

## Origin of solid bitumens, with emphasis on biological marker results

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**Abstract**—Solid bitumens are allochthonous, non-disseminated organic matter found associated with sedimentary rocks. Common worldwide examples include gilsonite, grahamite and ingramite. Their occurrence in petroliferous basins makes knowledge of their origin of interest to organic geochemists and petroleum explorationists. Using current analytical methods, it is usually possible to assign an origin to these materials, based on chemical characteristics of the whole material and its extractable fraction. In this study, 27 solid bitumens and their extracts have been studied, and the following analyses were performed: elemental (H, C, N, Ni and V) and isotopic ( $\delta^{13}\text{C}$ ) analyses of whole bitumen and extracts thereof; pyrolysis-gas chromatography of whole bitumen, and gas chromatography of extractable aliphatic hydrocarbons; carbon-13 NMR aromaticity measurements of the whole bitumen, using CP-MAS techniques; and GCMS studies of biological markers in the distillable (400–900°F) hydrocarbons. Results which have a bearing on the genesis of these materials are presented and discussed.

Results indicate that (a) the classical generic names assigned to each bitumen, based on solubility, fusibility and H/C ratios, are neither source-distinctive nor indicative of genesis; (b) the relative amounts of *n*-hydrocarbons in chromatograms and pyrograms are useful in assessing both origin and the nature of secondary alteration (e.g. biodegradation); (c) the solid bitumens examined can be successfully classified using a genetic scheme, based largely upon molecular and bulk maturation parameters. Using NMR-derived  $f_a$  values, H/C atomic ratios, moretane/hopane ratios, and ratios of sterane isomers, solid bitumens associated with oil source rocks can be genetically classified as either pre-oil or post-oil. Pre-oil solid bitumens are early-generation (immature) products of rich source rocks, probably extruded as very viscous fluids, which have migrated minimal distances to fractures. In contrast, post-oil solid bitumens are products of the alteration of a once-liquid oil, which was generated and migrated from a mature source rock. Following generation and expulsion, both pre-oil and post-oil solid bitumens are subject to the same modification processes, namely biodegradation, devolatilization and thermal alteration.

**Key words:** bitumen, bitumen origin, biomarkers, asphaltite, pyrobitumen, solid bitumen, thermal maturity, immature source rocks, aromaticity, oil alteration

### INTRODUCTION

The solid bitumens discussed here are allochthonous, localized organic matter found in, or closely associated with, sedimentary rocks. Common examples include grahamite, gilsonite, anthraxolite and albertite (Abraham, 1945). Solid bitumens have been encountered by geologists since the early stages of petroleum exploration, and their occurrence is common in petroliferous basins. Various origins have been assigned to these materials, ranging from identification as thermally immature to thermally postmature crude oil, and including several stages of possible alteration (e.g. devolatilization, biodegradation) between these two extremes (White, 1899; Taff, 1909; Ham, 1956; Williams and Goodarzi, 1981; and others). This wide range of potential origins suggests that knowledge of the genesis of these materials would provide important supporting data in assessing the thermal history of a basin. The present report is an attempt to define the chemical composition of solid bitumens, and determine their origin based upon these chemical characteristics. Note that our discussion of genesis here implies processes of solid bitumen formation, and is unrelated to specific source rocks or source environ-

ments. The source-related aspects of these materials will be explored in a later publication.

The traditional classification scheme for solid bitumens is entirely generic, relying upon the solubility, fusibility and hydrogen/carbon atomic ratio of the sample for naming purposes (Abraham, 1945; Hunt *et al.*, 1954; Fig. 1). While this generic classification scheme may be excellent for sorting museum collections of solid bitumens, it is of little use in establishing genesis. Nevertheless, the names provide an easily-understood jargon for rapid reference to specific solid bitumens, without the necessity of constantly reciting physical characteristics. For convenience, the traditional generic names will be used in this report, although the results discussed herein show that they bear no consistent geochemical significance.

Numerous studies involving solid bitumens are available in the literature; a complete review of these will be presented at a later date. Preliminary efforts were reviewed by Abraham (1945), who recites a complete account of the historic and geographic occurrences of solid bitumens and related materials. General theories for their origin have been presented (Taff, 1909; Brooks, 1936; Silverman, 1964,

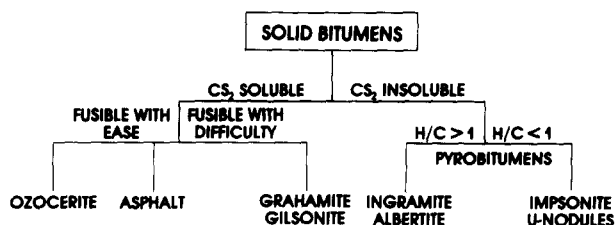


Fig. 1. Traditional (generic) classification scheme for natural solid bitumens, based upon solubility, fusibility and H/C atomic ratio. Modified after Abraham (1945) and Hunt *et al.* (1954).

1978; Curiale, 1981, 1983) and several workers have attempted to assign specific origins to particular solids found in certain regions (White, 1899; Hunt *et al.*, 1954; Bell and Hunt, 1963; Grantham, 1975; Nissenbaum and Goldberg, 1980; Bartle *et al.*, 1981; Ekinci *et al.*, 1981, 1982; Williams and Goodarzi, 1981; Curiale, 1981, 1983; Curiale *et al.*, 1983; Hayatsu *et al.*, 1983; Powell, 1984; McKirdy *et al.*, 1984; Rullkötter *et al.*, 1985). Although these studies and others (King, 1963; Hunt, 1963; Waples, 1977; Sikander and Pittion, 1978; Jacob *et al.*, 1981; Jacob, 1983; Kavari-Khorasani, 1983) have presented geochemical data for solid bitumens, little systematic effort at genetic classification resulted. The present study will propose such a process-related classification scheme.

#### SAMPLE AND METHODS INFORMATION

Twenty-seven solid bitumens from Spain, Mexico, Canada and the United States (Calif., Okla, Pa and Utah) were studied (Table 1). All are hand specimens from the collections of G. H. Smith and J. A. Curiale, and were sampled from surface outcrops or mine faces; they generally consist

of less than 5% host rock contamination. For samples whose field relationships are known, the sample was found either in wide veins and fractures in existing mines (Oklahoma grahamites and impsonites; Uinta Basin bitumens) or directly on the surface of the outcrop (Monterey asphalt). Descriptions of the host rocks and the basinal geology for most of the samples have been previously described (Hunt *et al.*, 1954; Bell and Hunt, 1963; Hunt, 1963; Curiale, 1981, 1983, and references therein; Grantham, 1975, and references therein; Khavari-Khorasani, 1983; Jacob, 1976; Curiale *et al.*, 1983), and will be discussed further in a later publication.

Extraction and separation steps are summarized in Fig. 2. Several analyses were conducted on each of the sample fractions obtained. Results will be discussed in detail where they are useful in assessing the genesis of the solid bitumens. Transition metals were analyzed by sample ashing and inductively-coupled plasma emission spectrometry, according to conditions described by Curiale (In press). Pyrolysis-gas chromatography was completed on all samples, using about 1 mg of sample in a Chemical Data Systems (coil) pyroprobe, heated at 20°C/ms to 750°C (held for 10 s). The pyrolyzate was cold-trapped at the head of a 12.5 m × 0.25 mm (i.d.) methylsilicone column; oven conditions were -20°C to 300°C at 4°C/min, held for 2 min.

