



## Geochemical significance of alkylbenzene distributions in flash pyrolysates of kerogens, coals, and asphaltenes

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**Abstract**—The distribution of C<sub>0</sub>–C<sub>5</sub> alkylbenzenes in flash pyrolysates of forty-seven immature kerogens and coals from different geographical locations and of different ages were studied using gas chromatography (GC) in combination with mass spectrometry (MS) in order to decipher the origin of aromatic moieties in macromolecular matter. All possible structural isomers of the alkylated benzenes were determined, and, in some cases, absolute yields were calculated. Sulphur-rich (Type II-S) kerogens yield higher absolute amounts of alkylbenzenes in comparison to Type I, II, and III kerogens. The variations in internal distribution patterns of C<sub>2</sub>–C<sub>4</sub> alkylbenzenes were analyzed using multivariate analysis techniques (principal component analysis; PCA). Major variations in alkylbenzene distributions were due to an increased abundance of specific alkylbenzenes, which are related to specific precursor moieties in the macromolecular structure assuming that they are mainly formed via  $\beta$ -cleavage. Alkylbenzenes possessing “linear” carbon skeletons are enhanced in flash pyrolysates of Guttenberg and Estonian Kukersite kerogens (Type I) and are proposed to be derived from linear precursors which have undergone cyclization/aromatization. Relatively high amounts of 1,2,3,4- and 1,2,3,5-tetramethylbenzenes were found in flash pyrolysates of Womble and Duvernay kerogens (Type II) which are likely to be derived from macromolecularly bound diaromatic carotenoids. The relatively high abundance of 1,2,3-trimethylbenzene and 1,3-/1,4-dimethylbenzene in pyrolysates of Monterey kerogens (Type II-S) is proposed to be indicative of the presence of bound nonaromatic carotenoids (e.g.,  $\beta,\beta$ -carotene) which have undergone aromatization and/or loss of methyl groups upon diagenesis. 1-methyl-4-isopropylbenzene, which appears in relatively high amounts in flash pyrolysates of Walcott Chuar kerogen (Type II) and Catalan coals (Type III), is thought to be derived from a heteroatom-bound precursor. These results demonstrate that the structure of monoaromatic moieties in kerogen is biologically controlled. The internal distribution patterns of alkylbenzenes of flash pyrolysates of kerogens and asphaltenes show a marked resemblance, the latter showing a slight enhancement of alkylbenzenes with longer carbon skeletons. These observations support the idea that asphaltenes are structurally related to kerogen and that aromatic moieties in asphaltenes are bound by fewer intermolecular bridges.

### INTRODUCTION

THE ELUCIDATION OF THE chemical structure of sedimentary high-molecular-weight organic matter (e.g., kerogen, asphaltenes, coal, humic substances) on a molecular level is a main objective in organic geochemistry, since it provides a basis for the understanding of the origin and composition of fossil fuels and for the reconstruction of palaeoenvironments. Many investigations have been performed to characterize kerogen, which represents the far greater part (ca. 95%) of the organic matter present in sediments (DURAND, 1980). The chemical composition of kerogen is a complex function of biochemical input, early diagenetic alteration processes, and degree of thermal evolution. The structure of kerogen has been explained as a heterogenous geopolymer, resulting from random polymerisation and condensation reactions of preserved monomers released from naturally occurring biopolymers by microbial degradation (TISSOT and WELTE, 1984). Recently, however, an alternative pathway for the formation of kerogens was proposed (TEGELAAR et al., 1989). Selective preservation of specific biomacromolecules occurring as such in refractory parts of organisms (e.g., cell walls, cuticles) during sedimentation and diagenesis is proposed to

explain the formation of kerogen. This new concept applied to kerogen formation also comprises the incorporation of low-molecular-weight functionalized lipids via an abiogenic reaction with inorganic sulphur species during the early stages of diagenesis in sulphate-reducing depositional environments. This “natural vulcanization” process has been shown to be an effective pathway by which functionalized low-molecular-weight molecules are bound with retention of their molecular features (e.g., KOHNEN et al., 1990). Oxygen linkages may also play an important role in building up a three-dimensional network. For example, nonhydrolysable, highly aliphatic biomacromolecules in outer cell walls of several species of algae have been found to be composed of ether-linked long *n*-alkyl chains (GATELLIER et al., 1993). Consequently, the composition of kerogen can be viewed as a physical mixture of selectively preserved and, to some extent, biochemically altered biomacromolecules. This concept, explaining the formation of kerogen, is based on the fundamentals of coal petrology, in which morphologically recognizable entities (macerals) are linked to specific precursor plant tissues. Light microscopic investigations of kerogens were in good agreement with the random polymerisation/condensation theory for kerogens since they were mainly classified as amorphous



TABLE 1 . Sample description

sample	code	origin	age	type	PC1	PC2	PC3
Alum Shale	ALU	Sweden	U. Cambrium	II	-0.50	1.49	1.38
Arang Coal	ARC	Indonesia	Tertiary	II/III	0.55	-1.49	1.78
Bakken Shale	BAK	U.S.A.	L. Devonian	II	4.79	3.36	0.00
Beulah Zap Lignite	BEU	U.S.A.	U. Paleocene	III	0.09	-2.79	0.46
Big Fork	BFO	U.S.A.	Ordovician	II	2.10	2.79	0.02
Campins	CAM	Spain	Oligocene	I-S	0.45	0.29	-0.36
Cerdanya	CER	Spain	Miocene	II/III	0.42	0.72	0.56
Duvernay	DUV	Canada	U. Devonian	II	7.08	2.98	-2.12
Esteruel	EST	Spain	Cretaceous	III	-1.74	-1.75	-0.63
Kukersite	KU1	Estonia	Ordovician	I	-4.71	1.14	-1.79
Kukersite	KU2	Estonia	L. Ordovician	I	-4.77	0.70	-1.50
Kukersite	KU3	Estonia	L. Ordovician	I	-5.05	1.17	-1.23
Gardanne Coal	GAR	France	?	III	-0.58	w0.09	0.18
Georgina Basin	GEO	U.S.A.	Cambrium	II	2.33	1.12	0.29
Grenz Bitumen	GRE	Switzerland	Triassic	II-S	0.62	0.92	-0.18
Guttenberg	GUT	U.S.A.	Ordovician	I	-5.31	1.16	-3.01
Illinois #6 Coal	ILL	U.S.A.	U. Carboniferous	III	-0.46	1.08	2.29
Jurf ed Darawish	JED	Jordan	Cretaceous	II-S	2.15	-0.87	-0.06
Kimmeridge Black Stone Band	KB1	U.K.	Jurassic	II	0.75	0.06	0.89
Kimmeridge Black Stone Band	KB2	U.K.	Jurassic	II	0.32	0.68	-0.63
Kimmeridge Black Stone Band	KB3	U.K.	Jurassic	II	1.45	1.32	-0.52
Lewiston-Stockton Coal	LEW	U.S.A.	U. Carboniferous	III	-0.71	0.71	2.31
Mequinensa	MEQ	Spain	Tertiary	III-S	-1.61	-2.47	-0.18
Messel Shale	MES	Germany	Eocene	I/II	-1.02	-0.72	-1.62
Monterey BP1	MO1	U.S.A.	Miocene	II-S	2.59	-4.04	-1.35
Monterey T6	MO2	U.S.A.	Miocene	II-S	4.42	-4.08	-0.94
Monterey TEM025	MO3	U.S.A.	Miocene	II-S	5.58	-4.95	-1.90
Monterey NB2	MO4	U.S.A.	Miocene	II-S	2.10	-2.30	-0.71
Mowry Shale	MOW	U.S.A.	L. Cretaceous	II	0.12	1.55	1.81
Mulhouse Ci/FMM//16.5-21.5	MU1	France	Pliocene	II	-1.70	-0.03	0.89
Mulhouse Mi1/6	MU2	France	Pliocene	II	-0.54	1.51	1.25
Mulhouse S//125-132	MU3	France	Pliocene	II	-2.01	0.25	0.19
Mulhouse S//452-457	MU4	France	Pliocene	II	-1.79	0.24	-0.14
Paris Basin GG-2-2	PAR	France	Toarcian	II	0.68	1.37	0.97
Paula	PAU	Spain	Tertiary	III	-2.00	-1.06	-0.42
Phosphoria Retort Shale	PHO	U.S.A.	Permian	II-S	0.13	0.02	0.70
Portalrubio	POR	Spain	Cretaceous	III	-1.81	-1.39	-0.58
Posidonia Shale	POS	Germany	Jurassic	II	-0.65	-0.81	1.86
Ribsalbes	RIB	Spain	Miocene	I-S	-1.39	-0.08	-1.92
Rubielos	RUB	Spain	Miocene	III	-1.59	-2.46	-0.93
Serpiano Shale	SER	Switzerland	Triassic	II-S	0.44	1.06	0.74
Siberian Platform	SIB	U.S.A.	L. Proterozoic	II	-1.79	0.60	0.28
Tarfaya	TAR	Marocco	Cretaceous	II-S	0.91	-0.82	0.45
Tasmanite	TAS	Australia	Permian	I	-1.05	-0.12	0.04
Vinini	VIN	U.S.A.	Ordovician	I/II	0.45	2.77	0.23
Walcott Chuar Group	WAL	U.S.A.	L. Proterozoic	I/II	-1.62	-3.70	4.31
Womble	WOM	U.S.A.	Ordovician	II	3.95	2.63	-0.91



