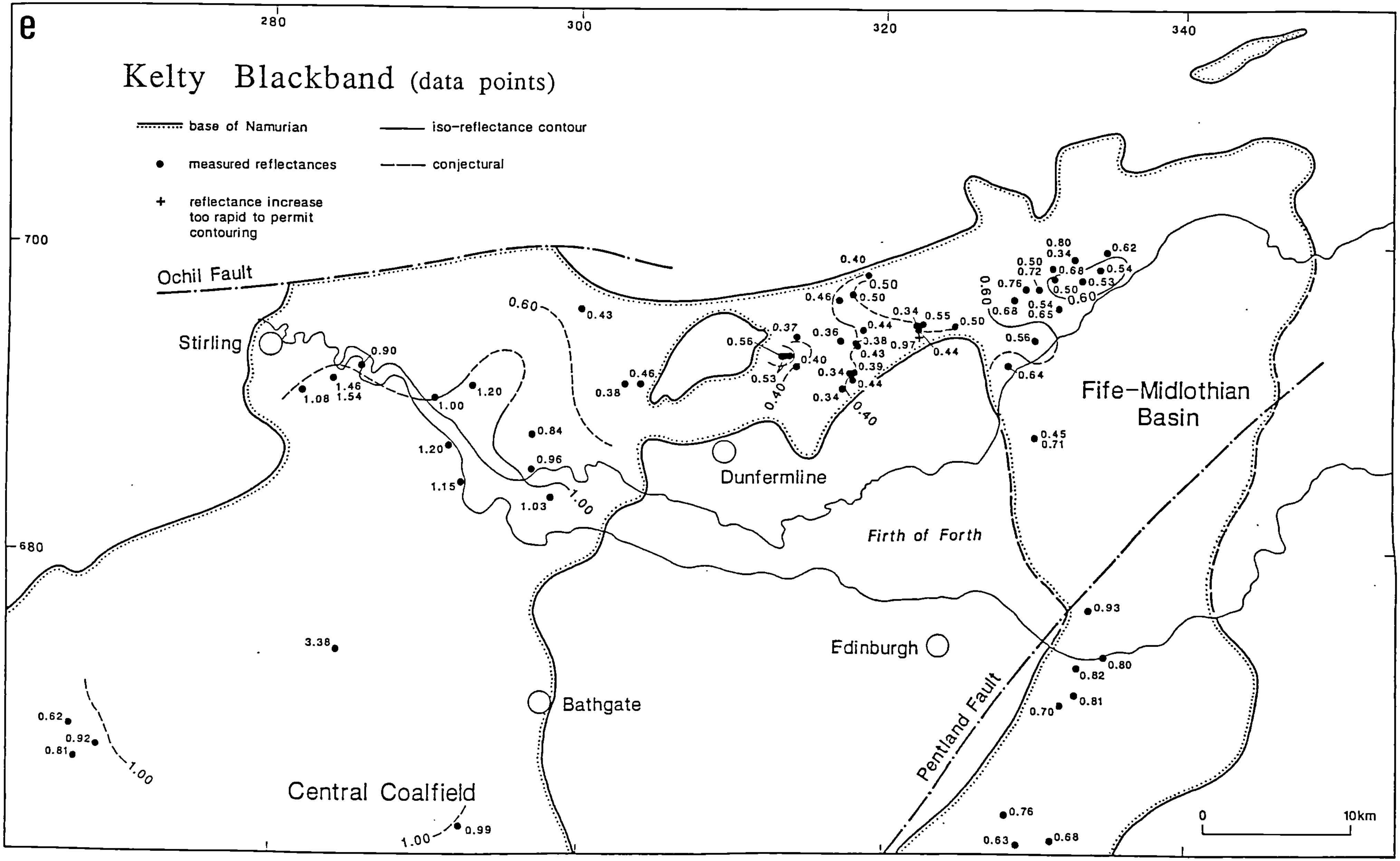
4.06
0.77
1.00


d
Index Blaes (mapped data)
base of Namurian
up to 0.60
0.80
0.60–1.00
1.00–2.00
2.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife–Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km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Kelty Blackband (data points)
base of Namurian
iso-reflectance contour
measured reflectances
conjectural
+ reflectance increase too rapid to permit contouring
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife-Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km
0.40
0.50
0.60
1.00
0.43
0.46
0.38
0.90
1.46
1.54
1.08
1.20
1.00
0.84
0.96
1.15
1.03
0.56
0.37
0.53
0.36
0.44
0.38
0.43
0.39
0.34
0.97
0.55
0.80
0.72
0.76
0.68
0.54
0.65
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0.53
0.64
0.45
0.71
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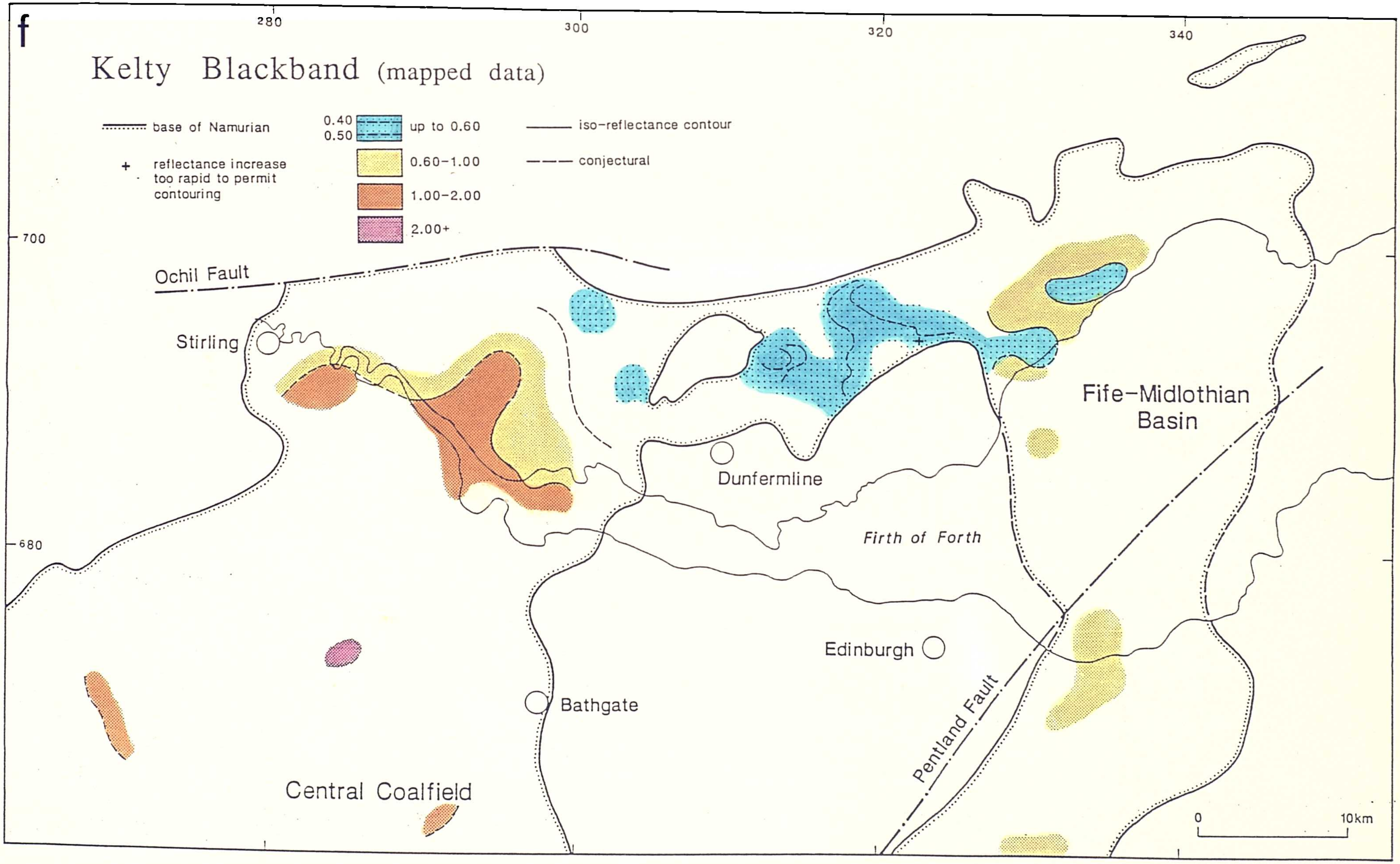
0.76
0.63
3.38
0.99
0.62
0.92
0.81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Kelty Blackband (mapped data)
base of Namurian
+ reflectance increase too rapid to permit contouring
0.40
0.50
up to 0.60
0.60–1.00
1.00–2.00
2.00+
iso-reflectance contour
conjectural
280
300
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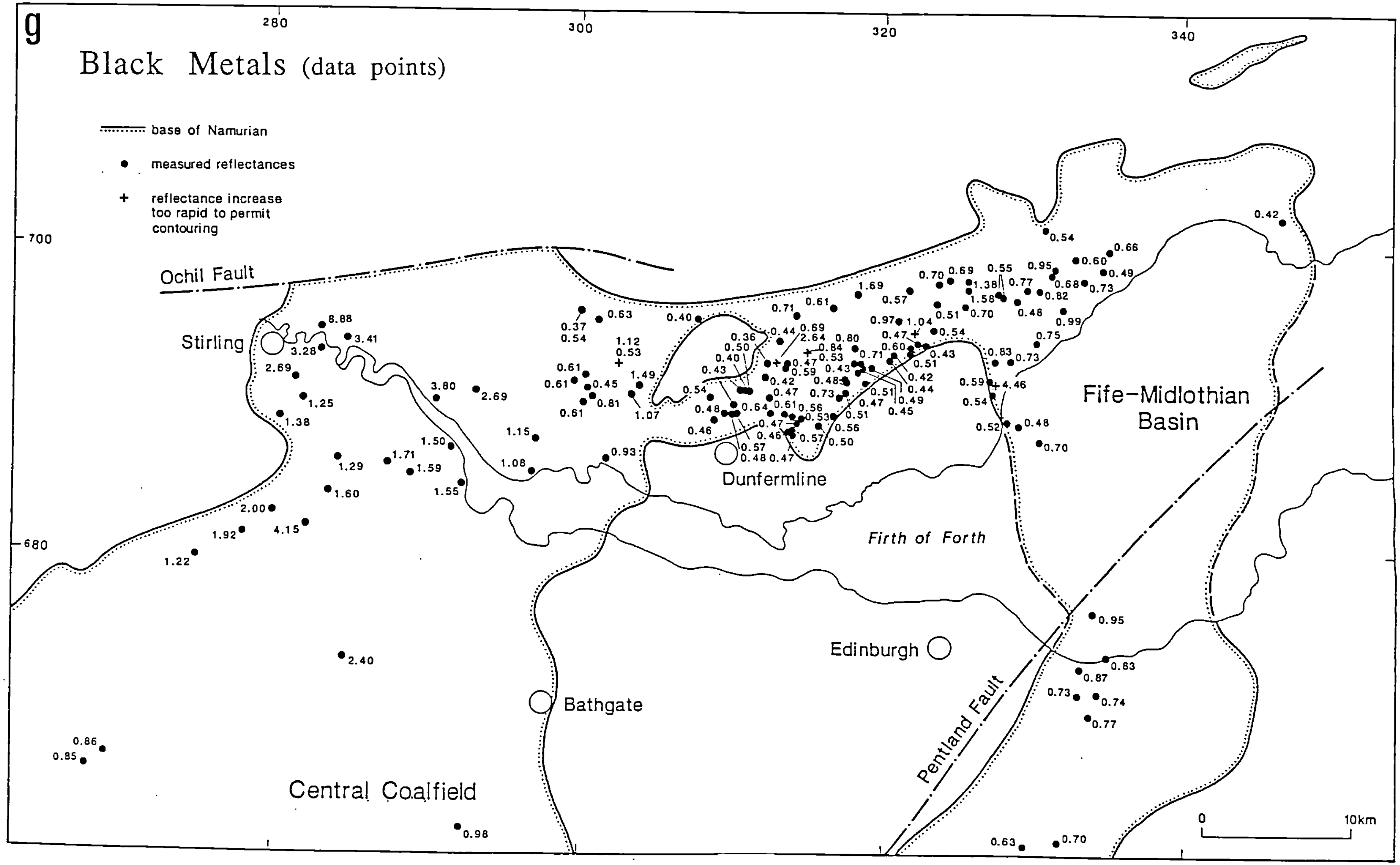
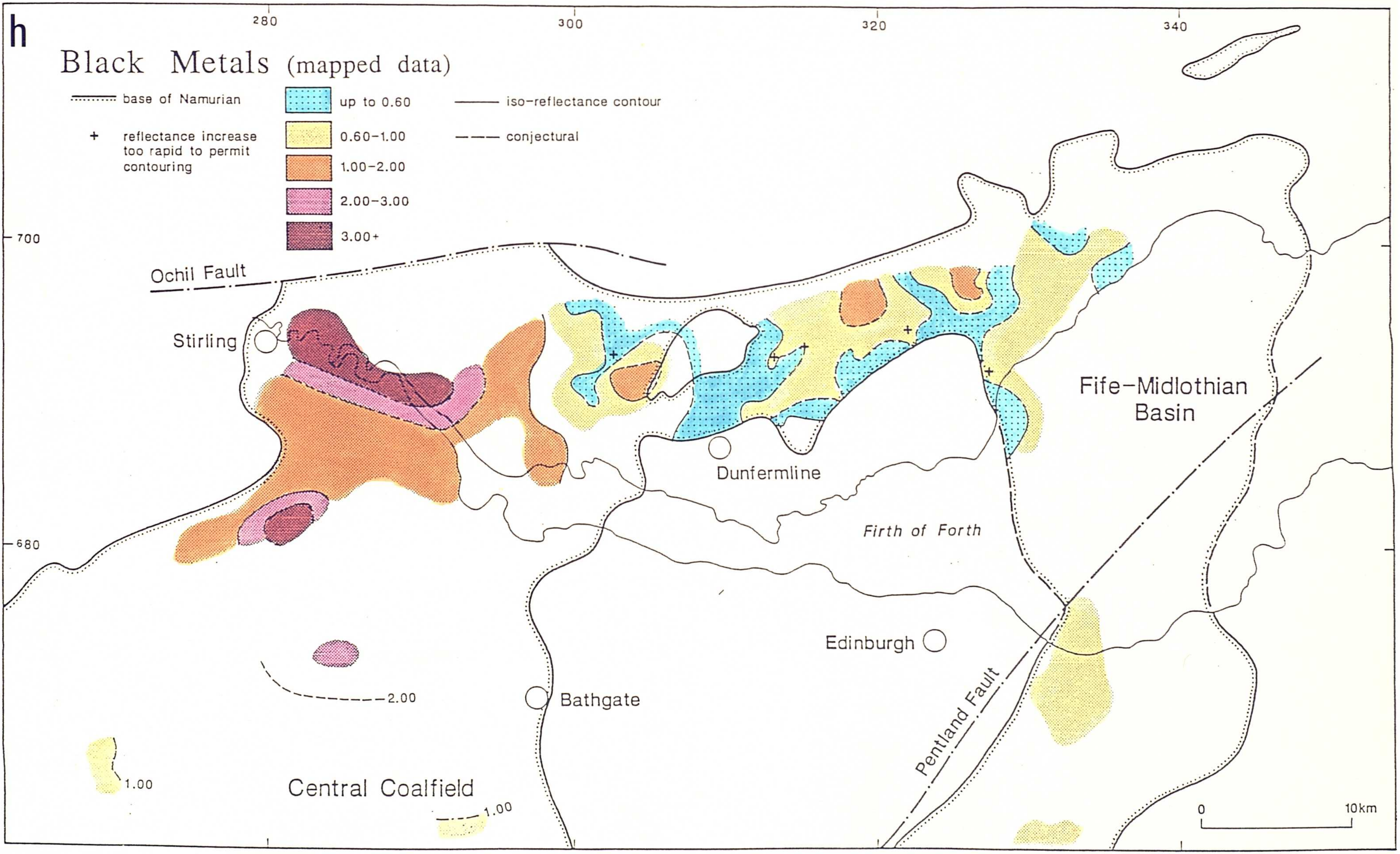
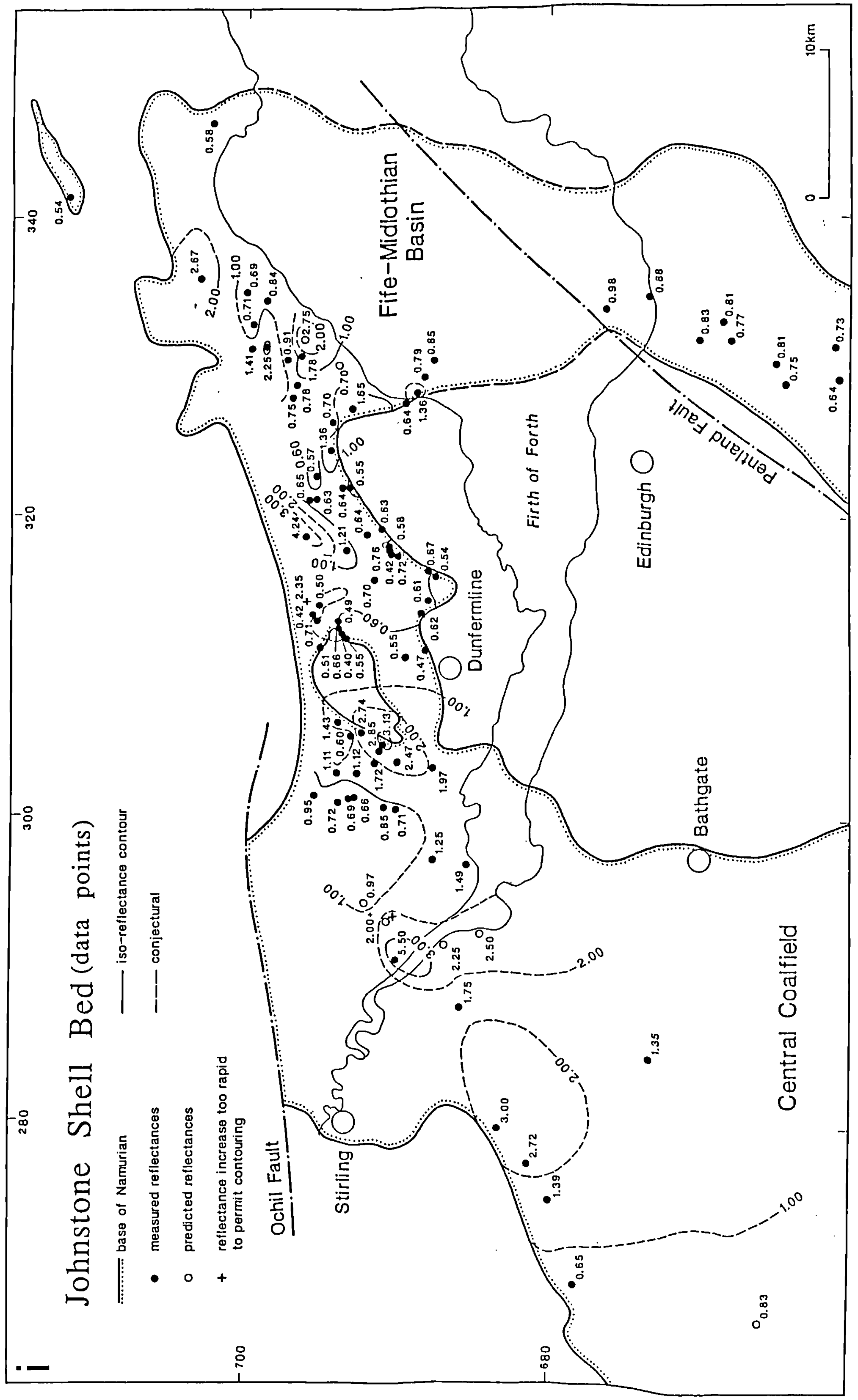
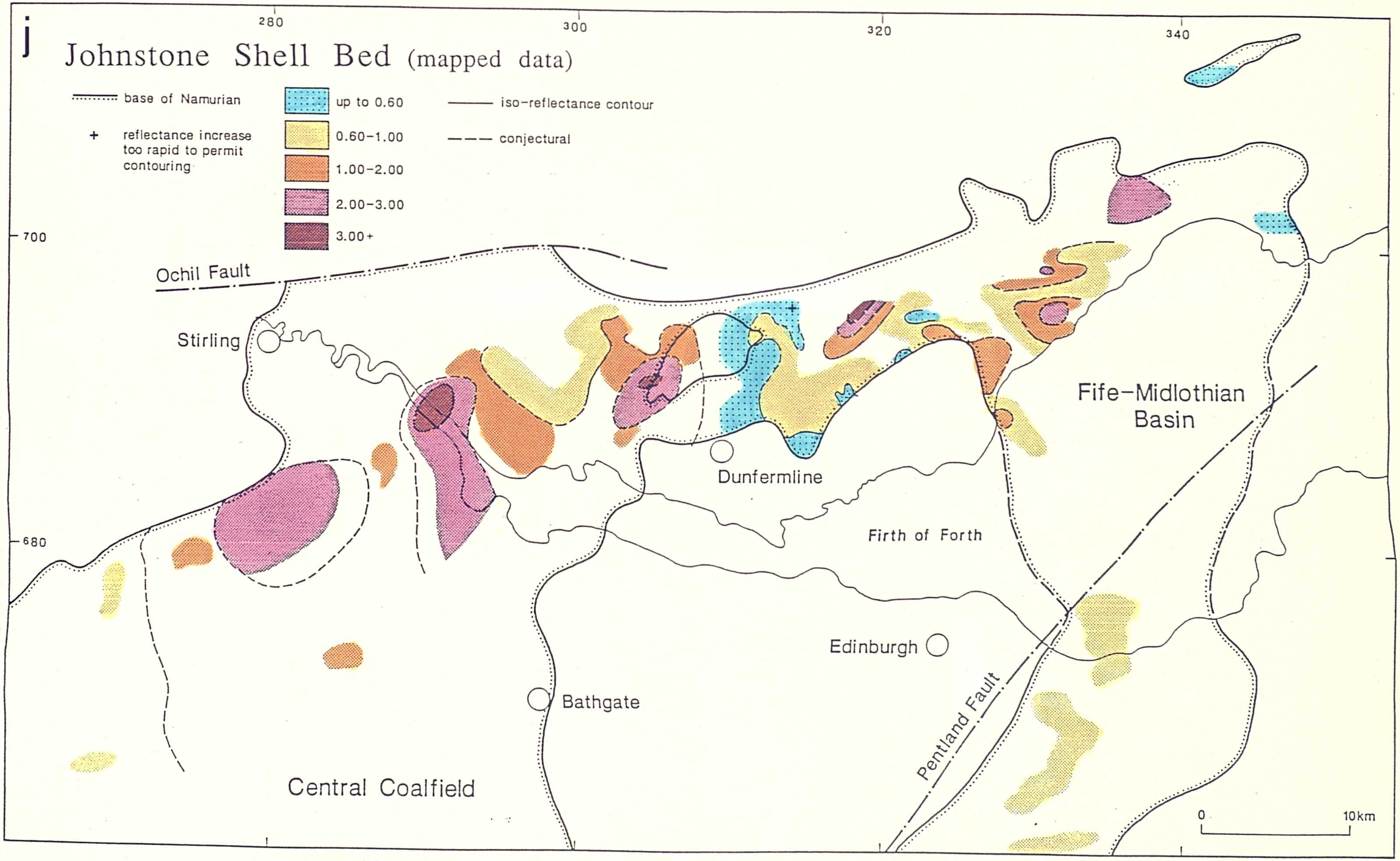
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife–Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km


g
Black Metals (data points)
base of Namurian
measured reflectances
reflectance increase too rapid to permit contouring
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Fife-Midlothian Basin
Firth of Forth
Edinburgh
Pentland Fault
Bathgate
Central Coalfield
0
10km


h
Black Metals (mapped data)
base of Namurian
+ reflectance increase too rapid to permit contouring
up to 0.60
0.60–1.00
1.00–2.00
2.00–3.00
3.00+
iso-reflectance contour
conjectural
280
300
320
340
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife–Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
2.00
1.00
1.00
0
10km



Johnstone Shell Bed (data points)


j
Johnstone Shell Bed (mapped data)
base of Namurian
+ reflectance increase too rapid to permit contouring
up to 0.60
0.60-1.00
1.00-2.00
2.00-3.00
3.00+
iso-reflectance contour
conjectural
280
300
320
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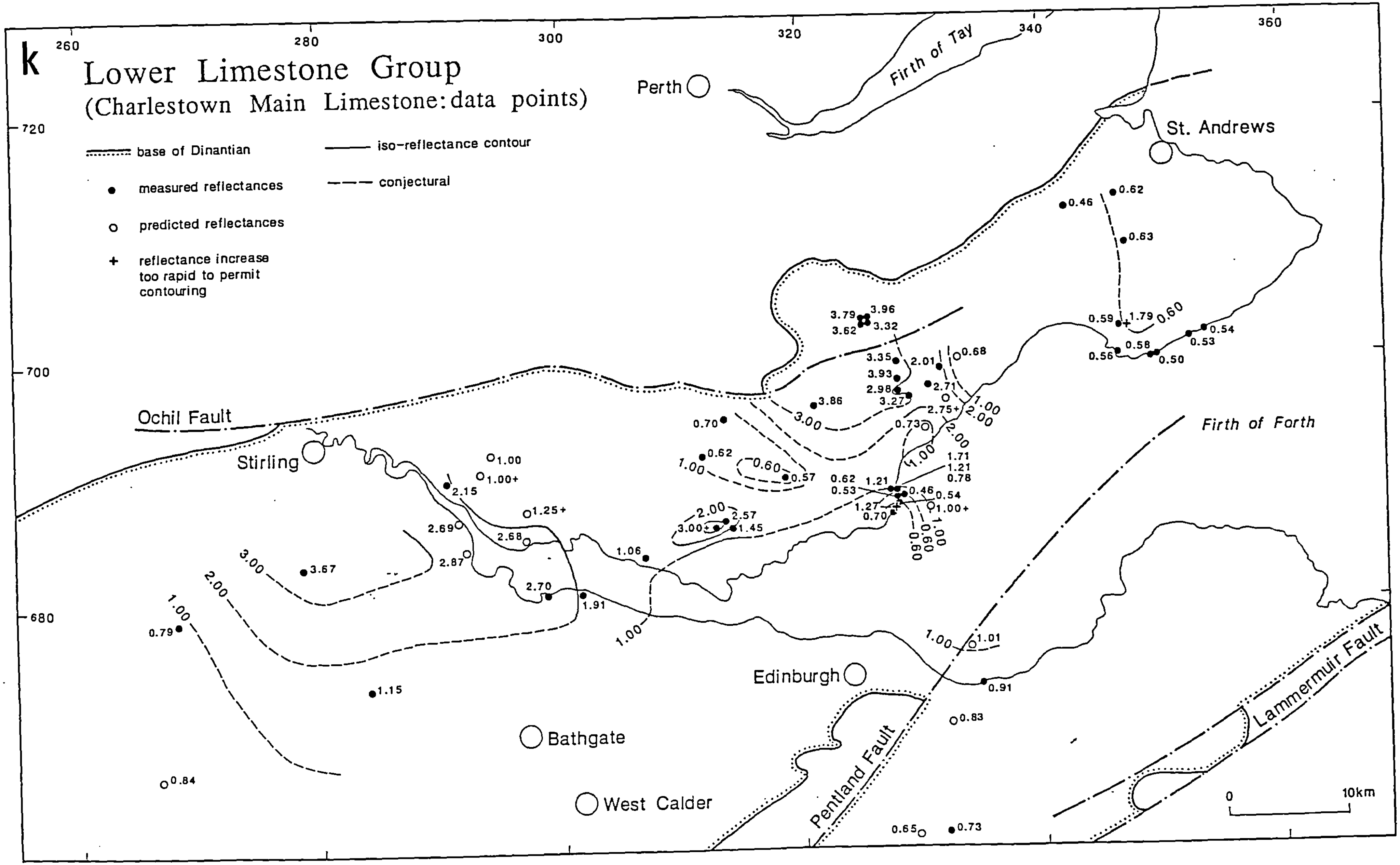
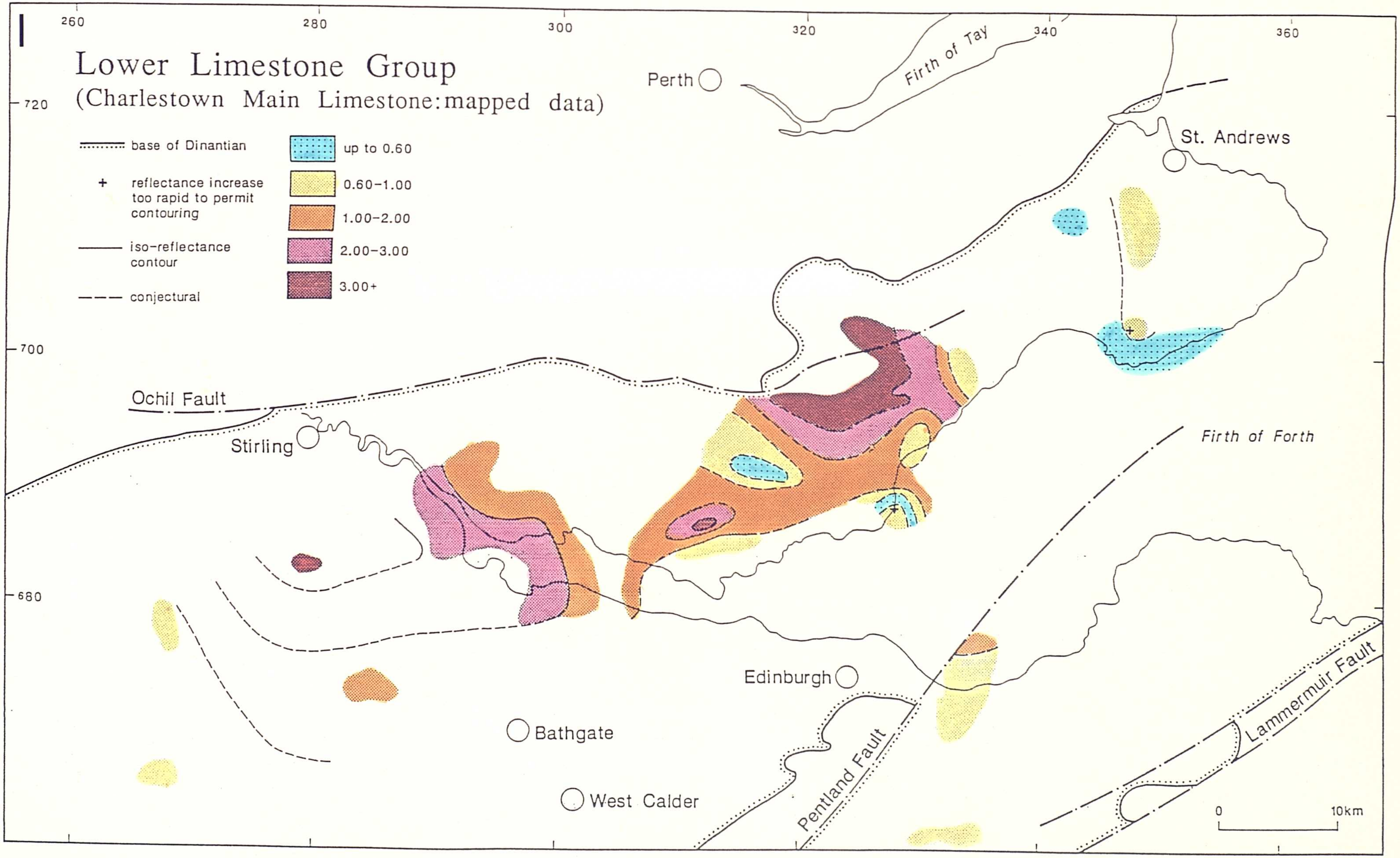
700
680
Ochil Fault
Stirling
Dunfermline
Firth of Forth
Fife–Midlothian Basin
Edinburgh
Bathgate
Pentland Fault
Central Coalfield
0
10km



k Lower Limestone Group
(Charlestown Main Limestone: data points)

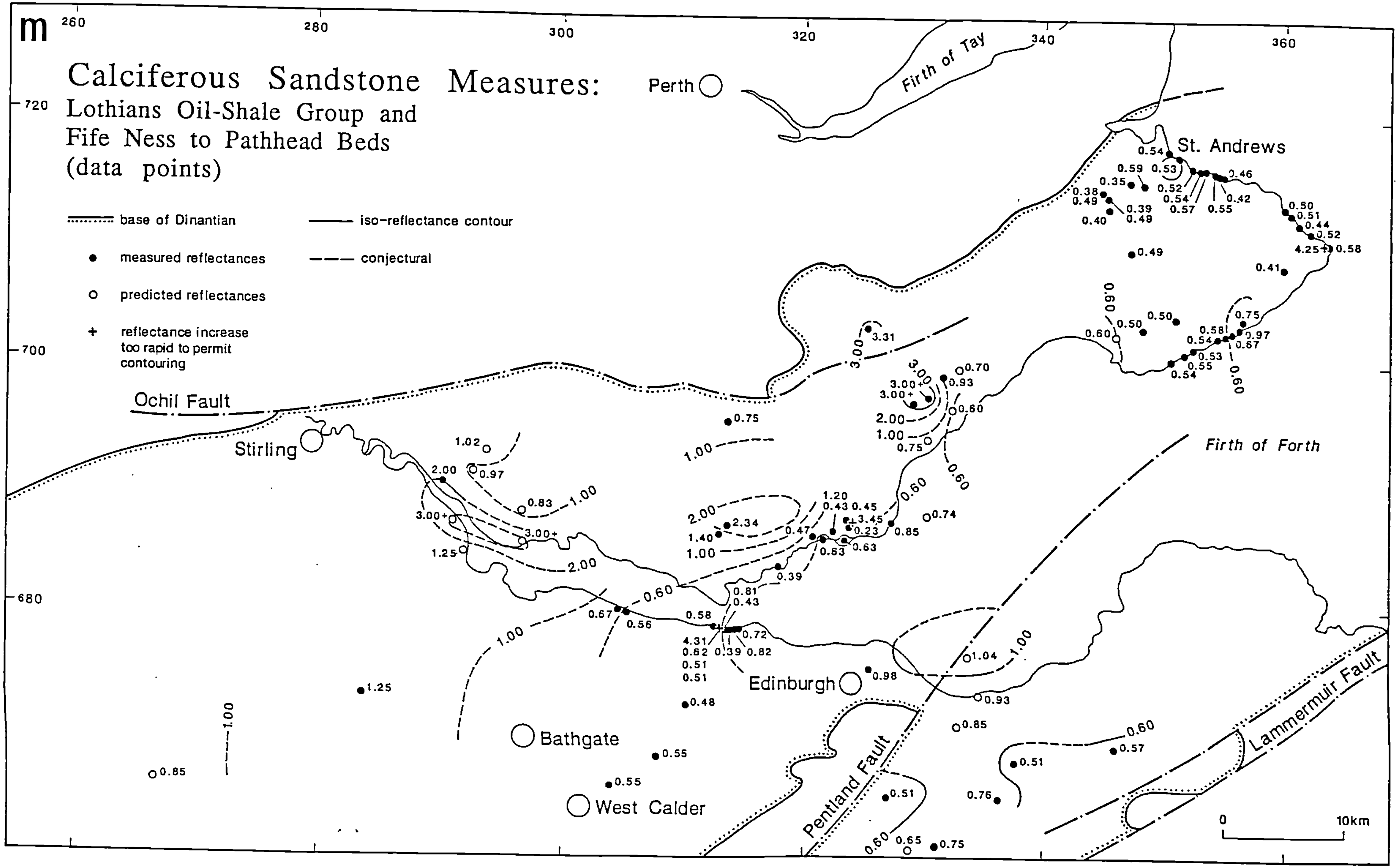


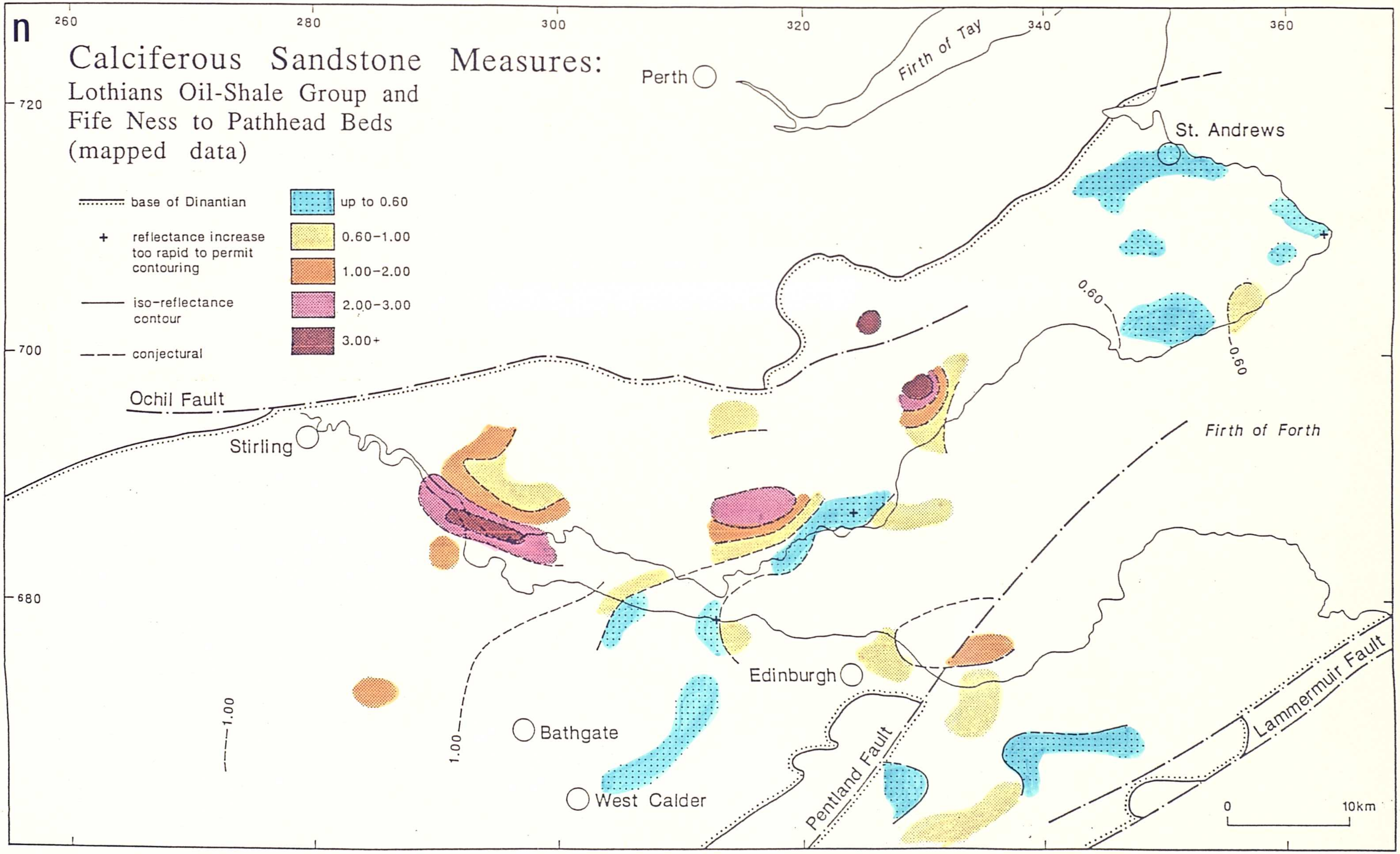
Lower Limestone Group
(Charlestown Main Limestone: mapped data)

m

Calciferous Sandstone Measures:

Lothians Oil-Shale Group and
Fife Ness to Pathhead Beds
(data points)





n

Calciferous Sandstone Measures:
Lothians Oil-Shale Group and
Fife Ness to Pathhead Beds
(mapped data)

collieries, Knox 1954), thus the thermal effects of the sill are probably responsible for at least some of the elevated ranks of coals and sediments in this area. The lack of vertical borehole-reflectance profiles for offshore localities precluded an assessment of the importance of the Midland Valley Sill in influencing organic maturation in the Leven district and immediately offshore.

The "hot spots" (%R_0av$\geq$1.00) in the Central Coalfield may be due to proximity to the Midland Valley Sill or to alkaline-dolerite sills, many of which are recorded in the Coal Measures sequence (e.g. Queenslie Bridge Borehole; see Appendix III) and were probably intruded not long after sedimentation occurred.

As mentioned in Section 4.2.3.1, high-reflecting vitrinites occur in samples located near major faults at the margins of Westphalian basins and could be due to oxidation by percolating mineral solutions. Subaerial oxidation may also have been important in increasing vitrinite reflectance in Coal Measures times, as inferred for the shale above the Bush Coal, West Wemyss (Sections 4.2.4.2.2 and 4.4.1.4.6.

Passage Group and Calmy Blaes

On the basis of the currently available reflectance data, the thermal effects of the Midland Valley Sill in the Passage Group (Figs 5.2a,b) and Calmy Blaes (Figs 5.2c,d) can only be detected in the Central Coalfield, where reflectances exceed %R_0av=1.00 (see Section 5.2.1). There is an overall increase in reflectance values moving towards the depocentres of the Fife-Midlothian and Stirling-Clackmannan Basins, which is probably related to increased burial depth as implied by isopach data (Browne *et al.* 1987).