Table 1. Sample identification

Sample	Location	Generic name
1	Sardis (east), Oklahoma	Grahamite
2	Jumbo, Oklahoma	Grahamite
3	Sardis (west), Oklahoma	Grahamite
4	Pumroy, Oklahoma	Grahamite
5	South Bald, Oklahoma	Grahamite
6	Page, Oklahoma	Impsonite
7	Uinta Basin	Gilsonite
8	Kiowa County, Oklahoma	Uraniferous nodule
9	Kiowa County, Oklahoma	Uraniferous nodule
10	Kiowa County, Oklahoma	Uraniferous (center)
11	Kiowa County, Oklahoma	Uraniferous (mid-radius)
12	Kiowa County, Oklahoma	Uraniferous (edge)
13	Mussel Rock, California	Asphalt
14	Washington Co., Penn.	Grahamite
15	Page, Oklahoma	Impsonite
16	Wasatch County, Utah	Albertite
17	Wasatch County, Utah	Ingramite
18	New Brunswick, Canada	Albertite
19	Mahogany Ledge (Colorado)	Gilsonite
20	Soldier Summit, Utah	Ozocerite
21	Bathurst Island, Canada	Gilsonite
22	Utah	Gilsonite
23	Tehuantepec, Mexico	Gilsonite
24	Northern Spain	Grahamite (impsonite)
25	Jumbo, Oklahoma	Grahamite
26	Coatzacoalcos, Mexico	Gilsonite (manjak)
27	Mexico	Gilsonite <sup>b</sup>

(a) Detailed location data for all Oklahoma samples will be found in Curiale (1981) and Curiale *et al.* (1983). (b) Probably from same sample location as sample 26.

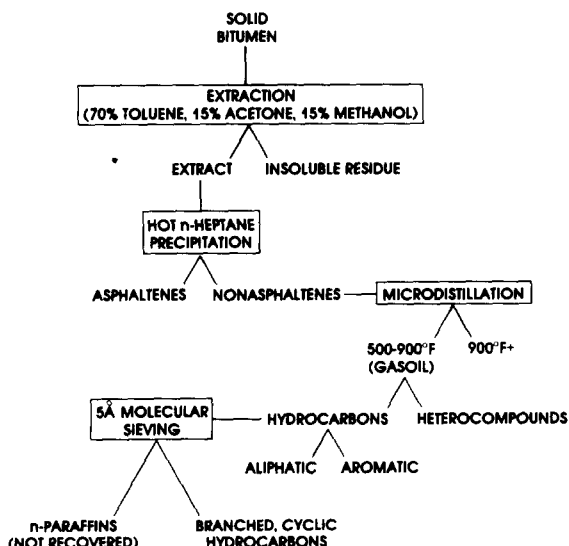


Fig. 2. Analytical flowchart for this study. Samples were crushed, powdered and extracted (room temperature) overnight. Gasoil hydrocarbons from all samples were molecular sieved using 1/16" 5A zeolite pellets, except sample 20 (see Table 1). Due to extremely high *n*-paraffin content, the *n*-paraffins in this sample were removed using silicalite (see text).

Conventional high resolution gas chromatography conditions were previously described (Curiale *et al.*, 1985). Gas chromatography-mass spectrometry runs were completed on total (gasoil) hydrocarbon fractions, having first been sieved to remove *n*-paraffins (O'Connor *et al.*, 1962). The extremely high relative concentrations of *n*-paraffins in one sample (20) necessitated the use of silicalite as an *n*-paraffin adsorbent (Dessau, 1980). (Preliminary testing of silicalite has shown no fractionation of the conventional biological markers.) GCMS instrument conditions are described by Curiale *et al.* (1985) and Curiale (In prep.). Whole hydrocarbon fractions were analyzed in order to facilitate direct comparison of aromatic steroids with aliphatic biomarkers. All reported biomarker ratios are obtained by area integration of peaks in mass chromatograms, uncorrected for fragmentation response factors. All stable carbon isotope ratios are reported in per mil notation, corrected to the PDB standard. Solid state carbon-13 NMR spectra were obtained with a JEOL 90 MHz spectrometer, modified with a Chemagnetics solids accessory package, at 22.5 MHz, using the CP-MAS technique. Carbon aromaticity ( $f_a$ ) values were obtained by splitting the field into aliphatic and aromatic regions (Barwise *et al.*, 1984).

Extractable organic matter data for the twenty-seven solid bitumens are presented in Table 2. EOM content varies from the extreme insolubility of the uraniferous bitumens (samples 8–12) to the complete solubility of the Monterey asphalt and some gilsonites (samples 7, 13, 22 and 23). All samples fall within either a low-solubility group (0.1–25.8%) or a high solubility group (64.0–100.0%). Aliphatic/aromatic hydrocarbon ratios for the distillable (400–900°F) extractable hydrocarbons vary dramatically (0.48–31.26). The highest ratios are present in the solid bitumens associated with the Green River Formation in and adjacent to the Uinta Basin (samples 7, 16, 17, 19 and 22). Despite the highly aliphatic nature of their extractable hydrocarbons, these albertites, ingramite, ozocerite and gilsonites range in solubilities from less than 7.0% up to 100.0%. All of the Uinta Basin samples (except sample 20,

Table 2. Compound class distributions

Sample	EOM <sup>a</sup>	Asphaltenes <sup>b</sup>	500–900°F <sup>c</sup>	Aliphatics <sup>d</sup>
				Aromatics
1	16.0	39.5	6.3	1.56
2	22.9	73.0	1.29	0.52
3	16.9	64.9	4.7	1.48
4	25.8	73.2	11.2	2.70
5	23.7	48.5	2.77	2.73
6	0.5	6.5	92.2	0.79
7	100.0	40.3	1.74	3.22
8	0.1	—	—	—
9	0.1	—	—	—
10	0.1	—	—	—
11	0.2	—	—	—
12	0.3	—	—	—
13	100.0	52.0	5.50	0.80
14	12.4	45.0	3.17	3.15
15	1.2	2.3	87.2	2.30
16	7.1	28.9	7.06	24.64
17	6.8	41.0	14.8	31.26
18	2.8	10.1	50.8	7.85
19	77.0	—	2.27	14.87
20	21.3	—	18.1	18.23
21	64.0	45.3	1.11	0.48
22	100.0	49.0	3.2	3.55
23	100.0	73.1	6.41	0.60
24	2.7	2.9	56.4	0.55
25	13.2	41.0	5.87	3.27
26	97.6	65.2	5.74	1.06
27	98.0	63.5	5.41	0.50

(a) Extractable Organic Matter (percent). (b) As percentage of EOM; precipitated with hot *n*-heptane. (c) Microdistillation cut of the non-asphaltene EOM. (%). (d) Hydrocarbon ratio in the 500–900°F cut.

Table 3. Elemental analyses and selected ratios

Sample	H (%)	C (%)	N (%)	ASH (%)	H/C	N/C
1	7.50	87.70	1.71	0.90	1.02	0.016
2	7.30	83.50	1.50	4.30	1.04	0.015
3	7.30	84.30	1.09	0.30	1.03	0.011
4	8.20	85.00	1.74	1.40	1.15	0.017
5	8.30	85.80	1.35	0.70	1.15	0.013
6	5.60	87.50	2.26	0.80	0.76	0.022
7	10.50	86.30	2.87	0.00	1.45	0.028
8	4.90	56.30	0.01	11.20	1.04	0.00
9	4.60	58.80	0.00	12.50	0.93	0.00
10	4.80	57.50	0.25	28.80	0.99	0.003
11	5.50	70.70	0.40	16.40	0.93	0.004
12	5.30	76.50	0.26	11.80	0.83	0.002
13	9.40	78.30	1.03	0.70	0.43	0.011
14	7.90	86.50	1.99	0.00	1.09	0.019
15	5.20	88.60	1.87	0.60	0.70	0.018
16	8.80	82.70	2.11	0.10	1.27	0.021
17	10.10	74.40	1.22	5.70	1.62	0.014
18	8.70	82.80	2.90	0.20	1.25	0.030
19	8.30	61.30	1.09	19.80	1.61	0.015
20	14.00	85.70	0.01	0.00	1.95	0.00
21	8.10	82.00	1.68	0.20	1.18	0.017
22	10.40	84.70	2.68	0.00	1.46	0.027
23	8.30	77.40	1.01	2.40	1.28	0.011
24	4.20	58.60	0.29	30.40	0.85	0.004
25	8.20	84.20	1.16	0.60	1.16	0.011
26	8.30	61.30	0.84	1.70	1.61	0.011
27	8.30	77.70	0.78	2.10	1.27	0.008

which is from the Wasatch Formation) are apparently sourced from the Green River Formation (Bell and Hunt, 1963; Hunt, 1963), which suggests that the high aliphatic/aromatic hydrocarbon ratio in these samples is a source-distinctive parameter.