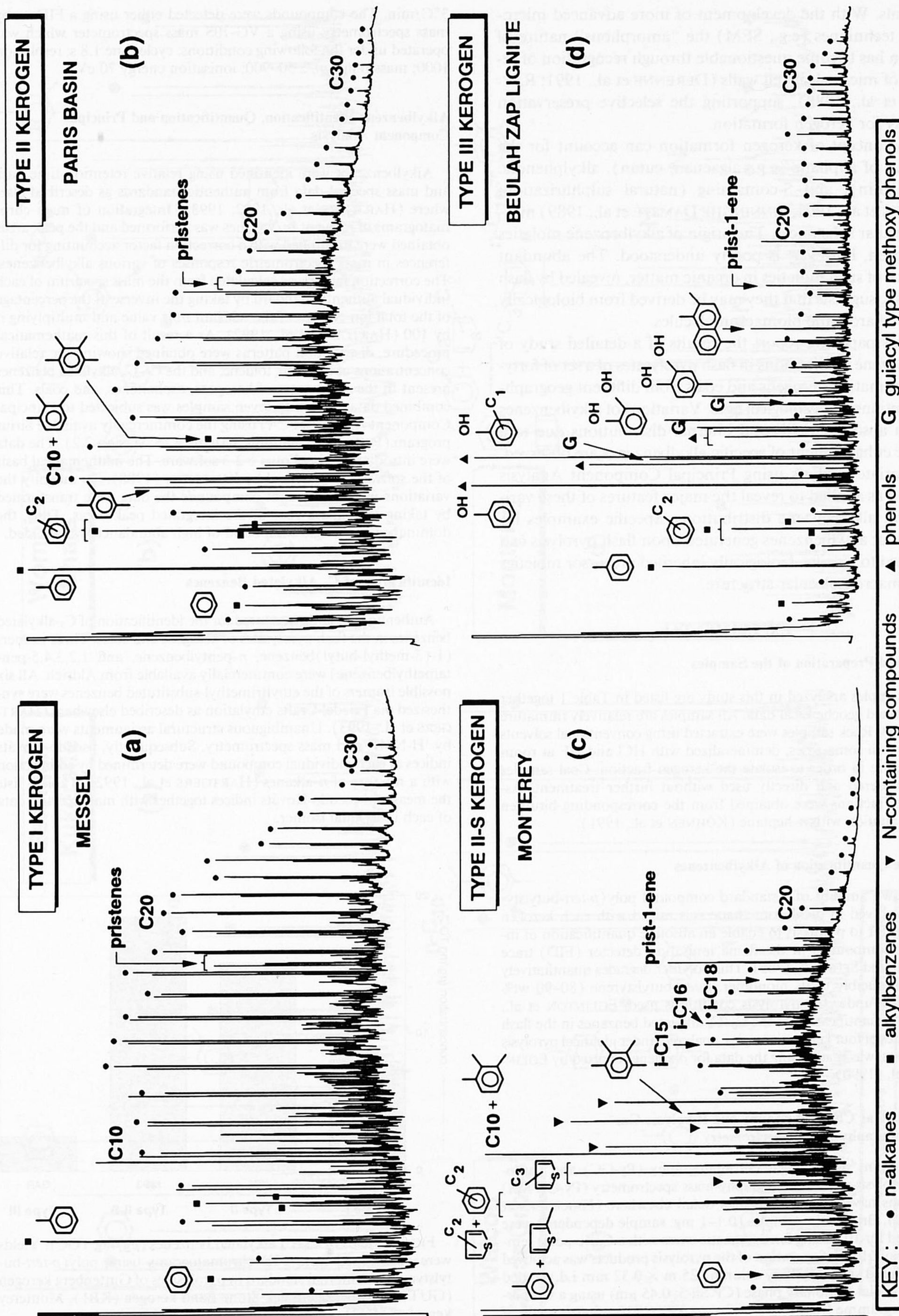


FIG. 1. FID traces of four typical flash pyrolysates (Curie temperature 610°C) of the kerogen of (a) Messel shale, (b) Paris Basin, (c) Monterey shale (MO3), and (d) Beulah Zap Lignite.



materials. With the development of more advanced microscopic techniques (e.g., SEM) the "amorphous" nature of kerogen has become questionable through recognition of remains of micro algal cell walls (DERENNE et al., 1991; RAYNAUD et al., 1988), supporting the selective preservation pathway for kerogen formation.

This concept of kerogen formation can account for the presence of aliphatic (e.g., algaenan, cutan), alkylphenolic (e.g., lignin), and S-containing (natural sulphurization; KOHNEN et al., 1991; SINNINGHE DAMSTÉ et al., 1989) macromolecular substances. The origin of alkylbenzene moieties in kerogen, however, is poorly understood. The abundant presence of such moieties in organic matter, revealed by flash pyrolysis, suggests that they may be derived from biologically produced aromatic biomacromolecules.

In this paper we report the results of a detailed study of alkylbenzene distributions in flash pyrolysates of a set of forty-seven immature kerogens and coals from different geographical locations and geological ages. Variations of alkylbenzenes in both absolute yields and internal distributions due to a relative enhancement of specific alkylbenzenes are observed. Multivariate analysis using Principal Component Analysis (PCA) was applied to reveal the major features of these variations in alkylbenzene distributions. Specific examples indicate that alkylbenzenes generated upon flash pyrolysis can be related to specific, biologically inherited precursor moieties in the macromolecular structure.

## EXPERIMENTAL

### Origin and Preparation of the Samples

The samples analyzed in this study are listed in Table 1 together with selected geochemical data. All samples are relatively immature ( $R_0 \leq 0.4$ ). Rock samples were extracted using conventional solvents and were, in some cases, demineralized with HCl and HF at room temperature in order to isolate the kerogen fraction. Coal samples were powdered and directly used without further treatment. Asphaltene fractions were obtained from the corresponding bitumen by precipitation with *n*-heptane (KOHNEN et al., 1991).

### Absolute Quantification of Alkylbenzenes

A known amount of a standard compound poly(*p*-tert-butylstyrene) dissolved in dichloromethane was mixed with each kerogen sample prior to pyrolysis to enable an absolute quantification of individual compounds in the flame ionisation detector (FID) trace (LARTER and SENFTLE, 1985). This polymer degrades quantitatively and reproducibly to its monomer, *p*-tert-butylstyrene (80–90 wt% conversion under the pyrolysis conditions used; EGLINTON et al., 1990). A quantification of the C<sub>0</sub>–C<sub>4</sub> alkylated benzenes in the flash pyrolysates of four kerogen samples, analyzed under identical pyrolysis conditions, was made using the data for *o*-xylene reported by EGLINTON et al. (1990).

### Pyrolysis-Gas Chromatography and Pyrolysis-Gas Chromatography-Mass Spectrometry

Curie-point pyrolysis-gas chromatography (Py-GC) and Curie-point pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) conditions have been described in detail elsewhere (HARTGERS et al., 1992). Briefly, the samples (0.1–1 mg; sample dependent) were pyrolyzed for 10 s using ferromagnetic wires with a Curie-point temperature of 610°C. Separation of the pyrolysis products was achieved using a fused silica capillary column (25 m × 0.32 mm i.d.) coated with an apolar stationary phase (CP Sil-5; 0.45 μm) using a temperature programme from 0°C (5 min) to 320°C (10 min) at a rate of

3°C/min. The compounds were detected either using a FID or by mass spectrometry using a VG-70S mass spectrometer which was operated under the following conditions: cycle time 1.8 s; resolution 1000; mass range *m/z* 50–900; ionisation energy 70 eV.

### Alkylbenzene Identification, Quantification and Principal Component Analysis

Alkylbenzenes were identified using relative retention time data and mass spectral data from authentic standards as described elsewhere (HARTGERS et al., 1992, 1993). Integration of mass chromatograms of relevant *m/z* values was performed and the peak areas obtained were multiplied with a correction factor accounting for differences in mass spectrometric responses of various alkylbenzenes. The correction factor was calculated from the mass spectrum of each individual authentic standard by taking the inverse of the percentage of the total ion current of the relevant *m/z* value and multiplying it by 100 (HARTGERS et al., 1992). As a result of this mathematical procedure, distribution patterns were obtained showing the relative concentrations of benzene, toluene, and the C<sub>2</sub>–C<sub>4</sub> alkylated benzenes present in the pyrolysates of kerogens, asphaltenes, and coals. This combined dataset of forty-seven samples was subjected to Principal Component Analysis (PCA) using the commercially available Sirius program (Pattern Recognition Systems A/S; version 2.2). The data were introduced using Lotus 1-2-3 software. The mathematical basis of the software is described by KVALHEIM (1988). To magnify the variations in low abundant compounds the data were transformed by taking the square root of the integrated peak areas. Thus, the dominance of a single compound of high abundance was avoided.

### Identification of C<sub>5</sub> Alkylated Benzenes

Authentic standards were used for the identification of C<sub>5</sub>-alkylated benzenes in the flash pyrolysates of kerogens and coals. Three isomers (1-(3-methyl-butyl)benzene, *n*-pentylbenzene, and 1,2,3,4,5-pentamethylbenzene) were commercially available from Aldrich. All six possible isomers of the ethyltrimethyl-substituted benzenes were synthesized via Friedel-Crafts ethylation as described elsewhere (HARTGERS et al., 1993). Unambiguous structural assignments were made by <sup>1</sup>H-NMR and mass spectrometry. Subsequently, pseudo-Kováts indices of each individual compound were determined by co-injection with a mixture of *n*-alkanes (HARTGERS et al., 1992). Table 3 lists the measured pseudo-Kováts indices together with mass spectral data of each individual isomer.