Although samples are sparse in the basinal tract joining the Fife-Midlothian and Stirling-Clackmannan Basins, the measured reflectances of the available samples are relatively low and indicate that the tract was maintained as a relative "high" during Upper Limestone Group and Passage Group times. Reflectances not thought to be suppressed and which are %R_0av$\leq$0.60 were recorded in many parts of central Fife at much lower stratigraphic levels, in the Black Metals and Johnstone Shell Bed (particularly the former) which suggests that sediments in the Passage Group and Upper Limestone Group strata over much of central Fife may also be of relatively low maturities.

The very low measured reflectances (%R_0av$\approx$0.40) recorded in west Fife for many samples of the Calmy Blaes reflect the abundance of liptinite (mainly alginite). The rank of many of the samples in west Fife is in all probability significantly underestimated. Insufficient samples from a given borehole were available with which to assess the extent of vitrinite-reflectance suppression through the construction of vertical reflectance profiles.

Index Blaes

The overall rank distribution seen in the Index Blaes maps (Figs 5.26c,d) is similar to that of the Passage Group and Calmy Blaes. The thermal effects of the Midland Valley Sill are more pronounced in the Central Coalfield-Stirling-Clackmannan Basin. The elevated ranks detected in the northeastern part of central Fife, north of Kirkaldy, are probably related to the presence of a large teschenitic intrusion which lies near the Index Limestone in this district. Rank increase in central Fife may also have been accelerated by proximity to alkaline-dolerite sills, which occur in great abundance, as part of several complexes, in the Namurian succession (Francis and Walker 1987).

Kelty Blackband

The ranks of all of the Kelty Blackband samples analysed in the Stirling-Clackmannan-Central Coalfield Basin have been modified by the Midland Valley Sill. Comparison of the present-day rank maps (Figs 5.26e,f) with the pre-Midland Valley Sill map (Fig.5.2f) indicates that in some regions (Rashiehill borehole, Fig.5.16c; Kincardine Bridge borehole, Fig.5.19a) relatively high ranks ($\%R_o>1.00$) were attained prior to sill intrusion, through "normal" coalification.

Any possible effect of the Midland Valley Sill on sediment maturities in central Fife could not be established. The ranks (based on vitrinite reflectance) of many of the samples in central Fife may be significantly underestimated due to the very high liptinite contents (mainly sporinite) of the majority of samples (see Section 4.2.3.4). As with the map of the Calmy Blaes, that of the Kelty Blackband contains an overprint of organic-matter type. The points in Fig.5.26e with dual readings refer to borehole localities at which "true" (higher reflectance values) could be estimated by projecting the horizon of the Blackband to the regional coalification gradient constructed from the data for unsuppressed vitrinites. The true values were used for contouring.

Black Metals and Johnstone Shell Bed

Rank variation at these stratigraphic levels is very pronounced (Figs 5.26g,i), and the resulting maps (Figs 5.26h,j) are complex. Some of this complexity may simply reflect the greater availability of samples at these horizons.

Consideration of the borehole-reflectance profiles and the position of the Black Metals and Johnstone Shell Bed relative to the Midland Valley Sill reveals that both these stratigraphic levels lie within the aureole of the sill in all borehole sequences studied in the Fife and Stirling-Clackmannan-Central Coalfield Basin.

This observation, coupled with the fact that major changes in sediment maturity generally occur over several hundreds of metres, is strong evidence that major rank variations within the base of the Limestone Coal Group are largely due to the influence of the Midland Valley Sill rather than to the effects of alkaline dolerites or extrusives (see Section 5.3.2.1.1). The complex rank patterns mainly reflect the varying distance of the strata from the intrusion and the differing physical properties of the sediments at the time of intrusion. High-reflecting vitrinites occur sporadically in relatively low-maturity areas (marked by "+" on the maps). In addition to localised "hot spots" associated with quartz dolerites, it is possible that these high sediment maturities could also arise through close contact with alkaline-dolerite intrusions or extrusive masses.

At both horizons, the sill exerts its greatest effect in the western part of the study area where the vitrinites have been elevated to anthracitic/meta-anthracitic ranks. It is interesting to note that although ranks at the base of the Limestone Coal Group in the Stirling-Clackmannan Basin were at levels at which mosaic development might be expected following sill intrusion, such textures are very rarely (and poorly) developed (only recorded in the Inch of Ferryton and Gartarry Toll bores). This observation agrees with the data provided by NCB (1960) rank maps based on coking potential and volatile-matter yields. These maps indicate that many west Fife/Stirlingshire Limestone Coal Group coal samples have very poor coking potentials, yet reflectance data from the present study suggest that they ought "normally" to form mosaics (i.e. have good coking potentials). The anomalously poor coking properties of the coals in west Fife/ Stirlingshire indicate that mosaic development in the area is not simply a function of rank, but is related to the rate at which regional coalification proceeded before sill intrusion (inducing carbonisation). Similar conclusions can be drawn from the work of Pearson (1988) who noted that coals with anomalously low coking potentials occur in parts of the Durham coalfield which lie close to the Alston Block. Radioactivity from the underlying potassic granite which constitutes this structural high is thought to have provided the heat source for the rapid coalification which affected many of the coals overlying or draping over the "block" (Ridd *et al.* 1970; Jones and Creaney 1977; Creaney 1980).

The areal extent of the zone of relatively low-maturity strata ($\%R_oav<0.60$) depicted on the maps may be exaggerated because the optical properties of vitrinites in samples with reflectances lower than c.$\%R_oav=0.50$ have probably been influenced by the presence of abundant liptinite. Some samples lying in the higher rank category ($\%R_oav=0.60-1.00$) may also be affected in this way. The suppression phenomenon is likely to be more pronounced in the Johnstone Shell

Bed than in the Black Metals because of the higher overall liptinite content in the former. Whether samples lying in the $\%R_oav=0.60-1.00$ interval lie within aureoles or whether their ranks have been imposed solely through regional coalification could not be unequivocally established because of a lack of data from boreholes drilled in the area.

In the Midlothian Basin there is no known intrusive igneous activity, thus, as with the previous horizons, the trend towards increased rank at the level of the Black Metals and Johnstone Shell Bed moving offshore probably relates to increased burial.

Lower Limestone Group

Although the available data points are relatively few and are unevenly distributed (Fig.5.26k), the high reflectances shown for strata throughout most of central Fife, and further to the west (Fig.5.26l), clearly indicate that the thermal effects of the Midland Valley Sill are still very pronounced in this part of the succession.

Calciferous Sandstone Measures (Strathclyde Group: Lothians Oil-Shale Group and Fife Ness to Pathhead Beds)

The effects of the Midland Valley Sill are still recorded in strata of the Strathclyde Group throughout most of central and western Fife (Figs 5.26m,n). As mentioned earlier, the tract of low-maturity strata lying between Burntisland and Bathgate overlies the Burntisland Arch. That relatively low maturities are recorded in this terrain is an indication that the area remained as a "high" throughout post-Dinantian times. It is also possible that the existence of this positive structural feature could have influenced the course of the intrusion of the Midland Valley Sill at this stratigraphic level.

The possibility that the reflectances of vitrinites in sediments in the Lothians may have been influenced by the presence of abundant alginite in the sequence cannot be disregarded. The occurrence of relatively low-maturity samples in the area is, however, consistent with the geological knowledge that they lie on the line of the Burntisland Arch, and therefore low-rank strata may be expected. Again, borehole data were not available to construct vertical vitrinite-reflectance profiles in the area.

Much of the Strathclyde Group in east Fife is of low rank which indicates that this region remained as an area in which relatively little subsidence occurred throughout the remainder of the Carboniferous and later.

Calciferous Sandstone Measures (Inverclyde Group: Cementstone Group and Ballagan Formation)

Very few boreholes and field sections penetrate lowermost Carboniferous strata. Measured reflectances on basal Carboniferous samples were included in the regional rank map (Fig.5.2k). That the predicted reflectances at the base of the Carboniferous are reasonable estimates of present-day ranks seems likely in view of the similarities in the order of magnitude between the predicted and measured reflectances at localities in the same geographical area.

The value of $\%R_oav=2.00$ for the Ballagan Formation in the Inch of Ferryton well is probably enhanced due to the elevation of the background rank which is thought to have occurred as a consequence of the intrusion of the Midland Valley Sill (see Section 5.3.2.1.2.1). The low maturity of the Ballagan Formation bordering the Firth of Tay (Newburgh and East Dron bores) indicates there has been little overburden in this area. The organic content of the samples is not sufficiently high for vitrinite impregnation to be the cause of the low reflectances.

The rank map data, in conjunction with the borehole-reflectance profiles, show that the Midland Valley Sill has exerted a major influence on the level of organic maturation in the eastern and central Midland Valley, particularly within the base of the Limestone Coal Group, the Lower Limestone Group and the upper part of the Calciferous Sandstone Measures sequence.

The present study confirms the rank-map data of the NCB(1960) by demonstrating that, along a given stratigraphic level, higher ranks occur in the west of the area than in the east. The NCB data are also expanded since the current study shows that the higher maturities in the Stirling-Clackmannan-Central Coalfield Basin can be attributed to two components *viz.* the greater thermal effect of the Midland Valley Sill in the area, which is ultimately controlled by the higher regional level of coalification attained before sill emplacement.

5.3.2.2 Geochemical Aspects

Several previous studies have involved monitoring changes in the amount and composition of EOM in sediments approaching igneous bodies and these have also demonstrated changes in the distributions of acyclic alkanes (see Section 2.3.5). Relatively few investigations have been directed towards evaluating changes in polycyclic alkanes and aromatic steroid distributions in heat-affected sequences and there appear to be no studies that have investigated variations in the distributions of alkylated naphthalenes and phenanthrenes in such successions. These oversights are surprising given the current high level of sophistication of organic geochemical analytical equipment and the fact that the changes in the distributions of the compounds in all of the compound classes mentioned above are widely used as maturation indices in geological studies (see Section 2.3.3).

It is the aim of this section to rectify, in some measure, the deficiencies in knowledge relating to the distributions of saturated and aromatic hydrocarbons in organic matter of different types which has been exposed to geologically rapid heating through proximity to igneous intrusions. Comparisons are also made with the changes in molecular distributions brought about through the "normal" course of burial metamorphism.

Various commonly-used, molecular-maturation indices were determined in samples whose rank, defined by vitrinite reflectance, had been achieved through the rapid heating associated with intrusive igneous activity. These indices were compared with those determined from samples that have reached the equivalent rank through exposure to the "normal" background geothermal gradient. Humic coals and sediments whose gross maceral composition would place them on the type III coalification track on a van Krevelan diagram (referred to as "type III samples") were collected from within and outside of the thermal aureole of the Midland Valley Sill (or related quartz-dolerite dyke in the case of the Mid Calder samples). These two sample suites are taken to represent samples which have experienced rapid and slow rates of heating respectively. An indication of the influence of organic-matter type at the different maturity levels is given by including data from lamosites (type I kerogen). Vitrinite reflectance values for the lamosites have been adjusted to those of closely-associated, humic-rich sediments to correct for suppression effects which would otherwise significantly underestimate the maturities of these deposits (see Section 5.2.2).

The samples utilised in this study were taken from boreholes and field localities throughout the eastern and central Midland Valley. The main sources of the type III samples for this work were the Milton of Balgonie, Musselburgh, Righead, Kincardine Bridge, Blairmains and Carrington boreholes, with additional samples originating mainly from the east Fife coastal sections. Inclusion of the lamosites was undertaken for general comparative purposes: the division of the samples into "heat-affected" (through igneous activity) and "non heat-affected" (through normal burial metamorphism) is not made for this suite because it was not possible, for some samples, to determine whether or not ranks higher than %$R_o$av=0.70 were achieved through exposure to igneous intrusives. In any case, too few samples were available from which to establish meaningful trends. Although this section is largely concerned with polycyclic compounds, mention is firstly made of extract yields and parameters based on acyclic hydrocarbons.

5.3.2.2.1 Extract Yields and Gross Compositions

No significant trends in EOM yields were evident with increasing rank in each of the three sample sets ("heat-affected" type III, "non heat-affected" type III and lamosites). The lack of TOC data, to which EOM data should be normalised for effective comparisons, is probably a major cause for the variation (Table A.2).

A very general trend towards an increase in aliphatic hydrocarbon content of EOM at higher ranks is evident in the type I- and type III-rich samples, although no difference could be identified for type III samples exposed to different heating rates. As for the relatively low-rank coals and type III sediments, the EOM of those of high rank is still enriched in polar materials, unlike high-rank lamosites which are more aliphatic and aromatic rich. These EOM compositions still reflect the underlying influence of organic-matter type.

5.3.2.2.2 Acyclic Aliphatic Hydrocarbons

5.3.2.2.2.1 General Trends

The changes in distributions of acyclic saturated hydrocarbons in heat-affected successions are akin to those reported by other authors in sequences approaching igneous bodies (e.g. Perregaard and Schiener 1979; Clayton and Bostick 1986). The thermal effects of the intrusions on the organic matter are also similar to those observed during "normal" burial (Tissot *et al.* 1971).

The general sequence of changes observed in the saturated hydrocarbon fractions of coals and sediments containing type III organic matter is illustrated by the gas chromatograms in Fig.5.27. Basic geochemical parameters calculated from the traces are shown in Appendix Table A.3.

The relatively high pristane content, characteristic of low-rank terrigenous samples investigated in this study, diminishes with increasing rank as dilution through *n*-alkane generation occurs. The odd carbon-number preference evident in the high and medium molecular-weight *n*-alkane ranges decreases as the *n*-alkane envelope becomes progressively "smoother" and skewed towards medium and low molecular-weight homologues. The skew is particularly pronounced at very high ranks (*c.*%R_o=2.50+).

Although Pr/Ph ratios of the type III samples are very variable up to ranks of *c.*%R_o=1.00, presumably reflecting the persistence of environmental variations, there is an overall decrease in the ratio at higher ranks. Polycyclic alkanes which are evident at the high molecular-weight end of the gas chromatograms in the lower-rank samples are increasingly swamped by acyclic alkanes as hydrocarbon generation proceeds.

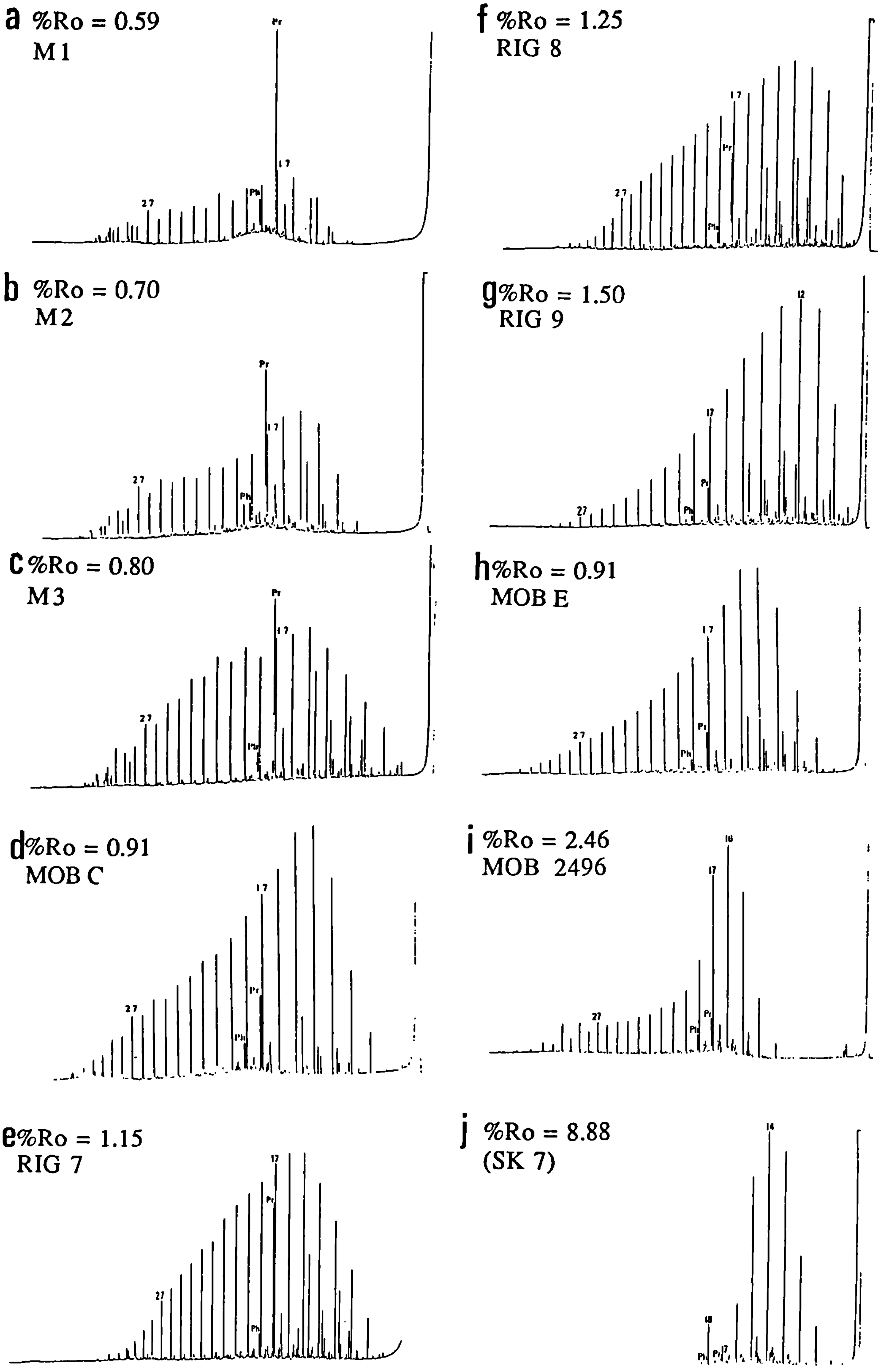


Fig.5.27 Gas chromatograms showing changes in the distributions of saturated hydrocarbons with increasing rank in coals and sediments containing predominantly humic macerals.

The general changes in the shape of the *n*-alkane distributions outlined above also apply to lamositic shales although the bimodality of the *n*-alkane envelope is often more pronounced in the low-rank samples, reflecting the lamalginite precursor (Section 4.3.3.1.2). The skew towards medium and low molecular-weight *n*-alkanes is less well developed, but this is probably due to the sheared nature of several of the high-rank lamosite samples studied (from Mid Calder), with consequent loss of "light ends" through evaporation/water washing in the natural environment.

Unlike the terrestrial samples, the Pr/Ph ratios in the lamosites do not show much variation through the rank range. The relatively low Pr/Ph ratios recorded in lamosites reflect a type/environmental signature.

The variation in acyclic alkane distributions with increasing rank in the sample suites studied is shown in Fig.5.28. No specific trends in the terrigenous samples could be confidently attributed to differing rates of heating.

5.3.2.2.2.2 Polycyclic Alkanes and Variations in Maturity Parameters based on Hopanes and Steranes

Terpanes

Salient changes occurring in terpane distributions with increasing rank in the coals and terrestrial sediments are shown in Fig.5.29. Ratios derived from these and other m/z 191 mass fragmentograms are shown in Table A.4.

That changes in molecular distributions can be more sensitive to increased thermal stress than is vitrinite reflectance in low-rank samples is indicated by the occurrence of an obviously more immature terpane profile in the coal StA6 (Fig.5.29b) than in the coal SM6 (Fig.5.29a), although measured vitrinite reflectances would indicate the reverse. Hopenes were identified in the former sample (see Section 4.3.3.3.7.1).

Increasing organic maturation is accompanied by a reduction or loss of thermodynamically unstable compounds or by the transformation of compounds with relatively unstable, biologically-inherited configurations to those with more stable stereochemical structures. Thus, ββ hopanes disappear rapidly (by $\%R_o \approx 0.60$), there is a progressive decrease in the relative concentrations of βα hopanes, and extended hopanes with a 22S stereochemistry increase relative to their 22R epimers. The trisnorhopane Ts also increases relative to Tm. These transformations in terpane distributions are well known and have been documented for coals and sediments unaffected by igneous intrusions (e.g. Ensminger *et al.* 1974, 1977; Seifert and Moldowan 1978; Mackenzie and Maxwell 1981), as well as in heat-affected successions (Altebäumer *et al.* 1983; Gilbert *et al.* 1985).

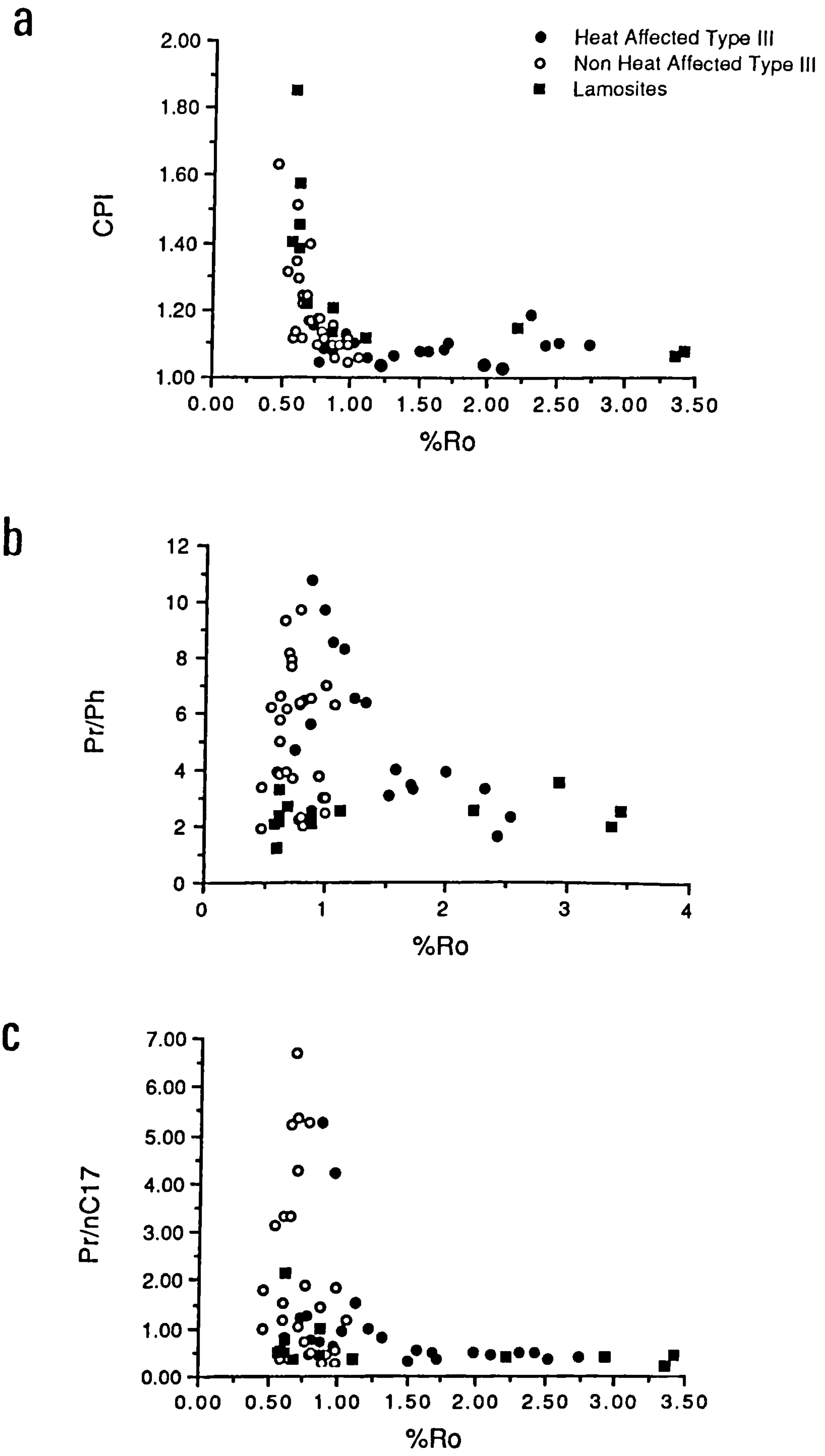


Fig.5.28 Plots showing values of basic geochemical parameters at different ranks as defined by vitrinite reflectance.

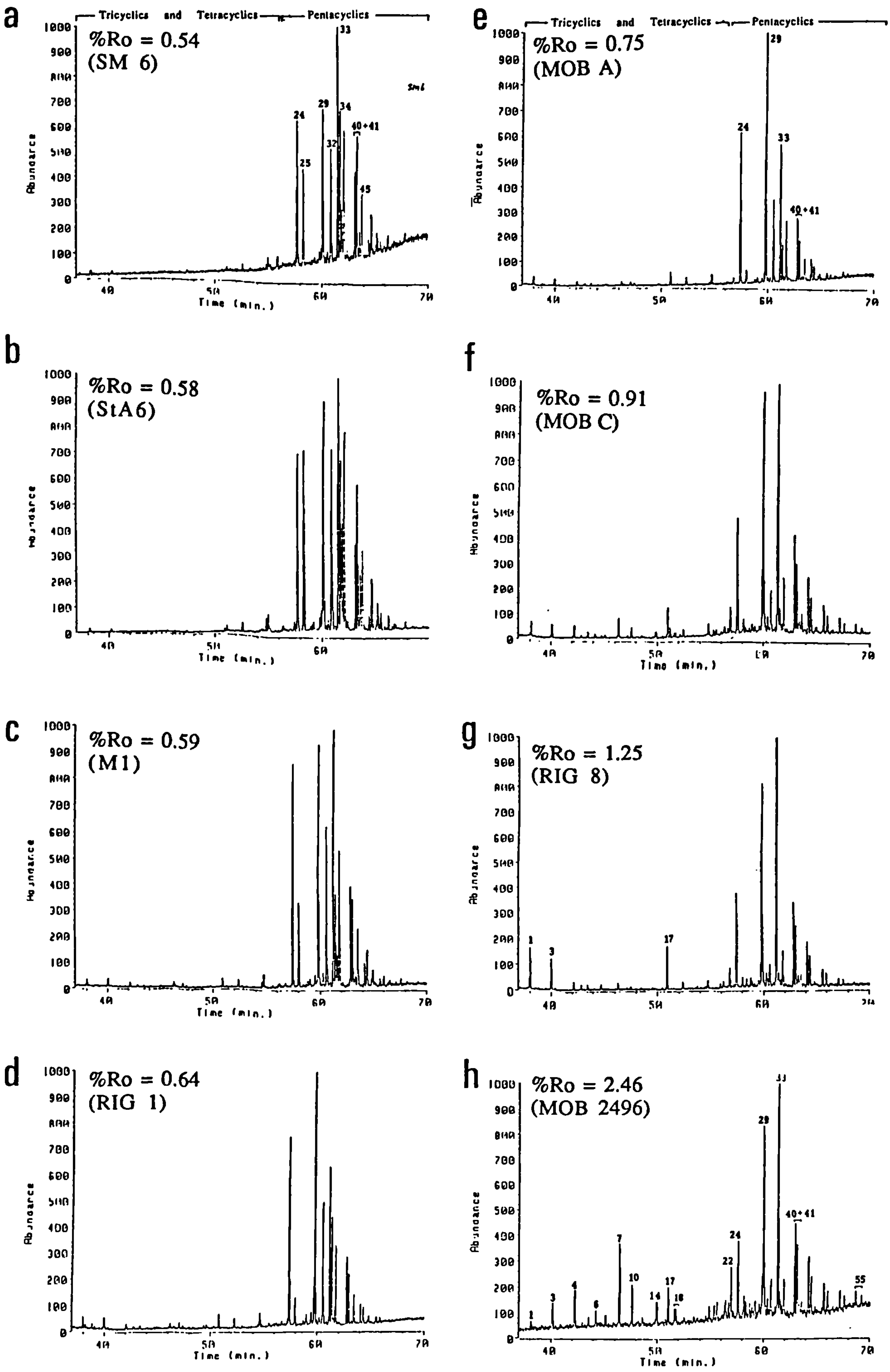


Fig.5.29 M/z 191 mass fragmentograms showing changes in terpane distributions with increasing rank in coals and sediments containing predominantly humic macerals (peak assignments in Table 4.5).

A change not commonly documented in the geological environment (but see Rodrigues *et al.* 1987) is the increased relative concentration of tricyclics and tetracyclics seen in samples of increasing rank. Concentrations of 3- and 4-ringed terpanes higher than those found in original extracts have been reported in pyrolysates (Aquino Neto *et al.* 1983; Ekweozor and Strausz 1983; Cassani and Eglinton 1986; Peters *et al.* 1990). The quantitative data of Ekweozor and Strausz (1983) indicate that the increase probably reflects the neoformation of tricyclics and tetracyclics from kerogen rather than an enhanced thermal stability, relative to the pentacyclic terpanes.

Unlike the tricyclics and tetracyclics, bicyclic alkanes were present in most samples in amounts suitable for measurement. An overall increase in bicyclics relative to pentacyclics (parameter j, Table A.4) was observed with increasing rank (Fig.5.30a) although, in the absence of quantitative data, it is not possible to say whether this is due to neoformation or cracking of pentacyclic terpanes. In view of the occurrence of bicyclic alkanes in the pyrolysates of pentacyclic triterpenoids (Hayatsu *et al.* 1987), the latter mechanism is at least possible.

A further change evident with increasing rank in the humic sample suite is the reduction in the relative concentration of the unknown C_{29} pentacyclic terpane, peak 34 (parameter f, Table A.4 and Fig.5.30b). As discussed in Section 4.4.1.4.2, the compound appears to be a marker for coals and sediments rich in vascular-plant matter; thus the abundance of this compound in terrigenous samples could be used as a maturity indicator. The utility of this compound as a maturation parameter extends to ranks of $\%R_o \approx 0.90$.

In general, the changes in pattern of the m/z 191 mass fragmentograms with increasing rank recorded in the lamosites parallel those outlined above for the humic samples. Although an increase in tricyclic and tetracyclic terpanes relative to pentacyclics is evident in the lamositic shales with increasing rank, the increase is much less significant than in the humic sample suite. The relative abundance of 3- and 4-ringed terpanes to 5-ringed terpanes is of the same order of magnitude in lamosites with $\%R_o > 3.00$ as that shown by the humic-rich sample in Fig.5.29e ($\%R_o = 0.75$). Akin to the coals and terrigenous samples, bicyclic terpanes are relatively abundant and show an overall decrease with increasing rank (Fig.5.30a).

Major differences between the terpane distributions of the lamosites and terrigenous samples through the rank range lie in the Tm/Ts and hopane/moretane ratios. The relatively high amounts of Ts recorded in low-rank lamosites (Fig.4.12) show little change in concentration relative to Tm at higher ranks. Thus Tm/Ts ratios appear to be insensitive to increased thermal stress in lamositic shales. Hopane/moretane ratios also show little response through the rank range,

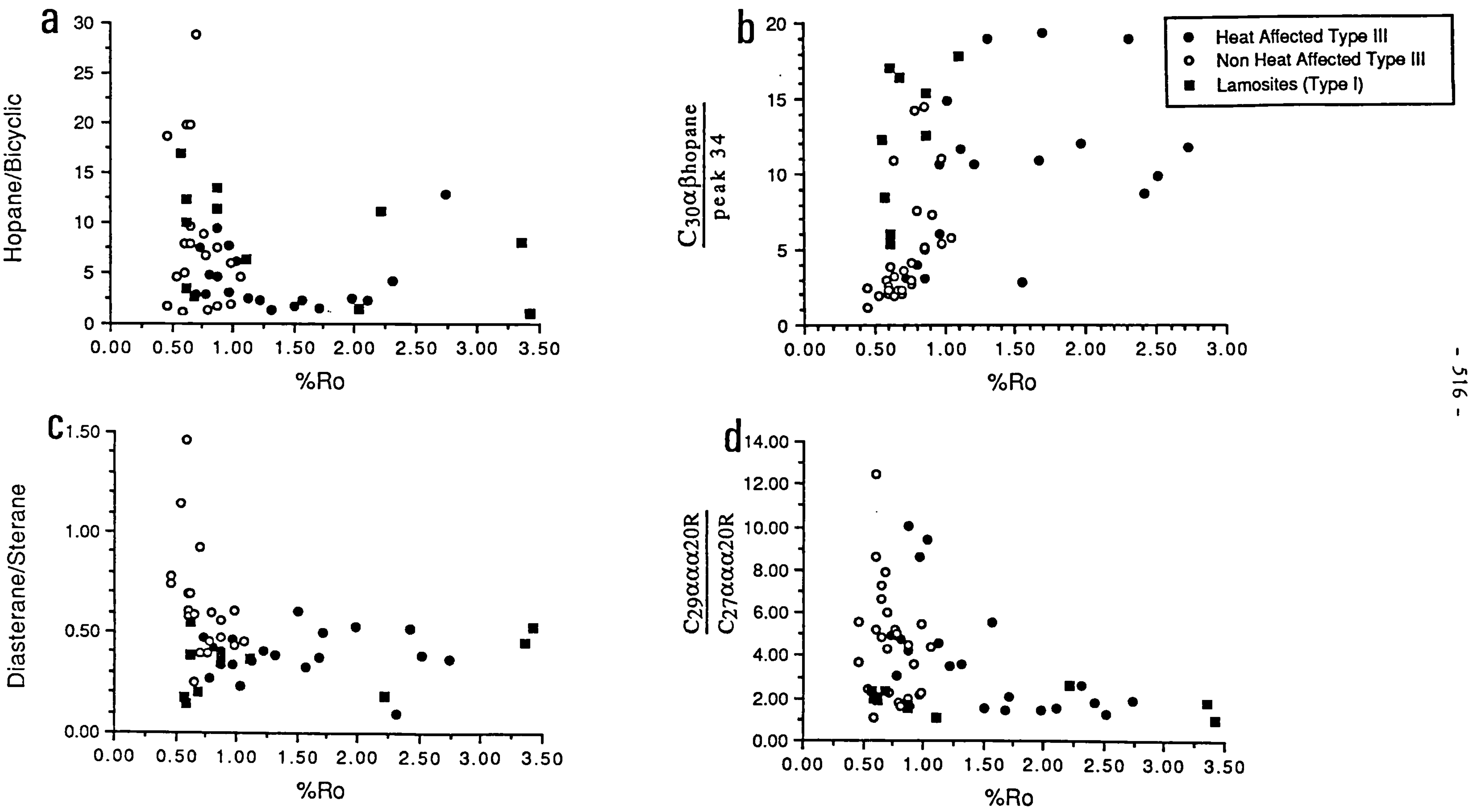


Fig.5.30 Changes in distributions of polycyclic alkanes with increasing rank (see Tables A.4 and A.5 for data).

having almost reached their equilibrium values in low-rank samples (see Section 4.3.3.1.2.1). The "anomalous" value of Tm/Ts and hopane/moretane ratios within the lamositic shale suite clearly indicate that these widely-used maturity parameters are susceptible to the influence of organic-matter type.

Steranes

Changes in the general pattern of steranes with increasing rank in the humic sample suite are illustrated in Fig.5.31. As for the hopane mass fragmentograms, the salient changes that are apparent are well documented and form the basis of commonly-used maturity parameters (see Section 2.3.3.4.1). The main features are a progressive increase in the 20S epimer of the regular steranes with respect to the biologically-derived 20R configuration, the increase in $\alpha\beta\beta$ steranes and the loss of the $\beta\alpha\alpha$ configuration. Rearranged steranes (diasteranes) show a general decrease relative to their non-rearranged counterparts (Fig.5.30c). Less well documented in the natural environment is the shift in the profile of the regular steranes from distributions dominated by C_{29} homologues to those in which C_{27} compounds are more prominent (parameter m in Table A.5; Fig.5.30d). This shift is also evident within the diasteranes. Changes in the carbon-number distribution of steranes analogous to those noted in this study have been reported following laboratory pyrolysis experiments (Seifert 1978; Rullkötter *et al.* 1984a; Cassani and Eglinton 1986; Jones *et al.* 1987), although diasteranes were either negligible or absent in the pyrolysates.

A similar overall sequence of changes is recorded in the sterane profiles of the lamosites although, in contrast to the terrigenous sediments, the $C_{29}/C_{27}\alpha\alpha\alpha 20R$ ratio does not vary markedly throughout the rank range.

The changes in the terpane and sterane distributions outlined above represent general trends which were observed with increasing rank. Values of the molecular parameters commonly used as maturity indices are plotted against sample rank (vitrinite reflectance) for all specimens in the different sample suites under consideration in Fig.5.32. The principal features evident from the plots are summarised below:-

1. Most apparent is the reversal in the trends of the majority of ratios which occurs at relatively high levels of maturity. Thus, many samples which have experienced rapid heating from igneous activity and which have maturities greater than those expected in the wet-gas window ($>\%R_o \approx 2.00$) have biomarker ratios comparable with those of samples in the early zones of catagenesis

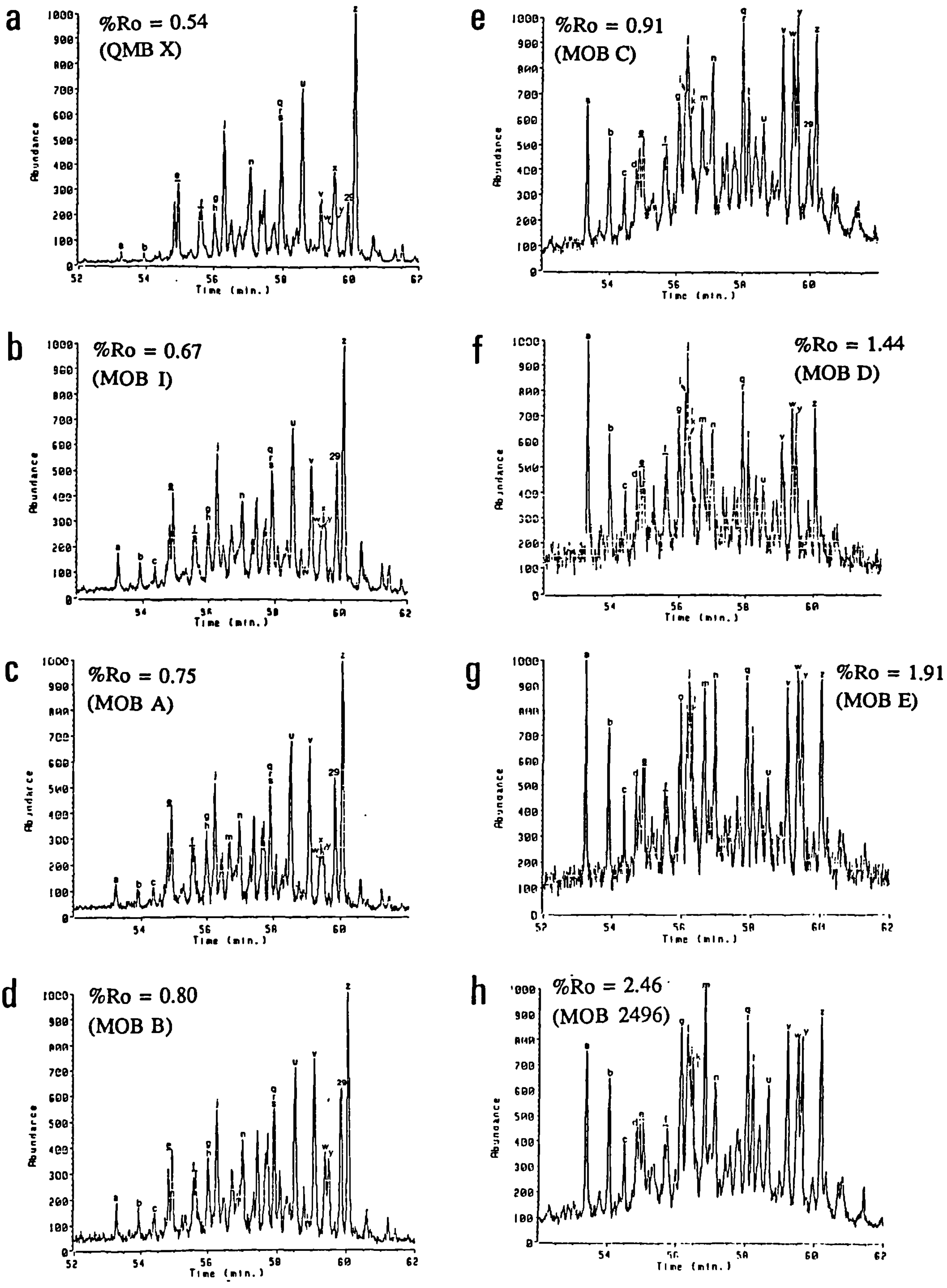


Fig.5.31 M/z 217 mass fragmentograms showing changes in sterane distributions with increasing rank in coals and sediments containing predominantly humic macerals (peak assignments in Table 4.6).