## RESULTS—ELEMENTAL AND ISOTOPIC ANALYSES

Table 3 lists carbon, hydrogen, nitrogen and ash contents of the solid bitumens. Most conspicuous in these data are the seven samples (8–12, 19, 24) having ash contents greater than 10%. Infrared spectra confirm that these high ash contents are caused by the association of minerals with the organic matrix: broad bands centered at 9.72 and 11.4 microns in the infrared can be assigned to silicates (Socrates, 1980). H/C and N/C atomic ratios are extremely variable for these samples. H/C ratios range from 1.95 to 0.70, indicating extensive variability in original source organic matter input and thermal history (although the highest value here is for sample 20, an ozocerite consisting of 90 + % *n*-paraffins—see Marschner and Winters, 1976). The wide range in N/C ratios (0.001–0.030) also suggests source facies or maturity variations, although the relationship between N/C ratios and rank level noted by Waples (1977), Boudou *et al.* (1984) and Boudou (1984) is not apparent in this data set: the relationship between H/C and N/C is non-correlative ( $r = 0.18$ ). Concentrations of the transition elements vanadium and nickel are listed in Table 4, along with the ratio of these two elements, a commonly-used oil-oil correlation parameter (Bonham, 1956; Stone, 1967; Lewan, 1980). Literature data, as well as unpublished results from in-house efforts, show that most crude oils and source rock extracts have  $V/(V + Ni)$  ratios greater than 0.25 (Lewan, 1984). It is therefore interesting that of the six samples with ratios less than 0.25, five are found within the Green River Formation (Hunt, 1963; samples 7, 16, 17, 19 and 22). The relative depletion of vanadium in these samples is consistent with previous studies of organic matter metal content in the Uinta Basin, and supports a lacustrine depositional environment (Hodgson *et al.*, 1963; Lewan, 1980, 1984).

Despite current efforts to utilize metalloporphyrins as thermal maturity indicators (Didyk *et al.*, 1975; Mackenzie

Table 4. Transition metal concentrations

Sample	Ni (ppm)	V (ppm)	V(V + Ni) <sup>a</sup>
1	428.0	419.0	0.49
2	422.0	544.0	0.56
3	459.0	436.0	0.49
4	359.0	1000.0	0.74
5	361.0	770.0	0.68
6	492.0	945.0	0.66
7	176.0	1.0	0.01
8	33.0	1100.0	0.97
9	47.0	1600.0	0.97
10	4500.0	16900.0	0.79
11	2700.0	4800.0	0.64
12	2100.0	1400.0	0.40
13	160.0	422.0	0.73
14	304.0	1100.0	0.78
15	477.0	1000.0	0.68
16	205.0	13.0	0.06
17	82.0	11.0	0.12
18	168.0	2.0	0.12
19	134.0	32.0	0.19
20	7.7	8.6	0.53
21	530.0	1670.0	0.76
22	188.0	< 10.0	< 0.05
23	204.0	1230.0	0.86
24	44.0	21.0	0.32
25	400.0	910.0	0.69
26	207.0	1200.0	0.85
27	205.0	1200.0	0.85

(a) weight/weight.

*et al.*, 1981), specific transition metal concentrations are rarely used to assess rank level. Preliminary results presented here imply that nickel concentrations, and particularly Ni/C atomic ratios may have an empirical utility as maturation indicators in non-uraniferous solid bitumens. In general, Ni/C ratios increase monotonically with increasing maturity (Fig. 3), suggesting that Ni is preferentially retained during the maturation process. One must be cautious however: Ni found in solid bitumens may simply be associated with aromatic rather than aliphatic carbon for source type reasons. At this point it is only possible to note

that, whether due to rank level or source-induced factors, Ni/C ratios appear to vary directly with aromaticities and inversely with H/C ratios in these solid bitumens.

Stable carbon isotope ratios for whole solid bitumen, extractable organic matter, and aliphatic and aromatic hydrocarbon fractions (where sample size permitted) are presented in Table 5. In general, the isotopically lightest samples are the uraniferous nodules and the ozocerite. All non-uraniferous Oklahoma samples fall in the narrow range of  $-29.7\%$  to  $-29.1\%$ , supporting a common source as previously suggested (Curiale, 1981). Remaining whole samples (except for the unusually heavy sample 24) fall between  $-30.2\%$  and  $-28.1\%$ . All but four samples have the usual relationship of aliphatic hydrocarbons being isotopically lighter than aromatic hydrocarbons (Stahl, 1978; Sofer, 1984); the four exceptions are all gilsonites (Fig. 4). Isotopic data patterned after Stahl's (1978) isotope type-curves (Fig. 5) are useful in solid bitumen correlations. Pattern similarities for most Green River Formation associated solid bitumens (samples 16, 17, 19 and 22; exception = sample 7) shown in Fig. 5 strongly suggest a common origin for these materials. Further, post-sourcing alteration has apparently not significantly altered the carbon isotope ratio relationships for these samples. Other sample sets also clearly show a common source, such as the three Mexican solid bitumens, samples 23, 26 and 27. The Monterey asphalt (sample 13) is also shown to be different from all others analyzed (Fig. 5).

Examination of data in Table 2 and 5 suggests that an apparent relationship exists between the content of aliphatic hydrocarbons in the extractable organic matter, and the carbon isotope ratio of the aliphatics. Figure 6 shows that the samples whose extractable hydrocarbons are rich in aliphatic components will also contain the isotopically lightest aliphatic hydrocarbons. Inasmuch as the aromatic hydrocarbon isotope ratios are roughly correlative with these aliphatic hydrocarbon isotope ratios (Fig. 5), a similar relationship would obtain for aromatics (see data in Tables 2 and 5). If we then consider the aromaticity of the hydrocarbon fraction as being a rank-related parameter, it would appear that the more aromatic the extractable hydrocarbons, the greater the relative concentration of isotopically heavy carbon in the hydrocarbon fractions.

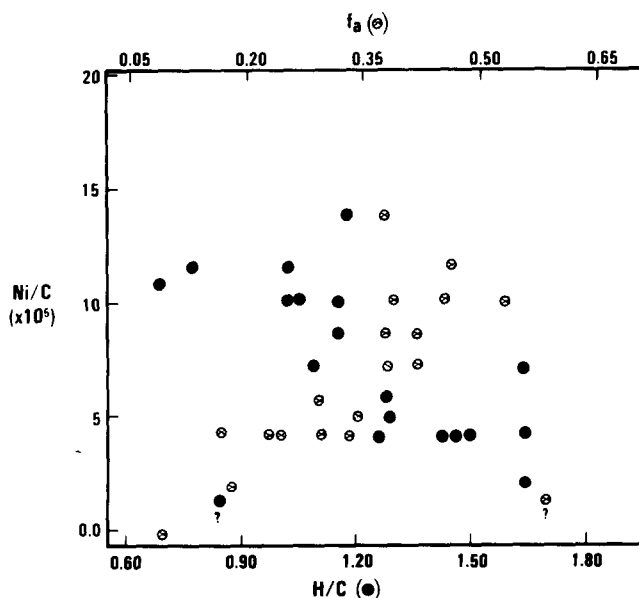


Fig. 3. Graph showing the increase in Ni/C atomic ratio with increasing rank level, as measured by aromaticity ( $f_a$ ) values and H/C atomic ratios. [Note that sample 24 (designated by question mark) does not correspond with the trend for the remaining samples.] The cause for this relationship is unknown.