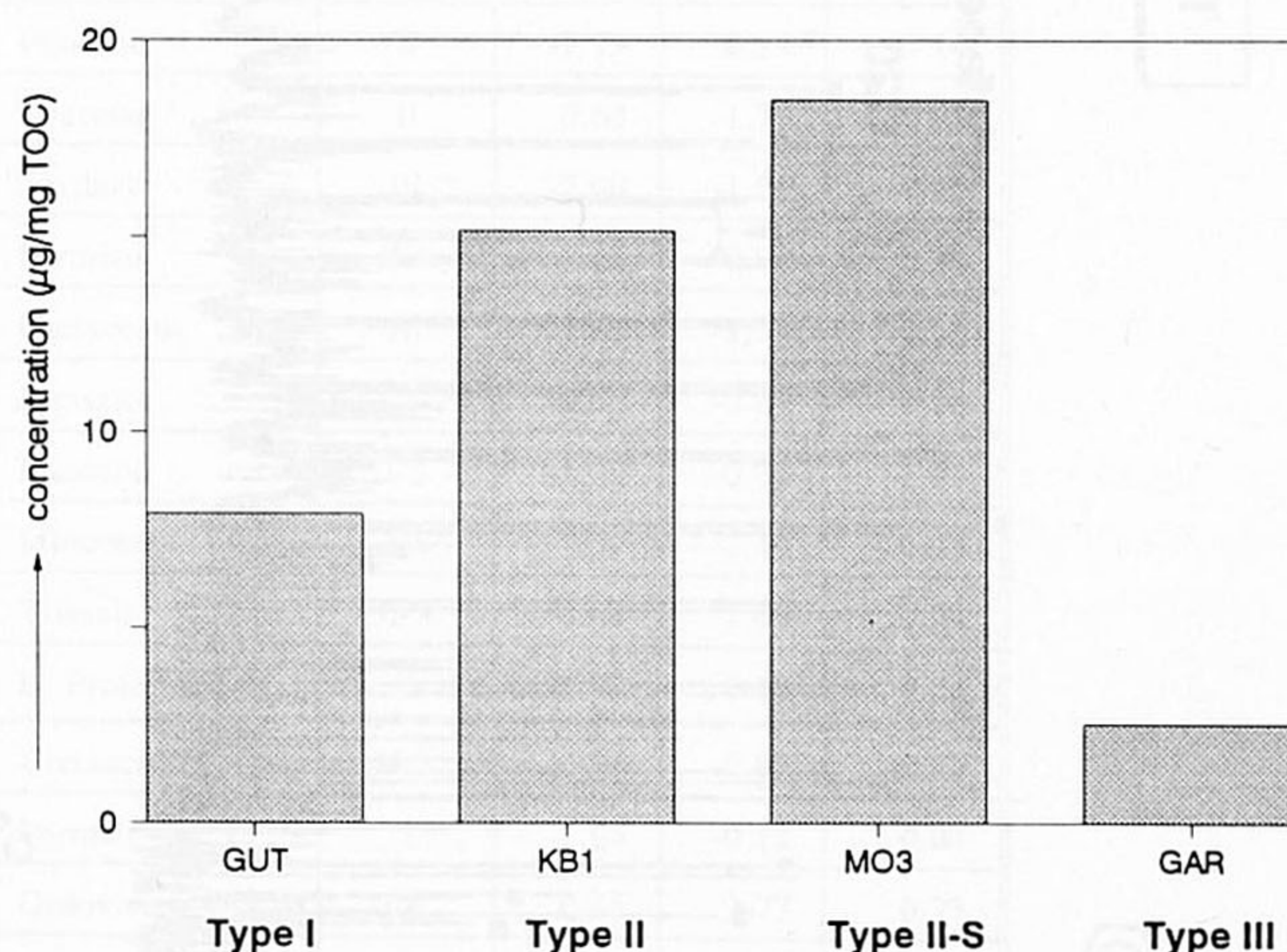
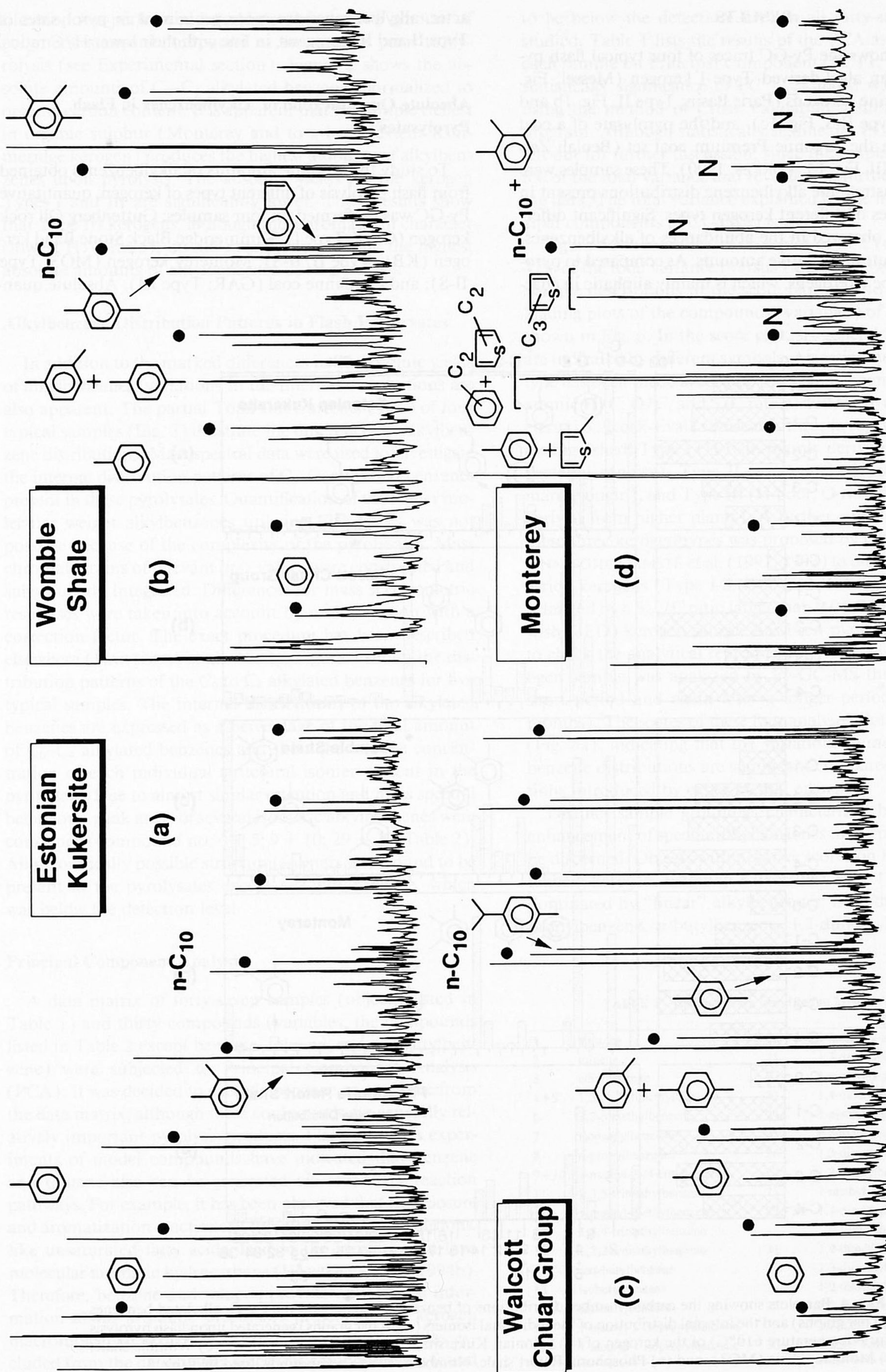


FIG. 2. Yields of C<sub>0</sub>–C<sub>4</sub> alkylated benzenes (μg/mg TOC). Yields were determined from FID chromatograms using poly(*p*-tert-butylstyrene) as internal standard in pyrolysates of Guttenberg kerogen (GUT), Kimmeridge Black Stone Band kerogen (KB1), Monterey kerogen (MO3), and Gardanne coal (GAR).





**KEY :** • n-alkanes    N n-alkylpyrroles

FIG. 3. Partial Total Ion Current (TIC) traces of the flash pyrolysates (Curie temperature 610°C) of the kerogen of (a) Estonian Kukersite, (b) Womble shale, (c) Walcott Chuar Group, and (d) Monterey shale (MO3).



## RESULTS

Figure 1 shows the Py-GC traces of four typical flash pyrolysates of an algal-derived Type I kerogen (Messel, Fig. 1a), two marine kerogens (Paris Basin; Type II, Fig. 1b and Monterey; Type II-S, Fig. 1c), and the pyrolysate of a coal selected from the Argonne Premium coal set (Beulah Zap lignite; Type III, Fig. 1d; VORRES, 1990). These samples were chosen to illustrate the alkylbenzene distributions present in the pyrolysates of different kerogen types. Significant differences can be observed in the abundances of alkylbenzenes, both in absolute and relative amounts. As compared to pyrolysates of Type I kerogens, which is mainly aliphatic in char-

acter, alkylbenzenes are more prominent in pyrolysates of Type II and III kerogens, in line with their lower H/C ratios.

#### Absolute Quantification of Alkylbenzenes in Flash Pyrolysates

To study the absolute amounts of alkylbenzenes obtained from flash pyrolysis of different types of kerogen, quantitative Py-GC was performed on four samples: Guttenberg Oil rock kerogen (GUT, Type I); Kimmeridge Black Stone Band kerogen (KB1, Type II/II-S); Monterey kerogen (MO3, Type II-S); and Gardanne coal (GAR; Type III). Absolute quan-