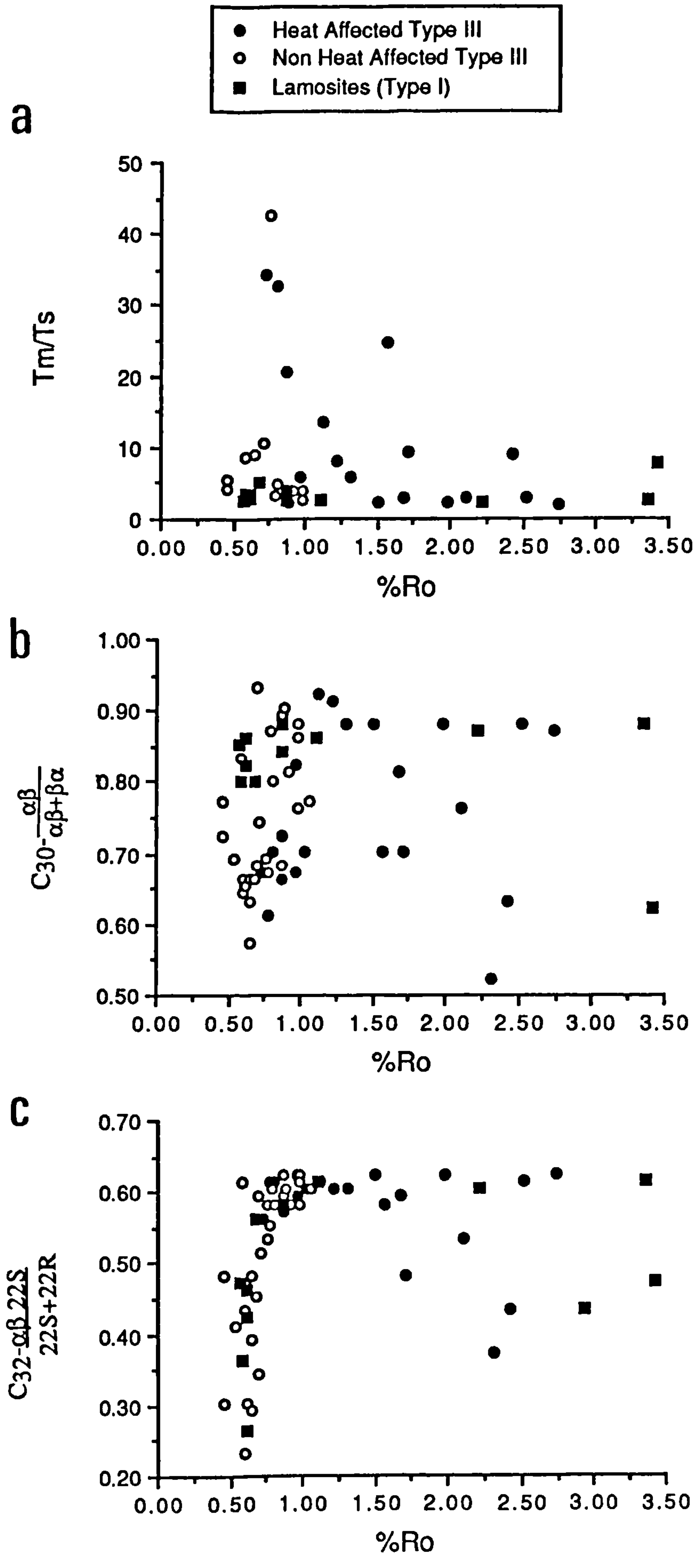


Fig.5.32 Plots showing values of various commonly-used molecular maturity parameters based on hopanes and steranes at different ranks (see Tables A.4 and A.5 for methods of calculation).

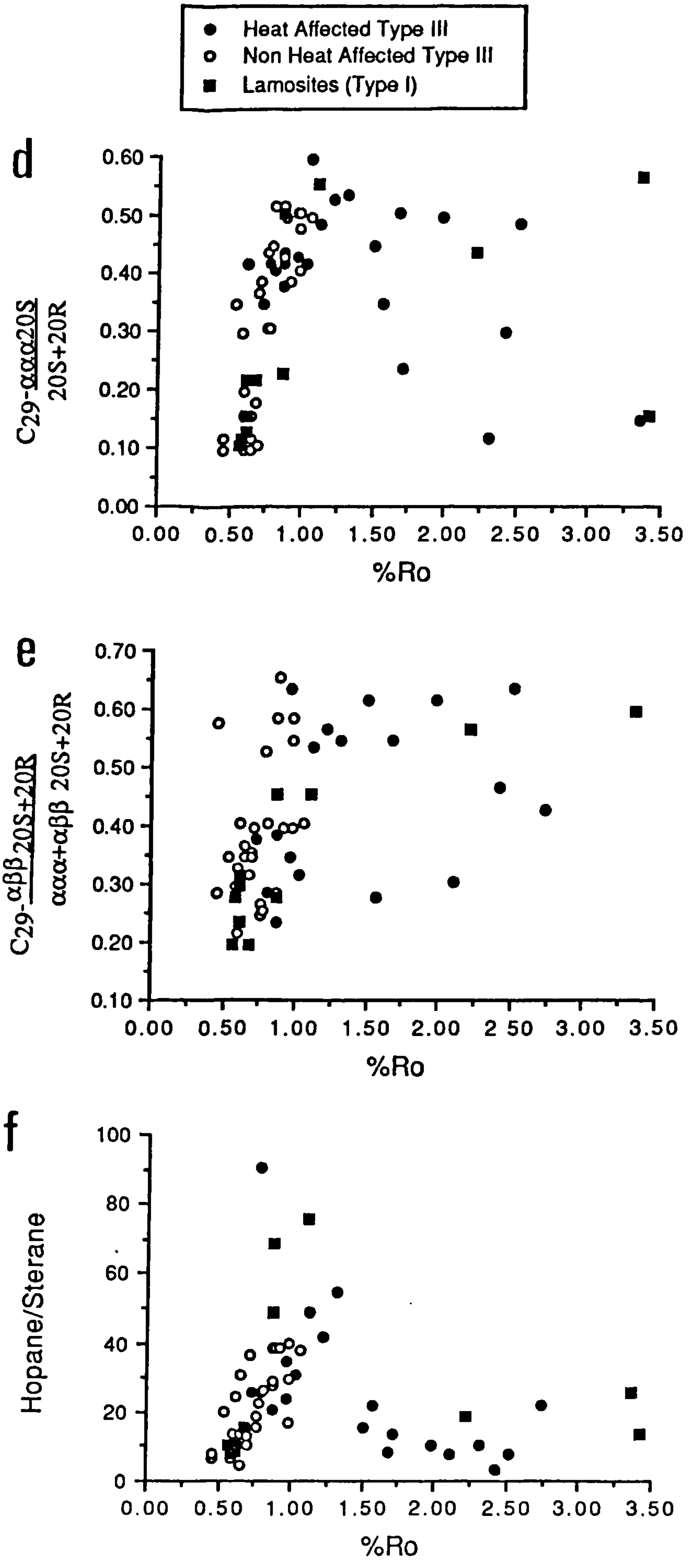

● Heat Affected Type III
o Non Heat Affected Type III
■ Lamosites (Type I)
d
C_{29}-$\frac{\alpha\alpha\alpha 20S}{20S+20R}$
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50
%Ro
e
C_{29}-$\frac{\alpha\beta\beta\ 20S+20R}{\alpha\alpha\alpha+\alpha\beta\beta\ 20S+20R}$
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00 0.50 1.00 1.50 2.00 2 50 3.00 3.50
%Ro
f
Hopane/Sterane
100
80
60
40
20
0
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50
%Ro

Fig.5.32 (cont.).

(<$\%R_o \approx 0.70$). Reversals in the trends based on triterpanes and steranes occur at ranks of $\%R_o \approx 1.30$).

2. For most of the indices, and most conspicuously for those from coals and terrigenous sediments, there is a general trend of rapidly heat-affected organic matter at a given rank developing a more immature molecular signature than organic matter that has attained the same rank solely through exposure to "normal" background geothermal gradients.

3. Although biomarker-maturity indices tend towards their equilibrium values with increasing rank, end-point values are not attained in many rapidly heat-affected samples which have reached maturity levels at which equilibrium would be expected.

The last observation is particularly well illustrated by the sterane distributions in Figs 5.31g and h. Although the geological αββ and 20S configurations are present, the abundances of these components relative to their presumed biological precursors are much lower than conventional biomarker theory would dictate, i.e. equilibration would be expected at these high ranks. Of all the ratios studied, that based on αββ steranes (parameter l, Table A.5) always fell significantly below the proposed end-point value (c.0.80, Seifert and Moldowan 1979; Mackenzie *et al.* 1980). Although an increase in hopane/sterane ratios has been noted with increasing depth in borehole sequences (Cardoso *et al.* 1986), a decrease is observed in this ratio at relatively high rank levels (Fig.5.32f; parameter i, Table A.4). Reversals in molecular ratios are not confined to saturated hydrocarbons (see next section).

5.3.2.2.3 Aromatic Hydrocarbons

5.3.2.2.3.1 General Trends

Changes in the overall pattern of aromatic hydrocarbon distributions with increasing rank in coals and humic sediments are illustrated by the gas chromatograms in Fig.5.33. Variation in the proportion of alkylated naphthalenes to phenanthrene is discernible over the rank range studied (Fig.5.34; parameter h, Table A.6). The relatively high concentration of phenanthrene (peak 19) noted in lower-rank samples (probably predominantly diagenetically derived) is reduced, relative to other components, with increasing rank, which probably reflects dilution by catagenetically-produced naphthalenes or, as Radke *et al.*(1982b) have postulated,

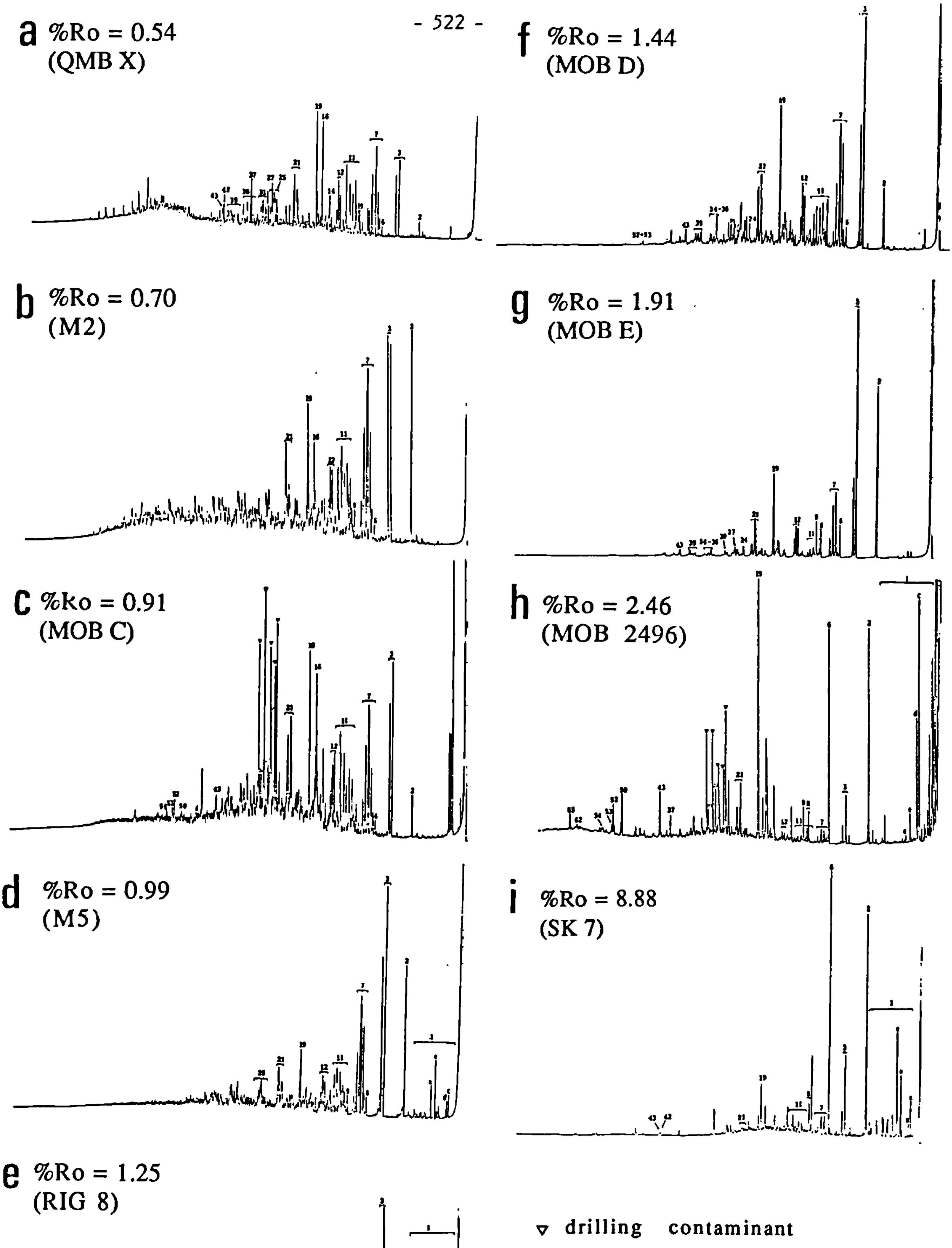


Fig.5.33 Gas chromatograms showing changes in distributions of aromatic hydrocarbons with increasing rank in coals and sediments containing predominantly humic macerals (peak assignments in Table 4.7).

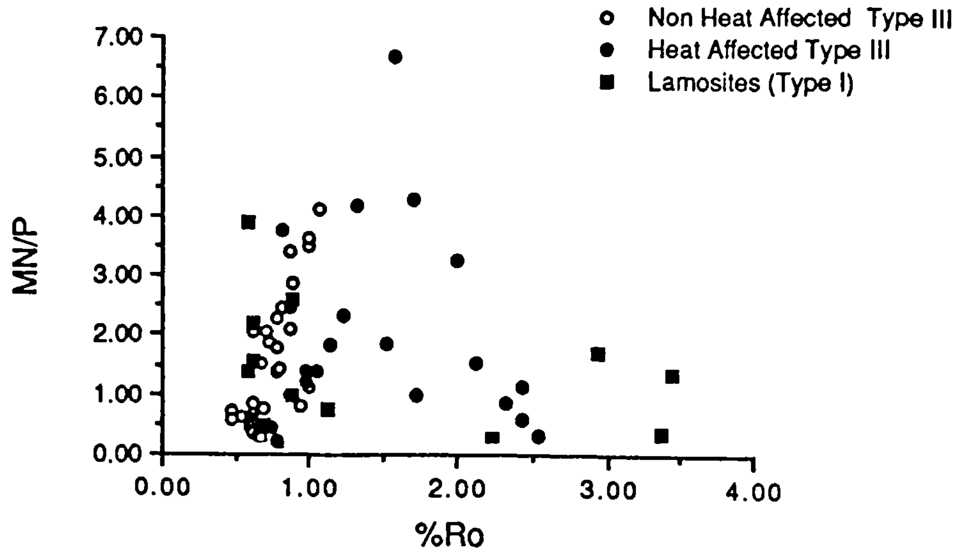


Fig.5.34 Plot showing variation of methylnaphthalene/phenanthrene ratios at different ranks (see Table A.6 for calculation).

is due to alkylation to methylphenanthrenes. The relative concentration of phenanthrene increases again in high-rank samples (c.$\%R_o \approx 1.50+$), in which parent PAH with ≥ 3 aromatic rings also become more prominent. This association is suggestive of a common source. Phenanthrene is a major product of fossil fuel combustion/pyrolysis processes (Lee *et al.* 1977), thus, like the high molecular-weight PAH (see Section 2.3.4.2), the phenanthrene in the high-rank samples probably is derived from the combustion/pyrolysis of organic matter through contact with hot igneous material, in this case the Midland Valley Sill. That biphenyl and related compounds are salient components in the aromatic hydrocarbon fractions of the high-rank coals and terrigenous samples (biphenyl dominates the distribution in the meta-anthracite; Fig.5.33i) lends support to the suggestion made previously (Section 4.4.1.4.6) that a major source of compounds with the biphenyl skeleton in Midland Valley samples originates from the high-temperature alteration of vascular-plant tissues.

The distributions of aromatic hydrocarbons at different ranks in the lamosites differ from those of the humic samples in that the complexity observed in the relatively low-rank samples (Figs 5.35a,b) persists to much higher ranks ($\%R_o \approx 2.00+$). Partially aromatised biogenic components, e.g. alkyltetralins and 1,2,5,6-Tetramethylnaphthalene, are still detected at high ranks although they are of minor abundance compared with alkylnaphthalenes and phenanthrenes, whose relative abundance increases with rising sample maturity. The prominence of the high molecular-weight "hump" in the samples with ranks of $\%R_o$av=0.81 and 2.16 (Figs 5.35d,f) may reflect the sheared nature of these specimens, in which

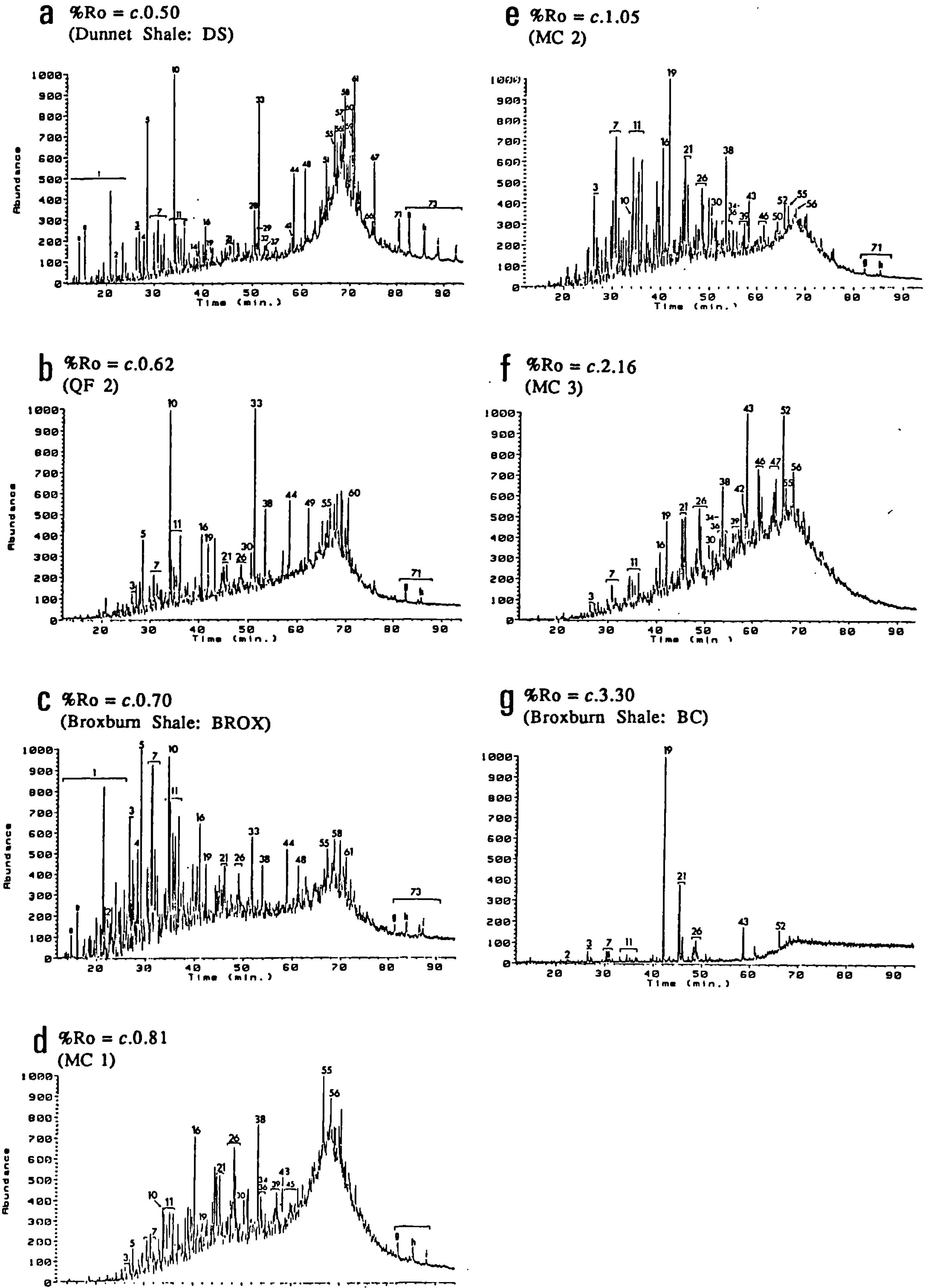


Fig.5.35 Total ion current (TIC) chromatograms showing changes in the distributions of aromatic hydrocarbons with increasing rank in lamositic shales (peak assignments in Table 4.7).

the lower molecular-weight compounds may have been reduced due to evaporative loss, water washing or biodegradation.

PAH with a pyrolytic-like distribution become increasingly prominent in the total ion chromatograms and begin to dominate the distributions in lamosites with $\%R_o \approx 2.00+$ (Figs 5.35f,g). The increase in baseline "noise" with increasing rank reflects an increased contribution from homologous series of alkylbenzenes.

Notwithstanding the differences in the overall pattern of aromatic hydrocarbon distributions between the lamosites and humic samples, overall changes in the distributions of alkylphenanthrenes and alkylnaphthalenes are similar, although for some ratios based on these compounds, the rate of change differs (see next section).

5.3.2.2.3.2 Variations in Maturity Parameters based on Alkylated Naphthalenes and Phenanthrenes

Changes in the overall shape of the aromatic hydrocarbon envelope are accompanied by changes in the proportions of different isomers present within the alkylnaphthalene and alkylphenanthrene series (Fig.5.36). Variations in the isomer distributions in these compound classes involve rearrangements which occur in response to increased thermal stress, where methyl groups shift from α-positions to sterically less crowded β-positions with increasing rank (Section 2.3.4.4). As outlined in the introduction, the current project is not so much concerned with the fact that these changes occur *per se*, since these are well documented (see Radke 1987 for a review): this study is more concerned with the rate of change of various maturity parameters based on these aromatic hydrocarbons in organic matter of different types exposed to different heating rates. Plots showing the changes in the different molecular-maturity indices, based on alkylated naphthalenes and phenanthrenes, with increasing rank are shown in Fig.5.37. The plots are presented as pairs so as to include and exclude the meta-anthracite. The data are summarised as follows:-

1. Reversals are observed in the ENR, DNR, TNR-1 and MPI parameters over the rank range studied (parameters defined in Section 2.3.4.4 and in Appendix II p.243).

2. For the ratios based on aliphatic hydrocarbons, the aromatic hydrocarbon distributions in the heat-affected terrigenous samples are generally more immature than those in the non heat-affected samples of similar rank. This difference is particularly pronounced for the TNR-1 ratio (Figs 5.37g,h) in which the samples exposed to different heating rates follow distinctly different trends

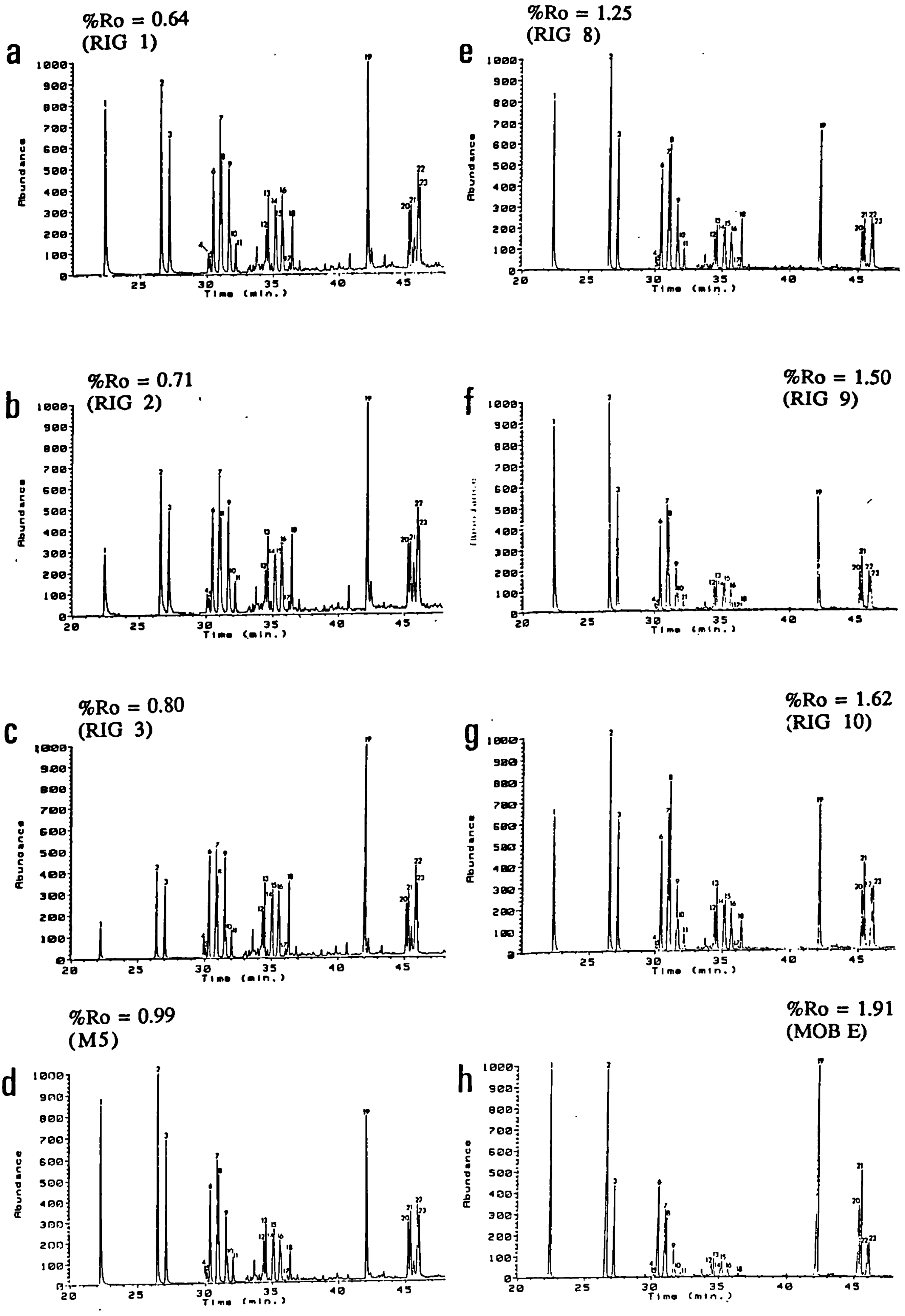


Fig.5.36 Added mass fragmentograms (m/z 128, 142, 156, 170, 178, 192) showing changes in the distributions of naphthalenes and phenanthrenes with increasing rank in coals and sediments containing predominantly humic macerals (peak assignments in Table 5.2).

Table 5.2 Peak assignments for isomers of alkylated naphthalenes and phenanthrenes (see Fig.5.36).

Peak No	Name	Abbreviation	Substitution
1	Naphthalene	N	_
2	2-Methylnaphthalene	2-MN	β
3	1-Methylnaphthalene	1-MN	α
4	2-Ethylnaphthalene	2-EN	β
5	1-Ethylnaphthalene	1-EN	α
6a	2,6-Dimethylnaphthalene	2,6-DMN	β,β
6b	2,7-Dimethylnaphthalene	2,7-DMN	β,β
7a	1,3-Dimethylnaphthalene	1,3-DMN	α,β
7b	1,7-Dimethylnaphthalene	1,7-DMN	α,β
8	1,6-Dimethylnaphthalene	1,6-DMN	α,β
9a	1,4-Dimethylnaphthalene	1,4-DMN	α,α
9b	2,3-Dimethylnaphthalene	2,3-DMN	β,β
10	1,5-Dimethylnaphthalene	1,5-DMN	α,α
11	1,2-Dimethylnaphthalene	1,2-DMN	α,β
12	1,3,7-Trimethylnaphthalene	1,3,7-TMN	α,β,β
13	1,3,6-Trimethylnaphthalene	1,3,6-TMN	α,β,β
14a	1,3,5-Trimethylnaphthalene	1,3,5-TMN	α,β,α
14b	1,4,6-Trimethylnaphthalene	1,4,6-TMN	α,α,β
15	2,3,6-Trimethylnaphthalene	2,3,6-TMN	β,β,β
16a	1,2,7-Trimethylnaphthalene	1,2,7-TMN	α,β,β
16b	1,6,7-Trimethylnaphthalene	1,6,7-TMN	α,β,β
16c	1,2,6-Trimethylnaphthalene	1,2,6-TMN	α,β,β
17	1,2,4-Trimethylnaphthalene	1,2,4-TMN	α,β,α
18	1,2,5-Trimethylnaphthalene	1,2,5-TMN	α,β,α
19	Phenanthrene	P	-
20	3-Methylphenanthrene	3-MP	β
21	2-Methylphenanthrene	2-MP	β
22a	9-Methylphenanthrene	9-MP	α
22b	4-Methylphenanthrene	4-MP	α
23	1-Methylphenanthrene	1-MP	α

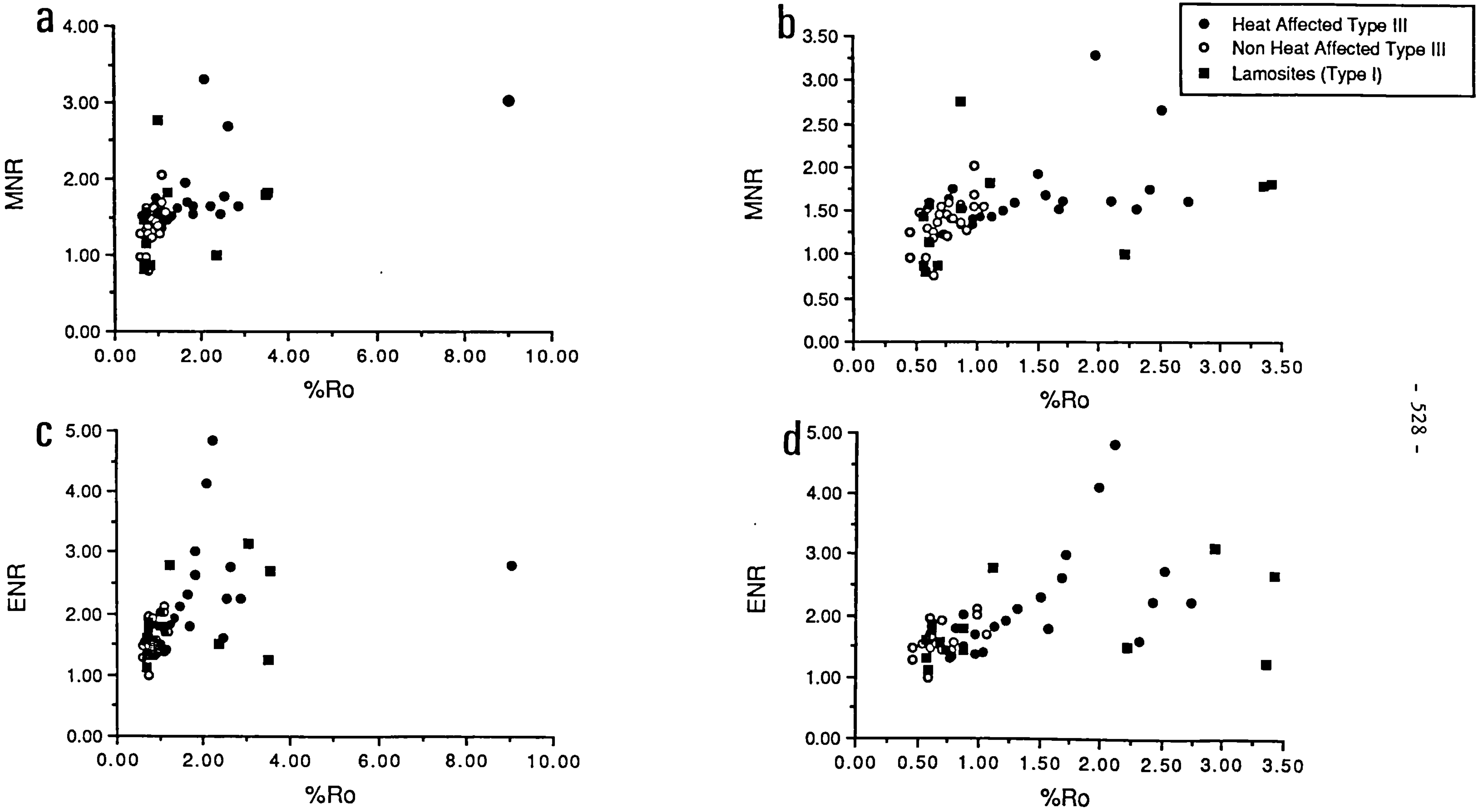


Fig.5.37 Plots showing values of commonly-used molecular-maturity parameters based on aromatic hydrocarbons at different ranks (see Table A.6 for methods of calculation).

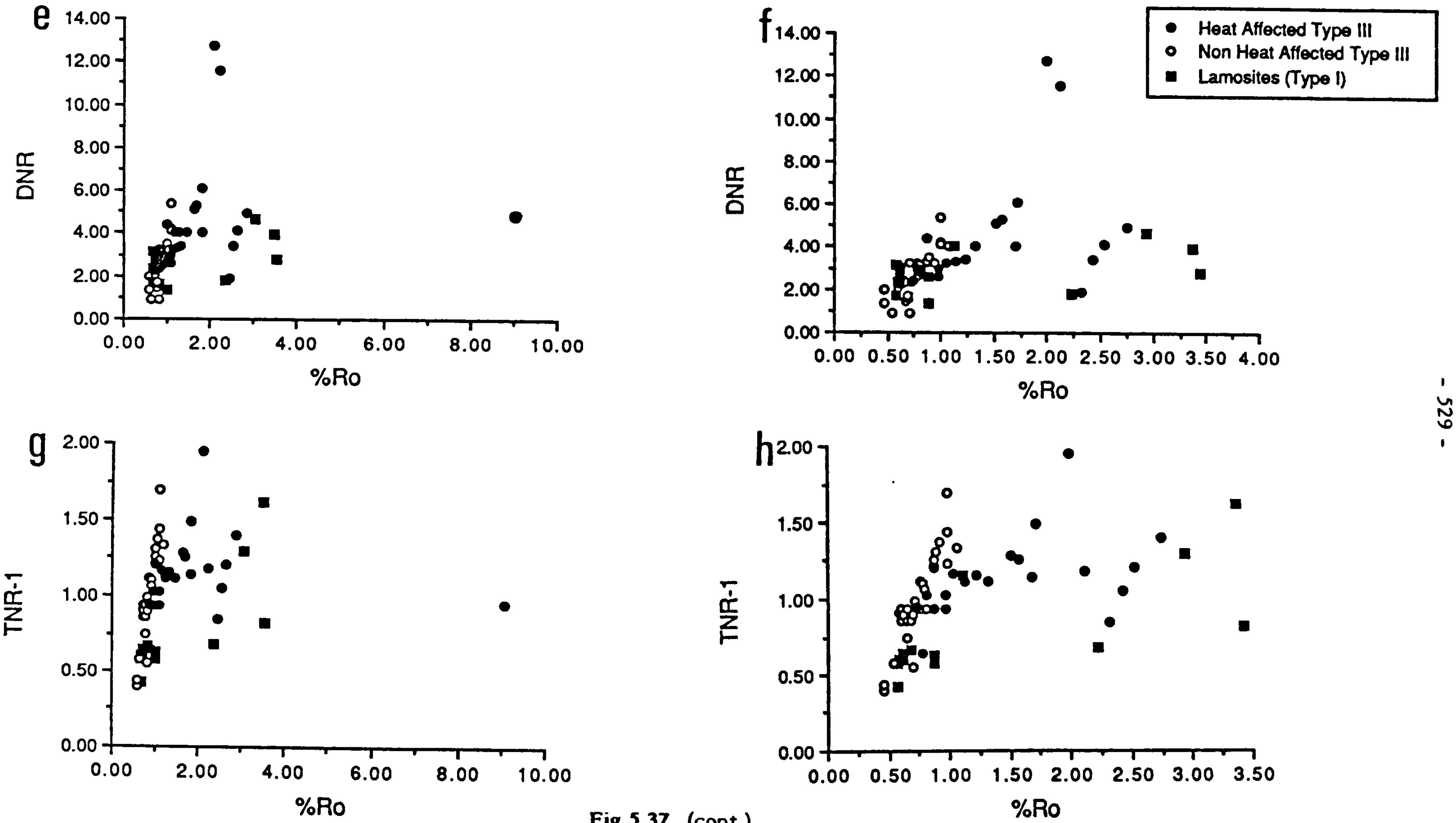

e
DNR
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
%Ro
f
DNR
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
%Ro
● Heat Affected Type III
○ Non Heat Affected Type III
■ Lamosites (Type I)
g
TNR-1
2.00
1.50
1.00
0.50
0.00
0.00
2.00
4.00
6.00
8.00
10.00
%Ro
h
TNR-1
2.00
1.50
1.00
0.50
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
%Ro

Fig.5.37 (cont.).

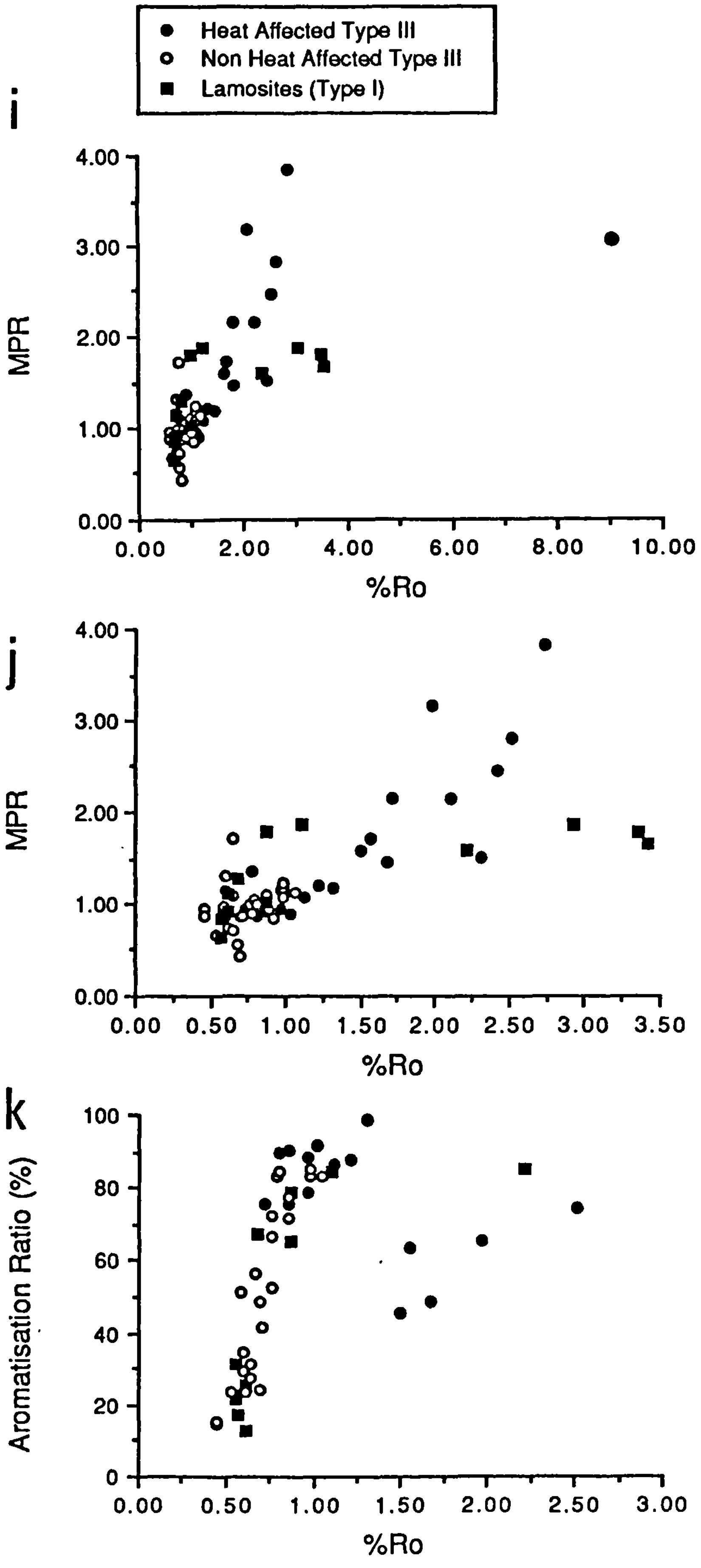

● Heat Affected Type III
○ Non Heat Affected Type III
■ Lamosites (Type I)
i
MPR
4.00
3.00
2.00
1.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
%Ro
j
MPR
4.00
3.00
2.00
1.00
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
%Ro
k
Aromatisation Ratio (%)
100
80
60
40
20
0
0.00
0.50
1.00
1.50
2.00
2.50
3.00
%Ro

Fig.5.37 (cont.).