Table 5. Carbon isotope ratios and carbon aromaticity

Sample	Whole Bitumen <sup>a</sup>	Extract <sup>a</sup>	Aliphatic HC <sup>a</sup>	Aromatic HC <sup>a</sup>	$f_a^c$
1	-29.5	-29.2	-28.9	-27.4	0.52
2	-29.6	-29.1	-28.4	-27.2	0.45
3	-29.7	-29.4	-28.5	-27.7	0.46
4	-29.4	-28.9	-30.4	-28.6	0.38
5	-29.6	-29.4	-30.1	-28.5	0.41
6	-29.3	-26.7	-28.5	-26.6	0.71
7	-28.0	-28.6	-29.1	-29.6	0.22
8	-31.9	b	b	b	0.48
9	-31.8	b	b	b	0.59
10	-31.0	b	b	b	0.44
11	-30.7	b	b	b	0.48
12	-29.5	b	b	b	0.52
13	c	-22.3	-23.4	-22.5	0.29
14	-29.4	-28.7	-30.0	-26.0	0.41
15	-29.1	-27.1	-28.6	-26.1	0.71
16	-29.9	-28.8	-32.4	-26.6	0.34
17	-30.2	-29.8	-31.1	-27.6	0.18
18	-28.1	-29.1	-30.8	d	0.33
19	c	-29.7	-32.7	-28.6	0.16
20	-31.9	-30.9	-31.9	-29.0	0.09
21	-29.0	-27.9	-29.0	-28.6	0.37
22	c	-29.0	-32.1	-30.3	0.24
23	c	-26.7	-24.8	-26.5	0.29
24	-26.8	-27.6	-27.7	-25.0	0.58
25	-29.8	-27.7	-30.0	-28.0	0.39
26	c	-26.1	-26.9	-27.1	0.37
27	c	-25.9	-26.7	-27.0	0.37

(a)  $\delta^{13}\text{C}$ , relative to PDB standard, in ‰ notation. (b) Extractable yield too low for class separation. (c) Not determined. (d) Aromatic HC yield too low for reliable analysis. (e) Whole solid bitumen.

#### RESULTS—AROMATICITY (NMR) ANALYSES

Using solid sample magic angle spinning techniques (Wemmer *et al.*, 1981; Maciel and Sullivan, 1982), carbon aromaticities of the twenty-seven solid bitumens have been determined, and are reported in  $f_a$  units, as a percentage of total carbon (Table 5). Values vary from 0.09 for sample 20 (the Utah ozocerite) to 0.71 for samples 6 and 15 (the Oklahoma impsonites). Both  $f_a$  and atomic H/C ratios are now commonly used as rank level indicators in geochemical organic matter, and the relationship between these indicators has been studied (Barwise *et al.*, 1984; Hayatsu *et al.*, 1984; Hayamizu and Ohshima, 1985). The wide range of

aromaticities for the solid bitumens of the present study appears to correlate extremely well with H/C ratios (Fig. 7;  $r = 0.93$ ). Further, a consistent distinction can be made at about  $f_a = 0.37$  and H/C = 1.20: grahamites, impsonites and uraniferous bitumens are more aromatic than these values, while gilsonites, ingramite, asphalt and albertites are less aromatic. The implications of these data on solid bitumen genesis will be discussed later.

#### RESULTS—GAS CHROMATOGRAPHY

Gas chromatography of the aliphatic hydrocarbon fraction and pyrolysis-gas chromatography of whole solid bitu-

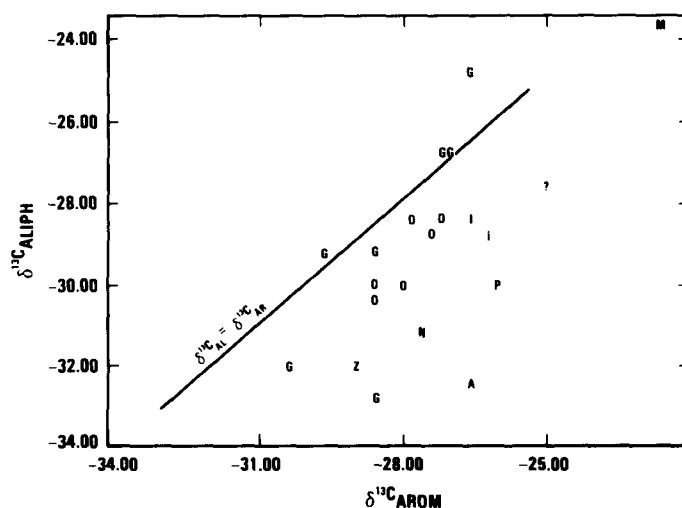


Fig. 4. Carbon isotope ratio plot (aliphatic hydrocarbons vs aromatic hydrocarbons). Note that all four samples with aliphatic ratios heavier than aromatic ratios are gilsonites. Sample code: M = 13; O = 1-5, 25; I = 6, 15; Z = 20; A = 16, 18; N = 17; P = 14; ? = 24; G = 7, 19, 21-23, 26, 27. See Table 1 for sample numbering.

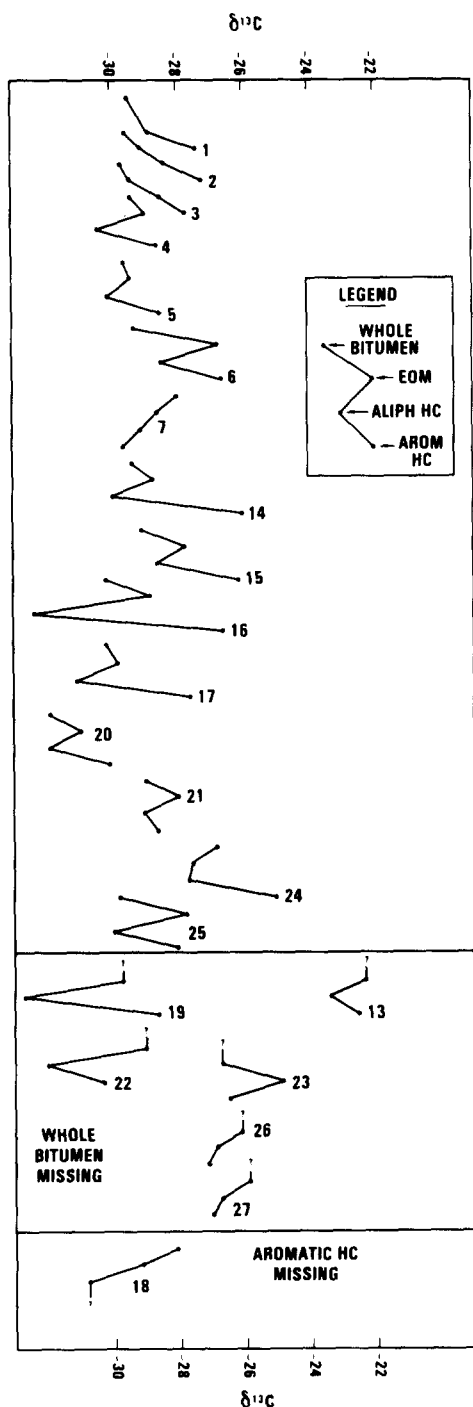


Fig. 5. Carbon isotope ratio patterns for whole sample and extractable fractions, designed after Stahl's (1978) isotope type-curves. Note that the Mexican gilsonites and the Monterey asphalt are distinct from the other samples. Sample number designations are listed in Table 1.