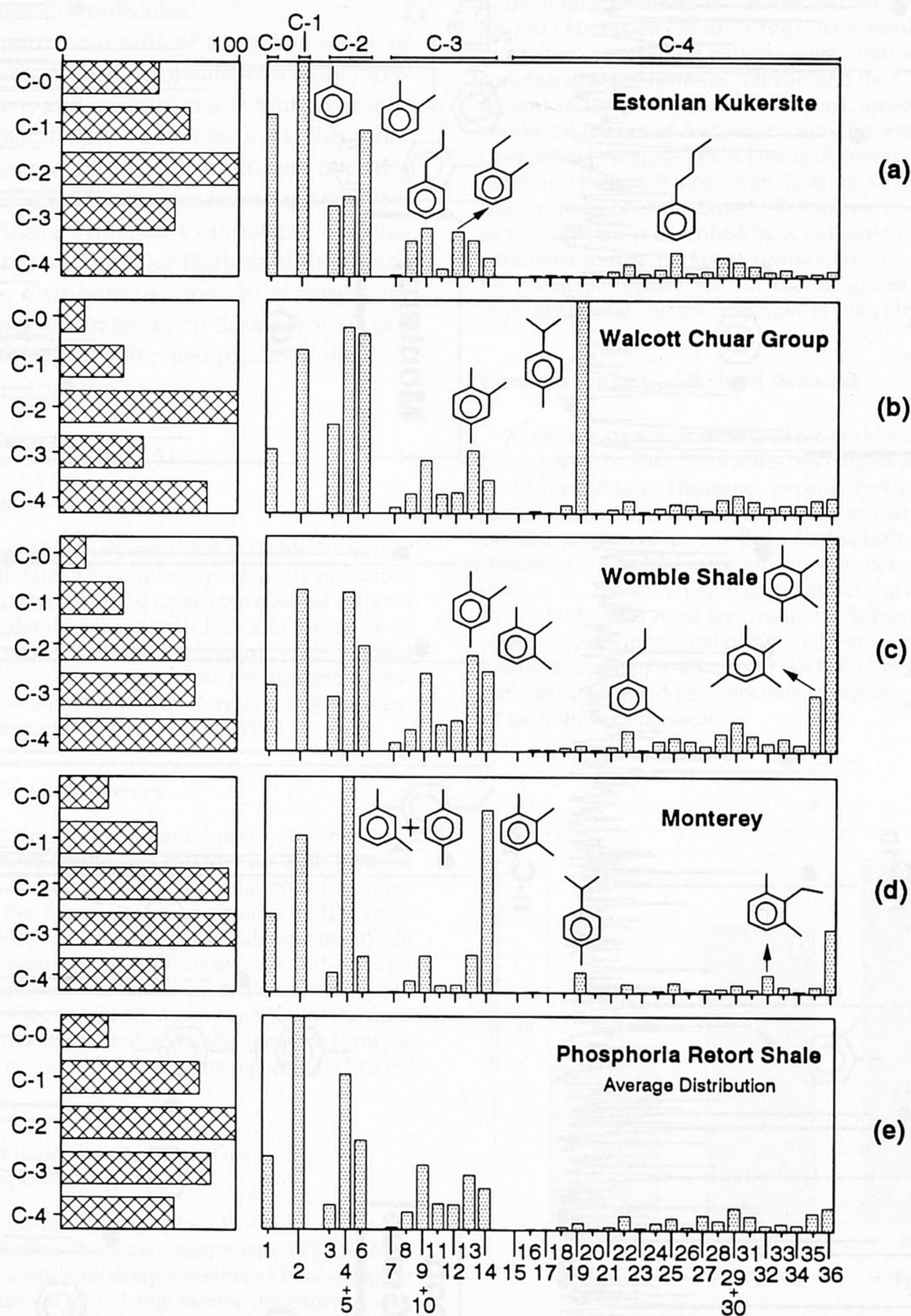


FIG. 4. Bar plots showing the carbon number distributions of benzene, toluene, and the C<sub>2</sub>-C<sub>4</sub> alkylated benzenes (left bar graphs) and the internal distribution of the individual isomers (right bar graphs) generated upon flash pyrolysis (Curie temperature 610°C) of the kerogen of (a) Estonian Kukersite, (b) Walcott Chuar Group, (c) Womble shale, (d) Monterey shale (MO3), and (e) Phosphoria Retort shale. Numbers refer to compounds listed in Table 2.



tification was performed by addition of a known amount of polymeric standard compound to the samples prior to pyrolysis (see Experimental section). Figure 2 shows the absolute amounts of C<sub>0</sub>–C<sub>4</sub> alkylated benzenes normalized to organic carbon content. It is apparent that the sample richest in organic sulphur (Monterey and to a lesser extent Kimmeridge kerogen) produces the highest amounts of alkylbenzenes upon pyrolysis. The absolute yields for the kerogen Types I and III are significantly lower. These results show that Type III kerogens, although most aromatic in character (lowest H/C ratio), do not necessarily generate the highest absolute amounts of alkylbenzenes upon pyrolysis.

### Alkylbenzene Distribution Patterns in Flash Pyrolysates

In addition to the marked differences in the absolute yields of alkylbenzenes, variations in the internal distributions are also apparent. The partial Total Ion Currents (TIC) of four typical samples (Fig. 3) illustrate the differences in alkylbenzene distributions. Mass spectral data were used to investigate the internal distribution patterns of C<sub>0</sub>–C<sub>4</sub> alkylated benzenes present in these pyrolysates. Quantification of the higher molecular weight alkylbenzenes utilizing FID traces was not possible because of the complexity of the pyrolysates. Mass chromatograms of relevant *m/z* values were constructed and subsequently integrated. Differences for mass spectrometric responses were taken into account by multiplication with a correction factor. The exact procedure has been described elsewhere (HARTGERS et al., 1992). Figure 4 shows the distribution patterns of the C<sub>0</sub> to C<sub>4</sub> alkylated benzenes for five typical samples. The internal distributions of the alkylated benzenes are expressed as a percentage of the total amount of C<sub>0</sub>–C<sub>4</sub> alkylated benzenes and show the relative concentration of each individual structural isomer present in the pyrolysate. Due to almost similar retention and mass spectral behaviour, peak areas of several isomeric alkylbenzenes were combined (compound no. 4 + 5; 9 + 10; 29 + 30; Table 2). All theoretically possible structural isomers were found to be present in the pyrolysates except *tert*-butylbenzene, which was below the detection level.

### Principal Component Analysis

A data matrix of forty-seven samples (objects; listed in Table 1) and thirty compounds (variables; the compounds listed in Table 2 except benzene, toluene, and *tert*-butylbenzene) were subjected to Principal Component Analysis (PCA). It was decided to exclude benzene and toluene from the data matrix, although these compounds are generally relatively important pyrolysis products. Flash pyrolysis experiments of model compounds have indicated that benzene and toluene also can be generated via secondary reaction pathways. For example, it has been observed that ring closure and aromatization reactions of functionalized hydrocarbons, like unsaturated fatty acids, lead to the formation of low-molecular aromatic hydrocarbons (HARTGERS et al., 1994b). Therefore, benzene and toluene provide only partial information about aromatic precursors present in the kerogen macromolecular structure. Also, *tert*-butylbenzene was excluded from the data-matrix since this compound was found

to be below the detection level in all forty-seven samples studied. Table 1 lists the results of the PCA as the scores of each sample on Principal Component (PC) 1, 2, and 3. The statistical significance of PC 1, 2, and 3 was ensured by using the method of Cross Validation within the SIRIUS program. Although statistically significant, PC 4 and 5 were left out for further discussion, since they explained only for 8% of the total variance and revealed no further structure in the data. The total variance explained by the first three principal components (PC1–PC3) is ca. 75%.

Figure 5a shows a scores crossplot of PC1 (explaining ca. 41% of the total variance) versus PC2 (ca. 23% of variance). Sample descriptions in the score plot refer to Table 1. The loading plots of the compounds (variables) of PC1–PC3 are shown in Fig. 6. In the score plot, six general kerogen types are indicated by different symbols. An assignment to kerogen type has been made according to elemental composition (i.e., atomic H/C, O/C, and S/C ratios) and/or pyrolysis parameters (i.e., Rock-Eval). Basically, three kerogen types can be distinguished: Type I (H-rich, mainly derived from algal or bacterial sources), Type II (moderately H-rich, mainly of marine origin), and Type III (H-poor, O-rich, predominantly derived from higher plants). A further sub-classification of these three kerogen types was proposed by ORR (1986) and SINNINGHE DAMSTÉ et al. (1992, 1993) to distinguish organic S-rich kerogens (Type I-S, II-S, and III-S) which are characterized by a S<sub>org</sub>/C ratio larger than 0.04. The Jurfed Darawish (JED) kerogen sample has been pyrolyzed four times to check the analytical reproducibility. To this end, the kerogen sample was analyzed by Py-GC-MS three times in a short period and again after a longer period of time (12 months). The scores of these four analyses plot close together (Fig. 5a), indicating that the variations found in the alkylbenzene distributions are significant compared to the variations introduced by experimental errors.

Distinct sample groupings characterized by the relative enhancement of specific alkylbenzenes in the pyrolysates can be discerned. Objects with negative scores on PC1 (i.e., Guttenberg kerogen, Estonian Kukersites; Type I kerogens) are dominated by "linear" alkylbenzenes: i.e., ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, 1,2-dimethylbenzene, and

TABLE 2. Alkylbenzenes identified in kerogen pyrolysates.

1	benzene	20	1-methyl-2-isopropylbenzene
2	toluene	21	1,3-diethylbenzene
3	ethylbenzene	22	1-methyl-3-propylbenzene
4+5	1,3-/1,4-dimethylbenzene	23	1,4-diethylbenzene
6	1,2-dimethylbenzene	24	1-methyl-4-propylbenzene
7	isopropylbenzene	25	<i>n</i> -butylbenzene
8	<i>n</i> -propylbenzene	26	1,3-dimethyl-5-ethylbenzene
9+10	1-methyl-3-/4-ethylbenzene	27	1,2-diethylbenzene
11	1,3,5-trimethylbenzene	28	1-methyl-2-propylbenzene
12	1-methyl-2-ethylbenzene	29+30	1,4-dimethyl-2-ethylbenzene + 1,3-dimethyl-4-ethylbenzene
13	1,2,4-trimethylbenzene		
14	1,2,3-trimethylbenzene	31	1,2-dimethyl-4-ethylbenzene
15	<i>tert</i> -butylbenzene	32	1,3-dimethyl-2-ethylbenzene
16	isobutylbenzene	33	1,2-dimethyl-3-ethylbenzene
17	<i>sec</i> -butylbenzene	34	1,2,4,5-tetramethylbenzene
18	1-methyl-3-isopropylbenzene	35	1,2,3,5-tetramethylbenzene
19	1-methyl-4-isopropylbenzene	36	1,2,3,4-tetramethylbenzene