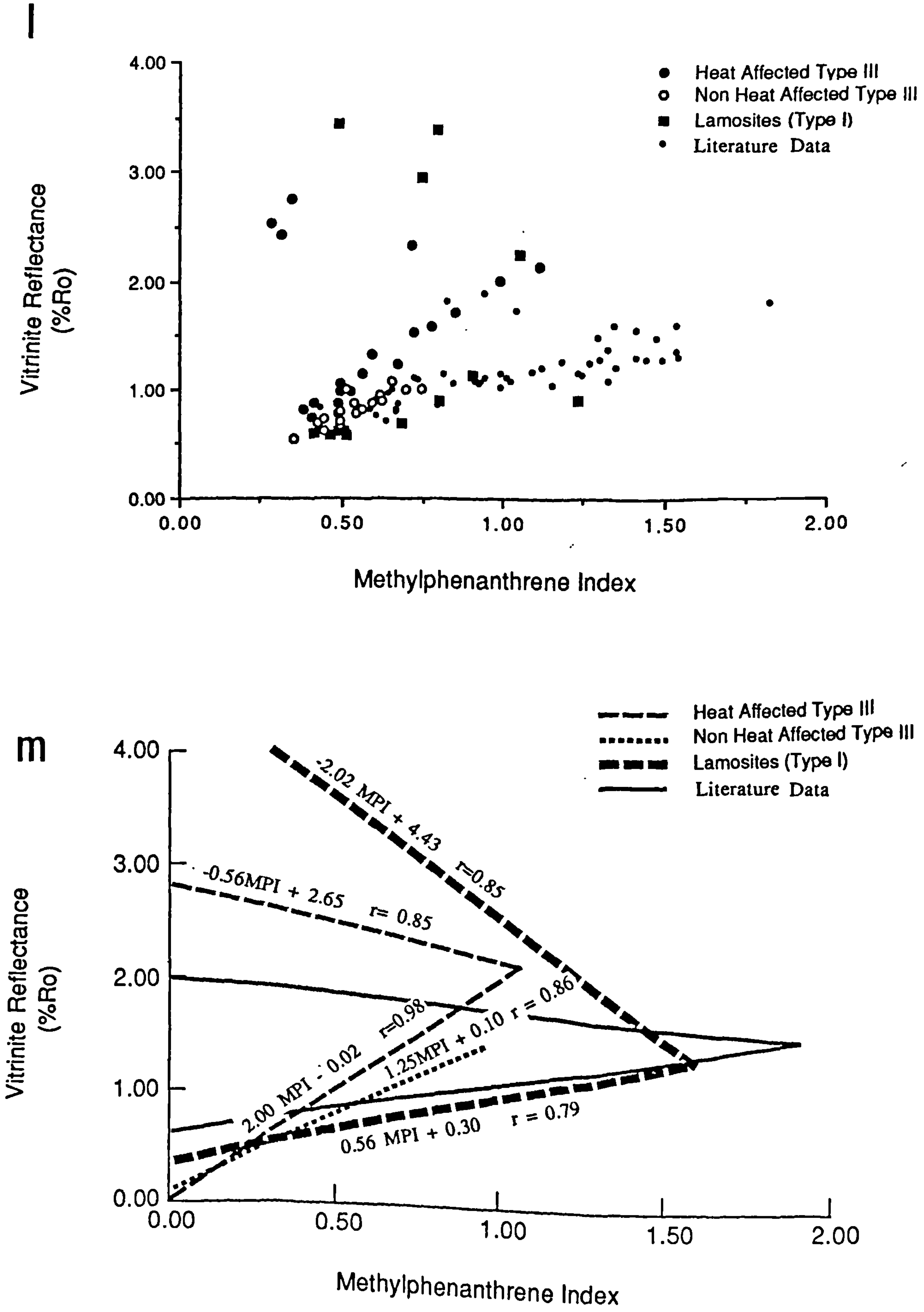

l
4.00
3.00
2.00
1.00
0.00
0.00
0.50
1.00
1.50
2.00
Vitrinite Reflectance (%Ro)
Methylphenanthrene Index
● Heat Affected Type III
○ Non Heat Affected Type III
■ Lamosites (Type I)
• Literature Data
m
4.00
3.00
2.00
1.00
0.00
0.00
0.50
1.00
1.50
2.00
Vitrinite Reflectance (%Ro)
Methylphenanthrene Index
Heat Affected Type III
Non Heat Affected Type III
Lamosites (Type I)
Literature Data
-2.02 MPI + 4.43
r=0.85
-0.56MPI + 2.65
r= 0.85
r=0.98
2.00 MPI - 0.02
1.25MPI + 0.10 r = 0.86
0.56 MPI + 0.30
r = 0.79

Fig.5.37 (cont.).

at ranks <$\%R_o \approx 2.00$. Only the plot for the TNR-1 ratio is presented here: that for the TNR-2 ratio (Radke *et al.* 1986) displays identical trends although, as noted by Radke (1987), the correlation between this parameter and vitrinite reflectance is higher than for the TNR-1 ratio devised by Alexander *et al.* (1985).

3. In contrast to the maturity parameters based on steranes and triterpanes, those based on alkylated naphthalenes and phenanthrenes continue to increase in heat-affected sediments to rank levels of $\%R_o \approx 2.00$ before decreasing.

4. For the lamosites, the rate of change of ratios based on methylphenanthrenes (Figs 5.37i,j,l,m) differs from that for the coals and terrigenous sediments. The methylphenanthrene ratio (MPR; Fig.5.37j) reaches a plateau at $\%R_o \approx 1.10$ in the lamosites while ratios in the coaly samples continue to increase with further maturation. Whether the value for the meta-anthracite forms part of a general trend or is part of a reversal could not be established due to the data gap in the $\%R_o$=4.00-8.00 range. Methylphenanthrene indices from igneous-affected Midland Valley humic coals and terrigenous sediments lie on a maturation track which differs significantly from the "conventional" pathway constructed using existing literature data (Radke *et al.*. 1982a,b). A reversal in the MPI does not occur until $\%R_o \approx 2.00$ for the heat-affected coals and terrigenous sediments studied. Different trends were also evident for lamosites and for coaly material that has not been heat affected. The trend shown for the terrigenous samples was established excluding the meta-anthracite since the nature of the trend for samples with $\%R_o$>3.00 is not known.

5.3.2.2.3.3 Aromatic Steroids

The only changes apparent in the distributions of C-ring monoaromatic steroids with increasing rank were the diminishing concentrations of 5α(H) isomers and an enhancement of short-chain components. Both of these factors have been previously reported (Mackenzie *et al.* 1981; Mackenzie 1984; Rioli *et al.* 1986). Data from geological samples (Moldowan and Fago 1986; Riolo *et al.* 1986) and laboratory-kinetics experiments (Abbott *et al.* 1988) have indicated that rearranged C-ring monoaromatic steroids are more stable than their non-rearranged counterparts, i.e. the former should increase relative to the latter with increasing rank. No such changes were apparent in the current study. The difference in the relative abundance between the two C-ring monoaromatic classes in the terrigenous and lamositic-sample suites was maintained throughout the rank range.

An increase in the relative concentration of low molecular-weight triaromatic and methyltriaromatic hydrocarbons was observed with increasing sample maturity, in agreement with previously established trends (Mackenzie *et al.* 1981; Mackenzie 1984). Although no changes in the pattern of C_{27}-C_{29} homologues in the triaromatics were noted in the different sample suites, variations were evident in the nuclear methyl-substituted triaromatic series of the lamositic shales. Increased exposure to thermal stress was paralleled by an increase in compounds eluting as peaks 4, 5 and 7 in the m/z 245 mass fragmentograms (Fig.5.38). No such variation was evident in the type III series; the methyltriaromatic distribution in the high-rank samples was very similar to that at low rank (e.g. Fig.4.57b). Increased relative contributions from low molecular-weight components (peaks 1 and 2) were seen at higher ranks.

Changes in the relative amounts of C-ring, non-rearranged, monoaromatic and triaromatic steroids occur throughout the rank range as the former components aromatise to the latter with increasing rank (Mackenzie *et al.* 1981; Shi Ji-Yang *et al.* 1982). The manner in which this "aromatisation ratio" (parameter m, Table A.6) changes with rank in the Midland Valley samples was shown in Fig.5.37k. As with many of the other maturity indices studied, a reversal is apparent, which occurs at $\%R_o \approx 1.20$.

5.3.2.2.4 Reversals in Molecular-Maturity Parameters

Earlier sections have shown that reversals occur in the trends of many commonly-used maturity indices, based on both saturated and aromatic hydrocarbons, with increasing rank. This work therefore verifies the reversals in biomarker-maturity ratios which have been recorded by other workers, as discussed below.

The apparent increase in the immaturity of many samples, as expressed by a decrease in biomarker ratios beyond the oil window, parallels the reversals in maturation trends that have been reported following the pyrolysis of organic matter at high temperatures (Lewan *et al.* 1986; Rullkötter and Marzi 1989; Abbott *et al.* 1990; Peters *et al.* 1990). While the attainment of high temperatures in pyrolysis work (typically at least 300°C) appears to be a prerequisite for the reversals, that these occur in some rank types (phosphatic and carbonate-rich shales, Lewan *et al.* 1986; Peters *et al.* 1990) and not in others (siliceous rocks; Peters *et al.* 1990) points also to a mineral-matrix control on some isomerisation-based biomarker reactions (Peters *et al.* 1990).

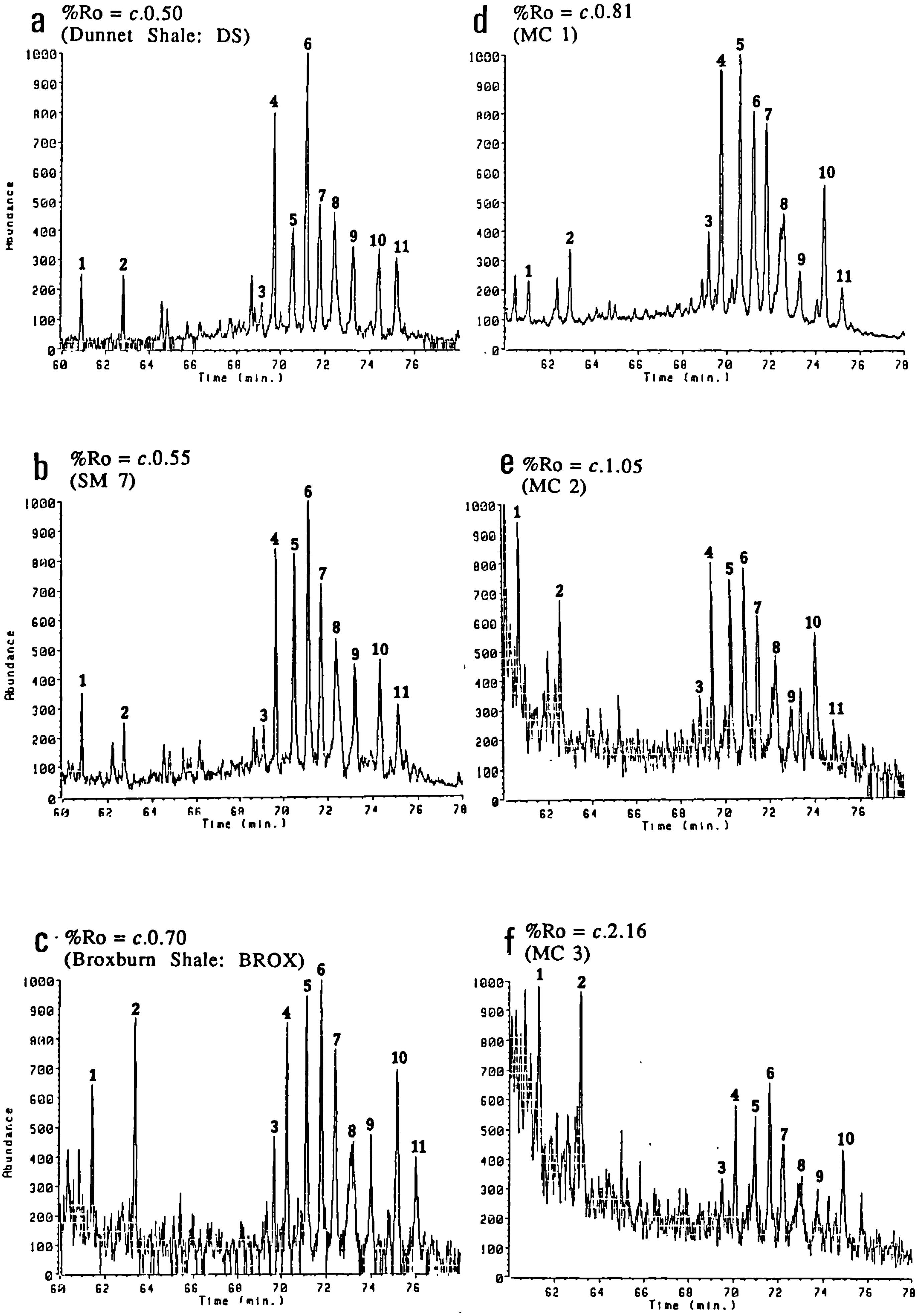


Fig.5.38 M/z 245 mass fragmentograms showing changes in the distributions of nuclear methyl-substituted triaromatics with increasing rank in lamositic shales (see Table 4.9b for peak assignments).

Support for lithologically-mediated reversals is based on observations in the natural environment. The increasing departure of the 22S/22S+22R homohopane ratio from its equilibrium value in a sequence within the Monterey Formation can be correlated with a progression from a siliceous to a phosphatic/carbonate lithofacies (Curiale and Odermatt 1989). A mineralogical control has also been invoked by Strachan *et al.* (1989) to account for the marked deviation from the equilibrium plateau (towards lower values) of the 20S/20S+20R sterane ratio in the high-maturity zone ($\%R_0$=1.62-2.56) of an Australian well. The reasoning of Strachan *et al.* (1989) stems from the radical differences in the kinetics of sterane isomerisation between adjacent shales and coals. The sediments in the high-rank zone, at the base of the well, are thought to be more coaly than those in the overlying sequence because sterane isomerisation in coals has been shown (by the same authors) to be less responsive to temperature increase than the equivalent process in shales. A further possibility considered by Strachan *et al.* (1989) is the preferential destruction of the 20S sterane epimer at the high temperatures encountered at the base of the well. Peters *et al.* (1990) offered the same explanation to account for the lowering of ratios seen in high-temperature bomb experiments.

The reversals in the Midland Valley sample suite and elsewhere clearly contradict the conventional premise that the isomerisation reactions on which the biomarker-maturation indices are based progress, with increasing sediment maturity, to an equilibrium value which is maintained at higher rank levels (Mackenzie *et al.* 1980; Mackenzie and Maxwell 1981). The importance of simple product-precursor conversion in controlling changes in biomarker ratios appears to be at least overstated, if not invalid. Peters *et al.* (1990) point out that a given ratio will not be determined solely by thermal isomerisation, but will also be influenced by the differential thermal destruction of isomers and by sample lithology. The more recent pyrolysis experiments of Wang (1990) and Abbott *et al.* (1990) have led to the further questioning of the validity of the "traditional" concept of biomarker isomerisation in governing the production of "geological" configurations observed in soluble extracts. These authors have highlighted the lack of importance of 20R to 20S isomerisation in steranes in the "free" state (i.e. in the bitumen fraction), which introduces the possibility that anomalously low biomarker ratios may result, at least in part, from the preferential release of "biological" isomers from the kerogen matrix. Additional relevant pyrolysis work by Eglinton (1988) and Eglinton and Douglas (1988) has shown that yields of steranes and hopanes increase to a maximum during kerogen pyrolysis (hopane yields are higher than steranes) and that maximum sterane yield precedes that of hopanes. These authors have suggested that the latter point is indicative of the stronger attachment of hopane structures to the kerogen. That the decrease in the abundance of hopanes is more abrupt than that for steranes in the pyrolysis experiments has been taken as an indication that hopanes are more thermally labile than steranes once they are released from kerogen. This possibility may account for the reversal in the trend of the hopane/sterane profile observed in the natural sample suite from the Midland Valley (Fig.4.32f). From experimental work it is becoming increasingly apparent that a given biomarker ratio is not simply a measure of the extent to which a given isomerisation reaction has progressed, but represents the net product of reactions involving conversion, generation and degradation. The relative importance of these processes will be governed by kinetic factors which will also change in different thermal regimes.

While lithological influences may dictate reversals in both laboratory and natural systems, the most significant controls on reversals of biomarker indices in the Midland Valley are heating rate and exposure to high temperatures. Matrix effects and differences in organic-matter type do not seem to be important in the Midland Valley, because reversals based on biomarkers have been recorded in lamosites as well as in coals and sediments whose gross kerogen composition is type III.

The observation that, for a given rank, maturity indices are lower for rapidly heat-affected organic matter than for that heated relatively slowly in the Midland Valley province emphasises the importance of heating rate in these reactions. An analogy exists in the work of Strachan *et al.* (1989) in which the importance of heating rate in controlling isomerisation reactions was predicted from reaction kinetics. Notwithstanding the differences in the kinetics of sterane-isomerisation reactions in coal-shale pairs, alluded to above, Strachan *et al.* (1989) have predicted, for a given temperature, a shift towards lower values of 20S/20S+20R ratios with increasing heat rate. Alexander *et al.* (1986b) also report differences in the behaviour of aromatic-maturity indicators in two sedimentary sequences with changes in heating rate.

The reversals recorded beyond the oil window in the Midland Valley, coupled with the results of high-temperature pyrolysis experiments, stress the importance of elevated temperatures in inducing reversals. It should be emphasised that the samples lying beyond the oil window have also experienced geologically rapid heating rates since they were collected from the thermal aureoles of sills. The relative influence of rapid heating rates and exposure to high temperatures in the attainment of maturities beyond the oil window could not be established because of the lack of samples in this higher maturity range with ranks that had been attained through the relatively slow heating rates of regional coalification. In view of the previously cited literature reports that low-maturity biomarker signatures are associated with samples exposed to rapid heating rates and/or high absolute temperatures, the balance of evidence suggests that a combination of both processes accounts for the reversals.

While the current work corroborates the reversal phenomenon which has, hitherto, been confined to parameters based on polycyclic alkanes (see Peters *et al.* 1990 for a review) and aromatic steroids (Rullkötter and Marzi 1989), the present investigation additionally shows that the reversals can also occur in maturity parameters based on alkylated naphthalenes and phenanthrenes. Previous studies have recognised that the dynamic ranges of ratios based on compounds within these classes extend to higher maturity levels than those for biomarker parameters. Radke *et al.* (1984) have established a good correlation between MNR, DNR and vitrinite reflectance up to rank levels of $\%R_0 \approx 1.50$. "Source effects" were invoked by these authors to explain differences that were observed, at a given reflectance level, between these ratios in two geographically distinct sets of coals (from West Canada and Germany). The differences in the same ratios that exist between the rapidly and slowly heated coals of similar ranks in the current study suggest that the disparities noted by Radke *et al.* (1984) may be a reflection of the exposure of the two suites of coals to different rates of heating.

No trends that can be specifically related to variations in organic-matter type can be detected in the distributions of MNR, DNR and ENR with increasing rank. Radke *et al.* (1986) also found no significant differences in the distributions of alkylnaphthalenes in sediments containing different kerogen types with increasing rank, although it should be noted that these authors were comparing type II and type III kerogens rather than type I and III as in the current work.

The scatter of points on the plot of MNR against reflectance for Midland Valley samples increases at ranks higher than $\%R_0 \approx 1.70$, but insufficient data are available to establish if the points beyond this rank level form part of a reversal. The dymanic range for the use of ENR, DNR and TNR-1 indices extends up to $\%R_0 \approx 2.00$, at least for organic matter that has experienced rapid heating. The applicability of the TNR-1 ratio as a rank indicator to levels within the wet-gas window (Alexander *et al.* 1985) is confirmed, but the present work suggests that the parameter may be usefully employed as a rank indicator up to the end of the wet-gas zone in organic matter which has been heated rapidly.

The rate of change of methylphenanthrene distributions in type III kerogens does not parallel that occurring in type II kerogen, which suggests that, in contrast to ratios based on alkylnaphthalenes, indices based on methylphenanthrene ratios are type-related (Radke *et al.* 1986; Radke 1988). The type-related effect on the MPR is evident from Fig.5.37i, in which the maturation track for the lamositic shales reaches an equilibrium plateau at $\%R_o \approx 1.10$, while ratios based on vitrinites in coals and terrestrial sediments continue to rise. Type-related trends are also apparent for the MPI. Values are lower for lamosites than for humic coals and sediments of the same rank, up to levels of $\%R_o \approx 2.00$: the converse is true at higher ranks.

The upper limit for application of the MPR has been stated as $\%R_o \approx 1.70$ (Radke *et al.* 1984). The current study shows that the working range of the MPR extends up to $\%R_o \approx 2.00$ for coals and terrigenous sediments exposed to high heating rates and also confirms a reversal in the MPR which was suggested by Radke *et al.* (1984), but which could not be proved because insufficient high-rank samples were available for analysis. These authors inferred a gradient reversal between $\%R_o = 1.70\text{-}2.50$ to explain the similarities between the MPR values of anthracites and low-volatile bituminous coals.

Marked differences in the rate of increase of the MPI with rank for the humic-rich materials which have been subjected to different heating rates are apparent from Figs 5.37 l and m. Furthermore, unlike the plots of Radke *et al.* (1982a) and Radke and Welte (1983) in which a reversal of the MPI occurs at $\%R_o \approx 1.35$, the utility of the MPI extends up to a rank of $\%R_o \approx 2.00$ at least for heat-affected coals and humic-containing sediments, before a reversal in the MPI trend occurs. Deviations from the maturation pathways originally defined by Radke and Welte (1983) have been reported by Boreham *et al.* (1988) for samples taken exclusively from Australian basins. Recalibration of the MPI with vitrinite reflectance for the Australian basins allows for an accuracy in defining the maturities of oils and sediments in which vitrinite is absent that is greater than would be achieved using the "standard" equation given by Radke and Welte (1983).

The differences in the reponse of the MPI to rank increase in different sample suites observed in this and other work suggests that this parameter is highly susceptible to differences in heating rate and organic-matter type. The variability of the maturation pathways of this ratio points to the probable existence of a geochemical "provincialism" effect for the MPI (and MPR) which is analogous to that reported for vitrinite coalification in different basins. Variations in the rate of rank increase in vitrinites of different basins are thought to reflect exposure to differing thermal and tectonic histories and also to the inherent variation which occurs in the constitution of the humic precursors (Jones *et al.* 1984). If the best use is to be made of parameters based on methylphenanthrene distributions, the indices should be calibrated against vitrinite reflectance in each basin under investigation.

5.3.2.2.5 Recalibration of the Methylphenanthrene Index

As shown above, trends in the changes of MPI with increasing rank (Figs 5.37 l, m) differ from the "conventional" patterns (Radke and Welte 1982; Radke *et al.* 1982a) from which vitrinite reflectance values can be determined through the use of the appropriate equations (see Section 2.3.4.4). Application of these "standard" formulae, which are widely used in basin evaluation studies, to the different sample-suite types currently considered gives rise to the distributions shown in Fig.5.39a.

At ranks less than $\%R_m \approx 0.90$, it is apparent that the non heat-affected coals and type III sediments lie within the standard error envelope constructed using the "standard" data of Radke and Welte (1983) and Radke *et al.* (1982a), although the overall trend of the data set, and also that of the heat-affected, humic samples, differs significantly from the Rc=Rm line at ranks less than $\%R_m \approx 1.35$. From Fig.5.39a it is evident that Rc will be underestimated at ranks greater than $\%R_m \approx 0.70$, particularly in heat-affected type III organic matter, and that the discrepancy between Rm and Rc will increase with rising rank up to $\%R_m \approx 1.35$. The calculated reflectances of lamosites with $\%R_m < 1.35$ are lower than predicted by the formula while the reverse applies at higher ranks.

In view of the deviations between observations in the Midland Valley data and those of "conventional" literature data, the equations derived from linear regression analysis in Fig.5.37m were used to recalibrate the MPI. The modified plot (Fig.5.39b) clearly shows a very good "fit" of data within the standard error envelope about the Rm=Rc line for type III kerogens. Discrepancies in the lamositic shale sample suite probably reflect the influence of organic-matter type and possibly also inaccuracies in the determination of Rm due to reflectance-suppression effects.

5.3.2.2.6 Effect of Different Background Geothermal Gradients on Molecular-Maturity Parameters

In the last section comparisons were made between molecular signatures which had been achieved through igneous activity and those that had been attained through regional coalification. This section considers the effects of different regional geothermal gradients on maturation profiles by comparing maturity

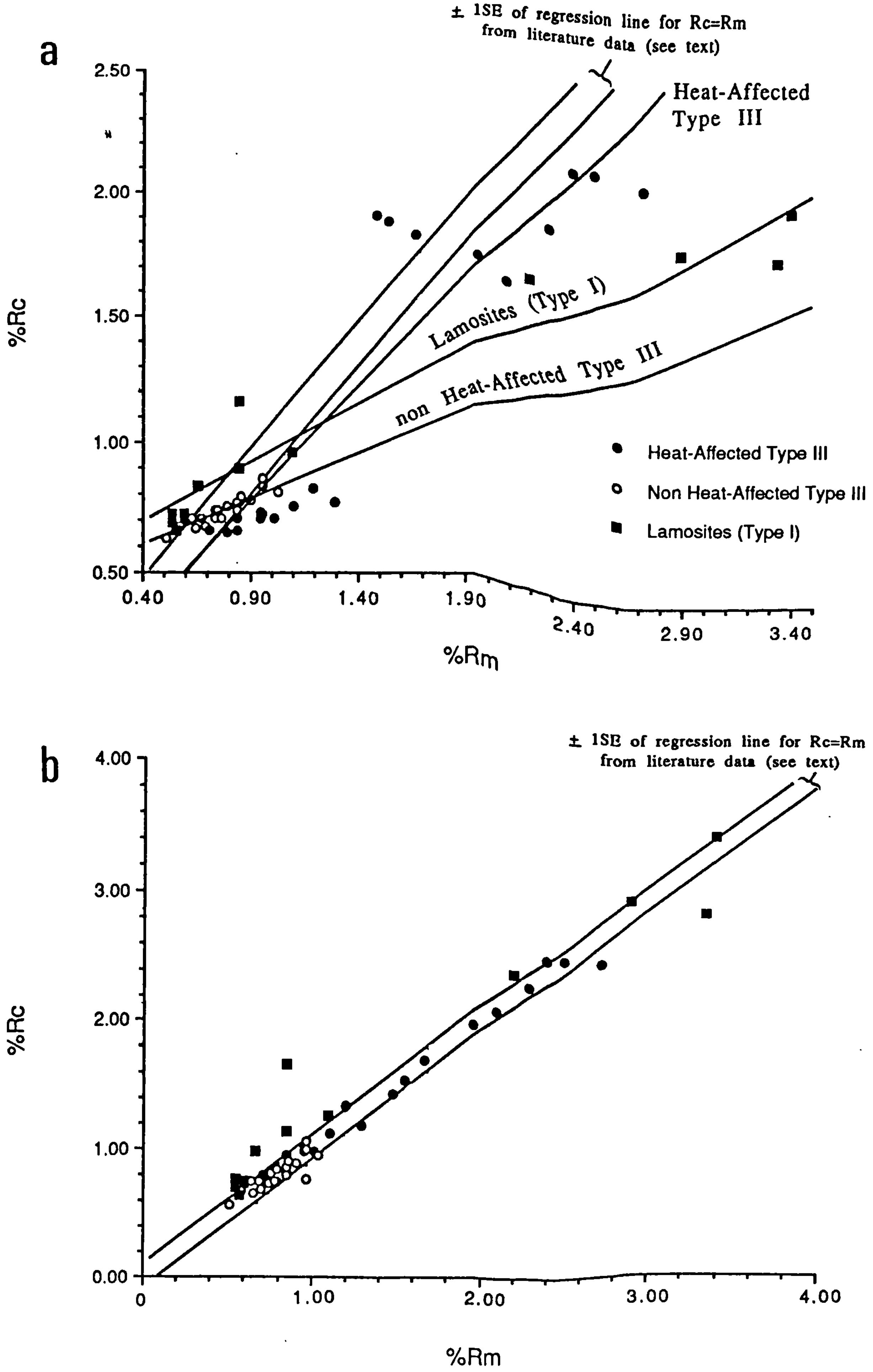


Fig.5.39 Plots showing relationship between measured (Rm) and calculated (Rc) vitrinite reflectance using equations formulated by Radke and co-workers (a) and equations formulated in this thesis (b).

indices at a given vitrinite reflectance level from samples in west Fife with ratios from samples at approximately the same rank from a sequence in the Fife-Midlothian Basin. The data presented in Section 5.2.1 indicated that organic matter in west Fife basins had been exposed to higher background temperatures and rates of heating than that in basins further to the east. Also included for comparison are heat-affected samples from both areas.

Since the comparison is essentially between the east and west of the study area, the sample set currently considered which is derived from the Fife-Midlothian Basin is hereafter referred to as originating from east Fife, although, strictly speaking, the succession from which it originates lies in central Fife (Balfour Anticline). The samples from the west were culled from *inter alia* Righead, Blairmains, Gartarry Toll (Brucefield), Kincardine Bridge and Orchard Head boreholes. The samples from further east were from the Milton of Balgonie-1 borehole. Because of limited sample availability, the majority of samples represent composites. The origin of each sample is indicated in Table A.2. The gross organic composition of all samples is that of type III kerogen.

Plots of the different molecular parameters determined at various vitrinite reflectance levels are shown in Fig.5.40. It is evident that, as for the heat-affected and non heat-affected samples in the previous section, the non heat-affected samples from west Fife generally show more immature molecular profiles based on saturated or aromatic hydrocarbons than do the relatively slowly heated samples further to the east. Similarly, the molecular fingerprints of the igneous-affected samples from the west are more immature than those for the heat-affected samples from the east. The disparity between the molecular signatures in sediments exposed to different heating rates is particularly striking when it is borne in mind that the samples from the east are all from the same borehole. The anomalously immature molecular distributions of the sample from the "west Fife heat-affected" suite with $\%R_o=1.50$ (RIG9) could be due to contamination by migrant (immature) hydrocarbons, because fluorescence microscopy revealed the presence of hydrocarbons infilling fusinitic cell cavities.

Although the heat-affected samples all lay in the thermal aureole of the same intrusion (Midland Valley Sill), the difference in the level of organic metamorphism, at a given reflectance level, determined by molecular parameters presumably reflects the different thermal histories of the samples before intrusion of the sill, i.e. regional coalification proceeded to a greater degree in west Fife basins than in those further east (Section 5.2.1). As discussed earlier, the major factors likely to account for the differences in the two areas are geothermal gradients and the physical state of the sediments at the time of intrusion.

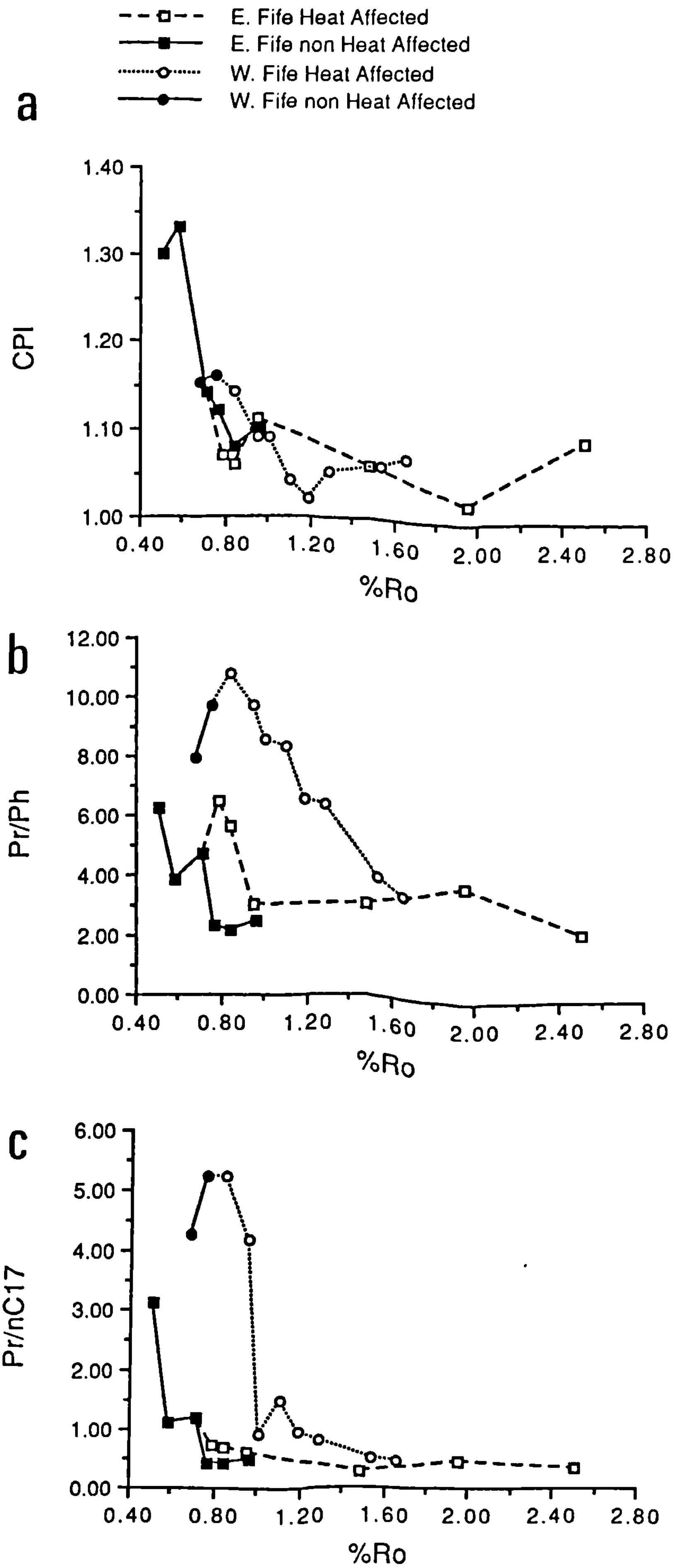


Fig.5.40 Variation of differing molecular indices with increasing rank (vitrinite reflectance) in coals and humic-rich sediments in "east" and "west" Fife (see text; parameters calculated in Tables A.3-A.6).
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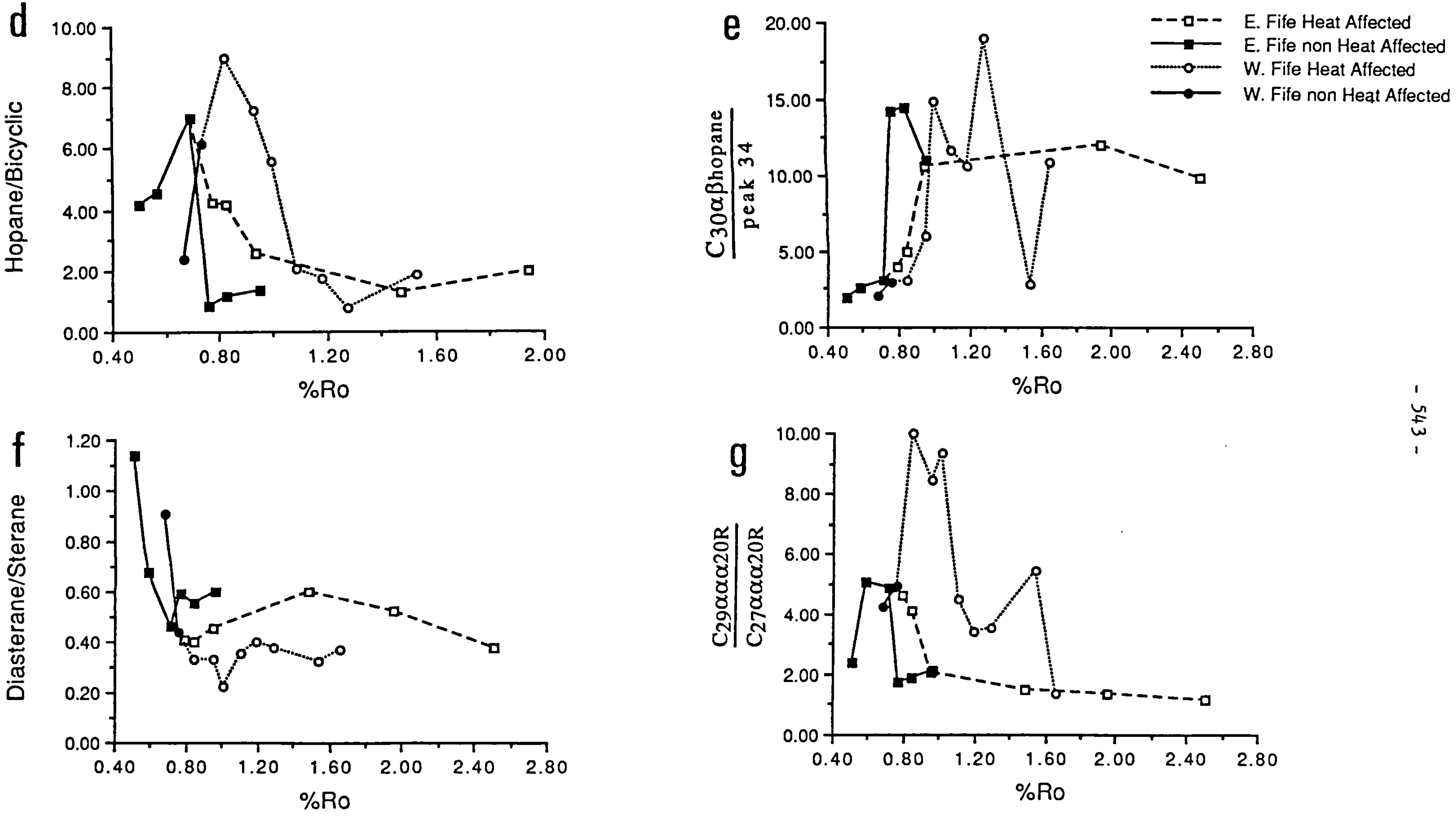

d
Hopane/Bicyclic
0.00
2.00
4.00
6.00
8.00
10.00
0.40
0.80
1.20
1.60
2.00
%Ro
e
$\frac{C_{30}\alpha\beta\text{hopane}}{\text{peak 34}}$
0.00
5.00
10.00
15.00
20.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
E. Fife Heat Affected
E. Fife non Heat Affected
W. Fife Heat Affected
W. Fife non Heat Affected
f
Diasterane/Sterane
0.00
0.20
0.40
0.60
0.80
1.00
1.20
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
g
$\frac{C_{29}\alpha\alpha\alpha 20R}{C_{27}\alpha\alpha\alpha 20R}$
0.00
2.00
4.00
6.00
8.00
10.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro

Fig.5.40 (cont.).

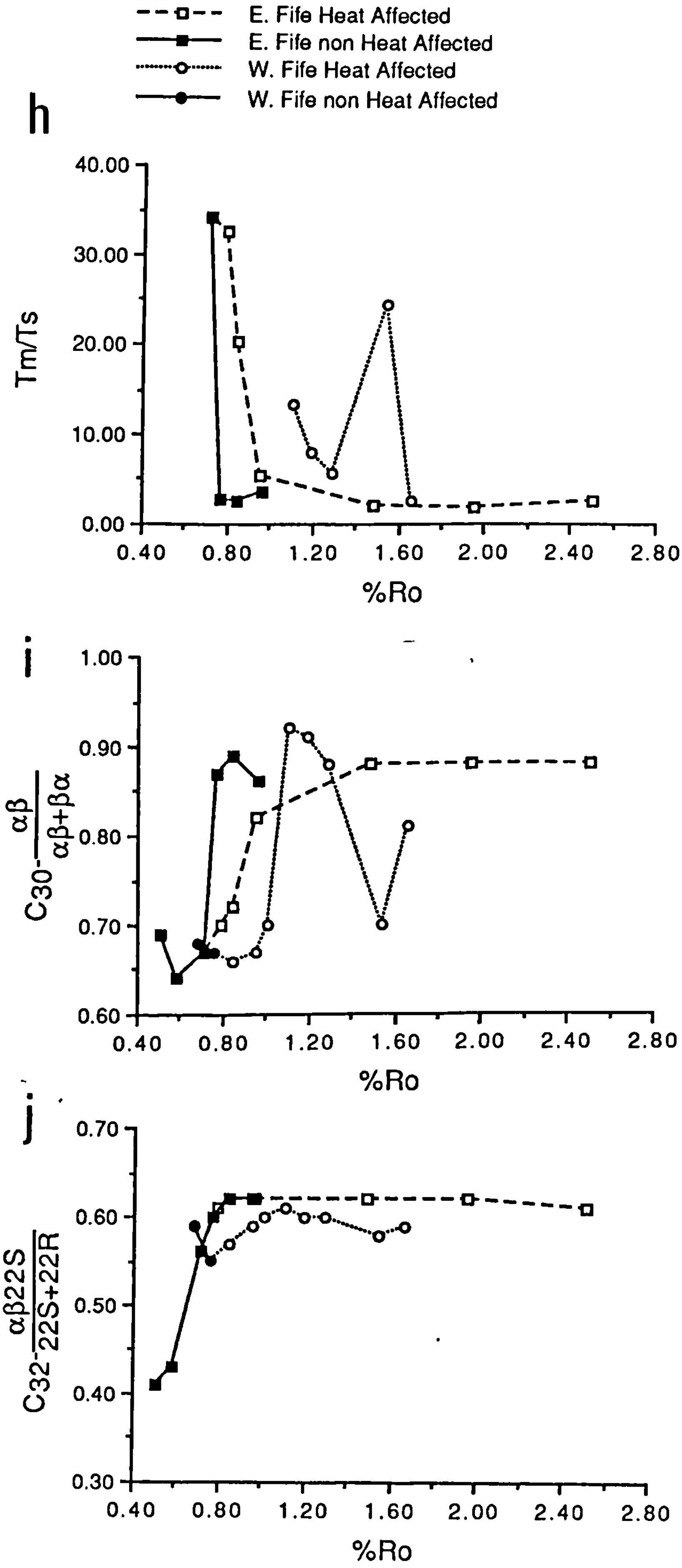

E. Fife Heat Affected
E. Fife non Heat Affected
W. Fife Heat Affected
W. Fife non Heat Affected
h
Tm/Ts
40.00
30.00
20.00
10.00
0.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
i
$C30\text{-}\frac{\alpha\beta}{\alpha\beta+\beta\alpha}$
1.00
0.90
0.80
0.70
0.60
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
j
$C32\text{-}\frac{\alpha\beta22S}{22S+22R}$
0.70
0.60
0.50
0.40
0.30
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro

Fig.5.40 (cont.).