mens were carried out; high-temperature, flash pyrolytic gas chromatograms for the twenty-seven solid bitumens are presented in Fig. 8. For most of the samples, the pyrograms reveal a series of doublets consisting of *n*-alkanes and their corresponding (early-eluting) 1-alkenes, characteristic of pyrograms of kerogens and other geochemical organic matter (Horsfield, 1984; Larter, 1984). When pyrogram groupings according to chromatographic simi-

larities are attempted, it is clear that the data group together by geographic and not physical characteristics. This would suggest that such groupings are based upon source similarities rather than generic name classifications. For example, all the Oklahoma Ouachita solid bitumens (including grahamites and impsenites) have similar pyrograms (Fig. 8). Likewise the Utah albertite/ingramite/gilsonites appear similar to one another, as do the Mexican gilsonites. Thus the solid bitumen pyrogram may be regarded as a genetic- rather than generic-related datum. Nevertheless, it is important to realize that the "pyrograms" actually represent the sum of volatilized and pyrolyzed organic matter, the proportions of which are unclear.

Among the pyrograms in Fig. 8, only those for the five uraniferous solid bitumens (samples 8–12) are totally deficient in *n*-hydrocarbons. Because of the almost complete insolubility of these samples, their pyrograms represent the only chromatographic/structural information available for them. As shown in Fig. 8, the pyrograms of these samples are extremely similar, suggesting that they are both (a) commonly sourced, and (b) similarly altered, a conclusion consistent with previous work on these samples (Curiale *et al.*, 1983). The other 22 pyrograms show a complete range of (qualitative) *n*-hydrocarbons, from the almost non-paraffinic sample 7 to the dominantly-paraffinic sample 20 (ozocerite).

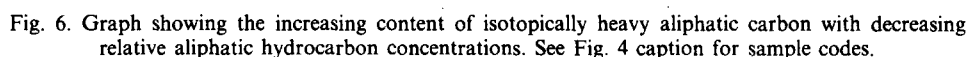
Of the non-uraniferous samples, only four are not dominantly *n*-paraffinic: samples 7, 13, 19 and 22. The absence of *n*-paraffins in extractable organic matter is often interpreted as the result of microbial degradation (Connan, 1984). However, if these (high-asphaltene) samples were biodegraded, one would expect *n*-hydrocarbons (often including *n*-alkenes) to be dominant in their pyrograms (Rubinstein *et al.*, 1979). The real cause of the low *n*-hydrocarbon content in the pyrogram is more likely the result of thermal immaturity, as suggested by the relatively high H/C ratios (Table 3) and the relatively low  $f_a$  values (Table 5). Thus the thermal stress upon the sources of these solid bitumens may simply have been insufficient to generate *n*-hydrocarbons. Consequently, the low relative concentration of *n*-hydrocarbons in the pyrograms may be an indication of thermal immaturity of the solid bitumen source materials. If so, an independent assessment of biodegradation can be made by observing the absence of *n*-hydrocarbons among the extractable hydrocarbons along with the simultaneous presence of *n*-hydrocarbons in the pyrogram (Connan, 1984; Rubinstein *et al.*, 1979).

Gas chromatograms of the extractable aliphatic hydrocarbons are shown in Fig. 9 for all solid bitumens except the uraniferous bitumens, from which too little extractable organic matter was obtained for further fractionation (Table 2). Five samples contain minor baseline "humps" and full suites of *n*-paraffins (samples 14, 18, 20, 24 and 25), and may therefore be considered to have escaped large-scale microbial attack. The remaining samples (excluding samples 7, 13, 19 and 22), while depleted in extractable *n*-hydrocarbons, show large suites of pyrolyzable *n*-hydrocarbons.

Generally, these three observations (occurrence of *n*-hydrocarbons in pyrograms and chromatograms, and the presence of a baseline "hump"), which are based on chromatograms of extractable and pyrolyzable hydrocarbons, can be paired with two geochemical processes, namely, thermal maturation and biodegradation. The following conceptual framework can be proposed to link these three chromatographic observations with these two geochemical processes, for the solid bitumens of this study.

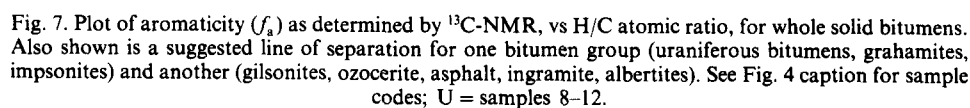
(A) Biodegraded samples from a thermally mature source unit will show a depletion of *n*-hydrocarbons in the extracted organic matter (Connan, 1984), a predominance of *n*-hydrocarbons in pyrolyzed organic matter (Rubinstein *et al.*, 1979), and a pronounced baseline "hump" of unresolved material in the extract (samples 1–6, 15–17, 21, 23, 26, 27).

(B) Biodegraded solid bitumen samples from a thermally



Because this conceptual classification system of solid bitumen chromatographic data is based solely on estimates of biodegradation and thermal maturity of source material

(i.e. other factors such as source rock organic matter variability have been excluded), it should be apparent that the divisional lines between the groups are not sharp. Figure 10 summarizes the confluences of the three observations and two processes in a single diagram. Superimposed on the figure are sample numbers of the non-uraniferous solid bitumens studied. In an effort to keep the diagram relatively uncluttered, the degree of each observation (i.e. the size of the baseline "hump", or the relative amount of *n*-hydrocarbons) has not been noted on the figure. Generally, extractable *n*-hydrocarbon concentration increases to the upper left, while the baseline rise increases to the right. Figure 10 provides a conceptual link between the characteristics of the organic matter at the time of sourcing (vertical axis) and the subsequent alteration that the organic matter encountered (horizontal axis). In general, the most aromatic samples (Fig. 7) tend to fall at the top of the diagram (the