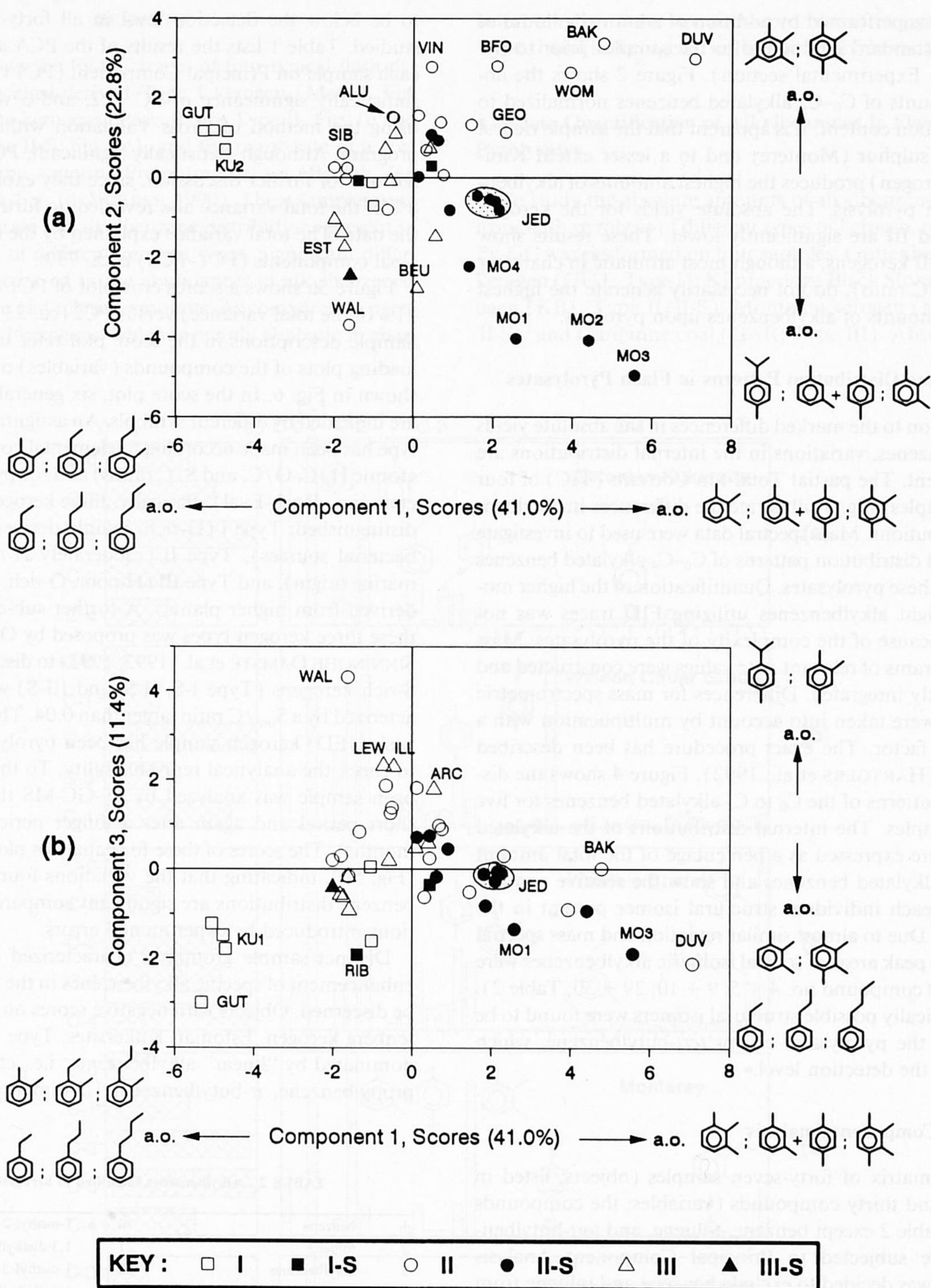


FIG. 5. Score plot of (a) PC1 vs. PC2 and (b) PC1 vs. PC3 showing the scores of individual objects (samples). Codes refer to sample names listed in Table 1. The variables (compounds) explaining the major variances are plotted along the axes. The result of PCA leaving out the quadruplicate analysis of the Jurf ed Darawish (JED) sample from the data set is similar.

1-methyl-2-ethylbenzene. These alkylbenzenes are thought to be formed by cyclization and aromatization of precursors possessing linear carbon skeletons, i.e., they are monosubstituted or are substituted at positions 1 and 2. The alkylbenzene distributions of objects showing positive scores on PC1 are dominated by 1,2,3-trimethylbenzene, 1,3- and/or

1,4-dimethylbenzene (which coelute), and 1,2,3,4-tetramethylbenzene. These compounds are generally enhanced in the pyrolysates of Type II and II-S kerogens.

Objects with a positive score on PC2 are characterized by a relative high abundance of 1,2,3,4- and 1,2,3,5-tetramethylbenzene. These objects, predominantly Type II kerogens,



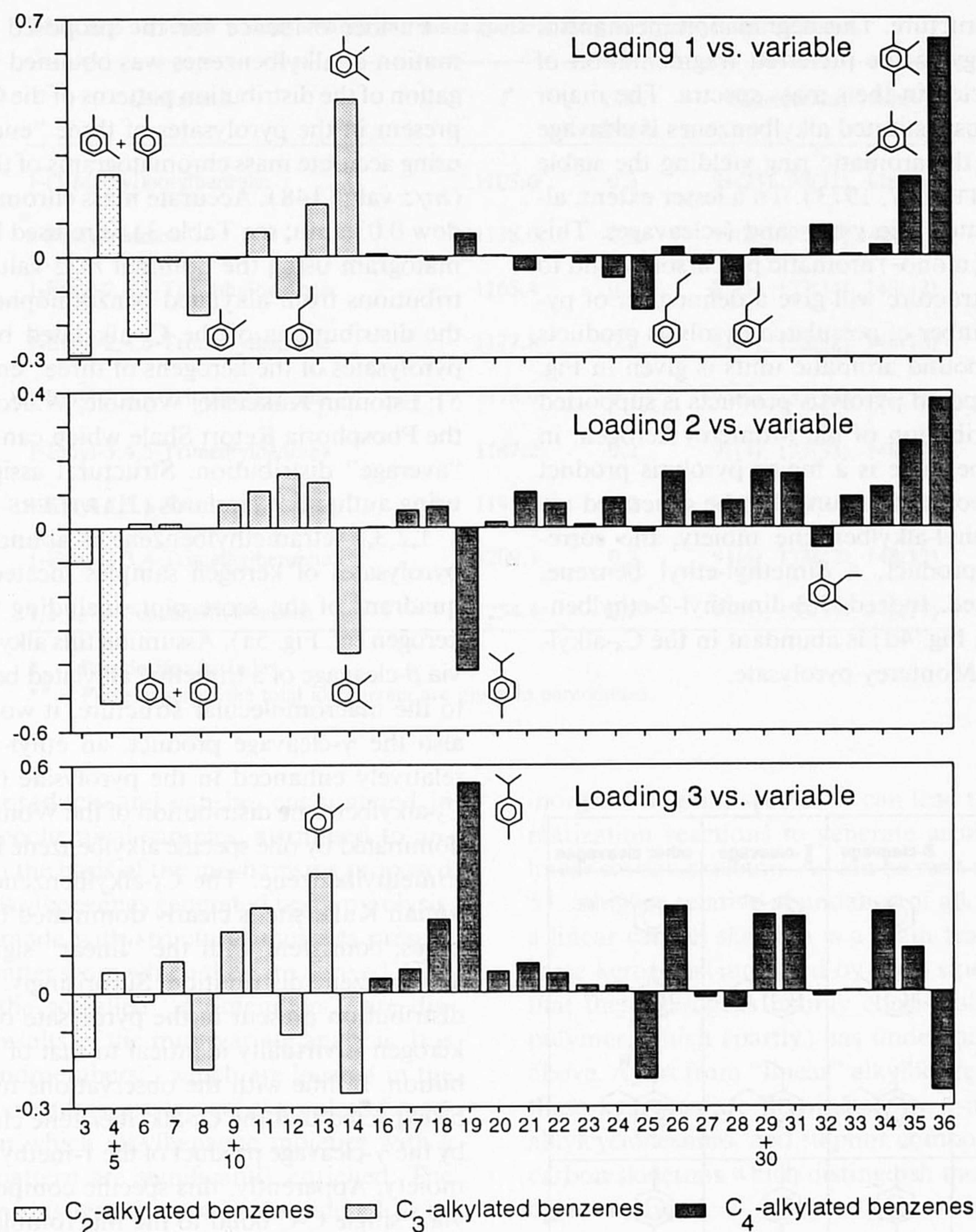


FIG. 6. Bar plots showing the loadings vs. individual variables (compounds) of PC1, PC2, and PC3. Numbers refer to compounds listed in Table 2.

are located in the upper right quadrant of the score plot. The negative scores on PC2 reflect the higher abundance of 1,2,3-trimethylbenzene, 1,3-dimethyl- and/or 1,4-dimethylbenzene, and/or 1-methyl-4-isopropylbenzene. Type II-S kerogens (plotting predominantly in the lower right quadrant of the score plot) and Type III kerogens (coals) are characterized by higher relative amounts of these compounds in their pyrolysates.

The score plot of PC1 (ca. 41% of variance) vs. PC3 (ca. 11% of variance; Fig. 5b) reveals a further distinction between the objects. Positive scores on PC3 are explained for the greater part by 1-methyl-4-isopropylbenzene, which is found to be an important pyrolysis product of Walcott Chuar Group (cf. Figs. 3 and 4). Also, a number of coal samples (e.g., Arang coal, Illinois #6, Lewiston Stockton) show a positive score on PC3 due to a relative enhancement of 1-methyl-4-isopropylbenzene. Furthermore, the Type I kerogens cluster together in the lower left quadrant, indicative of the "linear" character of alkylbenzene moieties.

Major variations in alkylbenzene distributions are found

for objects showing the largest scores for the principal components. These objects, the so called "endmembers", tend to move away from the origin of the score plot, which corresponds to the average alkylbenzene distribution of the pyrolysates of the samples analyzed. Multivariate analysis was also performed on the objects clustered around the origin of the score plot. The variations found for the principal components were explained by the same alkylbenzenes as found previously for the whole set of forty-seven samples.

## DISCUSSION

### Mechanisms of Formation of Alkylbenzenes

In order to relate alkylbenzenes in the pyrolysate to aromatic moieties present in the macromolecular structure of kerogens and coals, an understanding of the mechanisms of their formation is a prerequisite. Upon pyrolysis, alkylbenzenes are mainly generated via a homolytic cleavage of the C-C bond between the  $\alpha$ - and  $\beta$ -carbon atoms (" $\beta$ -cleavage") of the side chain by which the aromatic moiety is linked to



the macromolecular structure. This degradation mechanism is postulated in analogy to the preferred fragmentation of alkylbenzenes as reflected in their mass spectra. The major fragmentation of monosubstituted alkylbenzenes is cleavage of the C-C bond  $\beta$  to the aromatic ring yielding the stable tropylium ion (MCLAFFERTY, 1973). To a lesser extent, alkylbenzenes are generated also via  $\gamma$ - and  $\delta$ -cleavages. This implies that a specific (mono-) aromatic precursor bound to the macromolecular structure will give a defined set of pyrolysis products. A number of postulated pyrolysis products of macromolecularly bound aromatic units is given in Fig. 7. This concept of proposed pyrolysis products is supported by the pyrolysate distribution of the Monterey kerogen, in which 1,2,3-trimethylbenzene is a major pyrolysis product (Fig. 4d). If this compound is assumed to be generated via  $\beta$ -cleavage of a dimethyl-alkylbenzene moiety, the corresponding  $\gamma$ -cleavage product, a dimethyl-ethyl benzene, should also be enhanced. Indeed, 1,3-dimethyl-2-ethylbenzene (compound 32 in Fig. 4d) is abundant in the  $C_4$ -alkylbenzene cluster of the Monterey pyrolysate.

	presumed moiety in kerogen	$\beta$ -cleavage	$\gamma$ -cleavage	other cleavages
LINEAR				
NON-LINEAR				

FIG. 7. Postulated products of flash pyrolysis of macromolecularly bound monoaromatic moieties. Linear carbon skeletons are indicated by bold lines.