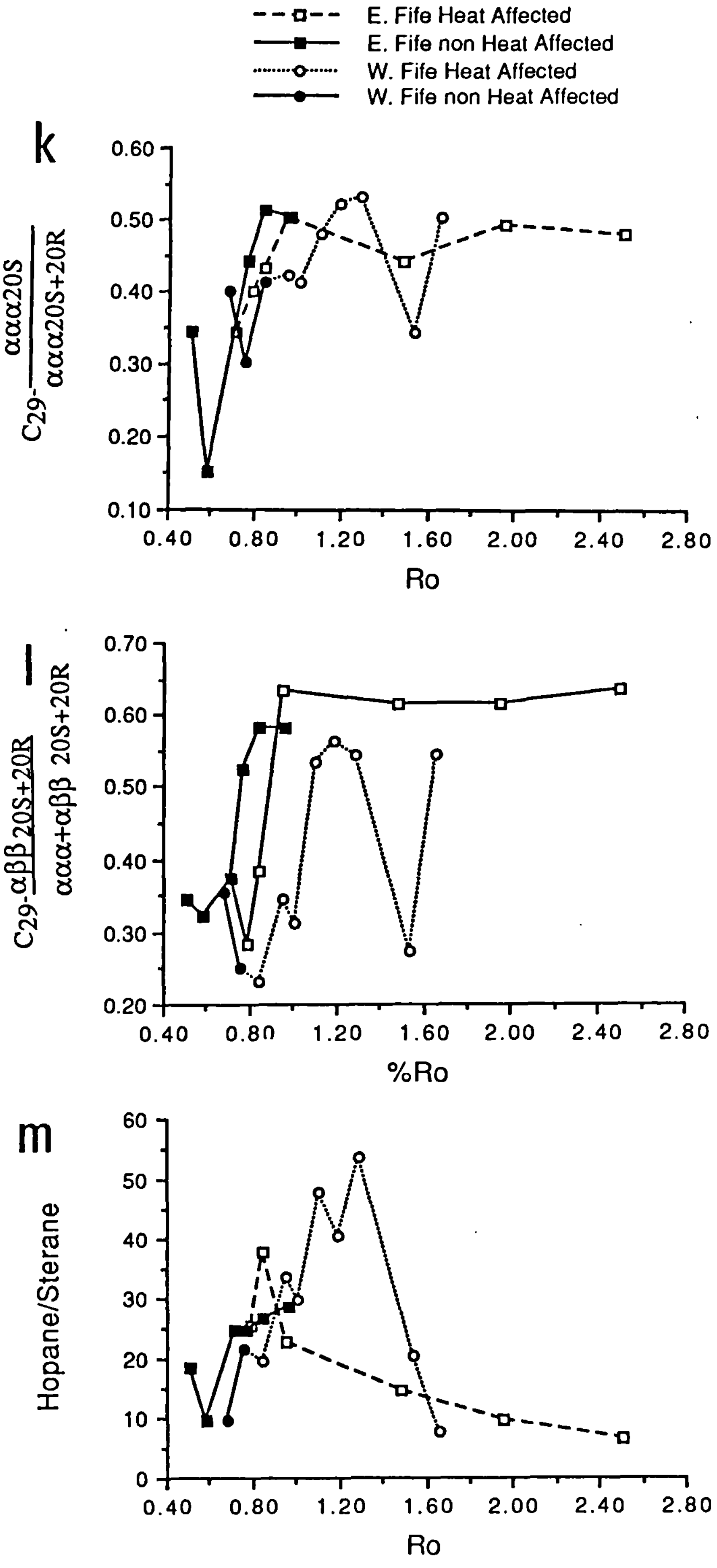

E. Fife Heat Affected
E. Fife non Heat Affected
W. Fife Heat Affected
W. Fife non Heat Affected
k
C_{29}-$\frac{\alpha\alpha\alpha 20S}{\alpha\alpha\alpha 20S+20R}$
0.60
0.50
0.40
0.30
0.20
0.10
0.40
0.80
1.20
1.60
2.00
2.40
2.80
Ro
l
C_{29}-$\frac{\alpha\beta\beta\ 20S+20R}{\alpha\alpha\alpha+\alpha\beta\beta\ 20S+20R}$
0.70
0.60
0.50
0.40
0.30
0.20
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
m
Hopane/Sterane
60
50
40
30
20
10
0
0.40
0.80
1.20
1.60
2.00
2.40
2.80
Ro

Fig.5.40 (cont.).

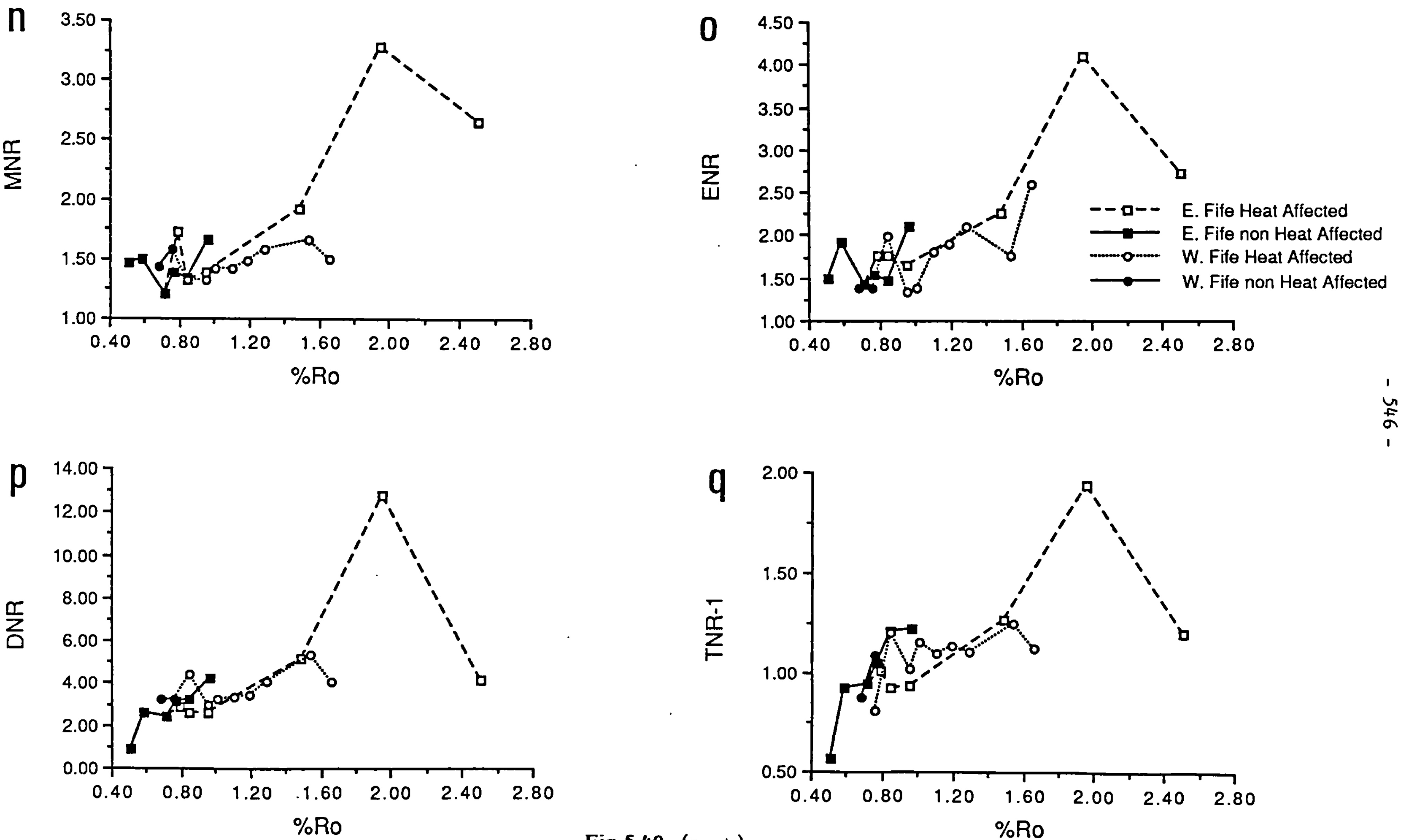

n
MNR
3.50
3.00
2.50
2.00
1.50
1.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
o
ENR
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
E. Fife Heat Affected
E. Fife non Heat Affected
W. Fife Heat Affected
W. Fife non Heat Affected
p
DNR
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.40
0.80
1.20
.1.60
2.00
2.40
2.80
%Ro
q
TNR-1
2.00
1.50
1.00
0.50
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro

Fig.5.40 (cont.).

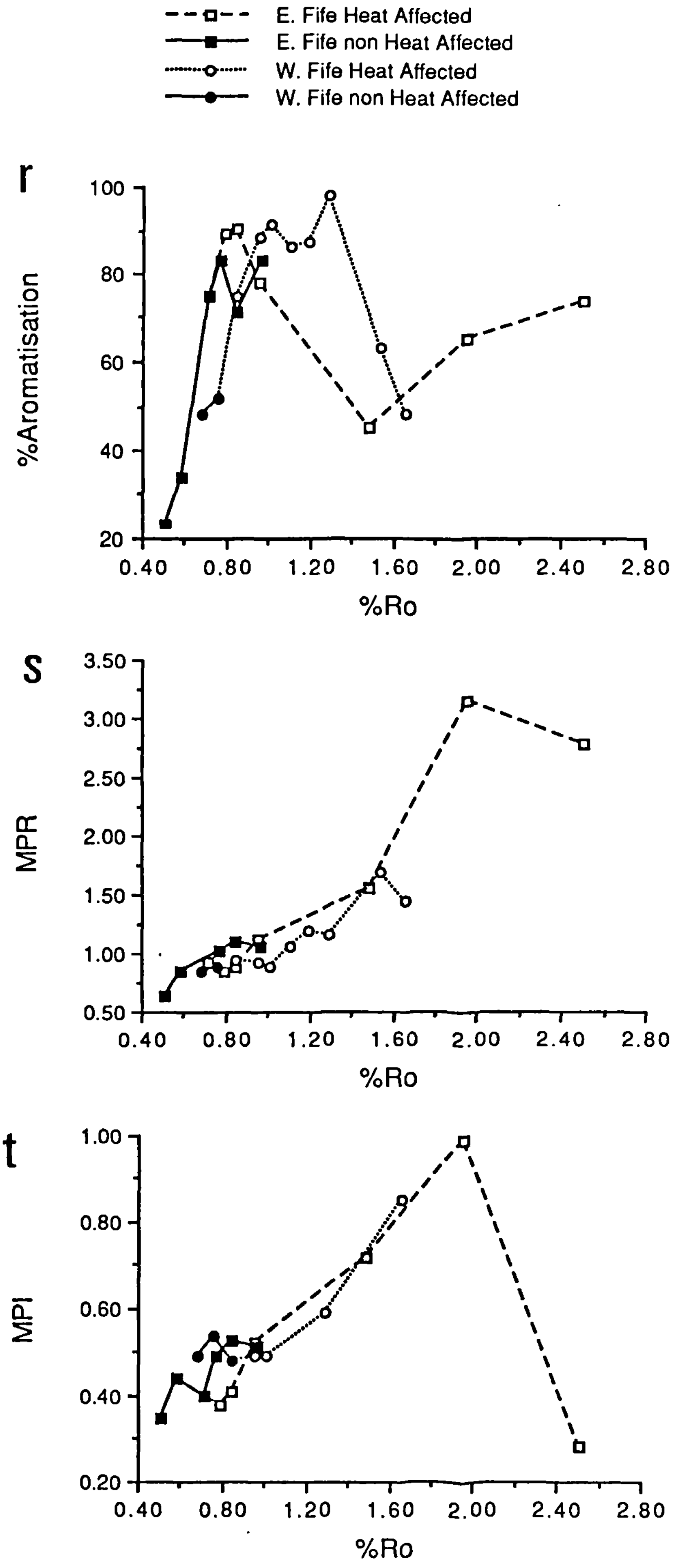

E. Fife Heat Affected
E. Fife non Heat Affected
W. Fife Heat Affected
W. Fife non Heat Affected
r
%Aromatisation
100
80
60
40
20
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
s
MPR
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro
t
MPI
1.00
0.80
0.60
0.40
0.20
0.40
0.80
1.20
1.60
2.00
2.40
2.80
%Ro

Fig.5.40 (cont.).

The results described in the last two sections have important consequences for hydrocarbon exploration. The marked variation which can exist in the distributions of saturated and aromatic hydrocarbons in samples which have attained the same rank as determined through vitrinite reflectance is an indication that basins in which heat flow is variable, either due to variation in the background geothermal gradient or due to igneous activity, require careful assessment to ensure complete and accurate appraisal for hydrocarbon exploration.

CHAPTER 6

OILS AND BITUMENS

6.1 INTRODUCTION AND SAMPLE INFORMATION

This chapter presents the results of the optical and geochemical analyses of oils and bitumens from various localities and from different geological settings. The hydrocarbon distributions of the oils and bitumens are compared with one another and with those of the different suites of samples discussed in Chapter 4, with the intention of establishing sample correlations, defining potential source rocks and assessing the maturities of the samples. Consideration is also given to the process of biodegradation, which has modified the compound distributions to varying degrees, and to the mode of formation of these "free" hydrocarbons. The localities, modes of occurrence and sources of the samples studied are shown in Fig.6.1 and Table 6.1.

The D'Arcy and Milton oils are both dark brown in colour and solid at room temperature. The bitumens from St.Catherine's Well, Mid Calder and Orrock Quarry are black and highly viscous. Samples for analysis were pared from inner surfaces with a clean knife and were dissolved in DCM/methanol prior to TLC. Both of the bitumens from the ironstone nodules analysed were dark brown and hard. The nodules themselves lay within the Broxburn Shale horizon at Mid Calder. Optical characterisation of the sample from the large nodule (Plate 6.1) was not possible because it partially dissolved in immersion oil. Its high solubility in organic solvents, coupled with the gross composition data (Table A.2), indicates that it probably lies on the asphalt-grahamite tract of bitumen evolution (Jacob 1989). The reflectances determined (in oil) on the bitumen sample from the small nodule lay in the range 0.38-0.83%. The sample displayed variable fluorescence colours (brown to orange) and moderate fluorescence intensities. The marked variation in the optical properties and the lack of correspondence between the EOM data in Table A.2 with those cited by Jacob (1989), precluded even a general classification of this bitumen.

The two samples from the Broachrigg borehole were sandstones which smelled strongly of hydrocarbons. The darker sample was dark brown in colour, medium-grained and was massive while the other was buff-coloured, fine grained, finely laminated and very compact. Microscopical examination revealed the presence of hydrocarbons filling secondary pore spaces in both samples (Plates 6.2 and 6.3; G.M.Harwood *personal communication*).

6.2 GROSS COMPOSITIONS

Data relating to the EOM and gross compositions of the oils and bitumens analysed are included in Table A.2 Variations in gross composition are shown in the ternary plot of Fig.6.2.

Plate 6.1 Bitumen in centre of large ironstone nodule from Mid Calder.

Plate 6.2 Hydrocarbons (black) filling secondary pore spaces in sandstone: transmitted light, air.

Brown sandstone from Broachrigg borehole; sample BEA 7169

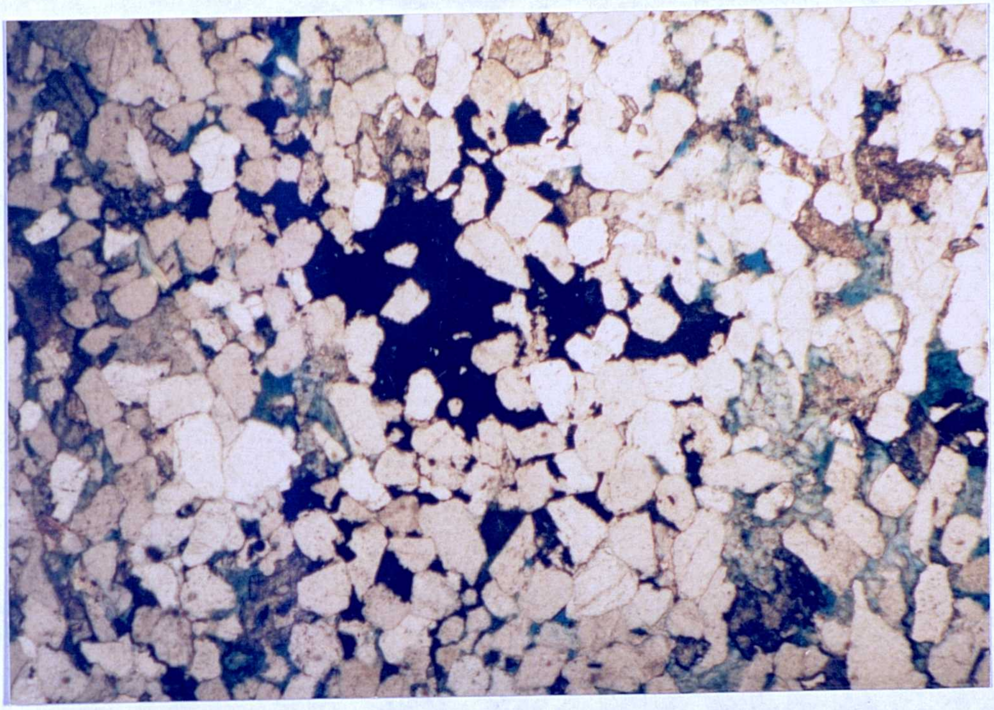
x35

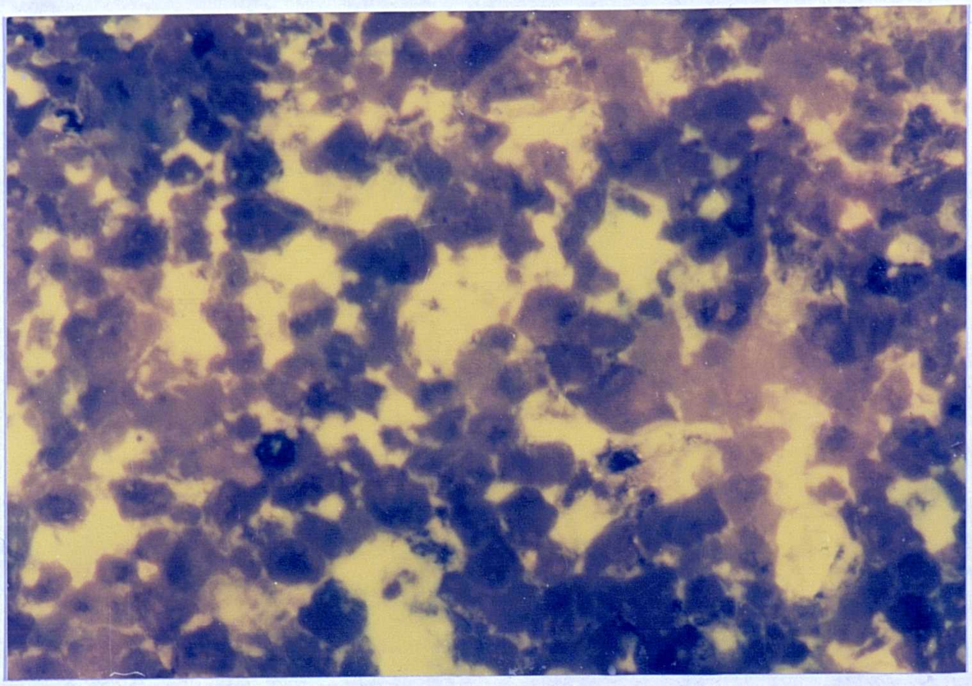
Plate 6.3 Hydrocarbons (yellow) filling secondary pore spaces in sandstone: blue-light excitation, air.

Laminated sandstone from Broachrigg borehole; sample BEA 7157

x75

how?





Text Name	Locality	Mode of Occurrence	Grid Reference	Stratigraphic Position	Source of Sample
D'Arcy Oil	D'Arcy Oil Bore (1919)	Sandstone at 1810'	NT 33623 66480	Lower Oil Shale Group	Dr. G. Durant
Milton Oil	Milton of Balgonie - 1 Borehole	Sandstone Interval at 3870-3912'	NT 33174 69933	Calciferous Sandstone Measures (Pathhead Beds)	Burmah/Premier
St. Catherine's Bitumen	St. Catherine's Well, Liberton	Natural Seep	NT 3273 6684	Upper Oil Shale Group	Field Sample
Orrock Bitumen	Orrock Quarry, Fife	Vugs in Basaltic Ash	NT 3218 6887	Calciferous Sandstone Measures (Burntisland Volcancis)	Field Sample
Dyke-Rock Bitumen	Mid Calder, Linhouse Water	Coating Quartz-Dolerite Dyke	NT 30796 66708	Faulted Junction Between Lower and Upper Oil Shale Groups	Dr. G. Durant
Petershill Bitumen	Petershill Reservoir	Veins in Limestone	NS 2985 6695	Lower Limestone Group	Dr. G.M. Harwood
Bitumen From Large Nodule	Mid Calder, Linhouse Water	Centre of Large Ironstone Nodule in Broxburn Shales	≈NT 3079 6671	Upper Oil Shale Group	Dr. G. Durant
Bitumen From Small Nodule	Mid Calder, Linhouse Water	Centre of Small Ironstone Nodule in Broxburn Shales	≈NT 3079 6671	Upper Oil Shale Group	Dr. G. Durant
Hydrocarbons in Brown Sandstone	Broachrigg Bore	Sandstone at 1921'	NT 329209 660867	Limestone Coal Group	BGS Corestore at Newbattle Abbey (BGS N^{O} = BEA 7169)
Hydrocarbons in Laminated Sandstone	Broachrigg Bore	Sandstone at 1831'	NT 329209 660867	Limestone Coal Group	BGS Corestore at Newbattle Abbey (BGS N^{O} = BEA 7157)

Table 6.1 Sample information for the oils and bitumens studied.

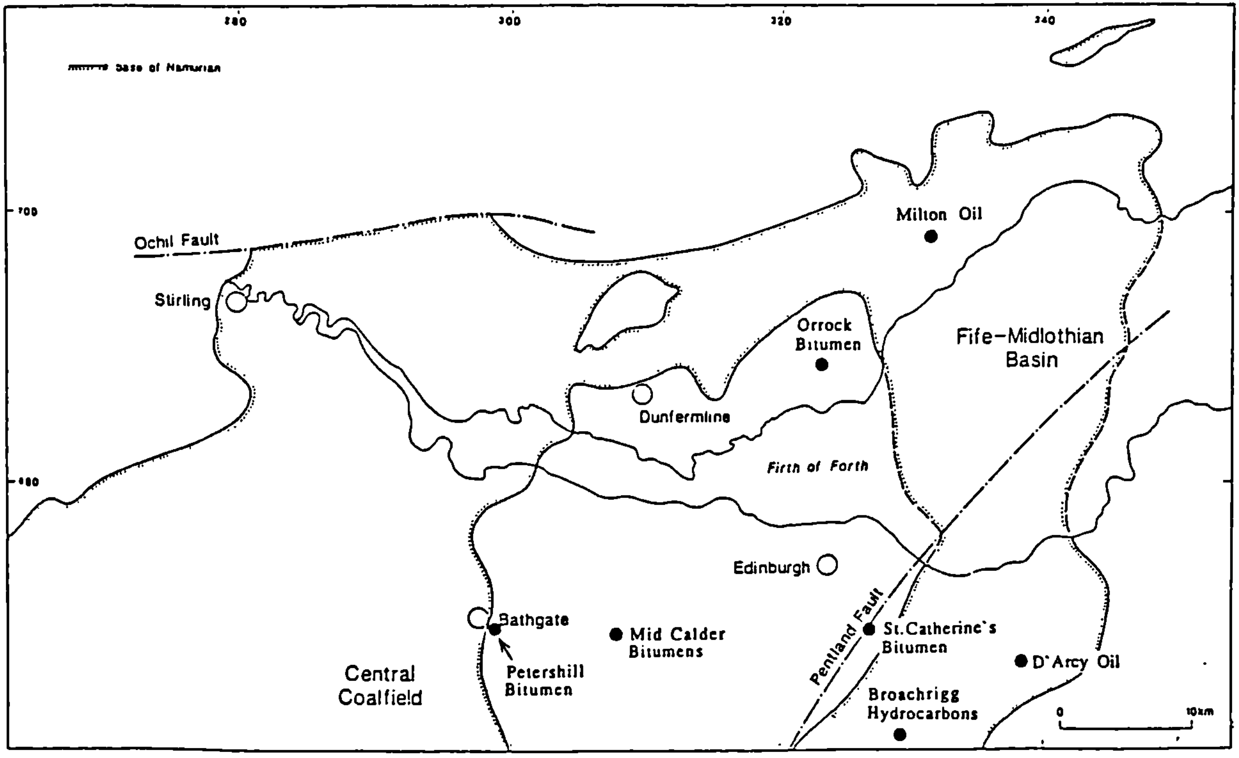


Fig.6.1 Locations of the oils and bitumens studied.

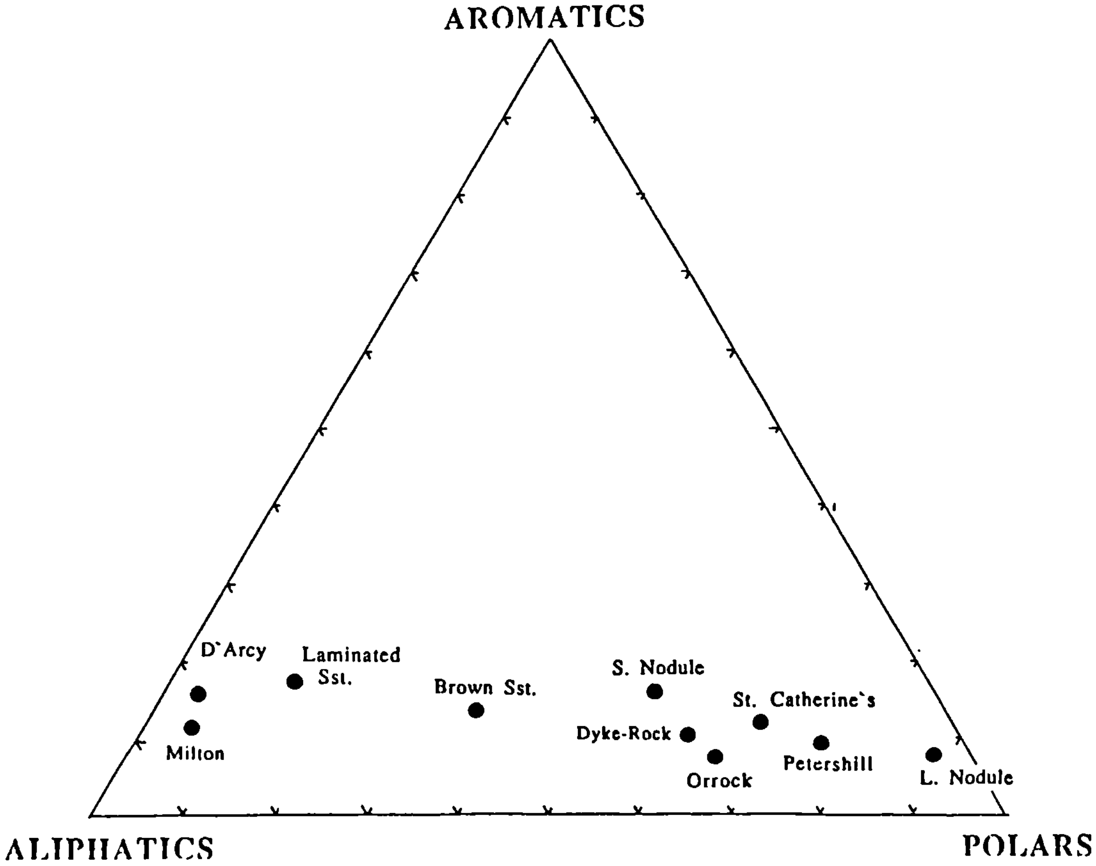


Fig.6.2 Ternary plot showing variation in gross composition of the oils and bitumens.

The D'Arcy and Milton oils and the extracted hydrocarbons from the laminated sandstone in the Broachrigg bore all have aliphatic hydrocarbon contents exceeding 60%, which classifies them as paraffinic oils (Tissot and Welte 1984). Apart from the brown sandstone, the organic matter of the remaining samples contains more than 50% polar compounds. Such constitutions are usually accredited to degraded oils in which the hydrocarbons have been removed by microbial activity, water washing and oxidation (Tissot and Welte 1984), although immature oils may also possess high contents of polar material (e.g. Spiro *et al.* 1983).

The composition of the extract from the brown sandstone enables the sample to straddle the "degraded oils" field of Tissot and Welte (1984; p.380). Whether the samples from the Midland Valley which are enriched in polar compounds represent the degraded products of pooled oils or are immature, bituminous exudates can be determined by evaluating the distributions of aliphatic and aromatic hydrocarbons.

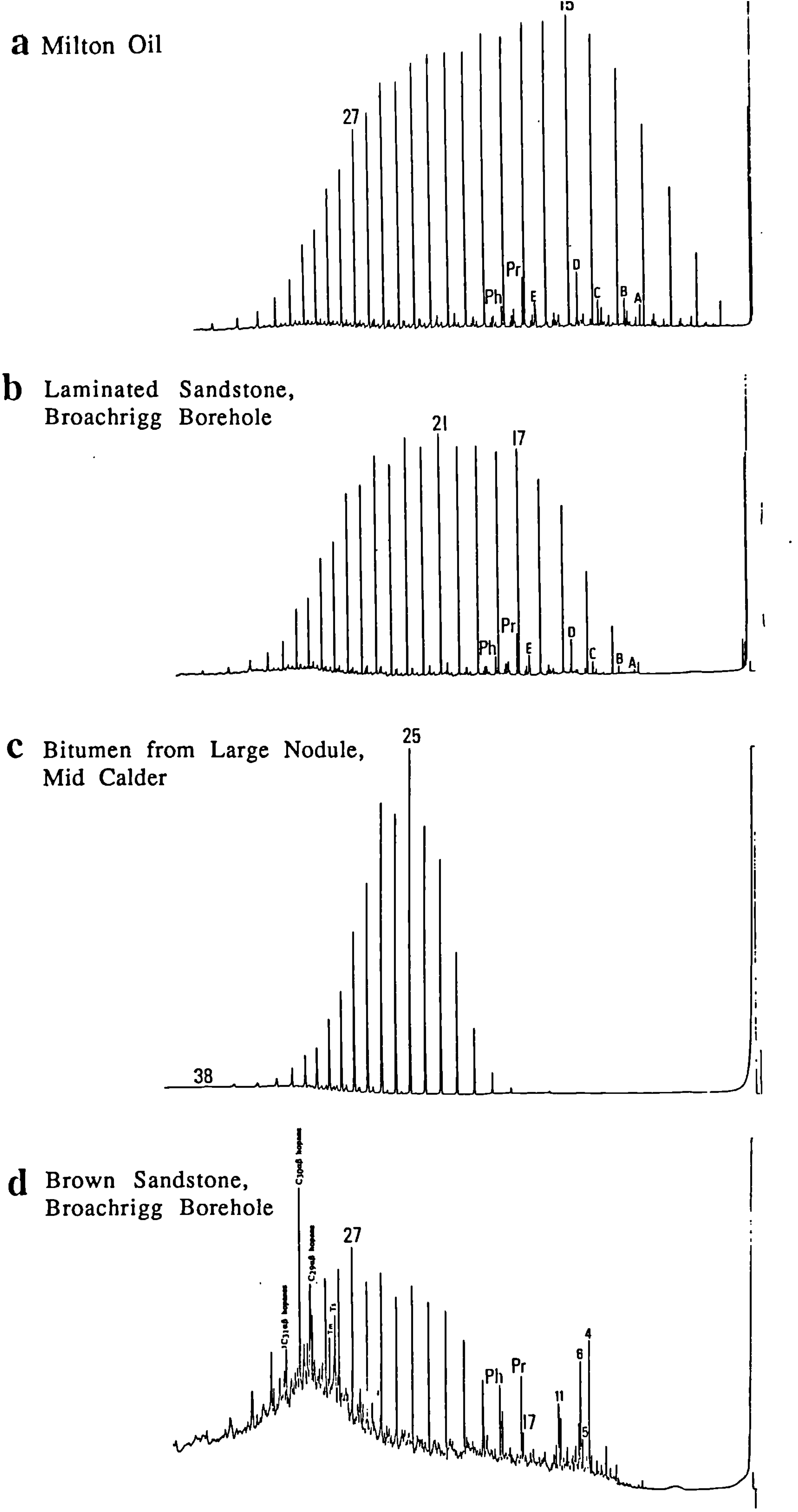
6.3 ALIPHATIC HYDROCARBONS

6.3.1 Gas Chromatography (GC)

Gas chromatograms of the saturated hydrocarbon fractions of the oils and bitumens are shown in Fig.6.3. Basic molecular parameters relating to these distributions are included in Table A.3. The distributions fall into four types categorised by the following features:-

(i) Marked predominance of *n*-alkanes over branched/cyclic components. These distributions are found in the D'Arcy and Milton oils (e.g. Fig.6.3a) as well as in the reservoired hydrocarbons in the laminated sandstone from the Broachrigg borehole (Fig.6.3b). The gas chromatogram of the saturated hydrocarbon fraction of the D'Arcy oil is almost identical to that of the Milton oil. The highly paraffinic nature of these samples is reflected in the very low isoprenoid/*n*-alkane ratios. The *n*-alkane envelopes display a front-end bias in the D'Arcy and Milton oils and maximise at n-C_{15}. The more symmetrical shape of the envelope of Fig.6.3b may be due to evaporative loss of the light ends and/or the lower maturity of the sample (see later). Odd-over-even carbon preferences are evident within the medium molecular-weight range in the above samples. CPI values in the high molecular-weight range are near unity.

(ii) Restricted range of high molecular-weight *n*-alkanes with a unimodal envelope. This type of pattern was recorded in the Mid Calder dyke-rock bitumen and in the bitumens from the nodules (e.g. Fig.6.3c), also from Mid Calder. The



a Milton Oil

b Laminated Sandstone, Broachrigg Borehole

c Bitumen from Large Nodule, Mid Calder

d Brown Sandstone, Broachrigg Borehole

Fig. 6.3 Gas chromatograms of the saturated hydrocarbon fractions of the oils and bitumens (peak assignments in Tables 4.4 and 4.12).

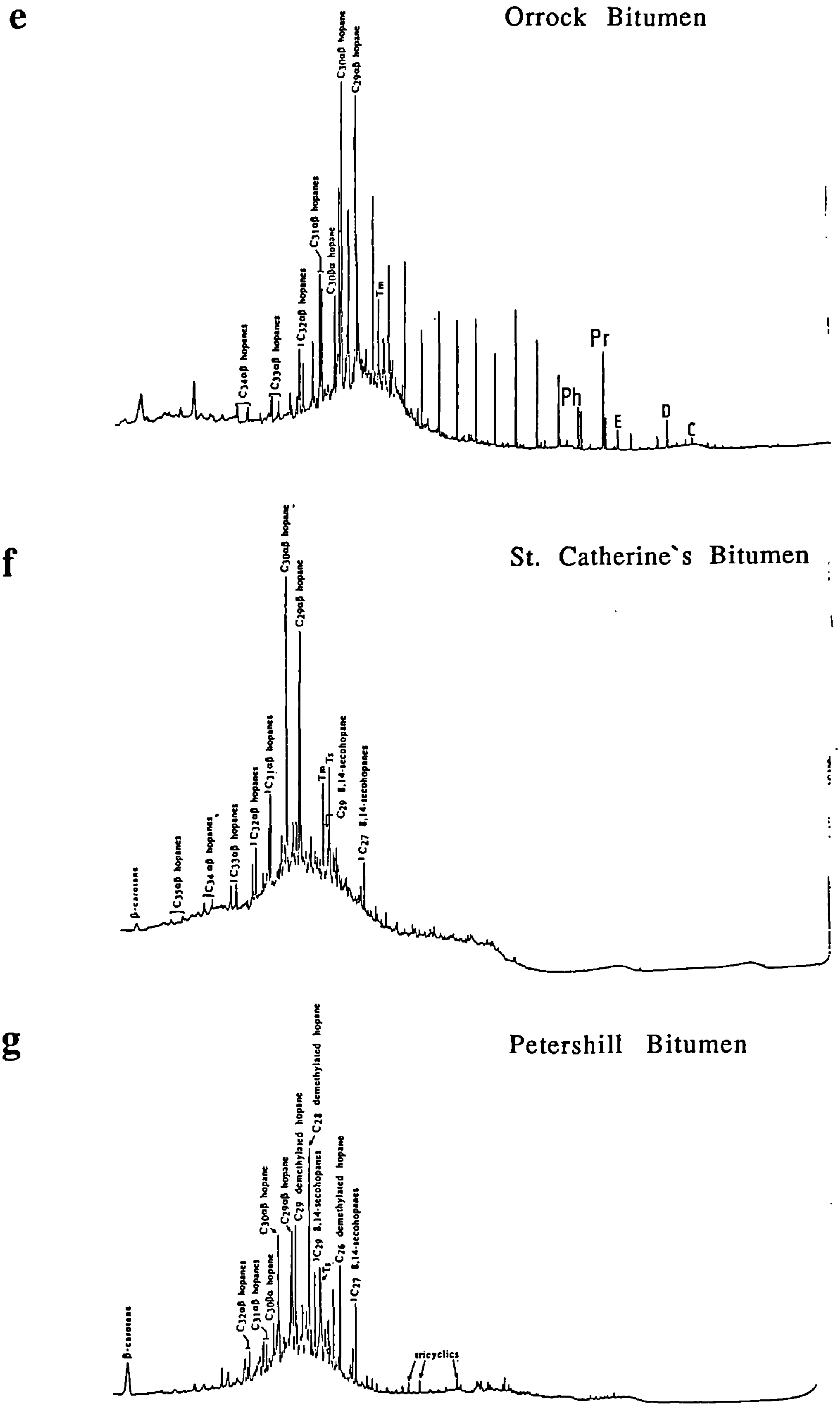

e
Orrock Bitumen
C34αβ hopanes
C33αβ hopanes
C32αβ hopanes
C31αβ hopanes
C30βα hopane
C30αβ hopane
C29αβ hopane
Tm
Ph
Pr
E
D
C
f
St. Catherine's Bitumen
β-carotane
C35αβ hopanes
C34 αβ hopanes
C33αβ hopanes
C32αβ hopanes
C31αβ hopanes
C30αβ hopane
C29αβ hopane
Tm
Ts
C29 8,14-secohopane
C27 8,14-secohopanes
g
Petershill Bitumen
β-carotane
C32αβ hopanes
C31αβ hopanes
C30βα hopane
C30αβ hopane
C29αβ hopane
C29 demethylated hopane
C28 demethylated hopane
C29 8,14-secohopanes
Ts
C26 demethylated hopane
C27 8,14-secohopanes
tricyclics

Fig.6.3 (cont.)

distributions maximise between *n*-C_{25} and *n*-C_{29}. The *n*-alkanes from the nodular bitumens show an OEP, with CPI values of *c*.1.1. Isoprenoid alkanes are barely detectable or absent, but iso- and anteiso alkanes can still be discerned. The *n*-alkanes in the dyke-rock bitumen are superimposed on a small unresolved complex mixture (hump); the chromatographic baselines are flat in the nodular bitumens.

(iii) Dominance of polycyclic alkanes (hopanes) over *n*-alkanes. Such distributions were derived from the hydrocarbons in the brown sandstone (Fig.6.3d) and the Orrock bitumen (Fig.6.3e). *N*-alkane distributions are biased towards the high molecular-weight components and maximise at C_{27}. Pronounced OEPs exist in the high molecular-weight range. *N*-alkanes below *n*-C_{17} are of minor abundance.

(iv) Absence of normal and branched alkanes. The bitumens from St.Catherine's Well and Petershill reservoir (Figs 6.3f and g respectively) show this type of distribution.The peak annotations in the gas chromatograms are derived from gc-ms analysis, the results of which are elaborated below.

6.3.2 Gas Chromatography-Mass Spectrometry (GC-MS)

6.3.2.1 Terpanes

Gc-ms analysis indicates that, for all samples, tri- and tetracyclic terpanes are greatly subordinate in abundance to the pentacyclics. In all samples, except the Orrock bitumen, the qualitative distributions of 3- and 4-ringed terpanes are virtually identical. The C_{24} 17,21-secohopane (peak 17) is generally the only tetracyclic component present: the remaining compounds eluting in the 37-55 minute range of the m/z 191 mass fragmentograms are tricyclic terpanes. The tricyclics are of approximately equal, or slightly higher, abundance to the C_{24} secohopane. A typical trace showing the distribution and abundance of the 3- and 4-ringed components relative to the pentacyclics is shown in Fig.6.4a.

As with the gas chromatograms, the results of gc-ms analysis allow groups of samples with similar geochemical characteristics to be delineated. M/z 191 mass fragmentograms of the D'Arcy and Milton oils and those of the hydrocarbons from the impregnated sandstones from the Broachrigg borehole (typified by Fig.6.4c) are almost identical (see Figs 6.4a-c). Molecular parameters derived from these traces are included in Table A.4. Only the region of the trace encompassing the pentacyclics is shown in Figs 6.4b and c as the remaining pattern is identical to that shown for the D'Arcy Oil.