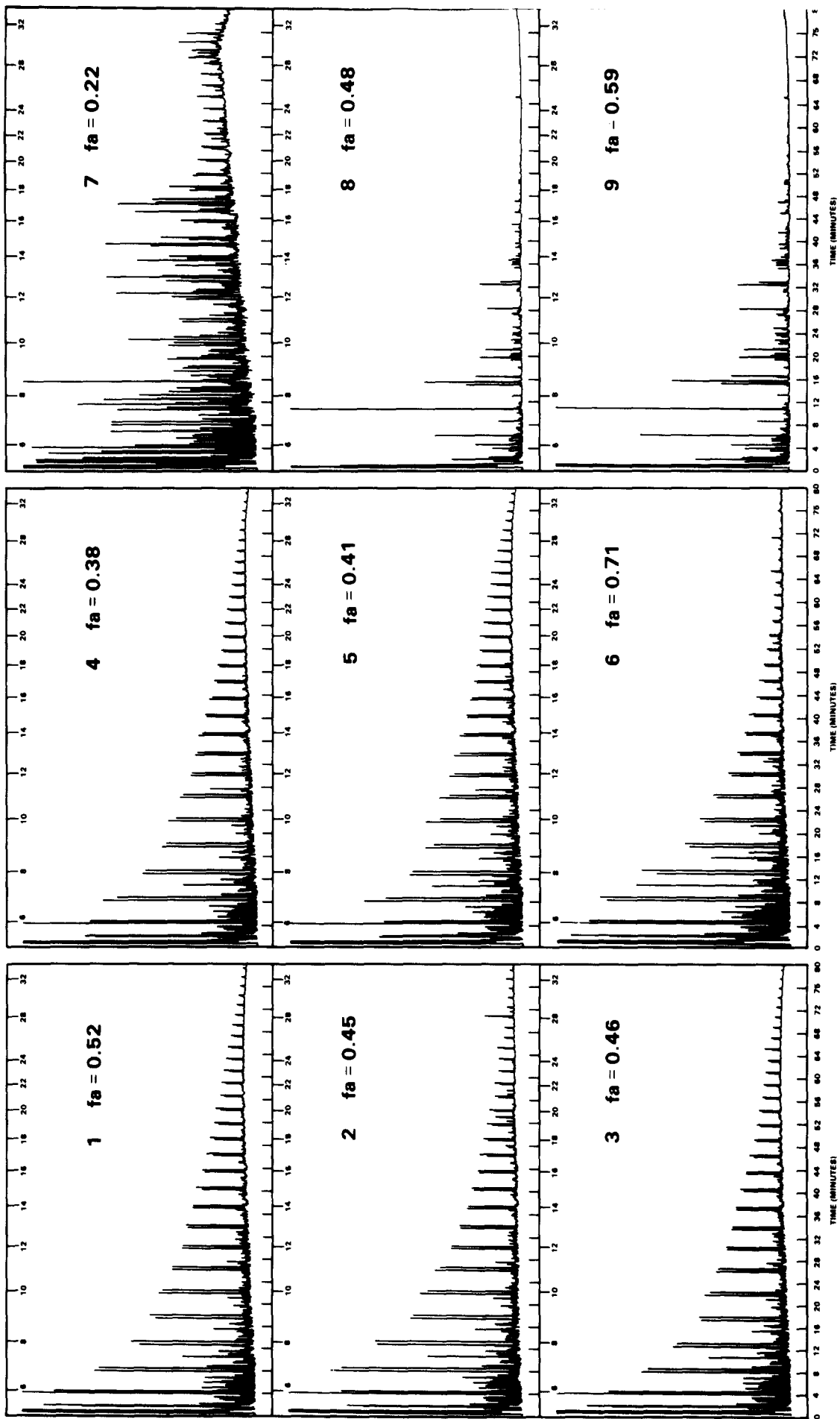


Fig. 8.



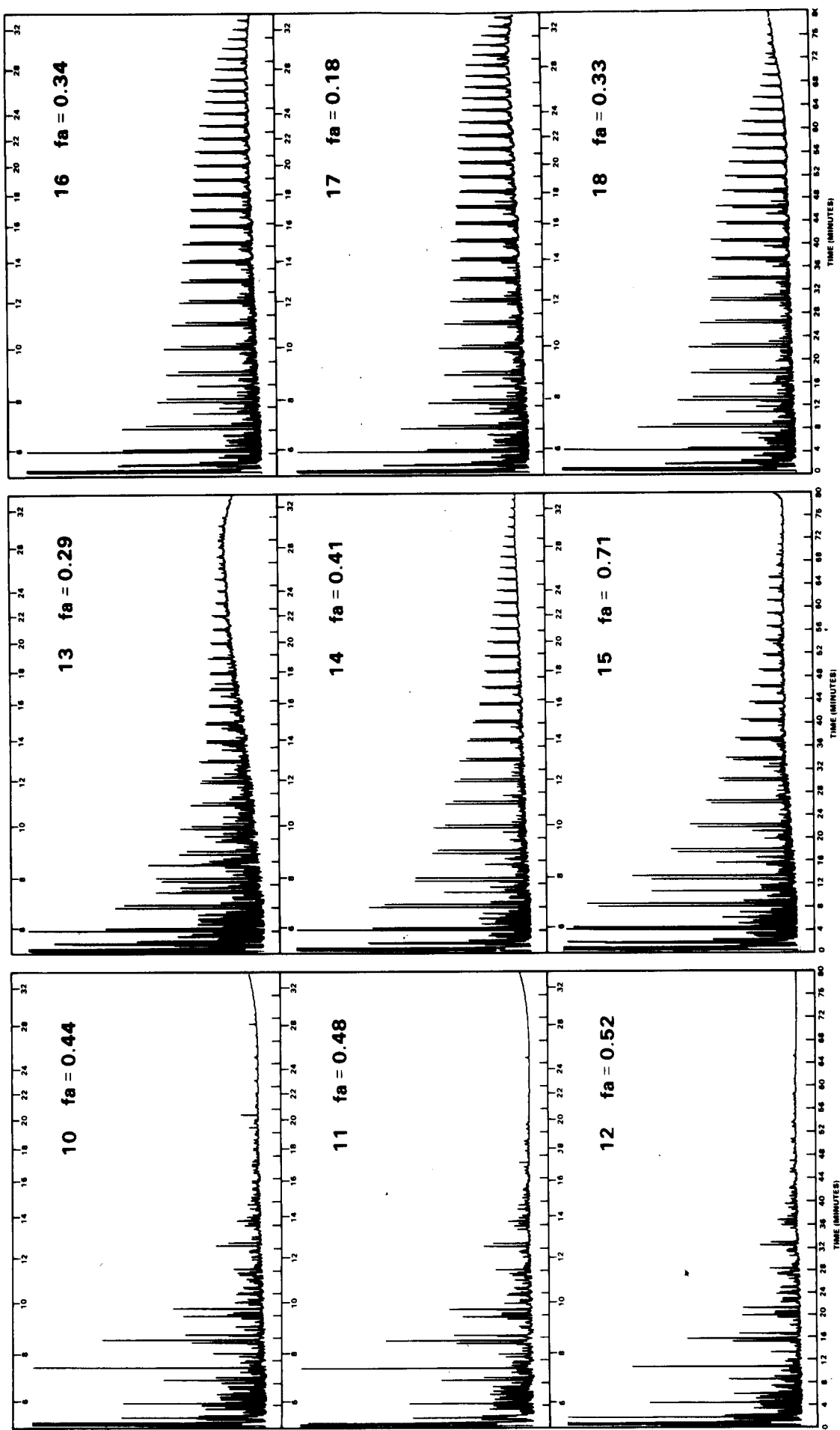


Fig. 8.