Further evidence for the proposed mechanisms of formation of alkylbenzenes was obtained by a detailed investigation of the distribution patterns of the  $C_5$ -alkylated benzenes present in the pyrolysates of three "endmember" kerogens, using accurate mass chromatograms of their molecular weight ( $m/z$  value 148). Accurate mass chromatograms (mass window 0.03 amu; see Table 3) were used because a mass chromatogram using the nominal  $m/z$  value also contains contributions from alkylated benzothiophenes. Figure 8 shows the distributions of the  $C_5$ -alkylated benzenes in the flash pyrolysates of the kerogens of three "endmembers" (cf. Fig. 5): Estonian Kukersite, Womble, Walcott Chuar Group, and the Phosphoria Retort Shale which can be considered as the "average" distribution. Structural assignments were made using authentic standards (HARTGERS et al., 1993).

1,2,3,4-tetramethylbenzene is abundantly present in the pyrolysates of kerogen samples located in the upper right quadrant of the score plot, including that of the Womble kerogen (cf. Fig. 5a). Assuming this alkylbenzene is generated via  $\beta$ -cleavage of a trimethyl alkylated benzene moiety bound to the macromolecular structure, it would be expected that also the  $\gamma$ -cleavage product, an ethyl-trimethylbenzene, is relatively enhanced in the pyrolysate (Fig. 7). Indeed, the  $C_5$ -alkylbenzene distribution of the Womble kerogen is clearly dominated by one specific alkylbenzene isomer, 1-ethyl-2,3,6-trimethylbenzene. The  $C_5$ -alkylbenzene distribution of Estonian Kukersite is clearly dominated by "linear" alkylbenzenes, consistent with the "linear" signature of the  $C_2$ - $C_4$  alkylbenzene distribution. Surprisingly, the  $C_5$ -alkylbenzene distribution present in the pyrolysate of the Walcott Chuar kerogen is virtually identical to that of the "average" distribution. In line with the observations made above, it would be expected that the  $C_5$ -alkylbenzene cluster was dominated by the  $\gamma$ -cleavage product of the 1-methyl-4-isopropylbenzene moiety. Apparently, this specific compound is bound either via a single C-C bond to the macromolecular matrix, or via a heteroatom such that the  $\gamma$ -cleavage product could not be generated.

As a result of these observations, it appears that  $\beta$ -cleavage and, to a lesser extent,  $\gamma$ - and  $\delta$ -cleavages of monoaromatic macromolecularly bound moieties are the major degradation mechanisms by which alkylbenzenes are generated upon pyrolysis. This observation is consistent with the proposed mechanisms for the formation of alkylthiophenes and alkylbenzothiophenes (SINNINGHE DAMSTÉ et al., 1989). This provides a tool to assess the monoaromatic precursor moieties by a detailed analysis of alkylated benzenes in the pyrolysate. The substitution pattern of the pyrolysis products found, therefore, provides clues regarding the structure of its precursor bound to the macromolecule.

#### Geochemical Significance of Alkylbenzenes in Flash Pyrolysates

*Tert*-butylbenzene was found to be below the detection level in all forty-seven samples studied. The absence of this compound seems to be in accordance with other studies (EGLINTON et al., 1991) and the fact that components possessing a *tert*-butyl group are a red herring in nature. To the best of our knowledge, *tert*-butyl substituted alkylbenzenes



TABLE 3 . Pseudo Kováts indices and mass spectral data of C<sub>5</sub> alkylated benzenes.

Compound	<i>I</i> <sup>*</sup>	S.D. ( <i>n</i> =3)	Characteristic ions <sup>**</sup>
1-(3-Methyl)butylbenzene	1103.6	0.3	91(23), 92(31), 148(5)
<i>n</i> -Pentylbenzene	1138.0	0.2	91(33), 92(21), 148(9)
1-Ethyl-2,4,6-Trimethylbenzene	1165.4	0.4	91(5), 133(34), 148(12)
1-Ethyl-2,4,5-Trimethylbenzene	1177.8	0.2	91(4), 133(38), 148(10)
1-Ethyl-2,3,5-Trimethylbenzene	1178.9	0.2	91(5), 133(34), 148(13)
1-Ethyl-3,4,5-Trimethylbenzene	1187.2	0.2	91(4), 133(38), 148(14)
1-Ethyl-2,3,6-Trimethylbenzene	1193.3	0.2	91(4), 133(32), 148(14)
1-Ethyl-2,3,4-Trimethylbenzene	1209.1	0.3	91(4), 133(42), 148(13)
1,2,3,4,5-Pentamethylbenzene	1254.4	0.2	91(4), 133(34), 148(17)

\* Pseudo Kováts Index.

\*\* Percentages of the total ion current are given in parentheses.

are not biosynthetic products and can be, encountered in flash pyrolysates of geochemical samples, attributed to anthropogenic input. On the basis of the mechanisms proposed for the formation of alkylbenzenes generated upon pyrolysis, a correlation can be made with structural moieties present in macromolecular matter from which they are derived. Five clusters of samples, the so-called "endmembers", are discerned based on the results of the multivariate analysis. It is thought that these "endmembers", which are located in the outer corners of the score plots, are typical examples of macromolecular matter in which alkylbenzene moieties with a specific substitution pattern are significantly enriched. The remaining samples, in this respect, can be considered to be representatives of mixtures of the "endmember" alkylbenzene moieties. Five clusters of "endmembers" are discussed in detail. They are characterized by

- 1) alkylbenzenes possessing a linear carbon skeleton (negative score on PC1 and PC3),
- 2) 1,2,3,4- and 1,2,3,5-tetramethylbenzene (positive score on PC1 and PC2),
- 3) 1,2,3-trimethylbenzene and 1,3-/1,4-dimethylbenzene (positive score on PC1 and negative score on PC2),
- 4) 1-methyl-4-isopropylbenzene (negative score on PC2 and positive score on PC3), and
- 5) 1,2,4-trimethylbenzene (positive score on PC3).

#### Alkylbenzenes with linear carbon skeletons

It has been shown previously that pyrolysates of Ordovician Type I kerogens contain relatively abundant homologous series of monosubstituted and 1,2-disubstituted alkylbenzenes (DERENNE et al., 1990; DOUGLAS et al., 1991). The high abundance of these "linear" alkylbenzene entities is explained by the fact that these kerogens are mainly comprised of an insoluble, highly aliphatic biopolymer algaenan present in the extinct alga *Gloeocapsomorpha prisca* (TEGELAAR et al., 1989). The functionalized "linear" moieties can react with

inorganic sulphur species or can lead to cyclization and aromatization reactions to generate aromatic moieties with a linear carbon skeleton. As can be seen in the score plots (Fig. 5), a higher relative abundance of alkylbenzenes possessing a linear carbon skeleton is a main feature of pyrolysates of these kerogens (indicated by open squares). It is concluded that these kerogens mainly consist of a straight chain biopolymer, which (partly) has undergone reactions described above. Apart from "linear" alkylbenzenes, the pyrolysates of these kerogens are dominated by *n*-alkanes, *n*-alkenes, *n*-alkylcyclohexanes, and sulphur compounds possessing linear carbon skeletons which distinguish them from the other kerogens analyzed.

#### 1,2,3,4-/1,2,3,5-tetramethylbenzene

The flash pyrolysates of a number of Type II kerogens are characterized by a relative high abundance of 1,2,3,4-tetramethylbenzene. In addition, the C<sub>5</sub>-alkylated benzenes in these pyrolysates are dominated by its pseudohomologue, 1-ethyl-2,3,6-trimethylbenzene (e.g., Fig. 8). Macromolecularly bound aromatic carotenoids (I-V; Appendix) are feasible geochemical precursors for these pyrolysis products, since they are characterized by specific aromatic substitution patterns (2,3,4- and 2,3,6-relative to the isoprenoid chain; LIAAEN-JENSEN, 1978) which would upon  $\beta$ -cleavage yield 1,2,3,4-tetramethylbenzene (DOUGLAS et al., 1991; HARTGERS et al., 1991; REQUEJO et al., 1992). Aromatic carotenoids and their diagenetic products, have been identified in several oils and extracts (OSTROUKHOV et al., 1982; REQUEJO et al., 1992; SUMMONS and POWELL, 1987). The abundance of 1-ethyl-2,3,6-trimethylbenzene, probably formed via  $\gamma$ -cleavage, indicates that these specific pyrolysis products are most likely derived from aromatic carotenoids possessing the 2,3,6 substitution pattern. These compounds are confined to the *Chlorobiaceae* family of photosynthetic sulphur bacteria (LIAAEN-JENSEN, 1978). Additional evidence is provided by