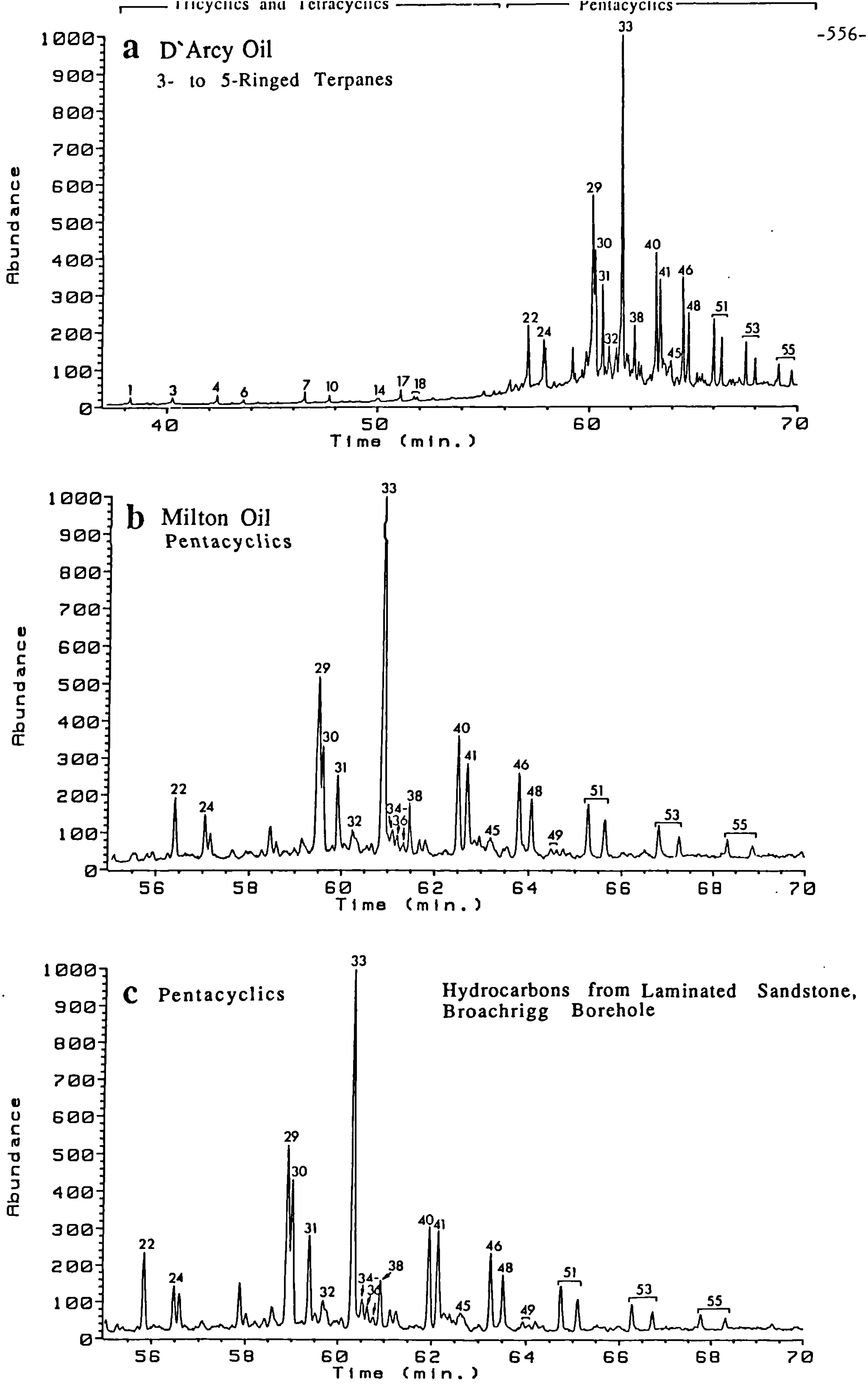


Fig. 6.4 M/z 191 fragmentograms illustrating the distributions of terpanes in the D'Arcy and Milton oils and in the hydrocarbons from the Broachrigg borehole (peak assignments in Table 4.5).

Isomerisation of the homohopanes at C-22 has reached equilibrium which, in conjunction with the low moretane content, indicates sample maturity, although a type control is possible for the latter parameter (see Chapter 4). The unknown C_{29} triterpane (peak 30), shouldering the $C_{29}\alpha\beta$ hopane, is in relatively high abundance in all samples of this suite, as is the later-eluting unknown C_{30} pentacyclic terpane (peak 31). The traces of all the above samples show a peak as a shoulder on Tm (peak 24) which mass spectral data (albeit "noisy") indicate is, at least in part, due to the coelution of a methyl-*n*-alkylcyclohexane with a C_{30} 8,14-secohopane (see later). The most significant difference in the terpane distributions of the four samples lies in the Tm/Ts ratios: those for the D'Arcy and Milton oils are higher than those for the Broachrigg samples.

Representative terpane distributions for the various bitumens from Mid Calder are shown in Fig.6.5. The distributions in the nodular bitumens(e.g. Fig.6.5b) are very similar, although the $C_{30}\alpha\beta$ hopane in the sample from the large nodule is of higher abundance, relative to the homohopanes, than it is in the smaller nodule. As for the oils and reservoired hydrocarbons, peak 30 is present in relatively large quantities in the nodular bitumens, although peak 31 is less conspicuous than in the former sample suite.

The bitumen coating the dyke-rock displays the greatest relative concentration of tricyclic terpanes encountered within the oils and bitumens studied, contrasting markedly with those for the nodular bitumens in which these components are barely detectable. Further differences between the Mid Calder samples lie in the enhanced concentrations of Tm and the $C_{29}\alpha\beta$ hopane seen in the dyke-rock bitumen and the low concentrations of peaks 30 and 31. Whilst the 22S epimer of the homohopanes $\geq C_{32}$ has a greater abundance than the 22R epimer in all of the Mid Calder samples, the equilibrium value is only found in the bitumen from the small nodule. The hopane profiles indicate that the dyke-rock bitumen is the least mature sample of the Mid Calder suite.

The similarities in the gas chromatographic traces of the Petershill and St.Catherine's bitumens (*viz.* lack of acyclic alkanes) are paralleled, to a certain degree, by similarities in the distributions of polycyclic alkanes. The bulk of the components visible in the gas chromatograms comprise hopanes. Although the ubiquitous hopanes and moretanes occur in the Petershill bitumen (Fig.6.6a), the pentacyclic terpane distribution is dominated by a series of compounds with a major fragment ion of m/z 177 (Fig.6.6b). The mass spectra of the most prominent of these compounds are shown in Fig.6.7. The mass spectra and relative retentions times of this suite of compounds correspond to those of the 25-norhopanes and 25-normoretanes (Rullkötter and Wendisch 1982; Volkman *et al.* 1983b). Peak assignments are shown in Table 6.2. Of all the samples submitted for gc-ms

Table 6.2 Peak assignments for demethylated hopanes.

A	18α(H)-22,25,29,30-tetrakisnorneohopane	(C_{26})
B	17α(H)-22,25,29,30-tetrakisnorhopane	(C_{26})
C	17α(H),21β(H)-25,30-bisnorhopane	(C_{28})
D	17β(H),21α(H)-25,30-bisnorhopane	(C_{28})
E	17α(H),21β(H)-25-norhopane	(C_{29})
F	17β(H),21α(H)-25-norhopane	(C_{29})
G	17α(H),21β(H)-25-norhomohopane (22S+22R)	(C_{30})
H	17β(H),21α(H)-25-norhomohopane (22S+22R)	(C_{30})
I	17α(H),21β(H)-25-norbishomohopane (22S+22R)	(C_{31})
J	17α(H),21β(H)-25-nortrishomohopane (22S+22R)	(C_{32})
K	17α(H),21β(H)-25-nortetrakishomohopane (22S+22R)	(C_{33})
L	17α(H),21β(H)-25-norpentakishomohopane (22S+22R)	(C_{34})

Table 6.3 Peak assignments for 8,14-secohopanes.

a	C_{27} 8,14-secohopane
b	C_{27} 8,14-secohopane
c	C_{27} 8,14-secohopane
d	C_{29} 8,14-secohopane
e	C_{29} 8,14-secohopane
f	C_{29} 8,14-secohopane
g	C_{30} 8,14-secohopane
h	C_{30} 8,14-secohopane
i	C_{30} 8,14-secohopane
j	C_{30} 8,14-secohopane

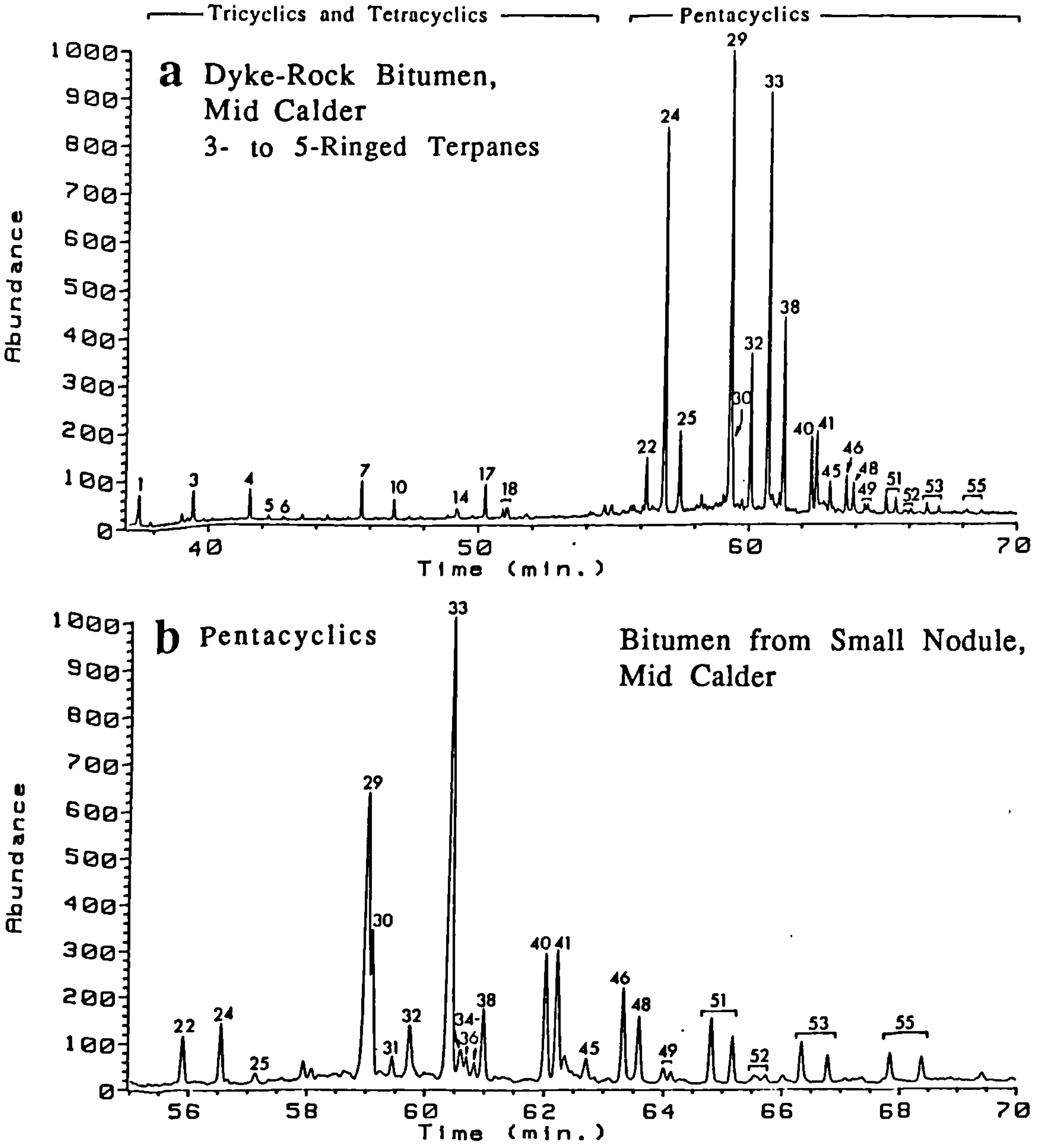


Fig. 6.5 M/z 191 fragmentograms illustrating the variation in terpane distributions in the samples from Mid Calder (peaks assignments in Table 4.5).

analysis throughout the course of the project, the 25-norhopanes were only detected in the Petershill bitumen.

Members of another series of terpanes that are prominent in the saturated gas chromatograms of the Petershill bitumen (Fig.6.3g) were identified as 8,14-secohopanes (Rullkötter and Wendisch 1982; Schmitter *et al.* 1982). Their mass spectra all contain a m/z 123 base peak, thus m/z 123 mass fragmentograms are used to monitor their distribution (Fig.6.8). Peak assignments are given in Table 6.3. One C_{27} and one C_{29} component have been reported in a bitumen from Hilderston (Robinson *et al.* 1986a). Mass spectra of the most prominent peaks in each homology are shown in Fig.6.9. Although at least four isomers per carbon

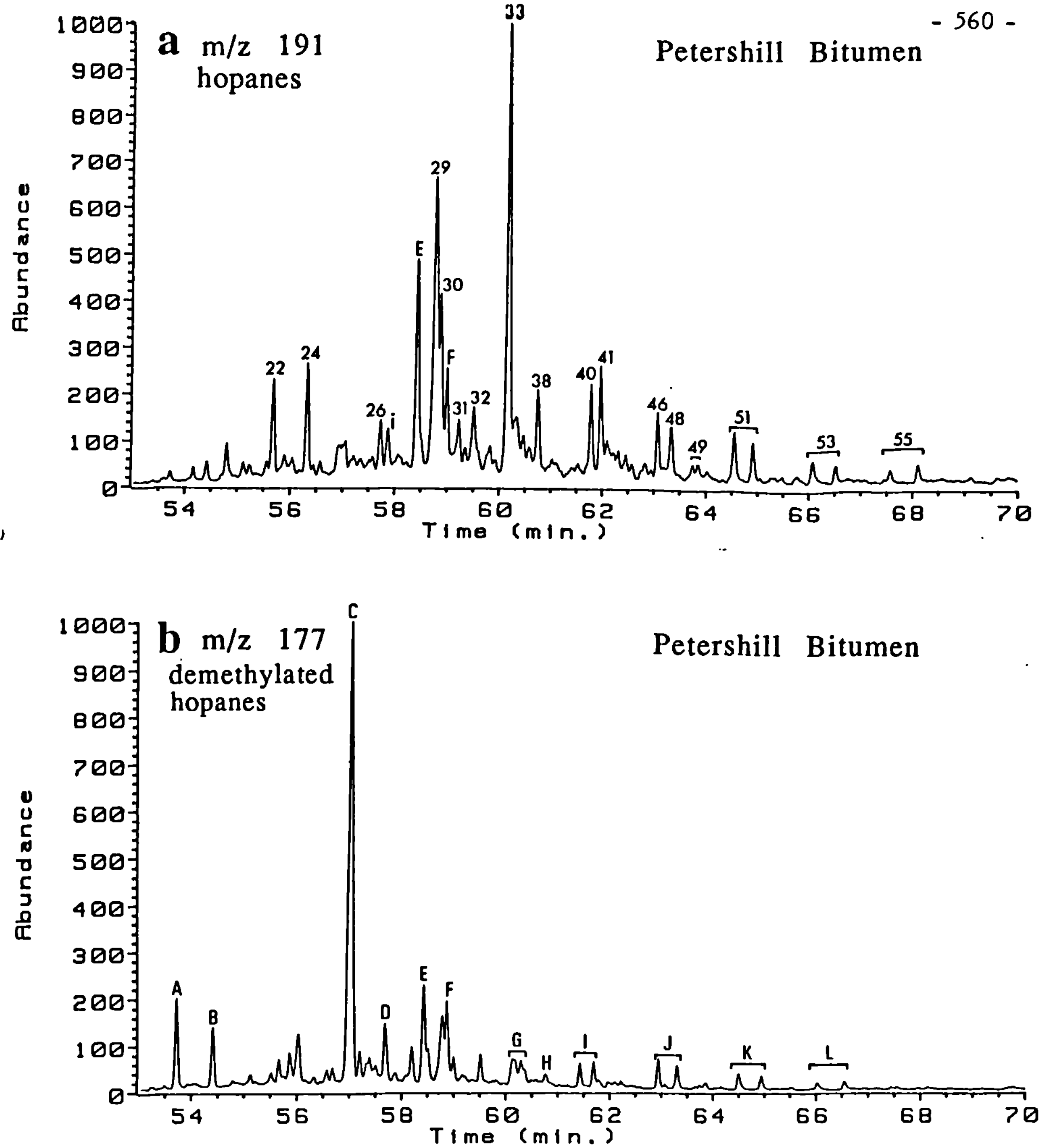


Fig. 6.6 Mass fragmentograms showing distributions of hopanes (a) and demethylated hopanes (b) in the Petershill bitumen (peak assignments in Tables 4.5 and 6.2).

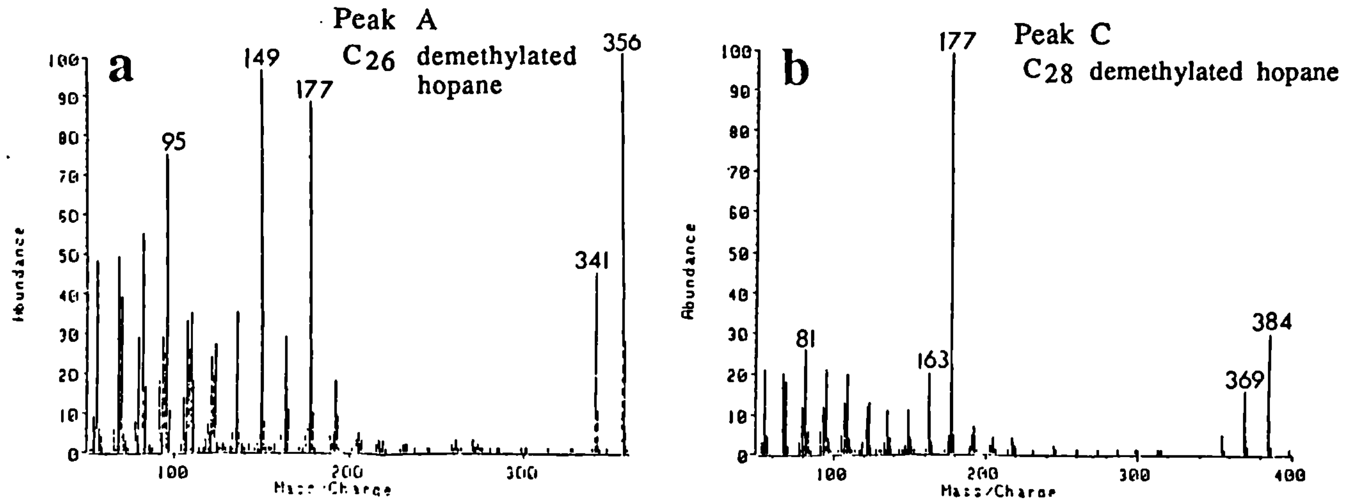


Fig. 6.7 Mass spectra of demethylated hopanes.

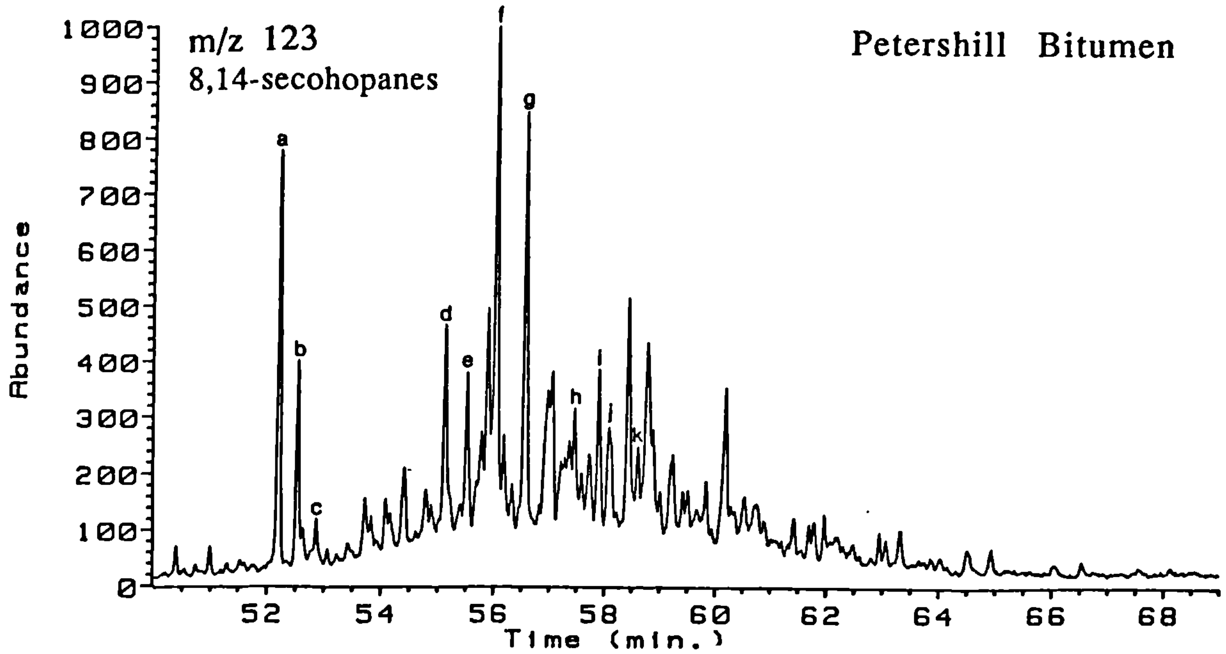


Fig.6.8 Mass fragmentogram showing distribution of 8,14-secohopanes in the Petershill bitumen (peak assignments given in Table 6.3).

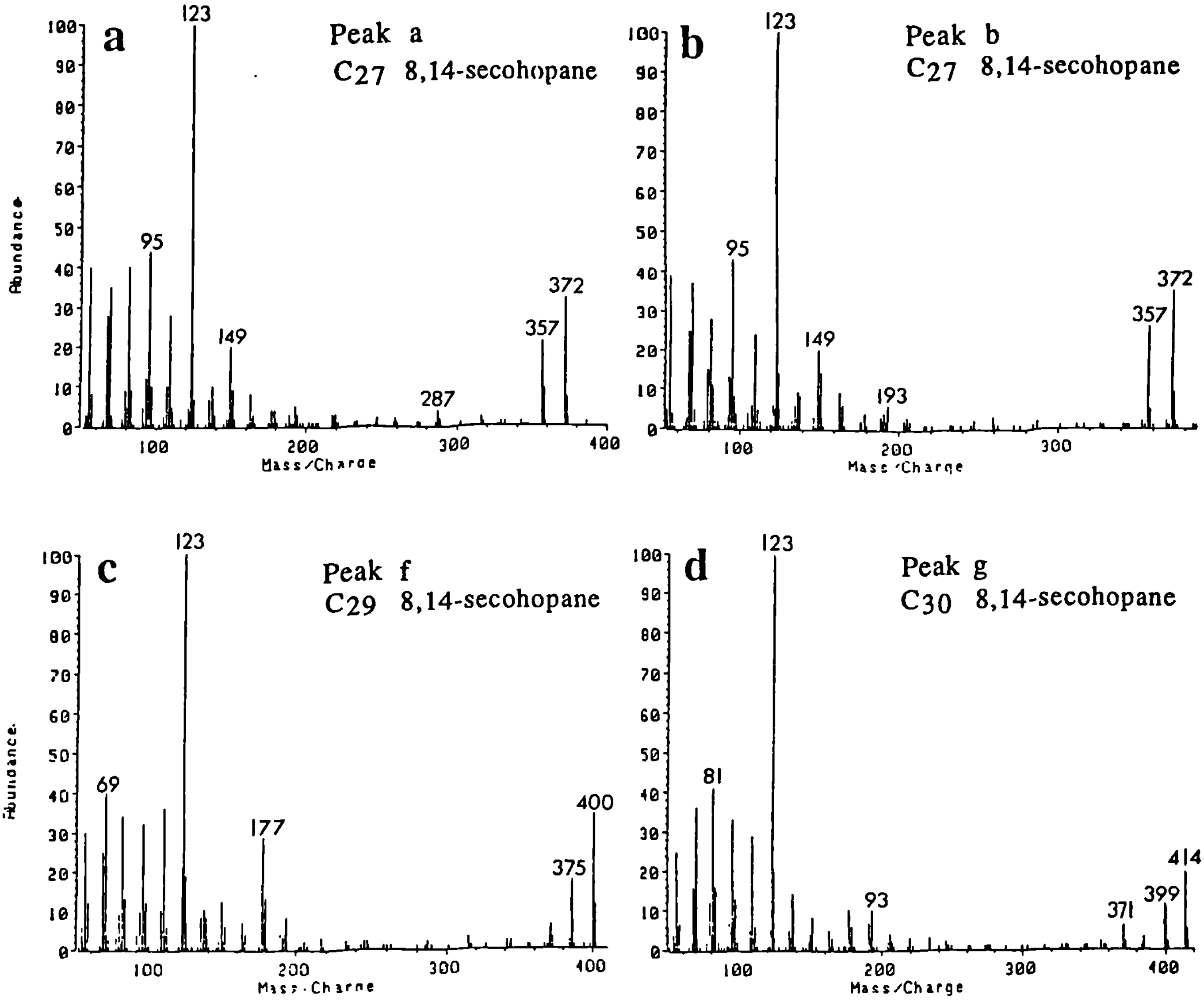


Fig.6.9 Mass spectra of prominent 8,14-secohopanes.

number in the C_{27}-C_{30} range have been identified (Schmitter *et al.* 1982; Wang *et al.* 1990), this complexity was not established in the Petershill bitumen. Wang *et al.* (1990) have extended the known range of 8,14-secohopanes to C_{31} and C_{32} homologues, each with at least three isomers. The poor quality of mass spectra and the complexity of the m/z 123 mass fragmentogram beyond 57 minutes prevented identification of 8,14-secohopanes >C_{30} in the Petershill (or any other) sample.

The mass spectrum (Fig.6.10) of the prominent compound eluting at the high molecular-weight end of the gas chromatogram (Fig.6.3g) closely corresponds to that of β-carotane (Murphy *et al.* 1967; Anders and Robinson 1971).

Apart from the absence of 25-norhopanes in the St.Catherine's bitumen, which partly accounts for the reduced complexity of the gas chromatogram (Fig.6.3f), the distribution of hopanes is very similar to that of the Petershill bitumen (Fig.6.6a). Peaks 30 and 31 are prominent, as are the C_{27}, C_{29} and C_{30} 8,14-secohopanes. A very small contribution from β-carotane occurs.

The terpane distribution of the Orrock bitumen differs significantly from those of the other oils and bitumens investigated. The m/z 191 mass fragmentogram (Fig.6.11a) reveals the prominence of a C_{24} tetracyclic terpane which forms part of a multiplet of C_{24} tetracyclic terpanes (Fig.6.11b). This distribution closely resembles those seen in the Orrock wood and "vitrinite" (Fig.4.64), in which the two tetracyclics labelled W and Y were also noted. Tricyclic terpanes are negligible in the Orrock bitumen.

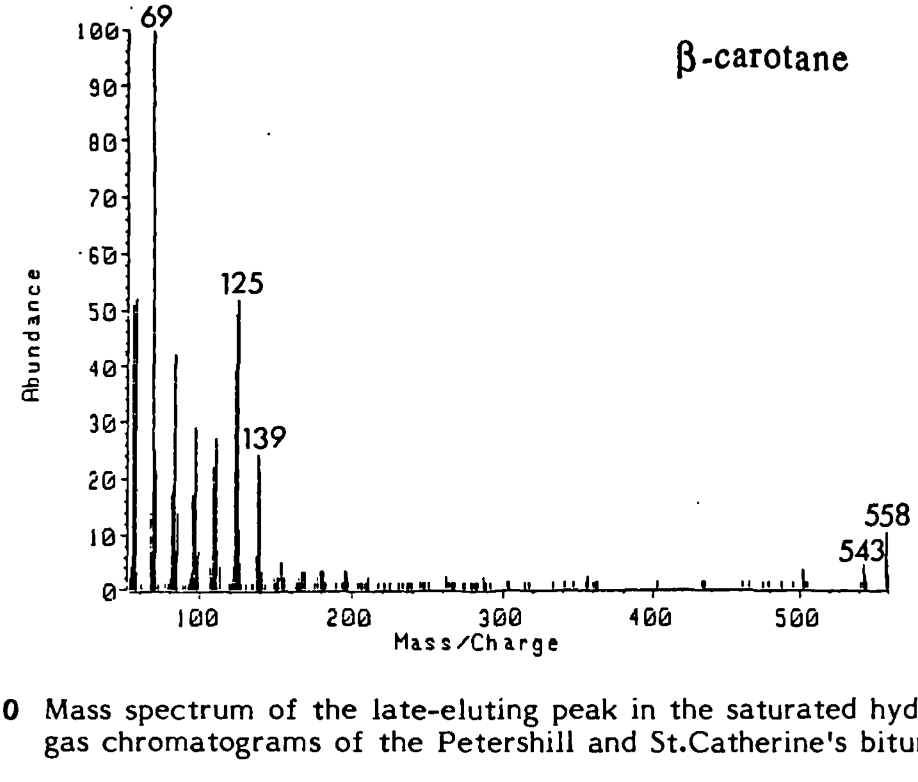


Fig.6.10 Mass spectrum of the late-eluting peak in the saturated hydrocarbon gas chromatograms of the Petershill and St.Catherine's bitumens.

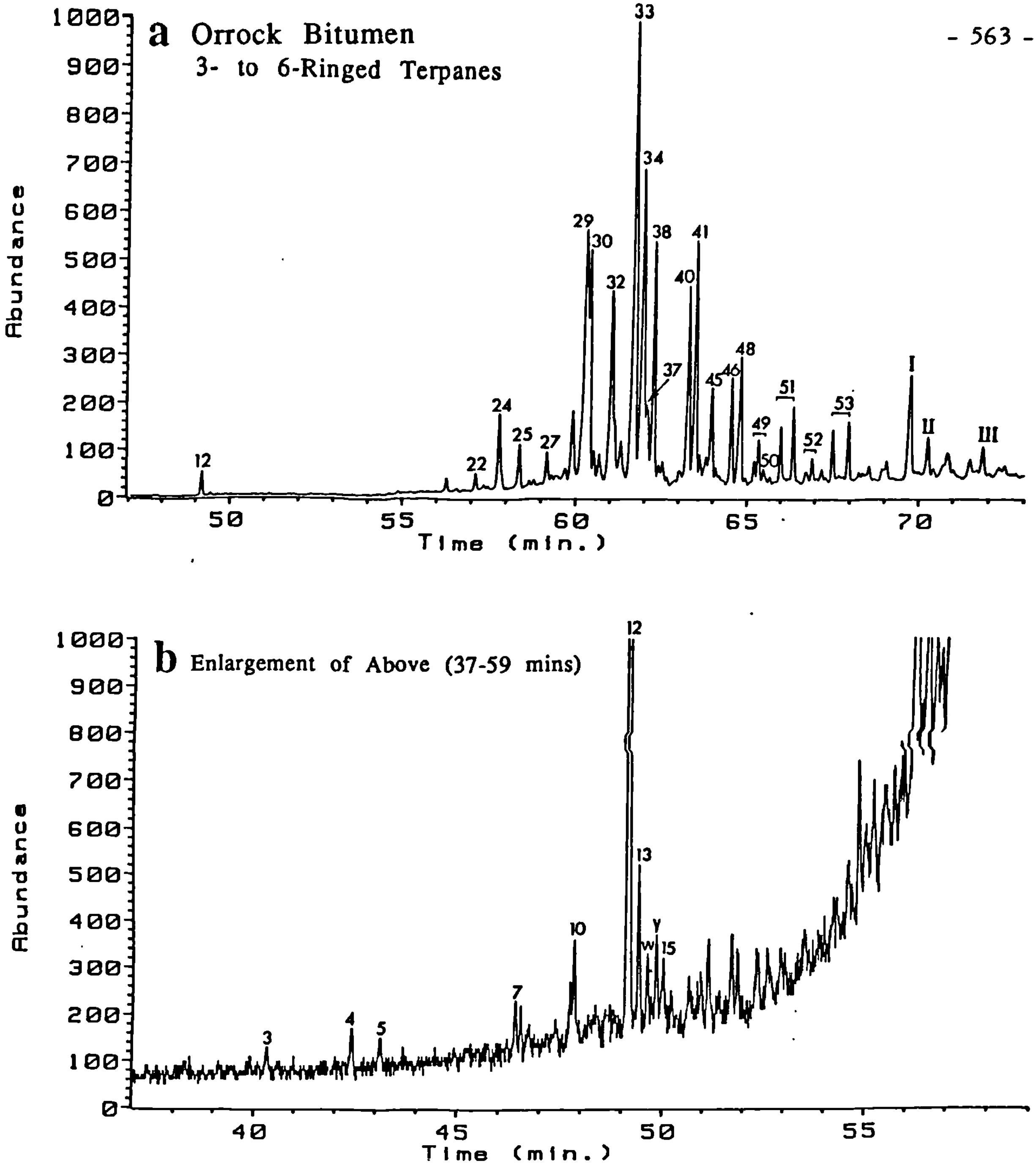


Fig. 6.11 M/z 191 fragmentograms showing the distribution of terpanes in the Orrock bitumen (peak assignments in Table 4.5).

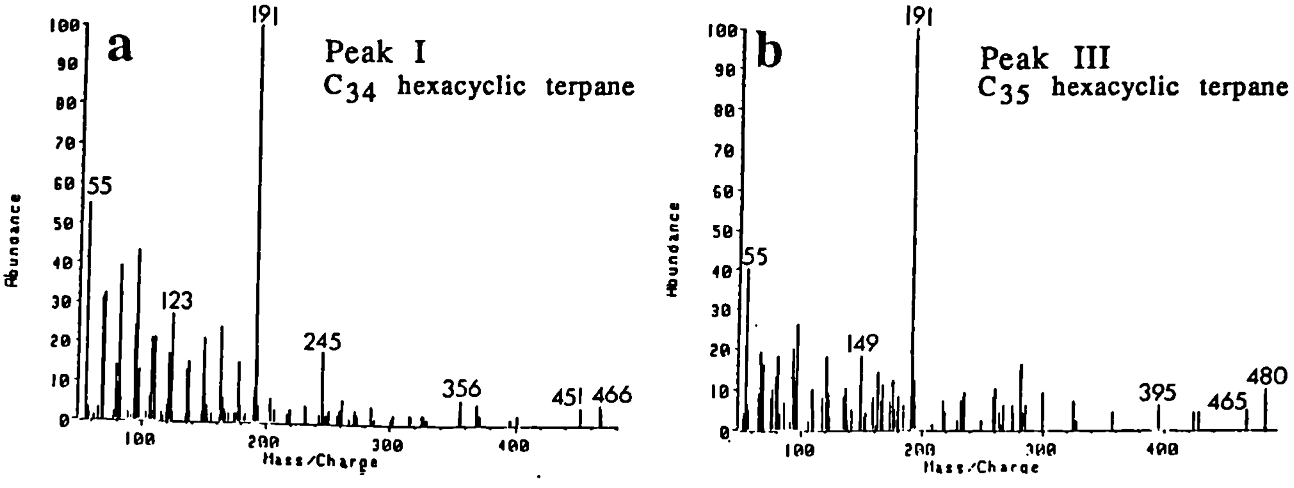


Fig.6.12 Mass spectra of hexacyclic terpanes found in the Orrock bitumen.

As for the majority of other oils and bitumens analysed, the unknown peak 30 is prominent and co-exists with peak 31, although the latter is of minor importance. Unlike the other samples, the unknown C_{29} triterpane (peak 34) eluting after the $C_{30}\alpha\beta$ hopane is high in abundance. A further salient feature is the dominance of homohopanes with the biologically-inherited 22R configuration over their 22S counterparts. This pattern confirms the immaturity of this bitumen. Coelution of the $C_{35}\alpha\beta$22R homohopane occurs with a compound (peak I) whose mass spectrum is given in Fig.6.12a. The mass spectrum of peak II is very similar. The molecular ion of 466 and the base peak of m/z 191 are indicative of a hexacyclic terpane. Peak III is thought to belong to the same series, as suggested by its mass spectrum (Fig.6.12b). The mass spectra of peaks I-III resemble those of hexacyclic hopanes described by Connan and Dessort (1987) in sediments and oils from highly anoxic evaporitic sequences. Notwithstanding the similarities in the mass spectra, the compounds documented by the above authors are not isomeric (i.e. only one compound per carbon number occurs) and they have significantly different retention times, relative to the pentacyclic hopanes, to the compounds found in the Orrock bitumen. These factors indicate that peaks I-III in Fig.6.11a may belong to a different hexacyclic terpane series.

6.3.2.2 Steranes

The quality of the m/z 217 mass fragmentograms of the oils and bitumens studied is generally poor because of very low sterane abundances, relative to the hopanes. Hopanes are approximately 20 to 70 times more abundant than steranes (parameter i in Table A.4) which leads to hopane fingerprints being superimposed on the sterane distributions in the m/z 217 mass fragmentograms.

The C_{29} regular steranes are of approximately equal abundance to, or show a slight predominance over, the C_{27} components in the majority of samples, which therefore places them within the estuarine/bay field of the Huang and Meinschein-type ternary plot (Fig.6.13). The enhanced concentrations of $C_{29}\alpha\alpha\alpha$20R seen in the bitumens from nodules places them within the "terrestrial" field.

The sterane distributions of the D'Arcy and Milton oils and of the hydrocarbons from the sandstones in the Broachrigg borehole are all markedly similar. Representative distributions for each pair of samples are shown in Figs 6.14a and b. The isomerisation of 20R to 20S epimers in the $\alpha\alpha\alpha$ steranes is at or near the end-point value, although the ratios of the isomerisation of $\alpha\alpha\alpha$ to $\alpha\beta\beta$ steranes are well below their proposed equilibrium values. The $\alpha\beta\beta$ steranes are present in slightly higher abundance, relative to $\alpha\alpha\alpha$ components, in the D'Arcy and Milton oils.

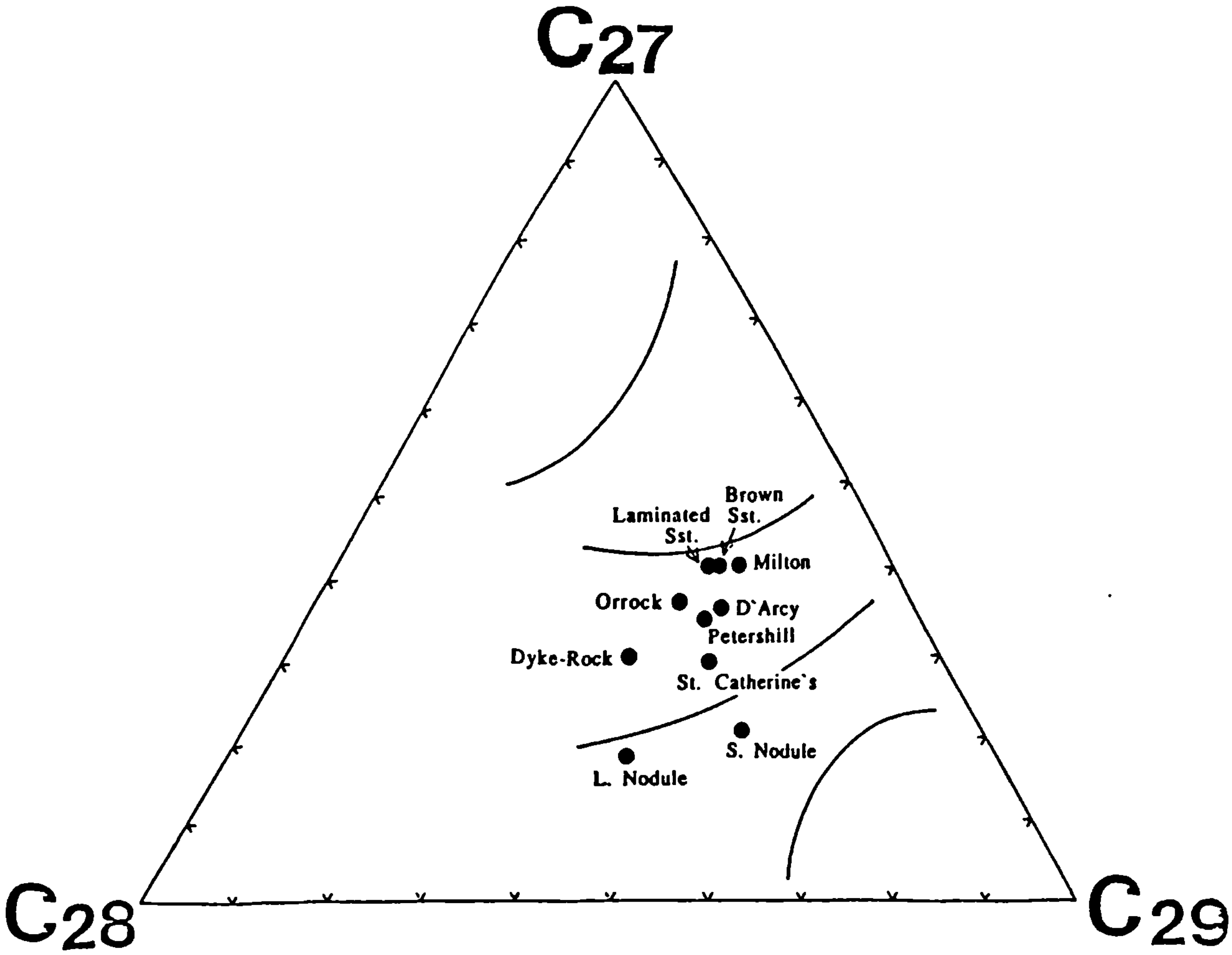


Fig.6.13 Ternary plot showing carbon-number distribution of steranes in the oils and bitumens (see Fig.4.18 for field definitions).