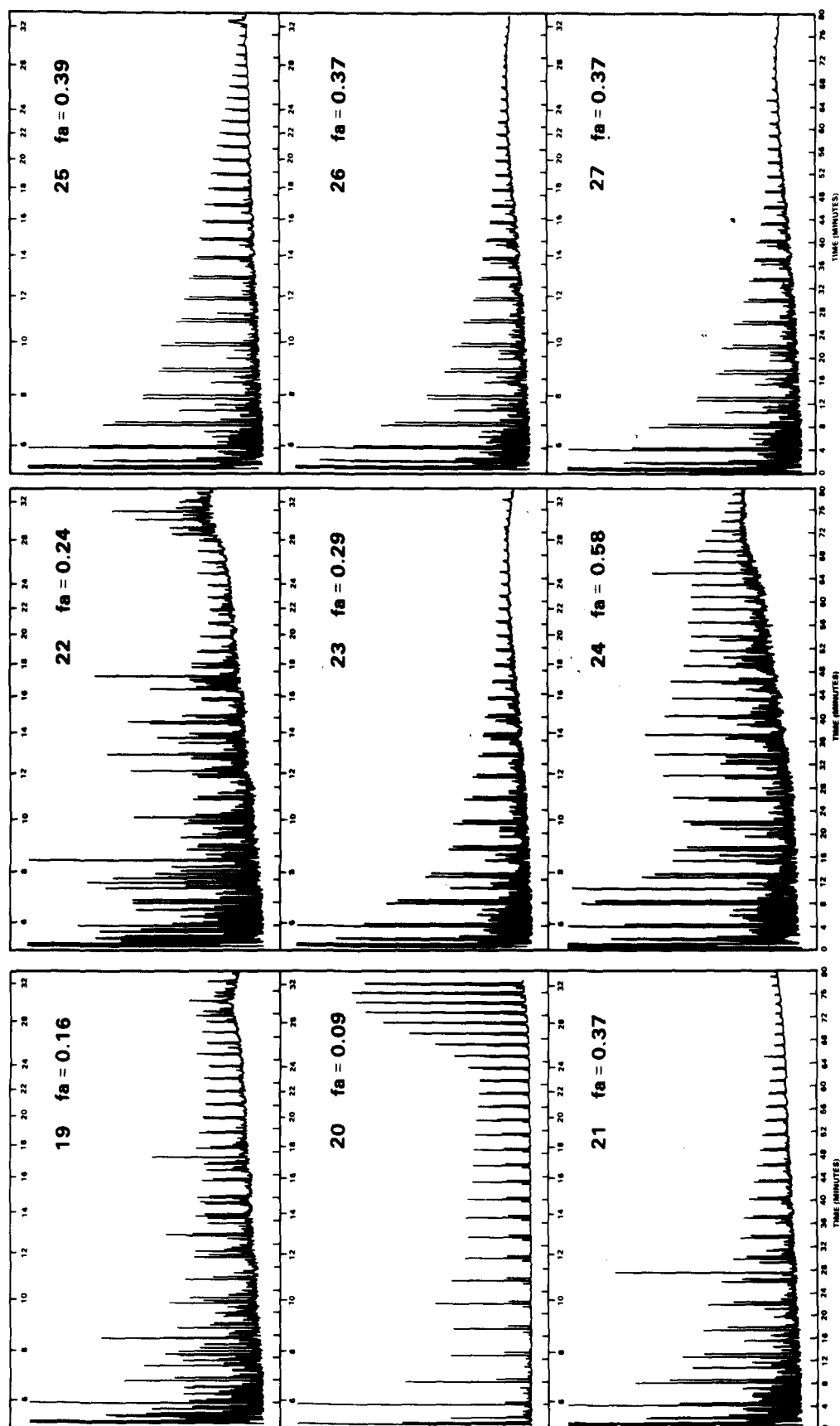


Fig. 8. Pyrolysis-gas chromatograms for the twenty-seven solid bitumens of this study. All samples were run by flash pyrolysis techniques (see text) at the same conditions. Carbon numbers for the *n*-alkanes are shown above each chromatogram, at the appropriate retention time. Also shown are  $^{13}\text{C}$ -NMR aromaticity values for each sample. Sample numbers correspond to those listed in Table 1.

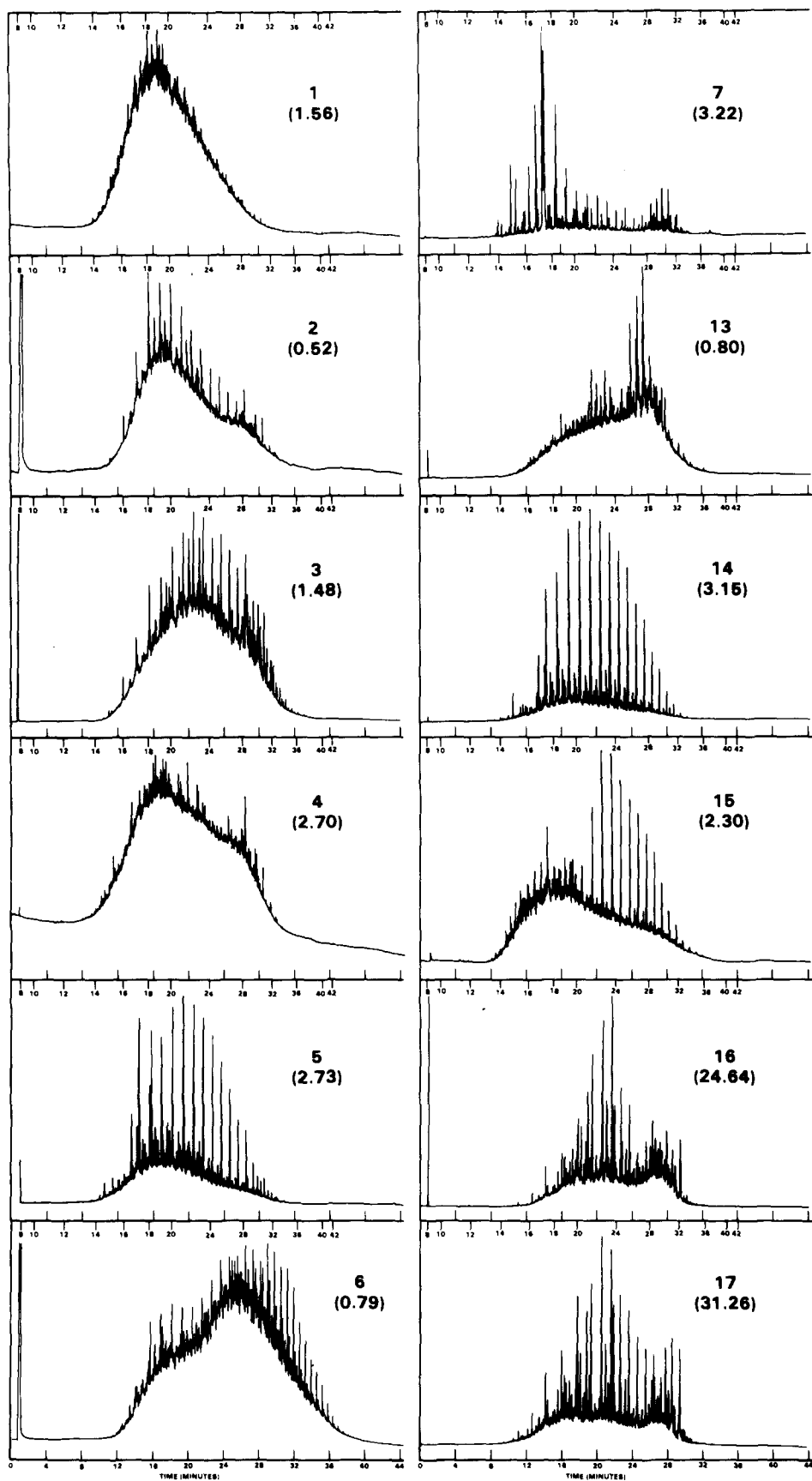


Fig. 9.