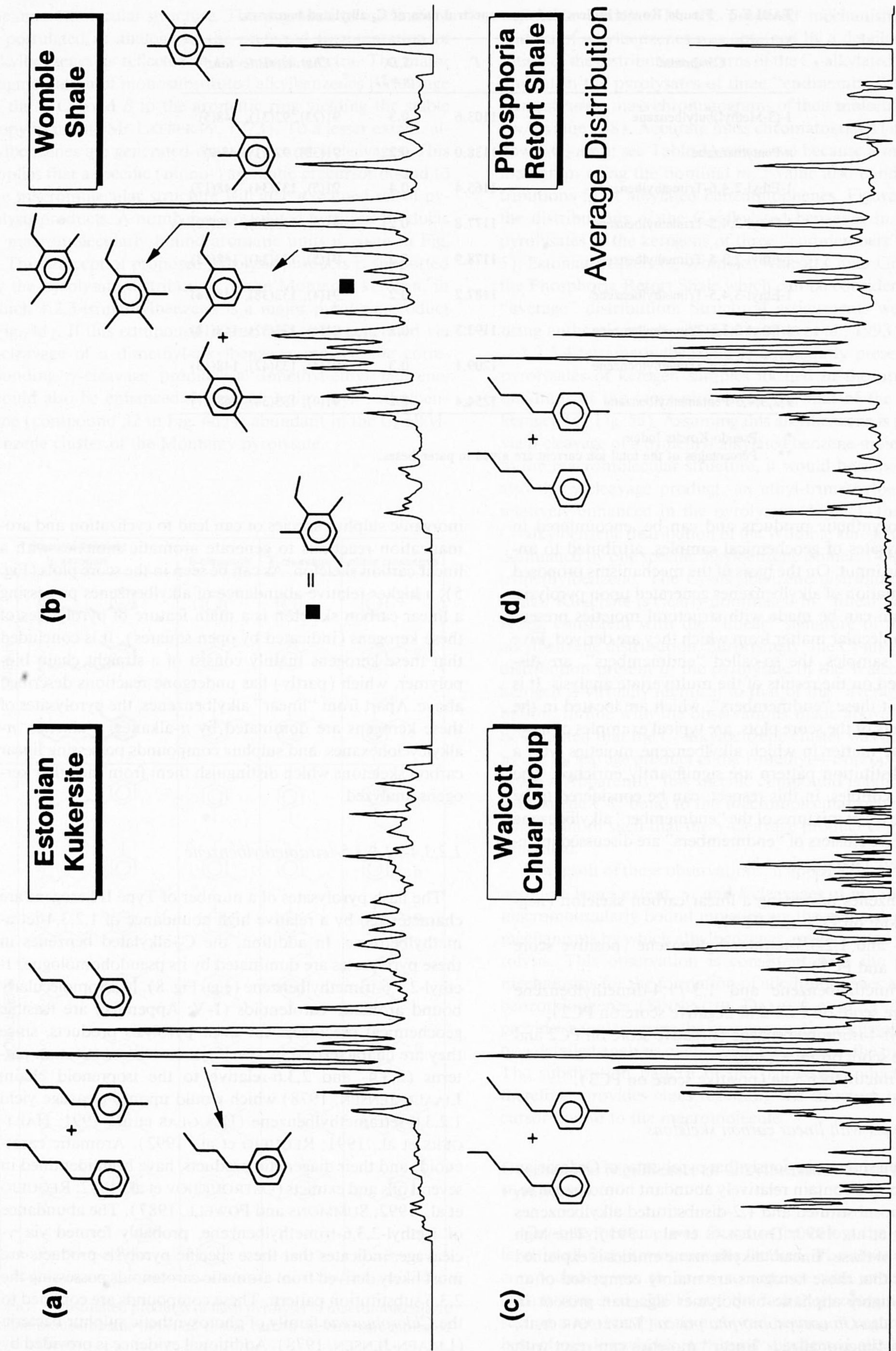


FIG. 8. Partial accurate mass chromatograms of  $m/z$  148 (mass window 0.03 amu) of the flash pyrolysates (Curie temperature 610°C) of (a) Estonian Kukersite, (b) Womble Shale, (c) Walcott Chuar Group, and (d) Phosphoria Retort Shale showing the distribution of  $C_3$  alkylated benzenes. Peak identifications are made using relative retention time and mass spectral data of authentic standards (Table 3).



compound specific isotope analysis of 1,2,3,4-tetramethylbenzene and its pseudohomologue from the pyrolysates, showing a substantial enrichment in  $^{13}\text{C}$  ( $\delta^{13}\text{C} = -19\%$ ) relative to algal derived *n*-alkanes ( $\delta^{13}\text{C}$  ranging from  $-29$  to  $-32\%$ ; HARTGERS et al., 1994a). *Chlorobiaceae* fix carbon through the reverse tricarboxylic acid (TCA) cycle leading to biomass containing relatively large amounts of  $^{13}\text{C}$  (SCHIDLOWSKI et al., 1984).

1,2,3,5-tetramethylbenzene covaries with 1,2,3,4-tetramethylbenzene on PC1 and PC2, suggesting a similar origin. 1,2,3,5-tetramethylbenzene was found to be substantially enriched in  $^{13}\text{C}$  as well ( $\delta^{13}\text{C} = -18\%$ ; HARTGERS et al., 1994a). Recently, we were able to isolate and to identify the structure of a novel octadecahydrodiaromatic carotenoid (VI) from sediments of the Western Canada Basin (HARTGERS et al., 1993). Its unprecedented 2,3,6- and 3,4,5- aromatic substitution pattern is consistent with the hypothesis that its precursor (VII) is also incorporated into the kerogen. This moiety yields upon pyrolysis, apart from 1,2,3,4-tetramethylbenzene, also 1,2,3,5-tetramethylbenzene. Although the origin of this novel carotenoid is still unknown, it is likely that it is derived from photosynthetic bacteria which fix carbon through the reverse TCA cycle.

#### *1,2,3-trimethylbenzene and 1,3-/1,4-dimethylbenzene*

These compounds are present in relative high abundance in the kerogen pyrolysates located in the lower right quadrant of the score plot (mainly Type II-S kerogens). It has been noted that Type II-S kerogens generate the highest absolute yields of alkylbenzenes upon pyrolysis compared to Type I and III kerogens (Fig. 2). The pyrolysates of Monterey kerogens, in particular, are dominated by 1,2,3-trimethylbenzene and dimethylated benzenes. It is proposed, that 1,2,3-trimethylbenzene and its pseudohomologue 1,3-dimethyl-2-ethylbenzene originate from nonaromatic carotenoids, such as  $\beta,\beta$ -carotene, which have upon catagenesis undergone aromatization followed by a loss of one or more methyl groups yielding alkyl-dimethyl and alkyl-methyl-substituted aromatic moieties. Flash pyrolysis of such moieties will yield 1,2,3-trimethylbenzene and 1,3-/1,4-dimethylbenzene (Fig. 7). Recently, five novel C-ring cleaved, triterpenoid-derived aromatic hydrocarbons have been identified in aromatic hydrocarbon fractions of immature Tertiary coals (DE LAS HERAS et al., 1991). Aromatization processes of triterpenoids involving C-ring opening and loss of the A-ring are proposed to explain the formation of those compounds, possessing a trimethylated phenyl group ethylene-linked to a naphthyl moiety. Although  $\beta$ -cleavage of these compounds is a possible source for trimethylated alkylbenzenes, their significance as a new geochemical source still has to be investigated.

#### *1-methyl-4-isopropylbenzene*

This alkylbenzene dominates the pyrolysate of the kerogen from the Walcott Chuar Group (Fig. 3). It is also present in relatively high abundance in the pyrolysates of coal samples. The origin of this compound is unclear, since the  $\text{C}_5$ -alkylbenzene distribution pattern of the Walcott Chuar Group does not significantly differ from the average distribution (Phosphoria Retort Shale). Therefore, it is unlikely that 1-

methyl-4-isopropylbenzene is generated via B-cleavage of a C-C bound precursor. Apparently, this compound is linked to the macromolecular structure either via a single C-C bond or, alternatively, via a heteroatom, for example, oxygen. A variety of 1-methyl-4-isopropylbenzene derivatives with hydroxy and methoxy groups are known higher plant constituents (RADKE, 1987). It is possible that such derivatives are incorporated into macromolecular material through heteroatom linkages. The occurrence of 1-methyl-4-isopropylbenzene in pyrolysates, therefore, seems to point to a contribution of higher land plant material. This is supported by the relatively high abundance of this compound in pyrolysates of coals (Type III kerogens). However, the input of higher plant material into the Walcott Chuar kerogen can be excluded, since this material originates from the Late Proterozoic (Table 1; SUMMONS et al., 1988) long before the evolution of higher plants. An other possible source is  $\alpha$ -terpineol (VIII), a cyclohexanoid terpenoid found in fungi (RATLEDGE and WILKINSON, 1988). The presence of a hydroxyl group at the isopropyl side chain of the cyclohexene ring enables the incorporation of this compound into macromolecular substances via ether linkages (Fig. 7).

#### *1,2,4-trimethylbenzene*

The relative enhancement of 1,2,4-trimethylbenzene and 1,2-dimethyl-4-ethylbenzene in, for example, the Alum Shale pyrolysate (Fig. 9a), may be indicative of the incorporation of plastoquinones (IX) into these kerogens. Plastoquinones are widely distributed in algae and cyanobacteria (RATLEDGE and WILKINSON, 1988). Reduction of the benzoquinone moiety, a likely process under anoxic conditions, can account for the formation of dimethylated alkylbenzene moieties with a 3,4-substitution pattern relative to the isoprenoid chain.

The detailed analysis of alkylbenzenes in pyrolysates on a molecular level can provide clues with regard to specific precursors which are incorporated in the kerogen, as illustrated above for some "endmembers" which are substantially enriched in a specific monoaromatic moiety (i.e., discrete structural components) within the macromolecule. This approach, therefore, provides useful information concerning the chemical nature of alkylbenzene moieties and their biologically derived precursors bound to the kerogen.

#### **Radiation-Induced Alterations of Organic Matter: An Implausible Source for Alkylbenzenes**

The high relative concentrations of low-molecular-weight alkylbenzenes and alkyl-naphthalenes in the pyrolysates of the Cambrian Alum Shale (Type II kerogen) were suggested to be due to radiation-induced random polymerization and aromatization reactions of nonfunctionalized alkyl chains or, alternatively, its structure had been directly inherited from biopolymeric or carotenoid-derived precursors in algae and bacteria (HORSFIELD et al., 1992). Recently, it was reported, that the overall composition of the Cerdanya kerogen pyrolysate is remarkably similar to that of the Alum Shale (SINNINGHE DAMSTÉ et al., 1993). The  $\text{C}_0$ - $\text{C}_4$  alkylbenzene distribution, also the dominant pyrolysis products of this Tertiary Catalan lacustrine oil shale, is very comparable to that of the Alum Shale (see Fig. 9). These authors proposed the unusual