M/z 217 mass fragmentograms of samples from Mid Calder are shown in Figs 6.14 c and d. The trace of the bitumen from the large nodule is very similar to that from the small nodule. The main variation in the sterane distribution of this sample suite lies in the relative proportion of C_{27}-$C_{29}\alpha\alpha\alpha$ steranes (Fig.6.13). The overall distributions are similar, however, in that diasteranes are negligible, there is a predominance of the20R over the 20S $C_{29}\alpha\alpha\alpha$ epimers and there is also a very low proportion of αββ steranes. The prevalence of the biologically-inherited stereochemistries in the Mid Calder suite is indicative of sample immaturity.

The immaturity of the Orrock bitumen that was apparent from terpane analysis is confirmed by the prevalence of biological configurations in the m/z 217 mass fragmentogram (Fig.6.14e). The αββ steranes are barely resolved from compounds with the immature βαα configuration. In contrast to other oils and bitumens, the diasteranes in the Orrock bitumen exceed the regular steranes in abundance. No maturity-related information could be gleaned from the steranes in the Petershill bitumen as coelution of the $C_{29}\alpha\alpha\alpha$20S and $C_{29}\alpha\beta\beta$ steranes

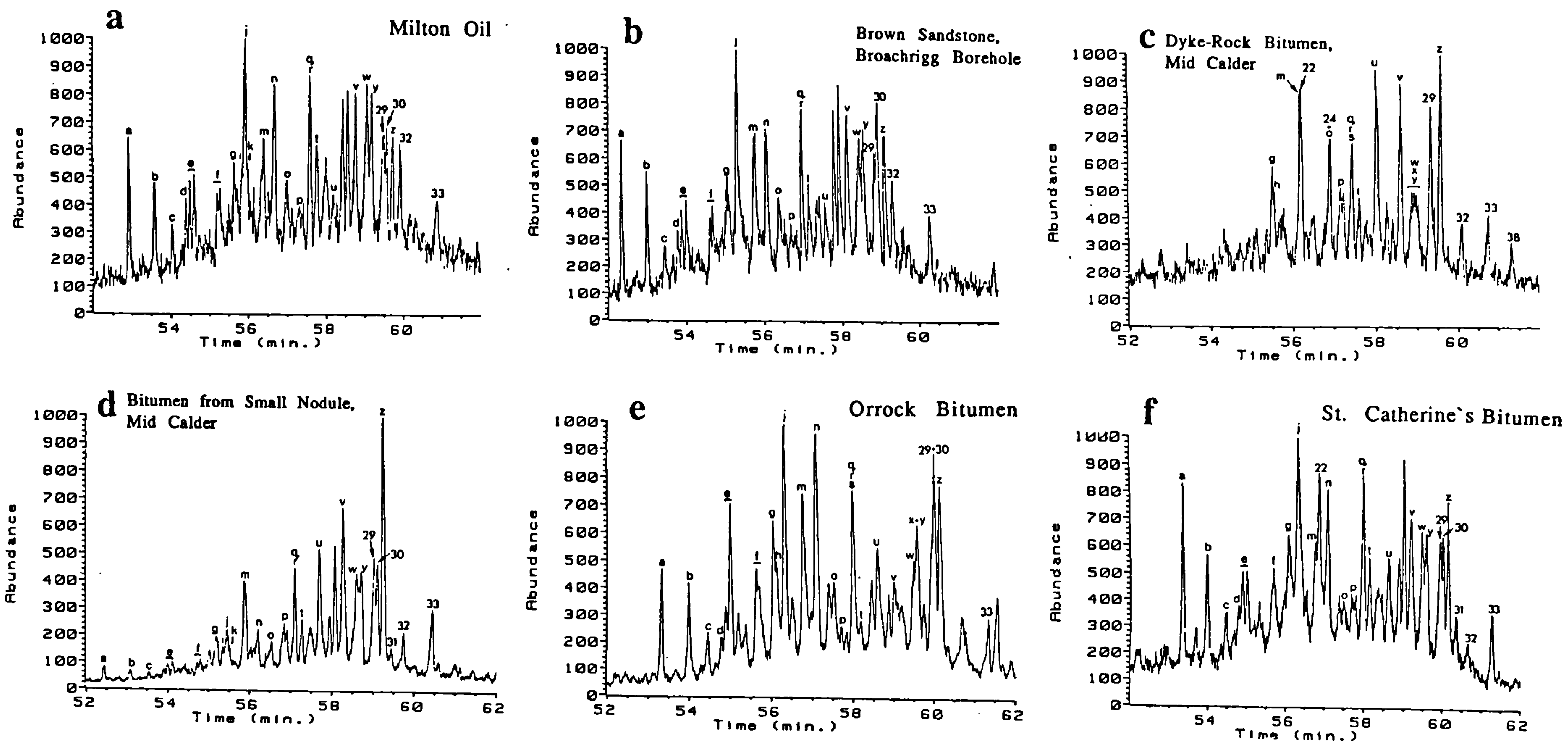


Fig.6.14 M/z 217 fragmentograms illustrating the variation in sterane distributions in the oils and bitumens studied (peak assignments in Table 4.6).

occurred with 25-norhopanes. The sterane pattern of the St.Catherine's bitumen (Fig.6.14f) is generally similar to that for the hydrocarbons extracted from the sandstones of the Broachrigg bore although the lower $C_{29}\alpha\alpha\alpha$20S and $\alpha\beta\beta$ contents are factors indicative of a lower maturity.

6.4 AROMATIC HYDROCARBONS

The similarity between the aromatic hydrocarbon distributions of the D'Arcy and Milton oils is revealed by the TIC traces in Figs 6.15a and b. Molecular parameters based on aromatic hydrocarbons are included in Table A.6. Both fractions contain a large proportion of unresolved material, particularly that of high molecular weight, which gives rise to a pronounced "hump". Readily discernible from the unresolved complex mixture (UCM) is a homologues series of naphthalenes and phenanthrenes, the former being more abundant. Also superimposed on the UCM is a homologous series of alkylbenzenes (extending at least to C_{38}) which is particularly prominent in the Milton oil. Monitoring of the m/z 105 fragment ion allows clarification of the alkylbenzene distribution (Fig.6.15c). Evaporative loss of low molecular-weight alkylbenzenes occurred prior to gc-ms analysis: gas chromatograms of the oils indicate that the C_3 alkylated members are *c.*50% higher in abundance than 2-Methylnaphthalene. The C_4 alkyltetralin, biphenyls and tetramethylnaphthalene are fairly prominent. Resolvable in the high molecular-weight hump are two compounds (peaks 55 and 56) which give major fragment ions of m/z 365 and which are thought to form part of a series of monoaromatic 8,14-secohopanes (Hussler *et al.* 1984). The distribution of these components in the oils is typified by that of the D'Arcy Oil (Fig.6.15d). The major peaks correspond to the earlier-eluting ones in Fig.4.25: their mass spectra were given in Fig.4.26.

The TIC traces of the hydrocarbons from the brown and laminated sandstones from the Broachrigg borehole (Figs 6.16a and b respectively) both show pronounced high molecular-weight UCMs from which two of the series of monoaromatic 8,14-secohopanes (with a distribution equivalent to that shown in Fig.6.15d) can be resolved. An alkylbenzene homology is evident in the laminated sample, but, despite the monitoring of ions with m/z 105, the homology could not be elucidated in the brown sandstone. Although swamped by the UCM, alkylated naphthalenes and phenanthrenes could be identified by mass fragmentography in both samples as could the benzohopanes.

The aromatic hydrocarbon fractions of the two bitumens from the nodules at Mid Calder bear a close resemblance to each other and are typified by the gas chromatogram in Fig.6.17a. The only compounds that could be identified were aromatic steroids and 8,14-secohopanes, the pattern of the latter components

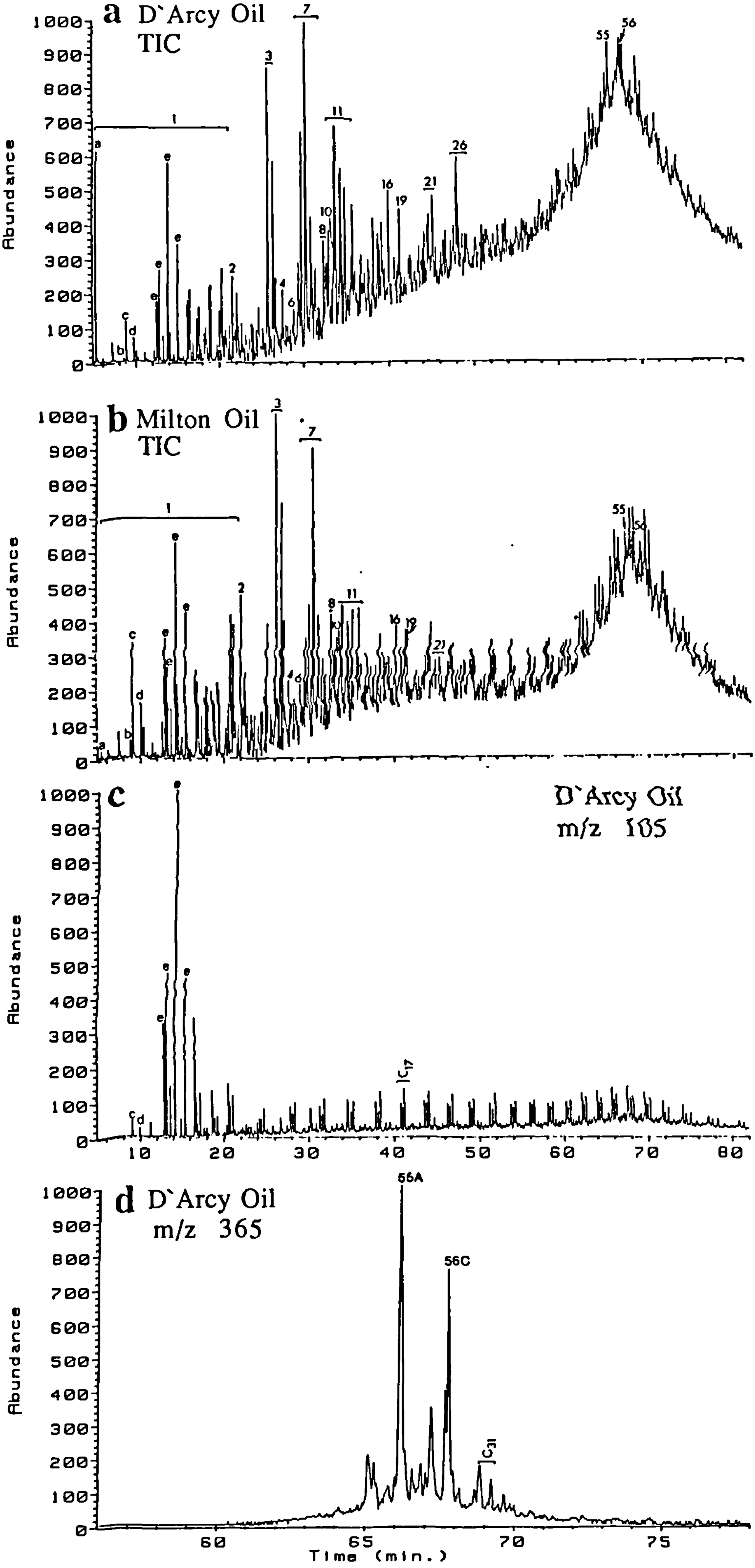


Fig.6.15 Distributions of aromatic hydrocarbons in the D'Arcy and Milton oils (peak assignment in Table 4.7).

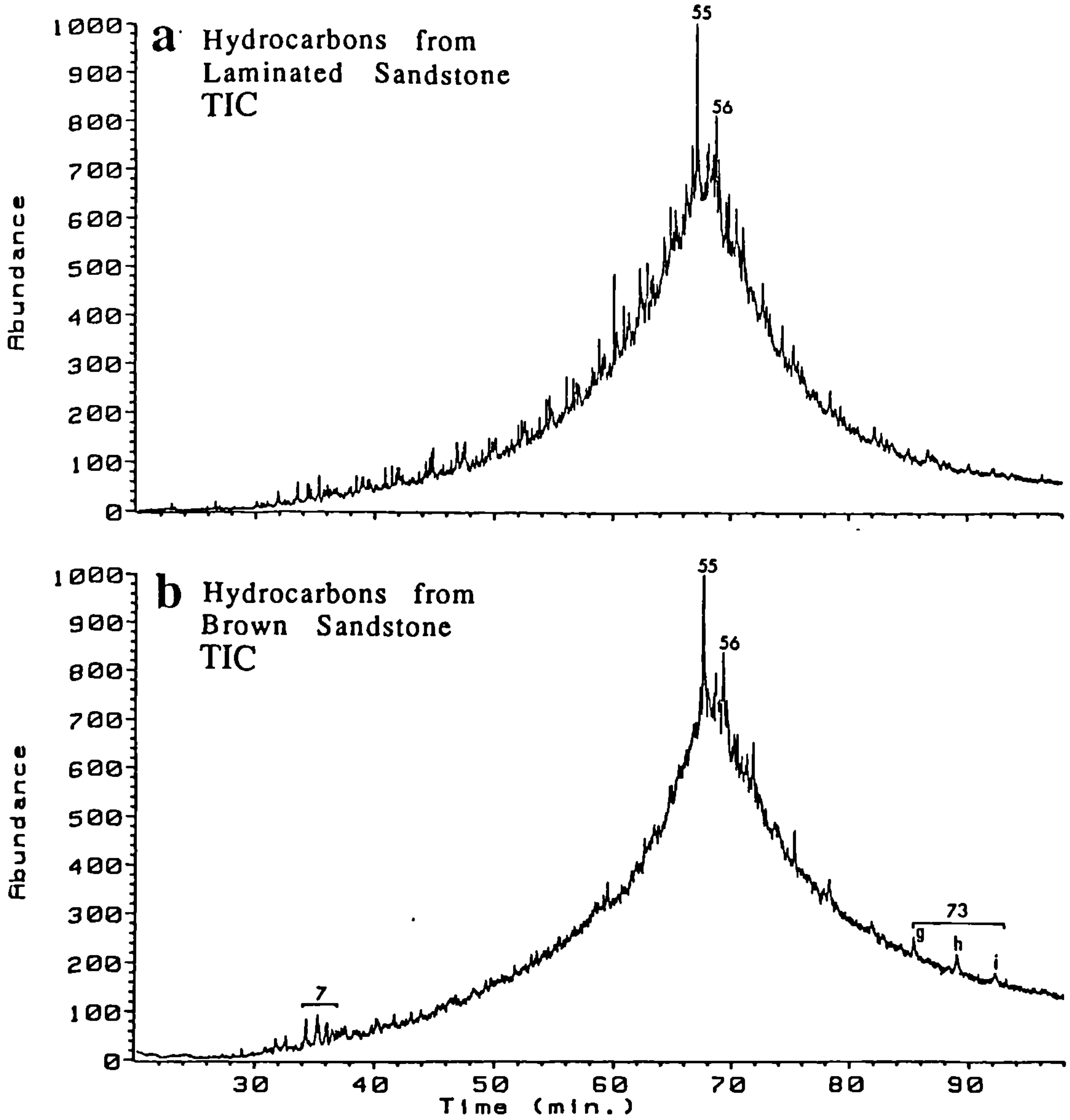


Fig.6.16 Distributions of aromatic hydrocarbons in the extracts from the sandstones from the Broachrigg borehole (peak assignments in Table 4.7).

closely resembling that shown in Fig.6.15d. In contrast, superimposed on the UCM of the dyke-rock bitumen is a prominent series of PAH with a pyrolytic-like distribution (Fig.6.17b).

The distributions of aromatic hydrocarbons in the Petershill and St.Catherine's bitumens (e.g. Fig.6.18a) bear a superficial resemblance to the distribution in the extract of the brown sandstone, in that they are dominated by a UCM from which two 8,14-secohopanes can readily be resolved. As for the other samples referred to above, the secohopane fingerprints are identical to that in Fig.6.15d. The majority of the remaining peaks in the hump are attributable to aromatic steroids and benzohopanes. Unlike the brown sandstone, no naphthalenes, phenanthrenes or alkylbenzenes could be detected.

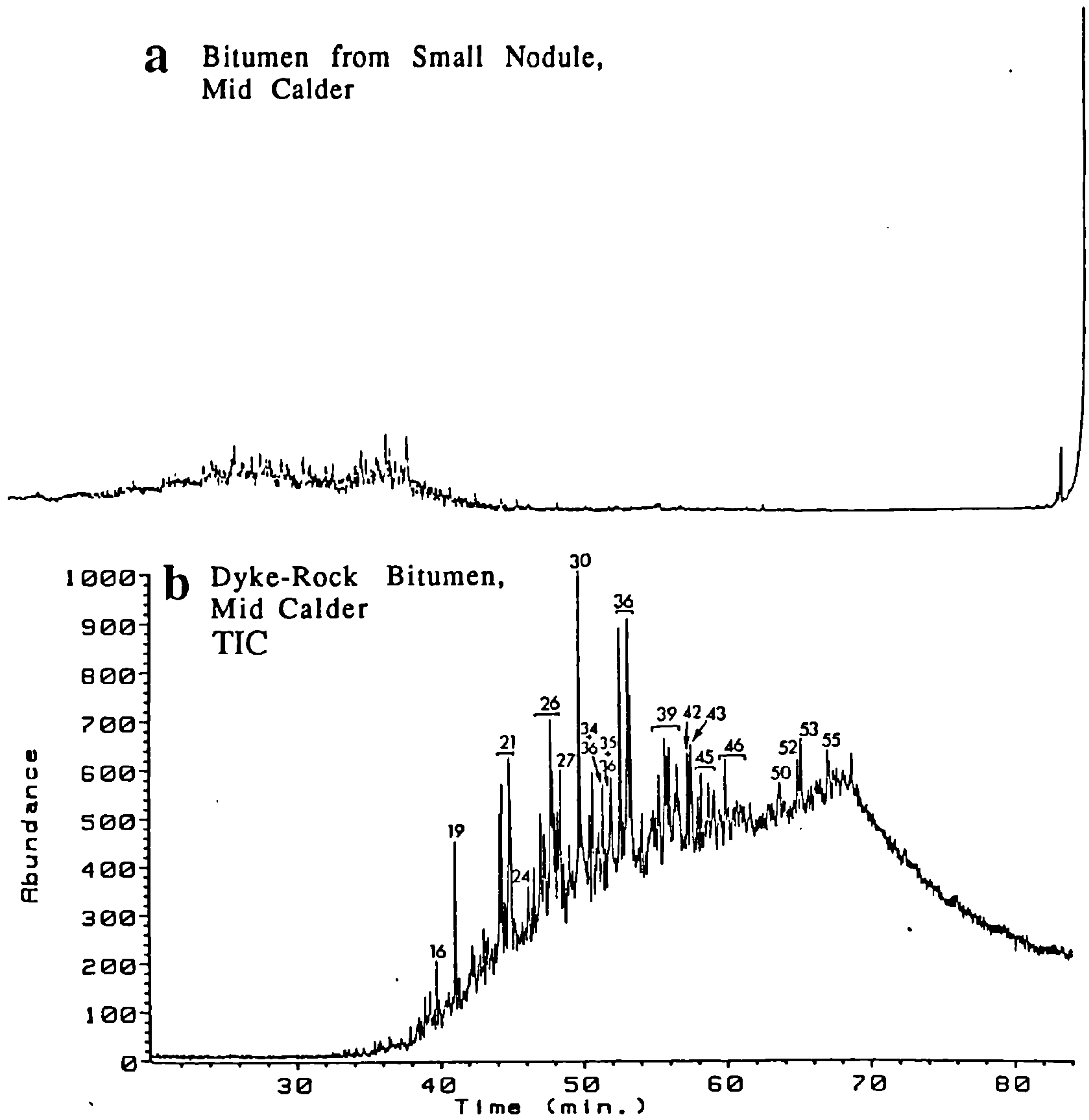


Fig.6.17 Distributions of aromatic hydrocarbons in the bitumens from Mid Calder (peak assignments in Table 4.7).

As did its saturated hydrocarbon fraction, the aromatic hydrocarbon distribution in the Orrock bitumen differs in several respects from those of the other samples. A double hump is present in the high molecular-weight region of the TIC trace (Fig.6.18b) and benzohopanes are relatively prominent. The 8,14-secohopane fingerprint is unique among the oils and bitumens studied because it contains doublets, with the later-eluting member of each pair of C_{29} and C_{30} components predominating (Fig.6.18c). In common with many of the other samples investigated, naphthalene, phenanthrene and their alkylated homologues are present. The C_4 alkyltetralin and 1,2,5,6-Tetramethylnaphthalene are prominent relative to the naphthalenes and phenanthrenes, as are several components (eluting at c.60 minutes) which were prominent in low-maturity lamalginite-rich shales. Parent PAH, particularly fluoranthene and pyrene, can also be recognised.

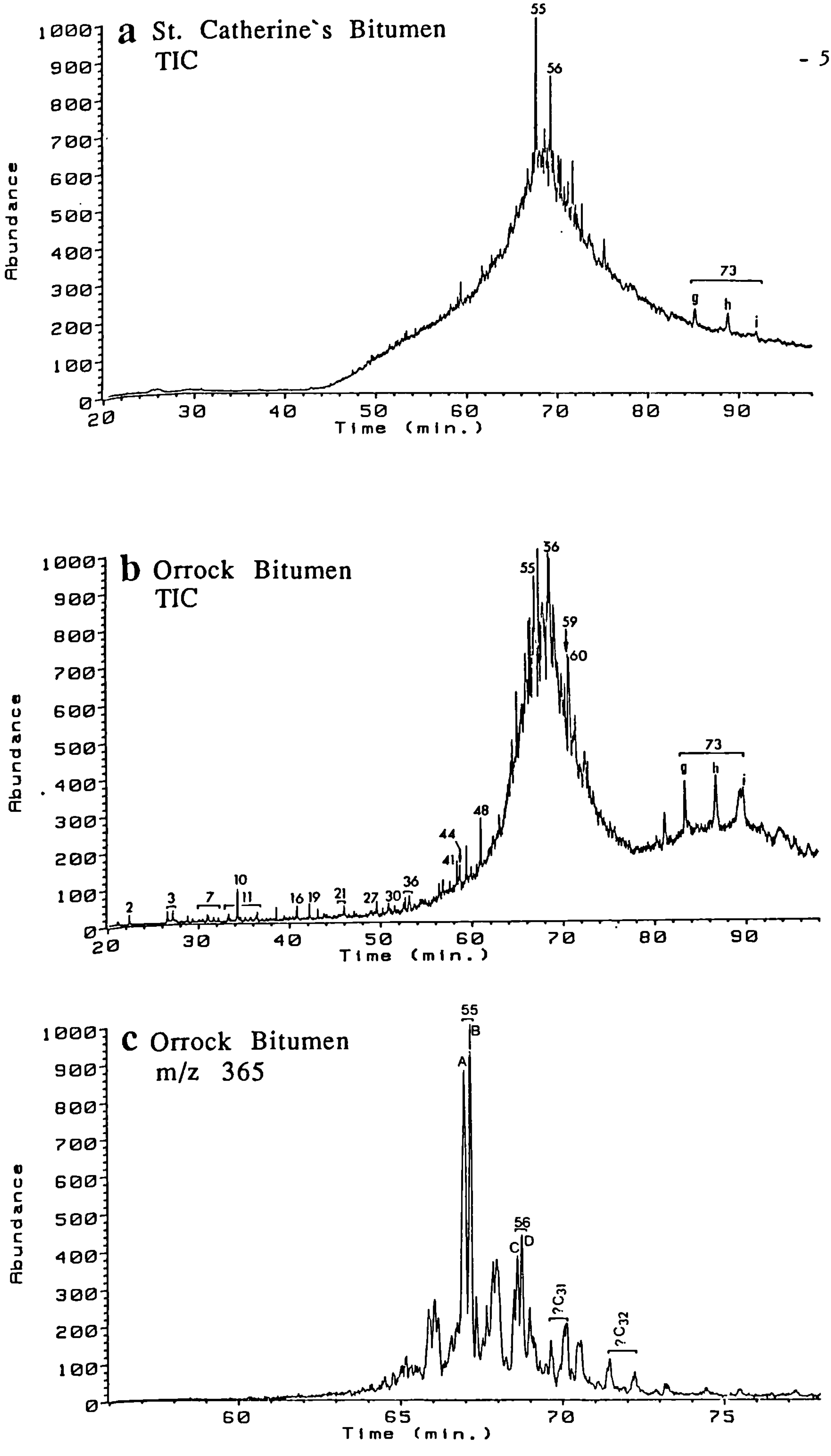


Fig.6.18 Distributions of aromatic hydrocarbons in the bitumens from St.Catherine's Well and Orrock Quarry (peak assignments in Table 4.7).

In all the oil and bitumen samples investigated, rearranged C-ring monoaromatics are moderately abundant and coelution with benzofluoranthenes and benzopyrenes occurs. The most salient difference apparent within the sample suite, that relates to the distribution of aromatic steroids, lies in the m/z 231/245 ratios. In all samples except the Orrock bitumen, the non-nuclear methyl-substituted triaromatics exceed the nuclear methyl-substituted triaromatics in abundance (parameter 1, Table A.6).

6.5 DISCUSSION

6.5.1 Biodegradation

Many qualitative similarities exist in the distributions of aliphatic and aromatic hydrocarbon components in the oils and bitumens examined, although the relative proportions of these fractions and their constituent compound classes differ greatly within the sample suite. The salient differences relate to the relative abundances of *n*-alkanes, acyclic isoprenoids and polycyclic alkanes. The variations reflect the degree of biodegradation suffered by the oils and bitumens.

From numerous studies of samples from the natural environment, and laboratory studies, the susceptibility to biodegradation of different compound classes in the aliphatic hydrocarbon fractions of crude oils is generally *n*-alkanes > acyclic isoprenoids > C_{14}-C_{16} bicyclics > regular steranes > hopanes > diasteranes > tricyclics (Seifert and Moldowan 1979; Alexander *et al.* 1983b; Volkman *et al.* 1983b; Connan 1984). Relatively few studies have focused on the degradative fate of aromatic hydrocarbons, but their generally accepted rate of alteration is considered to decrease with an increase in the number of aromatic rings and also with an increase in the extent of alkyl substitution. Thus, the relative ease of attack follows the sequence monoaromatics > diaromatics > triaromatics and within each class $C_1 > C_2 > C_3 > C_n$, where n is the number of carbon atoms in the alkyl substituents (Jones *et al.* 1983; Volkman *et al.* 1984; Jones 1986). These sequences only represent *general* trends; the specificity and sequence of reactions that occur in the different hydrocarbon classes are highly dependent on environmental factors (e.g. reservoir properties or laboratory conditions), the nature of the oil substrate and the nature of the microbial communities (and their nutrients) that degrade the oil (Atlas 1981; Goodwin *et al.* 1983; Volkman *et al.* 1983b, 1984; Jones 1986). It should also be borne in mind that the generalised degradation sequences have been established by observing the sequential removal of hydrocarbons from an initially undegraded oil or from a suite of oils in a given basin which derive from a common source rock from which they were released at similar levels of maturity.

The widely differing geographic locations, modes of occurrence and maturities of the Scottish oils and bitumens make derivation from a single pooled reservoir or expulsion from the same source horizon at the same level of maturity unlikely. Thus, there is no precursor oil whose biomarker distribution could constitute a comparative base. To state unequivocally how much of the variation in the hopane and sterane profiles (particularly the latter) is attributable to biodegradation is therefore difficult. The extreme recalcitrance of these components to biodegradation, coupled with the frequent prevalence of preferentially degradable components with biologically-inherited stereochemistries in several samples showing obvious signs of severe biodegradation indicates that major variation within the distributions of polycyclic alkanes is governed by factors other than microbial alteration, i.e. source and maturity. Despite the lack of comparative datum, the relative abundance of the different hydrocarbon classes in the Midland Valley oils and bitumens can be used to assess their general level of alteration.

The prominence of the highly soluble and readily degradable C_1-C_3 alkylated benzenes and the highly paraffinic nature of the D'Arcy and Milton oils are features typical of undegraded petroleums (Connan 1984; Volkman *et al.* 1984). The abundance of *n*-alkanes and the presence of a suite of alkylbenzenes in the EOM from the laminated sandstones in the Broachrigg bore indicate that the sample has experienced very little, if any, biodegradation. Water washing could account for the loss of low molecular-weight alkylbenzenes and a reduction in the concentration of *n*-alkanes $<C_{17}$. Alkylated naphthalenes and phenanthrenes are present, but are swamped by the significant UCM.

The close proximity of the hydrocarbon-bearing sandstones to one another in the Broachrigg borehole and their near-identical biomarker distributions and Rc values (see Table A.6) are indicative of expulsion from the same source rock at the same maturity level. Although lying only 90ft below the laminated sandstone reservoir, the prominence of bicyclic alkanes in the gas chromatograms of the saturated hydrocarbon fraction from the brown sandstone indicates that, not only has there been the preferential loss of medium/low molecular-weight *n*-alkanes, there has been an absolute reduction in the concentration of *n*-alkanes present. The increased percentage of aromatic hydrocarbons in the EOM from the brown sandstone is consistent with this inference. These observations, in conjunction with the removal of the alkylbenzene suite, suggest that the sample has undergone minor to moderate biodegradation on the scale of Alexander *et al.* (1983b) and Volkman *et al.* (1983b, 1984). This scale is adopted hereafter.

The difference in the level of alteration of the hydrocarbons in the Broachrigg sandstones is probably a reflection of the differing physical characteristics of the host sediments. The fine grain size and highly compact nature of the laminated sandstone are factors that are more likely to be inimical to the ingress of meteoric water than the coarse grains and massive character of the brown sandstone.

Within the Mid Calder sample suite, the loss of alkylated naphthalenes and, in the case of the bitumens from nodules, the alkylated phenanthrenes, coupled with the prominent UCM, points to moderate to extensive degradation. Assuming that the saturated hydrocarbon distributions have been affected by the biodegradation process, then because they are almost devoid of components other than high molecular-weight *n*-alkanes, they must be regarded as extremely unusual. Although departures from the general biodegradation orders cited previously do occur, the saturated hydrocarbon distributions in the Mid Calder suite represent major deviations. If the removal of medium and low molecular-weight *n*-alkanes were due to microbial activity, a concomitant enrichment in acyclic isoprenoids and bicyclics might be expected, akin to that seen in the brown sandstone. That this distribution does clearly not occur indicates that there may have been an absolute rather than a relative enrichment in long-chain *n*-alkanes in the Mid Calder samples.

High concentrations of very long-chain *n*-alkanes (C_{35}-C_{55}) have been reported in sediments contaminated by recent petroleum spills long after (1 year) the *n*-alkanes $<C_{35}$ had been removed (Oudot *et al.* 1981; Gassmann 1982). The suggestion that these compounds have been produced by *de novo* synthesis during the microbial degradation of oils is supported by the known bacterial production of very long-chain *n*-alkanes (Walker and Colwell 1976). The possibility that the high molecular-weight *n*-alkanes could have pre-existed in minute amounts and only became visible after the bulk of the other components had been degraded is considered unlikely because the high sensitivity of the analytical equipment employed in the studies referred to above should have been capable of demonstrating their presence in the original undegraded oil (Oudot *et al.* 1981). In recent sediments, the very high molecular-weight *n*-alkanes are only reported when degradation has reached an advanced stage, i.e. after significant alteration of steranes and hopanes (Connan 1984). As noted by Connan (1984), no literature is available detailing the occurrence of these long-chain alkanes in petroleum reservoirs.

While the lower content of C_{27} steranes in the nodular bitumens from Mid Calder could be construed as a facet of sterane biodegradation, the extent to which this has occurred (at most very minor), as well as the occurrence of acyclic isoprenoids and bicyclic alkanes in the samples, is inconsistent with the attainment of the very advanced stage of biodegradation that is seemingly a prerequisite for the neo-synthesis of long-chain *n*-alkanes in recent sediments. In summary, the co-existence of hydrocarbons that would generally be expected to be removed at relatively early or mid-stages of the biodegradation sequence (e.g. acyclic isoprenoids and bicyclic alkanes) with distributions typically indicative of late-stage alteration (presence of long-chain *n*-alkanes, absence of phenanthrene and methylphenanthrenes) is a clear indication that the environmental milieux which prevailed during the degradation of the Mid Calder samples differed considerably from those commonly operating in other geological environments and recent sediments.

An alternative explanation for the presence of long-chain *n*-alkanes in the Mid Calder bitumens is that the distinctive *n*-alkane envelopes represent distillation cuts. Industrial distillation processes indicate that the carbon-number distributions covering the ranges seen in the Mid Calder samples would be expected to be produced at temperatures exceeding 500°C (Hunt 1979). Since a high-temperature origin for the Mid Calder bitumens is considered likely (see Section 6.5.3), it seems that aspects of both biodegradation and high-temperature thermal activity are preserved in the hydrocarbon fractions of the Mid Calder sample suite, although the relative importance of the processes in producing the observed distributions is not known.

A further point of interest in relation to the Mid Calder samples is the occurrence of monoaromatic 8,14-secohopanes and a suite of pyrolytic-like PAH in the UCMs. That these components are preserved is an indication that they show a great resistance to biodegradation. The recalcitrance of pyrolytic/combustion-derived PAH in recent sediments to biodegradation has been noted in laboratory experiments (Jones 1986; Jones *et al.* 1986).

The lack of normal and acyclic isoprenoid alkanes in the St.Catherine's bitumen, coupled with the absence of bicyclic alkanes, indicates that the level of degradation is extensive.

In addition to the depletion of bicyclic alkanes, the presence of demethylated hopanes in the Petershill bitumen reveals that biodegradation has progressed further than it has in the St.Catherine's sample and lies between the "extensive" and "severe" categories on the scale of Alexander *et al.* (1983b) and Volkman *et al.* (1983b, 1984). The absence of alkylated naphthalenes and phenanthrenes in the traces of these samples supports their inferred advanced level of alteration.

Demethylated (25-nor) hopanes are commonly used as biomarkers for extremely degraded crudes in which they are thought to form by the bacterial removal of the methyl group at C-10 (Rullkötter and Wendisch 1982; Volkman *et al.* 1983b). Recent work evaluating the concentrations and distributions of hopanes and demethylated hopanes in undegraded and degraded oils (Peters and Moldowan 1991) has confirmed earlier suggestions (Volkman *et al.* 1983b) that a product-precursor relationship exists between the two types of hopane. This work has invalidated previous proposals that the abundance of 25-norhopanes in degraded crudes is *solely* due to their being "unmasked", as a result of concentration processes, as the more labile components have been removed (Goodwin *et al.* 1983; Howell *et al.* 1984).

Demethylated hopanes generally appear at the late stage of crude-oil degradation after significant alteration of steranes, although there are reports of demethylated hopanes occurring in oils in which the steranes are not altered (Brooks *et al.* 1988; Peters and Moldowan 1991). The Petershill bitumen apparently provides a further example of "anomalous" demethylated hopane occurrence. Also contradicting the generally observed pattern of degradation is the degradative removal of hopanes without the appearance of 25-norhopanes (Seifert and Moldowan 1979; Goodwin *et al.* 1983; Seifert *et al.* 1984). The vagaries of demethylated hopane occurrence cited above reflect the different environmental circumstances operating during biodegradation.

The restricted occurrence of the β-carotane to the highly-degraded St.Catherine's and Petershill bitumens points clearly to an association of this compound with microbial activity in the Midland Valley Carboniferous. The higher relative concentration of β-carotane in the Petershill bitumen correlates with the greater degree of biodegradation the sample is thought to have suffered. Since β-carotane is known to be very resistant to biodegradation (Jiang and Fowler 1986), the enhanced concentrations in the latter sample could reflect increased "unmasking" because of the greater removal of the less stable regular hopanes. Since carotenoids have been reported in extant bacteria (Schwendinger 1969), an alternative possibility is that the β-carotane could have originated from the direct input of carotenoid-containing bacteria which were degrading the bitumens. A bacterial source has been invoked to account for the intermittent occurrence of β-carotane in Chinese oil shales (Brassell *et al.* 1988).

The prominence of the aromatic 8,14-secohopanes in the St.Catherine's and Petershill bitumens emphasises the earlier comment that these compounds are extremely resistant to biodegradation. That these compounds are "preserved" by virtue of their resistance to biodegradation, rather than "produced" by the transformation of hopanoid precursors during post-diagenetic/catagenetic processes, is indicated by their presence in undegraded oils and bitumens and by their widespread occurrence in immature sediments (see Chapter 4). Resistance to bacterial attack is also inferred for the benzohopanes.

The preservation of the *n*-alkane envelope in the Orrock bitumen points to the sample being, at most, only mildly biodegraded, although the marked decrease in the *n*-alkanes $<C_{21}$ could have occurred during water washing through contact with hydrothermal fluids. The relatively high concentration of polycyclic alkanes in the saturated hydrocarbon fraction (Fig.6.3e) is not necessarily indicative of biodegradation (i.e. preferential removal of *n*-alkanes) since relatively high abundances of hopanes were detected in many low-rank samples (see Chapter 4). The inference of little/no biodegradation affecting the Orrock bitumen is corroborated by the presence of naphthalene and phenanthrene and their alkylated homologues, although their abundance is greatly subordinate to that of high molecular-weight unresolved material.

Because an increase in the magnitude of the UCM has been observed with the increasing biodegradation of aromatic (and saturated) hydrocarbons, the relative size of the UCM in chromatograms is often used as a qualitative indicator of the extent of biodegradation (Jones *et al.* 1983; Volkman *et al.* 1984). Caution is needed if this approach is to be used in the analysis of oils and bitumens from the Midland Valley because it is apparent that very pronounced UCMs can occur in samples which, on the basis of other evidence, have experienced little or no biodegradation.

A summary of the extent to which the analysed oils and bitumens have suffered biodegradation is given in Table 6.4. Although there is an expected general trend towards an increase in the proportion of polar material with the increasing extent of biodegradation (*cf.* Fig.6.2), the high percentage of polars in the Orrock bitumen indicates that, despite biodegradation exerting an important influence on the gross composition of the oils and bitumens, it is not the sole governing factor.

6.5.2 Correlation

Comparison of the biomarker distributions in the oils and bitumens with those of the extracts of immature sediments containing different types of organic matter (Chapter 4) enables their most likely source material(s) to be defined. The following discussion initially excludes the Orrock bitumen since this sample differs from the others in that it is thought to have a dual source: the remaining samples are thought to share a common, single, organic-matter source.

Excluding the Orrock sample, the qualitative distributions of the tricyclic and tetracyclic terpanes in the oils and bitumens are almost identical. They provide a strong indication that they originate from source rocks containing similar types of organic matter. Although of relatively low abundance in all types of organic

Level	Compositional Characteristics	Extent of Biodegradation	Midland Valley Oil/Bitumen
1	Abundant *n*-alkanes	Not degraded	D`Arcy and Milton oils, laminated sandstone Orrock bitumen
2	Light-end *n*-alkanes removed	Minor	
3	>90% *n*-alkanes removed		Brown sandstone
4	Alkylcyclohexanes and alkylbenzenes removed; acyclic isoprenoid alkanes and naphthalene reduced	Moderate	
5	Isoprenoid alkanes and methylnaphthalenes removed; selective removal of C_2 naphthalenes		Mid Calder bitumens
6	C_{14}-C_{16} bicyclic alkanes removed	Extensive	St. Catherine`s bitumen
7	>50%(20R)-5α(H),14α(H),17α(H) steranes removed	Very extensive	Petershill bitumen
8	Distributions of steranes and triaromatic steroids altered; demethylated hopanes abundant	Severe	
9	No steranes; demethylated hopanes predominate	Extreme	

Table 6.4 Extent of biodegradation of the oils and bitumens analysed using the scale of Volkman *et al.* (1984).

assemblage studied in the current project, the negligible contribution (if any) from tetracyclic terpanes, other than the ubiquitous C_{24} 17,21-secohopane (Aquino Neto *et al.* 1983), points to an algal source: more specifically lamalginite. This inference stems from the observations (discussed in Chapter 4) showing that relatively high concentrations of tetracyclic terpanes, coupled with an increase in the number of C_{24} tetracyclics present, were associated with telalginite and/or higher-plant input. Very strong corroborating evidence of lamalginite precursors is not only the presence , but more significantly the abundance, of the unknown C_{29} triterpane (peak 30) occurring as a shoulder on the $C_{29}\alpha\beta$ hopane. From the analysis of a wide range of low-maturity sediments containing different organic assemblages, it is evident that peak 30 is exclusively associated with algal matter in the Carboniferous sediments of the Midland Valley. The abundance of this compound in all samples, except the dyke-rock bitumen, is of the same order of magnitude as that seen in the lamositic shales, as well as in other shales containing abundant lamalginite thought to be of non-marine origin. Non-marine lamalginite is therefore the most probable progenitor material from which the bulk of the oils and bitumens were sourced.