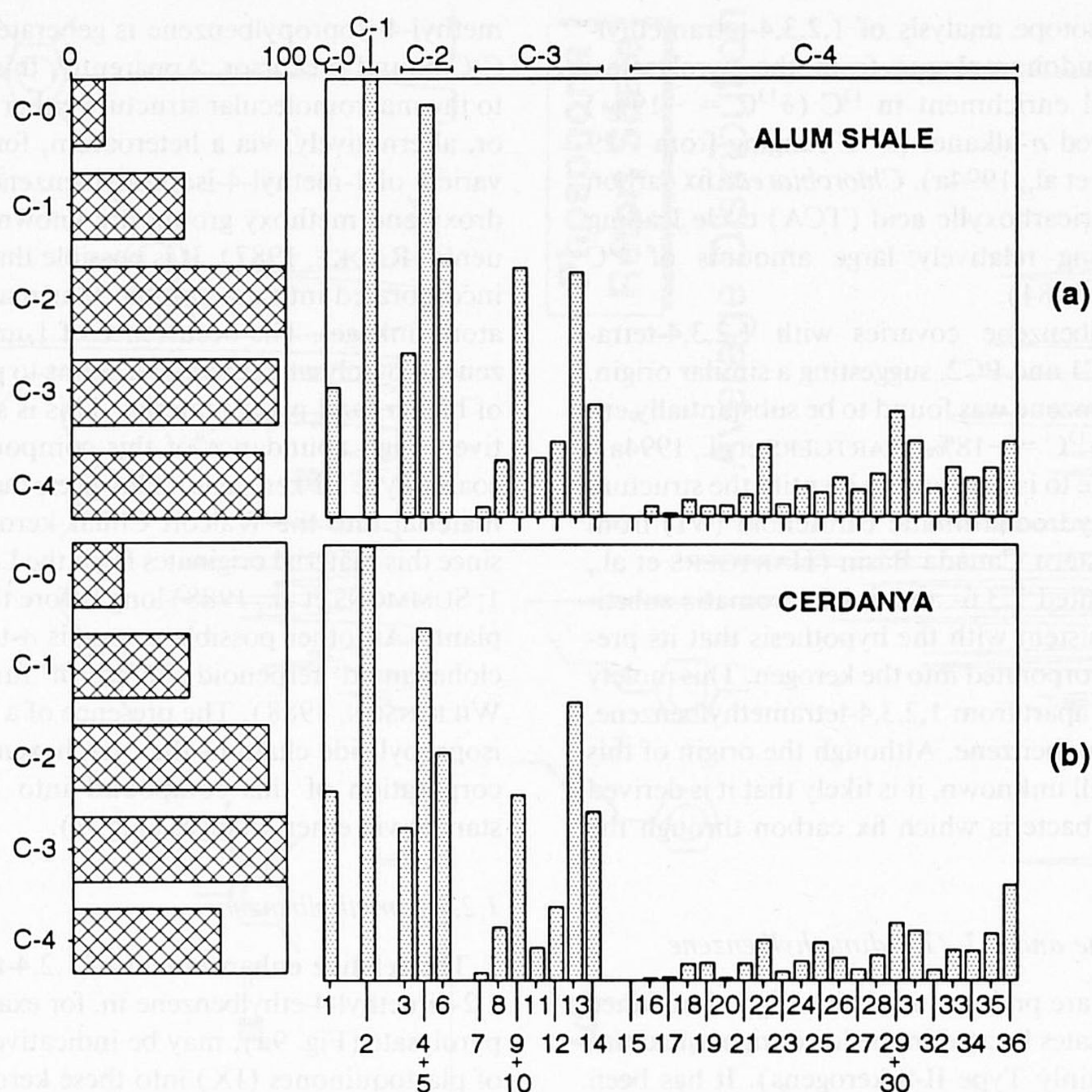


FIG. 9. Bar plots showing the carbon number distributions of benzene, toluene, and the C<sub>2</sub>-C<sub>4</sub> alkylated benzenes (left bar graphs) and the internal distribution of the individual isomers (right bar graphs) generated upon flash pyrolysis (Curie temperature 610°C) of the kerogen of (a) Alum Shale and (b) Cerdanya. Numbers refer to compounds listed in Table 2.

high abundance of alkylbenzenes to a significant contribution of remains of the microscopically recognizable freshwater alga *Pediastrum* to the kerogen. Although biomacromolecules so far identified in the cell walls of algae are mainly aliphatic in character, it was suggested that the bioresistant residue of *Pediastrum* is aromatic or partly aromatic. Judging by the minor differences in the alkylbenzene distribution of these samples and the absence of a high abundance of "linear" alkylbenzenes, it is deemed unlikely that radiation-induced aromatization reactions have played an important role in the formation of aromatic moieties in the Alum Shale kerogen. It seems that the peculiar "pyrolytic fingerprint" of the Alum Shale is a result of the absence of *n*-alkane/*n*-alkene doublets rather than the result of unusual diagenetic events.

#### Asphaltene-Kerogen Relationships

Figure 10 shows the distributions of alkylbenzenes generated by flash pyrolysis of the asphaltene and the extracted kerogen fractions of the Monterey oil shale, California, USA. The similarity of the internal alkylbenzene distributions as well as their relative concentrations is apparent, demonstrating the structural relationship between asphaltene and kerogen. The alkylbenzenes with longer carbon skeletons (C<sub>3</sub> and C<sub>4</sub> clusters) are slightly enhanced in the pyrolysate of

the asphaltenes compared to that of the kerogen. This is consistent with the concept that aromatic moieties in asphaltenes are bound by fewer intermolecular bridges (i.e., are less cross-linked). These findings support the idea that asphaltenes are intermediates in the generation of crude oil from kerogen (SOLLI and LEPLAT, 1986; BEHAR and PELET, 1984). Py-GC of asphaltenes and kerogens, integrated with other techniques, can be a useful tool for source rock correlations.

#### CONCLUSIONS

Analysis of alkylbenzene distribution patterns in pyrolysates of kerogens, coals, and asphaltenes can provide information about specific precursor moieties (i.e., discrete structural elements) within the macromolecule. The presence of some specific aromatic moieties appears to be biologically controlled and, therefore, can provide information about specific environmental conditions during sedimentation. Considering the results discussed above, the following conclusions can be made concerning the presence of monoaromatic moieties in geological macromolecules.

- 1) The absolute amount of alkylbenzenes are considerably higher in flash pyrolysates of Type II-S and Type II ker-



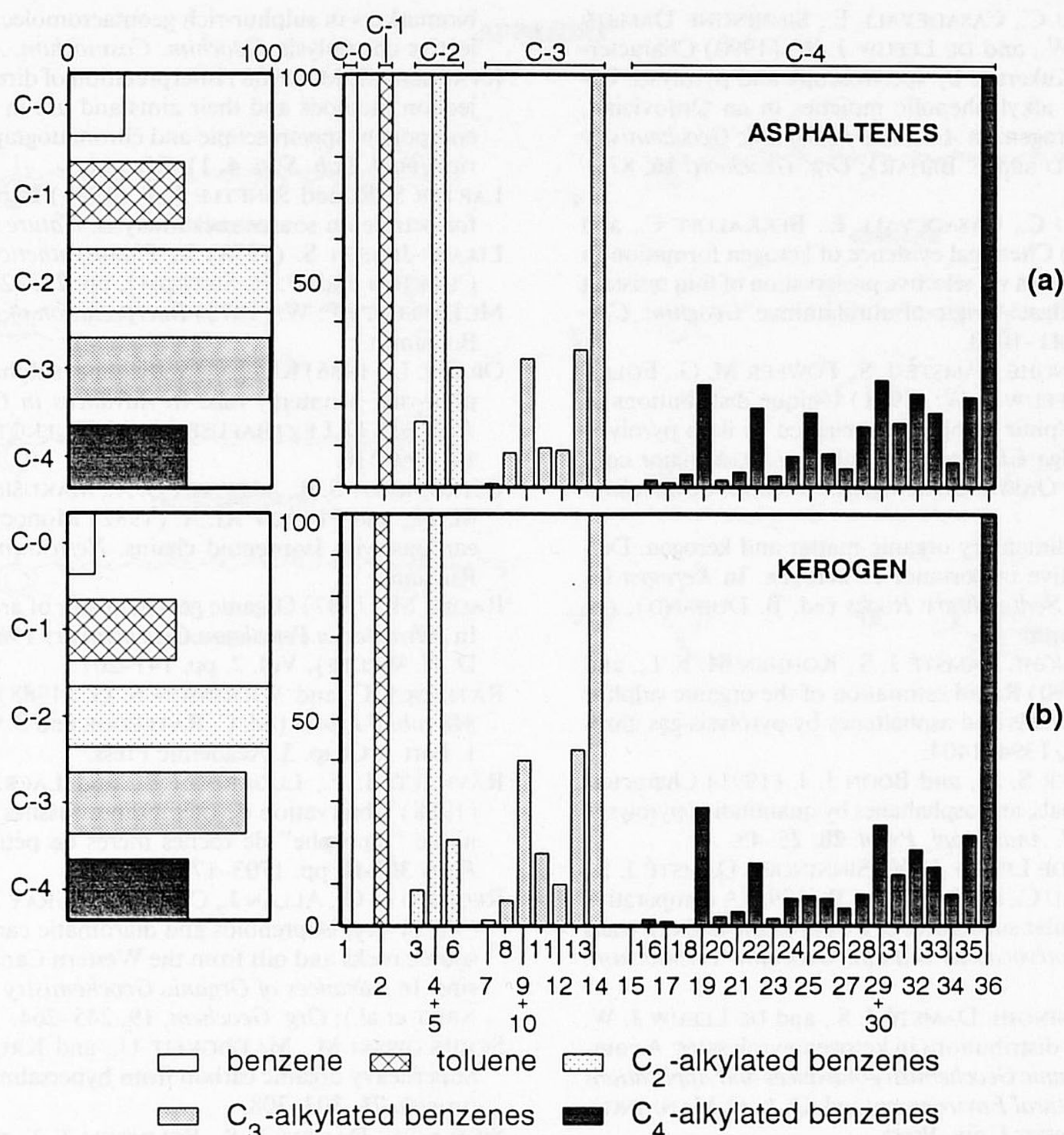


FIG. 10. Bar plots showing the carbon number distributions of benzene, toluene, and the C<sub>2</sub>–C<sub>4</sub> alkylated benzenes (left bar graphs) and the distribution of the isomers (right bar graphs) generated upon flash pyrolysis (Curie temperature 610°C) of (a) the asphaltenes and (b) kerogen of the Monterey oil shale, California, USA. The internal distributions of the alkylated benzenes were normalized to the most abundant component. Numbers refer to compounds listed in Table 2.

ogens in comparison to Type I and Type III kerogens. This demonstrates that Type III kerogens, although most aromatic in nature, do not necessarily generate the highest absolute amounts of alkylbenzenes upon pyrolysis.

- 2) Highly aliphatic Type I kerogens (Guttenberg, Estonian Kukersite) of algal origin are characterized by abundant alkyl moieties which upon diagenesis can convert partly into mono- and 1,2-di-substituted ("linear") alkylbenzene moieties.
- 3) The high abundance of 1,2,3,4- and 1,2,3,5-tetramethylbenzenes is a "pyrolytic" biomarker for macromolecularly bound aromatic carotenoids. Their structures and isotopic compositions indicate that they are derived from photosynthetic green sulphur bacteria (*Chlorobiaceae*). The presence of nonaromatic carotenoids (e.g.,  $\beta,\beta$ -carotene) is proposed to be envisaged by the relatively high abundance of 1,2,3-trimethylbenzene and 1,3-/1,4-dimethylbenzene in the pyrolysates.
- 4) The precursor of 1-methyl-4-isopropylbenzene is thought to be linked either via a heteroatom or, alternatively, via

a single C-C bond to the macromolecular matrix explaining the absence of the  $\gamma$ -cleavage product in the pyrolysate.

- 5) Alkylbenzene distribution patterns of asphaltenes and kerogens from the same oil shale appear to be very similar, lending further support to their structural relationship.

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APPENDIX