The hopane profile of the dyke-rock bitumen from Mid Calder differs from those of the other samples because peak 30 is relatively low in abundance and the $C_{29}\alpha\beta$ hopane is relatively high. The sample is still, nevertheless, likely to have been sourced from lamalginite-rich sediments. This is adduced from the close resemblance between its 3- and 4-ringed terpane distribution and those of the other samples. The carbon-number distribution of the regular steranes is similar to those of other samples for which there is stronger evidence for a lamalgal source although, as discussed in Section 4.4.1.4.5, sterane distributions alone are not unequivocal indices of source input. Consideration of the geological setting of the bitumen also favours lamalginite as the progenitor material, since the dyke on which the bitumen is coated is juxtaposed with lamalginite-rich sediments lying in the Upper Oil-Shale Group. The different nature of the hopane profile in the dyke-rock bitumen probably reflects its high-temperature origin and possibly also prolonged exposure to high temperatures, suggestions which are discussed more fully in the next section.

The occurence of the saturated 8,14-secohopane series in relatively large concentrations in the oils and bitumens is further evidence that they were sourced from non-marine, lamalginite-containing, sediments. The resistance of the 8,14-secohopanes to biodegradation is apparent from the prominence of these components in the saturated hydrocarbon fractions of highly degraded samples from which the more labile components have been removed (St.Catherine's and

Petershill bitumens). Gc-ms analysis revealed the presence of 8,14-secohopanes in all the oils and sediments studied (albeit in negligible amounts in the Orrock bitumen), and in all non-marine, lamositic, shales regardless of rank. Inspection of m/z 123 mass fragmentograms revealed only very small amounts of 8,14-secohopanes, relative to other hopanes, in other algal-containing sediments of marine or non-marine origin. A series of 8,14-secohopanes has been described from a Chinese torbanite (Wang *et al.* 1990), but none of these compounds was detected in any of the *Botryococcus*-rich shales in the Midland Valley, nor in any coals or sediments containing higher-plant matter unless accompanied by lamalginite.

Information derived from steroidal components supports the opinion of a source from non-marine lamalginite made on the basis of terpane analysis. As discussed in Chapter 4, the proportion of triaromatic steroids to nuclear methyl-substituted triaromatic steroids (m/z 231/245) was found to be a type-dependent parameter. Although the m/z 231/245 ratio exceeds unity in the majority of algal-rich sediments studied, the ratios in the oils and sediments (excluding Orrock) encompass the range of relatively high values (>1.4) which were derived from all but one of the lamositic shales studied (Section 4.4.1.4.1 and Fig.4.108).

Apart from the bitumens from nodules at Mid Calder, whose sterane distributions may have been influenced by biodegradation (see previous section), the close clustering of points on the Huang and Meinschein-type ternary plot (Fig.6.13) supports their inferred common source. The samples plot within the same general area as their suggested lamalginite-rich precursors, although sediments containing other types of maceral assemblage can plot in this area (see Chapter 4). From the foregoing account, biomarker evidence for a lacustrine source seems to override any suggestion derived from the ternary plot that the organic matter from which the oils and bitumens were sourced accumulated in an estuarine or bay regime. Thus, the analysis of oils and bitumens provides further evidence that the Huang and Meinschein plots have limited application in evaluating organic input and depositional environments in the Carboniferous of the Midland Valley.

Whilst the polycyclic alkane fingerprints of all the oils and bitumens studied provide the strongest evidence for their origin from non-marine, lamalginitic source materials, the analysis of acyclic alkanes provides confirmation. Because of the preferential susceptibility of acyclic alkanes to biodegradation, ratios based on these components are only truly representative of source-input and depositional environments for samples in which their distributions have not been modified by biodegradation or water washing. In such samples (D'Arcy oil, Milton oil and the hydrocarbons in the laminated sandstone) the Pr/Ph ratios are all very similar, lying in the range 2.23-2.33. These values are consistent with the relatively low values (c.1-2) cited by Powell (1986) as being characteristic of high-wax crudes derived from lacustrine sequences. The very low Pr/*n*-C_{17} ratios also suggest an origin from lamalginitic lacustrine source rocks because such ratios are thought to reflect the accumulation of organic matter in relatively open-water conditions (Lijmbach 1975; Powell 1984, 1986). These deductions concur with the known open-water regime under which lamellar algal matter accumulated in the areally extensive Lake Cadell (see Chapter 4 for further discussion).

The preceding evaluation indicates that the sediments containing lamalginite are the most likely source rocks for the oils and bitumens studied. From the organic petrological and geochemical work undertaken, the rocks with the greatest potential are the lamosites. It has long been known that these deposits, many of which were formerly worked as oil shales, are most abundant and reach their maximum thickness within the Lothians Oil-Shale Group. This part of the succession therefore constitutes the single most important source interval for the oils and bitumens of the Midland Valley.

As referred to earlier, deltaic sedimentation persisted throughout most of Fife whilst major oil-shale deposition was occurring over what is now the Lothians and Burntisland. The discovery of lamosites in the east Fife succession, however, indicates that the accumulation of lamositic shales was not restricted to the Lothians Oil-Shale Group province. Numerous thin, non-marine shales also occur in the fluvio-deltaic succession of Fife. While they do not appear to have the "feel" or characteristic features of lamosites (i.e. finely laminated, fissile, relatively lightweight), they do, nevertheless, contain abundant lamalginite. Consequently, although the greatest known thickness and areal extent of lamositic shale occurs in the area occupied by the Lothians Oil-Shale Group, in bulk terms it is likely that the thin, areally restricted, but numerous lamalginite-rich shales in Fife could, collectively, make the part of the sequence incorporating the deltaic Pathhead to Anstruther Beds sequence of Fife a viable source-rock interval.

Besides the probability that the D'Arcy and Milton oils and the hydrocarbons from the sandstones in the Broachrigg borehole all originate from a common type of source rock, the exceptionally close correlation between the qualitative terpane distributions of these four samples (see previous section) introduces the possibility that they derived from the same source horizon. If the Milton oil was locally sourced, then the source horizon probably lay on the "feather edge" of the Lothians oil-shale facies, because the line of demarcation between the lacustrine facies of the Lothians succession and the fluvio-deltaic facies of Fife probably lay close to the Balfour Anticline in which the oil is now reservoired. Alternatively, the Milton oil could have been generated in the Midlothian Basin, at the same time as the D'Arcy oil, and the former might have migrated northwards. Given that very little is known about the deep structure of the Fife-Midlothian Basin and that the onshore geology is very complex, particularly because of the multiplicity of faults, northwards migration must be regarded as highly speculative.

The Orrock bitumen differs from the other samples studied because aspects of hydrocarbon distributions characteristic of both higher-plant matter and lamalginite are represented in its molecular signature. The prominence of the unknown C_{29} triterpane (peak 30) is a lamalginite marker, as is the prominence of alkyltetralins, 1,2,5,6-Tetramethylnaphthalene and the compound eluting at *c.*60 minutes in the TIC trace of the aromatic hydrocarbon fraction. Unlike the other algal-rich sediments and the other oils and bitumens, the nuclear methyl-substituted triaromatics dominate over the non-methylated triaromatics, a feature characteristic of higher-plant matter (see Chapter 4). The unknown C_{29} triterpane (peak 34) eluting after the $C_{30}\alpha\beta$ hopane is highly conspicuous and, as discussed in Chapter 4, its abundance signifies contributions from vascular-plant matter. The most convincing evidence for terrigenous input is the distribution of tetracyclic terpanes. The association of a major contribution from the C_{24} tetracyclic terpane represented by peak 12 (prominent in the gas chromatogram) with the multiplet of the other C_{24} tetracyclics was only recorded in the wood and "vitrinite" from Orrock Quarry, the latter sample being a high-rank wood rather than a vitrinite *sensu stricto*. Thus, the Orrock bitumen represents a mixture of products of hydrocarbon generation from terrestrial matter and lamellar algal organic matter.

The occurrence of compounds thought to be hexacyclic terpanes is unique to the Orrock bitumen, but their significance in this sample is not currently known. Connan and Dessort (1987) have suggested that hexacyclic terpanes could be used as biomarkers for organic matter that accumulated in highly anoxic, evaporitic environments. In addition to the likelihood that the compounds in the Orrock bitumen are not the same as those identified by Connan and Dessort, there is no geological evidence suggesting that hypersaline or highly anoxic environments existed in the Burntisland area during or prior to the volcanic episode which gave rise to the accumulation of the Burntisland Volcanic Formation, into which Orrock Quarry is now cut. Furthermore, the prevalence of clasts containing the remains of higher-plant matter in Orrock Quarry (and in the other volcanic vents studied) suggests that volcanism occurred in environments dominated by terrigenous sedimentation. An additional factor worth noting is that none of the five samples analysed in this project which had ratios of Pr/Ph <1 contained hexacyclic terpanes, although, as Connan and Dessort (1987) noted, they apparently do not exist in all anoxic environments. Whatever the source of the hexacyclic compounds in the aliphatic hydrocarbon fraction of the Orrock bitumen, the concomitant relatively high abundance of benzohopanes in the aromatic fraction suggests that the environmental conditions that operated during and following the accumulation of the source material were conducive to the preservation of the 6-ringed skeleton of bacteriohopanetetrol, the precursor from which both series of compounds are thought to be derived (Hussler *et al.* 1984; Connan and Dessort (1987).

6.5.3 Maturity and Mode of Formation : Igneous *vs.* Non-Igneous Origin

While qualitative similarities exist between the hydrocarbon distributions of all the oils and bitumens studied, major differences exist between the molecular distributions of the various hydrocarbon classes which predominantly reflect variations in sample maturity.

In the preceding section, the D'Arcy and Milton oils and the hydrocarbons from the Broachrigg borehole were identified as belonging to a single family. Consideration of the maturity indices for these samples reveals that a consistent pattern emerges in that for most ratios the values for the D'Arcy and Milton oils are similar, as are the values for the Broachrigg samples, but the ratios for each pair of samples differ from one another. The maturity indices indicate that the former pair of samples is more mature than the latter. This assessment is based largely on the aromatic hydrocarbons because the majority of ratios based on hopanes and steranes are at or near their end-point values, or show insufficient variation from which relative maturities can be confidently predicted. Ratios based on steranes are probably not as reliable as those derived from hopanes or aromatics because of their very low relative abundance. The Tm/Ts ratios contradict the maturity trend established above, but this anomaly may reflect differences in source input (Seifert and Moldowan 1980), although these are likely to be very minor in view of the close qualitative resemblance of the biomarker distributions of the four samples. Differences in environmental oxicity is a more likely explanation since Tm is favoured over Ts in oxic environments (Moldowan *et al.* 1986). The higher levels of environmental oxicity (indicated by increased Pr/Ph ratios) in the D'Arcy and Milton oils parallel their higher Tm/Ts ratios.

Qualitative and quantitative molecular parameters indicate that the two pairs of samples were generated from the same source-rock type (possibly even the same horizon), but at different source-rock maturity. The samples are classified as "Mid Mature" oils because the molecular parameters, based on both saturated and aromatic hydrocarbons, indicate that the predicted maturity of the source rock at the time of generation lies in the range corresponding to a vitrinite reflectance of $\%R_o \approx 0.65\text{-}1.00$ (Cornford *et al.* 1983; Cornford 1986). The reservoired hydrocarbons in the Broachrigg borehole were generated in the early stages of the "Mid Mature" zone while the D'Arcy and Milton oils were generated at levels approaching peak hydrocarbon generation.

The absence of known intrusive igneous bodies in the Cousland Anticline and its immediate surroundings, and the knowledge that maturities in the Oil-Shale Group of the Midlothian Basin were at levels appropriate for hydrocarbon generation by the end of the Carboniferous (see rank-map and borehole data) are clear indications that the Broachrigg hydrocarbons and the D'Arcy oil were all generated through the normal course of burial metamorphism, without the intervention of igneous activity. Although ashes and lavas occur at the base of the D'Arcy Midlothian No.1 borehole (part of Arthur's Seat Volcanic Formation; Fig.5.7j) igneous extrusives are likely to have had a minimal effect on petroleum generation (see Chapter 5).

The sandstone in which the Milton oil was reservoired lies in a sequence which is intruded by the Midland Valley Sill. That the generation of this oil was not influenced by igneous activity is indicated by its marked similarity, both in gross composition and molecular signature, to the D'Arcy oil which is considered to be a "natural" petroleum. Furthermore, the maturation profile of the Milton of Balgonie borehole (Fig.5.16a) reveals that the maturities were sufficiently high within the Calciferous Sandstone Measures (Strathclyde Group) for petroleum generation to have occurred solely through exposure to the "normal" background geothermal gradient.

The maturity assessment of the St.Catherine's bitumen, based on hopane and aromatic steroids, conflicts with the maturity level based on sterane analysis, but, for the reason cited above, more credence is given to the former ratios. The higher hopane/moretane and aromatisation ratios for the St.Catherine's bitumen indicate that it is of approximately equal or slightly higher maturity to the D'Arcy and Milton oils. Removal of the alkylated naphthalenes and phenanthrenes by biodegradation precluded any further corroborating maturity evidence.

Because of the close qualitative resemblance of its biomarker profile to those of the other hydrocarbon accumulations analysed from the Midlothian Basin, and its location in an area devoid of intrusive igneous activity, the hydrocarbon seep at St.Catherine's Well probably constitutes the degraded remains of a natural petroleum. The occurrence of the petroleum as a natural seep on the line of the Pentland Fault makes it likely that the St.Catherine's "deposit" represents the products of hydrocarbon generation from several oil-shale horizons which have been tapped at depth by this major crustal lineament.

Molecular-maturation parameters determined on the bitumens from nodules at Mid Calder indicate that they are less mature than the oils and bitumens from the Fife-Midlothian Basin. Notwithstanding the microbial removal of aromatic components (other than steroids) from which maturity estimates could be made, the ratios based on the remaining compounds, coupled with gross compositional data and acyclic alkane distributions, indicate that the nodular bitumens possess the characteristics of immature conventional petroleums which have been severely biodegraded. Such petroleums are generated at maturities less than $\%R_0 \approx 0.70$. Consideration of geological factors and the biomarker reversal phenomenon illustrated in Chapter 5 indicates that the immature characteristics of the nodular bitumens belie their true thermal history, with the evidence pointing to a rapid, high-temperature genesis for these bitumens.

Ironstone concretions are not uncommonly encountered in Carboniferous sequences (e.g. Curtis *et al.* 1975; Love *et al.* 1983), but reports of those with central cavities containing hydrocarbons appear to be rare (Parnell 1984). Although much uncertainty surrounds their precise origin, nodule formation is thought to be strongly influenced by the redox conditions operating during sedimentation (Curtis and Spears 1968; Curtis *et al.* 1975; Pearson 1979). What is reasonably certain is that ironstone concretions form during diagenesis in uncompacted sediments. Organic matter is implicated in the formation of carbonate-bearing concretions by causing localised increase in pH, enabling carbonate to precipitate (Love *et al.* 1983). Some or all of the carbonate may actually originate from the organic matter through bacterial oxidation (Curtis *et al.* 1975; Pearson 1979).

A possible mode of formation for the nodules at Mid Calder may have involved the accretion of iron-bearing sediment around bitumen droplets which acted as nuclei. This postulated mechanism obviously requires the presence of free hydrocarbons in immature sediments. From the rank study in Chapter 5, it is apparent that such a requirement is met by assuming that hydrocarbon generation occurred as a result of alkaline-dolerite intrusion into wet, unconsolidated sediments in which the organic matter would be immature. Such a scenario seems feasible because the geological map of the Mid Calder district reveals the presence of a large teschenite sheet and at least one teschenitic lens within the sediments of the Upper Oil-Shale Group from which the nodules were taken.

Further evidence supporting a high-temperature origin of the Mid Calder nodular bitumens from immature organic matter stems from the comparison of their aliphatic and aromatic hydrocarbon distributions with those from organic materials in recent environments in which igneous-induced alteration of organic matter is thought to have proceeded in a manner analogous to that envisaged for the alkaline dolerites in the eastern and central Midland Valley of Scotland. *N*-alkane envelopes of the type seen in the nodular bitumens, which are characterised by monomodal, relatively narrow, high molecular-weight, carbon-number distributions, have been reported in petroliferous exudates from recent actively-spreading ocean basins in which intense hydrothermal activity prevails as a result of the creation of continental crust at spreading ridges by the emplacement of basaltic intrusions into soft sediments (Simoneit 1984; Kawka and Simoneit 1987; Simoneit and Kawka 1987; Brault *et al.* 1988). The generation of the geologically young (<5000 years; Didyk and Simoneit 1989) "hydrothermal petroleums" is instantaneous in geological terms and occurs predominantly by the action of hot hydrothermal fluids on immature organic matter. An overview of petroleum generation in submarine hydrothermal systems is found in Simoneit (1988, 1990).

Briefly, where hydrothermal systems operate below a thick blanket of sediment, for example in the Guaymas Basin (e.g. Simoneit and Lonsdale 1982; Simoneit 1984; Simoneit *et al.* 1984; Kvenvolden and Simoneit 1990) and the Escanaba Trough (Kvenvolden *et al.* 1988; Kvenvolden and Simoneit 1990), petroliferous substances are the products of hydrothermal processes acting on organic matter within the sediment pile. In unsedimented rift areas, such as the East Pacific Rise, trace amounts of petroleum are generated by the pyrolysis of suspended and dissolved organic detritus entrained within the hydrothermal plumes (Brault *et al.* 1988). In both situations, the hydrothermal fluids may either be driven by sill intrusions, with the concomitant expulsion of pore waters or, more importantly, by deep-seated magmatic intrusions which give rise to much larger-scale fluid movement (Einsele *et al.* 1980; Kastner 1982). Much of the petroleum genesis is thought to occur within the temperature range 300-350°C, which corresponds to measured temperatures of hydrothermal fluids emanating from vent sites along the spreading ridges and of fluids within the upper parts of the unconsolidated sediment pile (Simoneit 1984; Joyce 1988; Kvenvolden *et al.* 1988; Didyk and Simoneit 1989). Higher temperatures (400°C and above) probably occur in deeper parts of the sediment column as the deep-seated magma chambers are approached (Joyce 1988; Simoneit 1988).

An inherent feature of hydrothermal petroleums is their compositional variability, both in gross chemical composition and in the molecular-weight ranges of the components present (Simoneit 1984; Kawka and Simoneit 1987). Differences in source materials and formation temperatures are not thought to account for the wide variation observed. The most important factors governing compositional variability are post-generation fractionation processes operating during the rapid transfer of thermogenic products from hot zones to progressively cooler parts of the sediment column and/or sea floor. Fluctuating transport velocities and thermal gradients (lateral and vertical) impart a compositional fractionation effect on the newly-formed petroleums by inducing differential solubilisation and alteration of the hydrodynamic properties of the resulting mixtures. Differential condensation/precipitation of the petroleum occurs during mixing with ambient sea water. Biodegradation, also important in effecting the post-generative alteration of the exudates, may occur to varying degrees in samples that are accessible to microbe-laden sea water (most pronounced in sea-floor exudates). Differential thermal gradients also promote varying degrees of biodegradation, as evidenced by reports of hydrothermal petroleums in warmer areas, particularly near vent plumes, being more degraded than exudates accumulating in cooler ambient environments (Brault *et al.* 1988). Thus, the restricted high molecular-weight *n*-alkane distributions recorded in some samples from recent hydrothermal regimes are merely thought to represent facets of the complex fractionation processes occurring during the rapid transfer of hydrothermal fluids and petroliferous substances through porous sediments and/or during their discharge into the water column. Subsequent biodegradation and water washing may also contribute to the observed distribution (Simoneit 1984; Kawka and Simoneit 1987).

Although the intrusion of alkaline-dolerite sills in the eastern and central Midland Valley was not associated with a sea-floor spreading event, that the hydrocarbon distributions in the Mid Calder nodular bitumens show marked similarities with those observed in recent hydrothermal petroleums clearly points to the importance of hydrothermal processes in the generation and subsequent alteration of the nodular bitumens at Mid Calder. Biodegradation of the bitumens would probably have occurred in association with Carboniferous hydrothermal activity since susequent sequestering of the bitumens by the accretion of the iron-bearing concretionary matrix would have made them unavailable for further microbial attack.

Akin to recent hydrothermal petroleums, biomarker-maturation indices determined on the nodular bitumens from Mid Calder lie well below their end-point values. This feature is a further indication of their high-temperature genesis since laboratory-derived pyrolysates also frequently show biomarker distributions that are not only immature *per se*, but are less mature than the distributions seen in the corresponding bitumens of the unpyrolysed samples (Seifert and

Moldowan 1980; van Graas 1986 and references therein; Eglinton 1988). The incomplete isomerisation of biomarkers in Midland Valley sediments known, from optical examination, to have been exposed to high temperatures and heating rates due to their proximity to igneous intrusions (Chapter 5) lends further support to a pyrolytic origin for the bitumens from nodules. Thus, in summary, geological and organic geochemical evidence indicates that hydrocarbon distributions of the above two samples result from the post-generative fractionation and biodegradation of Carboniferous hydrothermal petroleum.

The molecular parameters derived from the dyke-rock bitumen give contrary indications about the sample's maturity relative to the nodular bitumens, but neverthelss indicate that the isomerisation reactions on which the parameters are based have not reached completion. The immature character of the bitumen, and the geological circumstances in which it is found (coating a quartz-dolerite dyke) as well as the similarity of its acyclic aliphatic hydrocarbon distribution to that of the bitumens in nodules are clearly suggestive of a high-temperature origin during and/or after which the movement of hydrothermal fluids played an important role. Although the shape of the *n*-alkane envelope for the nodular bitumens is, at least partly, attributable to the fractionation effects operating as a consequence of the intense hydrothermal activity associated with intrusive igneous activity in immature, unconsolidated sediments, geological evidence militates against the quartz-dolerite dyke having been intruded into sediments possessing the physical characteristics that they had at the time of alkaline-dolerite intrusion. By Permian times (the age of the dyke), sediment overburden (albeit probably not much during Silesian times) would have promoted sediment compaction and dewatering with concomitant maturation of the enclosed organic matter. Notwithstanding the more compact nature of the sediments during the Permian, fluid movement (emanating either from the intrusion itself or from remaining water in the sediments) probably still exerted an important control on the alteration of the bitumen after its formation. Fractionation effects, including biodegradation, may have been enhanced by fluid and bitumen movement up the dyke wall. Any biodegradation that occurred during Carboniferous times was probably augmented by microbial activity following recent subaerial exposure.

The juxtaposition of the dyke-rock bitumen with the Broxburn Shale is no guarantee that it was sourced from this horizon, since bitumen migration, enhanced by hydrothermal fluid flow, could have occurred up the dyke wall. Furthermore, although the enhanced concentration of $C_{29}\alpha\beta$ hopane in the bitumen could have been inherited from the Broxburn Shale, or a similar source-rock type, the relatively high contribution from this component (and Tm) may be a further reflection of its high-temperature origin since shifts within the carbon-number distributions of hopanes and steranes (towards lower homologues) have been noted in numerous pyrolytic studies (e.g. van Graas 1986). The relatively low abundance of peak 30 may also reflect a high-temperature origin since similarly low contributions from this component were observed in high-rank lamositic shales. The slight enhancement in C_{27} and C_{28} steranes may also be a consequence of the pyrolytic origin of the bitumen.

The aromatic hydrocarbon signature of the dyke-rock bitumen yields further information about its genesis. Although small amounts of PAH, with more than three rings and with unsubstituted members dominant, were detected in the nodular bitumens, and indeed in the majority of samples analysed in this thesis, the prominence of this "pyrolytic like" PAH pattern in the dyke-rock bitumen is significant. PAH distributions of this type have also been observed in hydrothermal petroleums forming at sea-floor spreading axes (Simoneit and Lonsdale 1982; Kawka and Simoneit 1987, 1990; Kvenvolden and Simoneit 1990), as well as in "hydrocarbon minerals" that have been documented in non-oceanic hydrothermal vent systems (Blumer 1975; Wise *et al.* 1986). An origin for these PAH distributions at temperatures much higher than those required for the formation of the bulk of the hydrocarbon components in hydrothermal petroleums (300-350°C) is evident from the known high temperatures (>600°C) used in anthropogenic combustion/ pyrolysis processes, which account for the formation of PAH with very similar distributions in recent sediments distant from any igneous or anthropogenic activity (Lee *et al.* 1977; 1981; Laflamme and Hites 1978; see also Section 2.3.4.2). The enhanced concentrations of pyrolytic-like PAH which are seen in exudates excrusting hot, hydrothermal vent chimneys, and also in those crystallising within the deeper parts of spreading-ridge systems, bear further testimony to the fact that these aromatic hydrocarbons represent high-temperature components of hydrothermal petroleums. The abundance of these high-temperature artefacts in the dyke-rock bitumen indicates that part of the organic matter from which it was sourced was subjected to temperatures far higher than those responsible for inducing the generation of the nodular bitumens, and possibly also that the dyke-rock bitumen has suffered prolonged exposure to high temperatures.

A point of interest arising from the study of oils and bitumens relates to the occurrence of 8,14-secohopanes. At least two members of the aliphatic series have been identified in a bitumen from a borehole at Hilderston, near Bathgate (Robinson *et al.* 1986a,b). Their occurrence has been cited as evidence supporting a high-temperature origin for the bitumen, where C-ring opening of hopanoid precursors is suggested to be due to thermally-induced rupturing of the inherently weak 8,14 bond caused by exposure to severe thermal stress during the intrusive igneous episode in which the sample is thought to have been generated. The geological occurrence of the Hilderston bitumen (veins in a quartz-dolerite dyke in an area long known to contain heavy-metal mineralisation; Stephenson *et al.* 1983) is compatible with the inferred high-temperature origin made on the basis of 8,14-secohopane occurrence.

The current work shows, however, that both aromatic and aliphatic 8,14-secohopanes are not exclusively associated with organic matter that has been exposed to high temperatures and cannot therefore be used as unequivocal markers for the pyrolytic genesis of the organic materials in which they occur. As stated earlier, the aromatic and aliphatic 8,14-secohopanes were identified in all the algal sediments studied, but were most abundant, relative to the regular hopanes, in the lamositic shales. They were also identified in all the oils and bitumens analysed, including the "natural" petroleums from the Fife-Midlothian Basin, whose genesis is not thought to be associated with igneous activity. The prominence of secohopanes in gas chromatograms and TIC traces is believed to result from their extreme resistance to biodegradation. The geochemical data for the Hilderston bitumen (Robinson *et al.* 1986a,b) reveal that it has all the hallmarks of heavy biodegradation; thus the dominance of 8,14-secohopanes in the sample is merely reflecting this characteristic.

Molecular ratios based on hopanes for the Petershill bitumen approach their end-point values and attest to the immaturity of the sample. The coelution of 25-norhopanes with steranes precluded an accurate maturity assessment based on the latter compounds. The Petershill bitumen is located in joints in the Petershill Limestone. Like the Hilderston bitumen, near to which it is geographically located, the bitumen occurs in an area where there has been extensive hydrothermal polymetallic mineralisation: in some areas the Petershill Limestone itself is mineralised (Stephenson *et al.* 1983). At the sampling site (Petershill Reservoir) the limestone lies only a few feet above a carbonaceous shale which, at least in part, is considered to be "sapropelic" (Jameson 1980, 1987). Geological factors and the immaturity of the bitumen, as determined geochemically, along with the similarity of the aromatisation ratio to that of the Mid Calder dyke-rock bitumen, make a high-temperature origin for the Petershill bitumen likely. A feasible scenario envisages hydrocarbon generation as occurring from the basal carbonaceous shale during the igneous episode which resulted in the intrusion of the quartz-dolerite dykes that transect the area and which also gave rise to extensive hydrothermal fluid movement. Subsequent biodegradation occurred either shortly after generation (early Permian) or later due to the percolation of meteoric waters through the joint system in the limestone. Since sedimentological evidence (e.g. collapse structures, erosion surfaces, plant growth) points strongly towards long periods of subaerial exposure for the Petershill Limestone Formation, much of the biodegradation may be ancient.

The location of the Petershill bitumen on the flanks of the Burntisland Arch militates against an origin through burial metamorphism. The background reflectance values of coals and sediments lying along the trend of this "high" are consistent with the immaturity expected of organic matter accumulating in an area which received little overburden after the Dinantian.

The presence of woody material in Orrock Quarry provides the most salient indication of limited burial of sediments overlying the Burntisland Arch. Molecular parameters collectively indicate that the Orrock bitumen is the most immature of those studied. Other distinguishing characteristics are the high relative concentrations of αββ steranes and diasteranes present. These observations were also made in the extracts of the very low-rank humic materials studied from the same quarry (Section 4.3.3.2.4). In a manner analogous to their postulated mode of formation in the above samples, the high proportions of αββ steranes and diasteranes probably reflect the acid-catalysed rearrangement of steroidal precursors at the active sites of clay minerals present in the ashy matrix enveloping the bitumen. Contact with a warm matrix may have accelerated the reactions.

Geological factors, and the saturated and aromatic hydrocarbon fingerprints (most notably the distribution of tetracyclic terpanes), indicate that the Orrock bitumen represents a mixture of exudates derived from the contact of warm/hot pyroclastic material with very immature humic matter (at the peat/lignite stage of coalification) and lamellar algal material probably at a similar level of coalification. Distillation of the liquid hydrocarbons from the immature organic matter would have occurred during incorporation of the organic clasts in streams of volcanic ejecta which subsequently accumulated to form the Burntisland Volcanic Formation. The accumulation of organic matter in terrigenous and lacustrine environments was contemporaneous with this major eruptive episode. Thus, both types of organic matter were probably incorporated simultaneously.

The presence of very immature organic matter in Orrock Quarry and the low levels of background maturity present in the Burntisland district mean that temperature increase through the background geothermal gradient is not likely to have had a major effect on the generation of hydrocarbons in this area.

CHAPTER 7

CONCLUSIONS

The foregoing chapters have illustrated that not only is there a wide variation in the types of organic materials contributing to the Carboniferous succession of the Midland Valley, there are also marked differences in the extent of organic metamorphism, both laterally and vertically, within the province. Variations in both rank and type have been detected through petrological and geochemical methods. The principal conclusions arising from this study are presented below.

1. Remains of marine and non-marine algae (telalginite and lamalginite) are common throughout the Carboniferous, although the organic matter predominantly originates from higher plants, particularly their vascular tissues (to give vitrinite and inertinite). The ubiquity of bicyclic sesquiterpanes and hopanes (the latter are particularly abundant) indicates that much of the organic matter has suffered microbial reworking, which was sometimes severe. The depositional environments in which the organic materials accumulated were predominantly oxic which may account for the absence of botryococcane in the sediment extracts, even though the remains of the presumed precursor (*Botryococcus braunii*) constitute the most common form of telalginite in the Carboniferous succession.

2. Variations in terpane distributions can be related to different organic inputs. Although tricyclic and tetracyclic terpanes are of generally negligible abundance compared with pentacyclic terpanes, tricyclics are generally enhanced, relative to the tetracyclics, in sediments containing lamalginite. Terrestrial sediments are marked by a dominance of tetracyclic terpanes (17,21-secohopanes) and often show a greater diversity of C_{24} tetracyclic components.

   High relative concentrations of an unknown C_{29} triterpane (shouldering the $C_{29}\alpha\beta$ hopane in m/z 191 mass fragmentograms) appear to be a good marker for sediments containing non-marine lamalginite, whilst a relatively high abundance of an unknown C_{29} triterpane which elutes after the $C_{30}\alpha\beta$ hopane is a good marker for coals and sediments rich in humic macerals.

   Steranes are almost exclusively subordinate in abundance to hopanes in the Midland Valley Carboniferous. Their carbon-number distributions relate predominantly to differences in organic-matter type rather than to depositional environment.

   Notwithstanding the overriding importance of terrigenous sedimentation in the Midland Valley, some molecular fingerprints that are commonly cited as indicators of higher-plant input may actually originate from algal precursors. Thus, the utility of these distributions (e.g. the abundance of long-chain *n*-alkanes with high CPIs and a predominance of C_{29} steranes) as terrigenous markers is overstated.

Aromatic hydrocarbon distributions also bear type imprints. Lamalginite-rich shales contain abundant partially aromatised naphthalene and phenanthrene derivatives whilst sediments containing higher-plant matter and/or telalginite are generally dominated by alkylated naphthalenes and phenanthrenes. Akin to some of the saturated hydrocarbons, the origin of some aromatic components may differ from that of conventional expectations. Thus, cadalene and tetrahydroretene may originate from algal or microbial precursors rather than from higher-plant progenitors. The possible dual origin of some aromatic and saturated hydrocarbons offers a clear warning that caution needs to be exercised in the assessment of source input and depositional environments based solely on molecular data.

3. In addition to organic-matter type, extensive volcanic and intrusive igneous activity within the Midland Valley has exerted an important influence on the development of the optical and geochemical properties of organic matter within the Carboniferous.

Of the two intrusive episodes, the later (early Permian) phase of tholeiitic magmatism effected the greater alteration of organic matter, with aureole development in non-multiple intrusions extending up to *c.*4 times the intrusion thickness. In contrast, the aureoles associated with the emplacement of the earlier, alkaline-dolerite intrusions extend for less than one intrusion's width. The markedly different extent of aureole development associated with the two intrusion suites reflects different levels of sediment compaction, water saturation and organic maturation at the time of intrusion. The alkaline dolerites were intruded shortly after sediment deposition, at which time the sediments would have been unconsolidated and water-laden and would have contained immature organic matter. The rapid cooling and inefficient transfer of heat brought about by this combination of factors probably also explains the limited effect that extrusive igneous activity has had on carbonaceous clasts incorporated into tuffaceous deposits in vents formed during Surtseyan-type volcanism in the eastern Midland Valley. Differences in the constitution of sediments and the maturity of their contained organic matter at the time of intrusion also explains the differences in the scale of aureole formation around the same intrusion (Midland Valley Sill) in different basins in the Midland Valley. Textural properties (mosaic development) and borehole-reflectance gradients indicate the attainment of higher organic maturation levels (and presumably also greater sediment compaction), in the Stirling-Clackmannan-Central Coalfield Basin than in the Fife-Midlothian Basin and surrounding areas before sill emplacement, thus accounting for the more extensive aureoles in the former province. The increase in the level of regional coalification that occurs at all stratigraphic levels in the Carboniferous moving westwards, and which cannot be explained by depth of burial alone, invites the corollary that the degree of sediment compaction is at least of equal importance to temperature in finally determining the level of organic metamorphism reached in sedimentary basins, whether temperature increase occurs rapidly through igneous activity or relatively slowly through the normal background thermal gradient.

The high degree of correlation which exists between the logarithms of intrusion thickness and those of aureole thickness in the Midland Valley also holds for intrusions in diverse provinces worldwide. This relationship suggests that the underlying factors invoked to explain aureole development in Scotland may govern aureole development more generally.

4. The integrated study of regional coalification patterns and the thermal anomalies associated with igneous materials shows that hydrocarbon generation in the Midland Valley has arisen both through the rapid heating associated with (mainly) intrusive igneous activity as well as through the relatively slow heating induced by the background geothermal gradient. The long-held view that the Dinantian oil shales of the Lothian Oil-Shale Group have sourced the "major" oil accumulations in Fife and the Lothians, and also many of the smaller shows, is confirmed by the close correspondence between their geochemical fingerprints based on saturated and aromatic hydrocarbons. There is no need to invoke igneous activity as a mechanism for inducing hydrocarbon generation from these shales. Reflectance profiles and rank-map data indicate that the major source horizons were well within the oil window through the "normal" course of burial metamorphism by the end of the Carboniferous. Notwithstanding this fact, reflectance data indicate that temperatures in the vicinity of both extrusive and intrusive igneous bodies (mainly the latter) were raised to levels sufficient to induce the generation of gaseous and liquid hydrocarbons from the appropriate types of organic matter.

Although microscopy and Rock-Eval data show that algal-rich shales have the greatest source-rock potential, the large volume of other, less oil-prone components in the Carboniferous succession may well be sufficiently high for the importance of a high initial H/C ratio for significant oil generation to be diminished. Thus, vitrinite and sporinite (and possibly inertinite) should not be discounted as potential contributors to the hydrocarbon potential of the Midland Valley on a basin-wide scale.

The hydrocarbon distribution which best characterises organic materials which have been exposed to high temperatures (including thermogenic bitumens) is the prominence, in aromatic hydrocarbon fractions, of parent PAH with three or more fused aromatic rings (a pyrolytic-like distribution). Such distributions are also prominent in low-rank, non heat-affected terrestrial sediments (and coals) in which the PAH are probably "concentrated" through sorption by relatively porous, vascular-plant tissues. This "contamination" by high-temperature artefacts of organic matter which has not in itself been exposed to high temperatures is virtually ubiquitous in the Midland Valley. The presence of a natural background level of pyrolytic-like PAH which originates from natural burning and/or pyrolytic processes may exist in other ancient geological provinces in which there has been prolific igneous activity.

5. Although an integrated optical and geochemical approach has provided a valuable insight into rank and type variation in the Midland Valley, the current study has also highlighted various limitations associated with vitrinite reflectance and molecular distributions as maturity indices which, if unrecognised or disregarded, could lead to erroneous interpretations of geothermal histories.

In view of the widespread use of vitrinite reflectance as a rank parameter, and its frequent use as a base level of comparison (undertaken in this study), it is strongly recommended that reflectance determinations are accompanied by a record of the volume of exinite present. This suggestion stems from the pronounced suppression in reflectance which can occur due to the presumed absorption of hydrocarbons from exinitic materials of various types.

From studying changes in the distributions of saturated and aromatic hydrocarbons with increasing rank, it is concluded that not only can exposure of organic matter to high temperatures and high rates of heating lead to a pronounced disparity between optical and geochemical parameters, those samples which have attained a given rank (vitrinite reflectance) through rapid heating appear to be more immature on the basis of their molecular signatures than samples which have achieved the same rank through the much slower heating of the "normal" coalification process.

Recording the changes in various molecular-maturation indices throughout the rank range invariably results in an apparent "reversal" in molecular ratios. Parameters based on alkylated naphthalenes and phenanthrenes are more useful for recording maturity changes in rapidly heated successions since "reversals" occur at higher ranks ($\%R_o \approx 2.00$) than for parameters based on steranes and triterpanes ($\%R_o \approx 1.20$). The reversal phenomenon provides an indication that the changes in molecular distributions on which maturity indices are based are not, as is conventionally assumed, simple $A \rightarrow B$ conversions, but involve much more complex interactions governed by relative rates of generation and degradation.

The results of the molecular maturation study do not negate the use of biomarkers and aromatic hydrocarbons as maturity indices, but they do have important consequences for hydrocarbon exploration. Inferences based solely on biomarkers may lead to significant underestimates of maturity in basins where organic matter has experienced high rates of heating either from igneous activity or from an abnormally high background geothermal gradient.

In addition to different rates of heating, erroneous assessments of sample maturity may occur because of a failure to recognise type imprints. The occurrence of high hopane/moretane and Tm/Ts ratios and low Pr/Ph ratios in lamositic shales is an indication that caution should be exercised in the utilisation of these ratios in lamalginite-rich sequences. A type control was also identified for ratios based on distributions of methylphenanthrene isomers, which could lead to anomalous maturity determinations.

There is a clear need for the complete integration of petrological, geochemical and geological information in basins containing a diverse array of organic components and/or where igneous activity has been pervasive.

The current study has shed much light on rank and type variation in the Carboniferous succession of the Midland Valley, thus rectifying a serious deficiency in published literature relating to the study of organic matter in the province which has developed over the past fifty years. Several lines of enquiry have evolved from this work which would merit further consideration. These would not only benefit the further evaluation of organic matter in the Midland Valley, but would heighten understanding of factors causing changes in the optical and geochemical properties of organic matter in other provinces worldwide.

(i) Although many type- and rank-related changes in hydrocarbon distributions have been identified in the current project, the great diversity of organic components in the Midland Valley Carboniferous means that there may well be more subtle, and potentially very useful, parameters which could assist in environmental or maturity interpretations in basin studies. The application of multivariate statistical techniques in assessing variations in molecular distributions may therefore prove advantageous. Detailed source information could also be gleaned through the application of recently developed isotope-gc-ms techniques which could also yield valuable information on the extent to which "terrestrial" hydrocarbon fingerprints or marker compounds occur in other types of organic matter.

(ii) Many different algal forms were recognised, but could not be specifically identified, although this may be due, at least in part, to the almost exclusive use of reflected-light microscopy in the present project. A micropalaeontological approach using combined transmitted-light and fluorescence microscopy may facilitate the identification of liptinitic moieties and thus lead to an increased understanding of the depositional environments and organic facies operating within the Carboniferous of the Midland Valley.

(iii) The concentrations of molecular components referred to in this thesis are all relative. Absolute quantitation needs to be undertaken to assess the variations in hydrocarbon content which exist in different types of organic matter and also how these amounts vary in response to the rapid or slow imposition of thermal stress. Quantitative data would be particularly valuable in elucidating the mechanism(s) of the apparent reversal in molecular-maturity ratios which is invariably seen at elevated ranks.

(iv) Vitrinite-reflectance suppression may be more widespread than is currently recognised. A wider study needs to be made of the circumstances in which anomalously low-reflecting vitrinites are found, and also of the "trapped" hydrocarbons in the vitrinite matrix. It would be instructive to see whether or not an increase in the "suppressed" reflectance is observed following treatment with appropriate solvents.

(v) The physical properties of sediments and their contained organic matter are recognised as important factors governing rank imposition. Much more intensive research needs to be undertaken of the relationship between sedimentological properties (e.g. permeability, porosity, fluid content and composition), heat flow and rank increase in geological environments. Such information would prove invaluable in maturation modelling studies.

The suggestions outlined above offer a clear indication that the Midland Valley of Scotland is a province in which there is still much scope for further research.

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