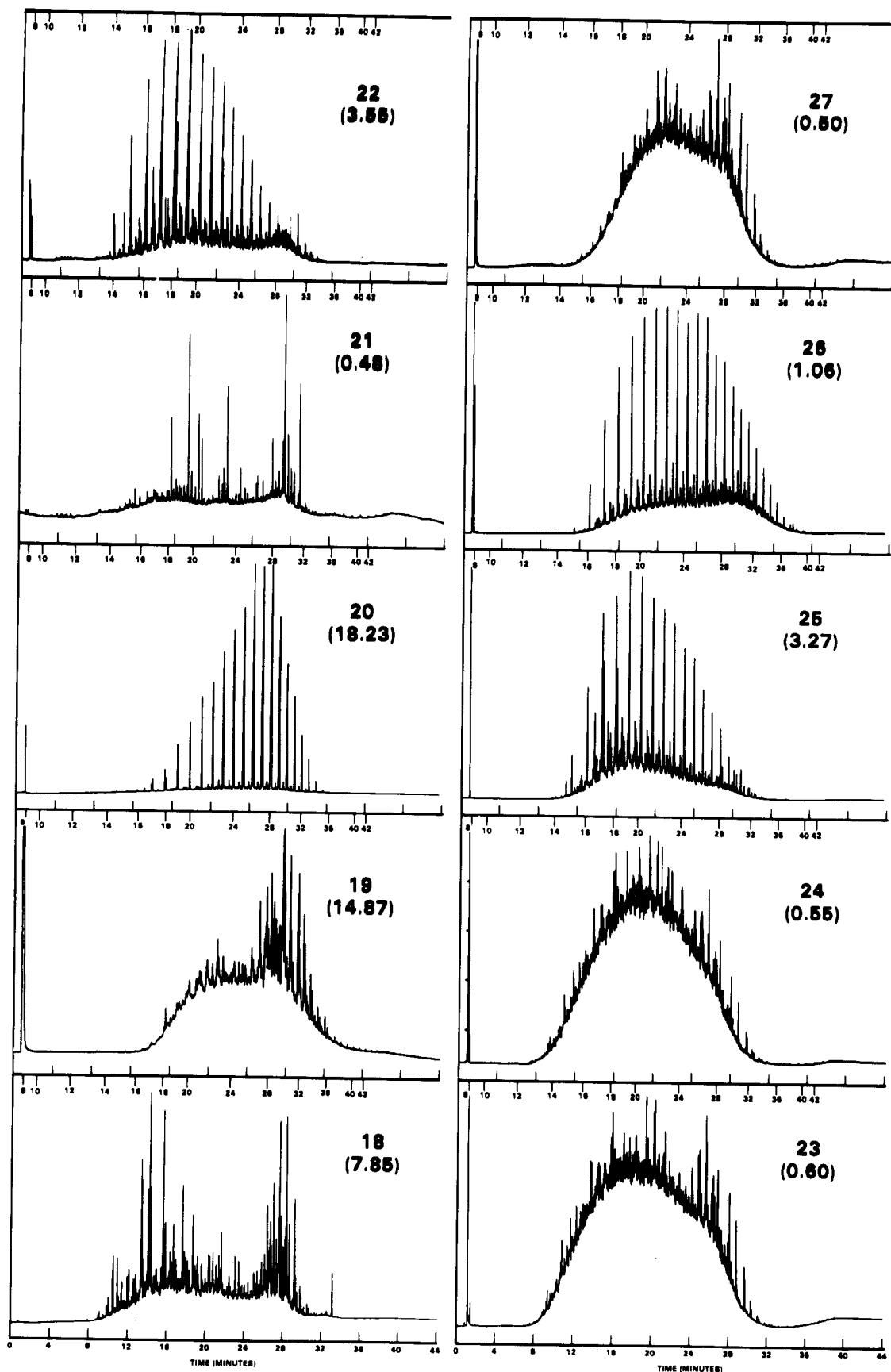


Fig. 9. High-resolution gas chromatograms of aliphatic hydrocarbons from the 22 non-uraniferous solid bitumens. See text for fractionation methods and run conditions. Carbon numbers for the *n*-alkanes are shown above each chromatogram, at the appropriate retention time. Also shown in parentheses are aliphatic/aromatic hydrocarbon ratios, for the 400–900°F distillate cut. Sample numbers correspond to those listed in Table 1.

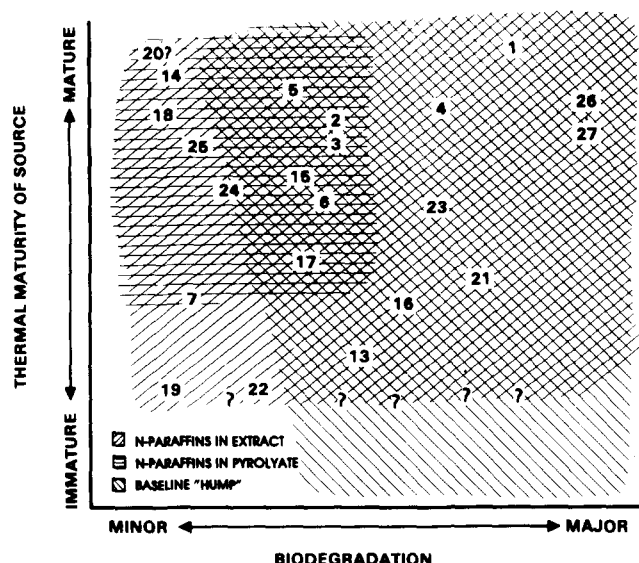


Fig. 10. Conceptual diagram illustrating the interrelationship of three chromatographic observations (occurrence of *n*-hydrocarbons in pyrograms and chromatograms, and the presence of a baseline "hump") with two geochemical processes, thermal maturation and biodegradation. Data are derived solely from inspection of extractable aliphatic hydrocarbon gas chromatograms and whole solid bitumen pyrograms. Numbers shown are the sample numbers listed in Table 1. This diagram is meant to be a conceptual rationalization of the chromatographic observations, and applies only to the solid bitumen set examined.

major exception, sample 20, may be the result of an unusual, localized source facies), although the possibility of further thermal maturation subsequent to the time of sourcing indicates that this need not necessarily be the case. The importance of Fig. 10 lies in its conceptual simplicity, and its ability to assign process-influenced geochemical characteristics to chromatographic observations. While the diagram does not implicitly provide genetic conclusions, the applications of this concept will be useful to later discussions of solid bitumen origins.

#### RESULTS—BIOLOGICAL MARKERS

Distributions of the common alicyclic and aromatic biological markers (steranes, aromatized steranes and terpanes) in the molecular-sieved gasoil hydrocarbons (Fig. 2) from several non-uraniferous samples were determined. Results are presented as "biomarker fingerprints," derived by area integration of the *m/z* 191, 217, 231 and 253 mass chromatograms. Relative uncorrected mass spectrometric responses are presented, normalized to the compound having the highest ion fragment area response. All samples were run at the same gas chromatographic-mass spectrometric conditions (after Curiale *et al.*, 1985; total hydrocarbons, MID runs) within a few days of one another; secondary ion fragmentation is considered to remain constant from run to run, for the same compound (Curiale, in prep). An example of the biomarker fingerprints to be used is given in Fig. 11. The distribution of 58 biological marker compounds is presented, including (from left to right in Fig. 11) six  $13\beta,17\alpha$ -diasteranes having 27–29 carbon atom skeletons; 15 regular steranes having

27–29 carbon atom skeletons; 8 monoaromatic steroid hydrocarbons; 5 triaromatic steroid hydrocarbons; 13 tricyclic terpanes from  $C_{20}$ – $C_{30}$ , excluding  $C_{22}$  and  $C_{27}$ , and including separate peaks for each epimer from  $C_{26}$ – $C_{30}$ ; and 11 pentacyclic terpanes, from  $C_{27}$ – $C_{32}$ , including separate peaks for each epimer from  $C_{31}$ – $C_{32}$ . Within each biomarker class separated in Fig. 11, specific biomarker compounds are listed from left to right in order of elution from a conventional non-polar gas chromatographic column (DB-5; Curiale *et al.*, 1985). The particular compounds shown are listed in the caption to Fig. 11.

Biomarker fingerprints for solid bitumen extracts containing enough hydrocarbons for separation and GCMS analysis are shown in Fig. 12. Although these samples cover a wide range of biomarker distributions, certain sample-to-sample similarities are apparent. For example, all grahamites examined (samples 2–5, 14, 25) show higher relative amounts of terpanes than steranes, with monoaromatic steroids absent in most cases. In contrast, three samples (the Monterey asphalt and Mexican gilsonites, 13, 23, 27) show a biomarker fingerprint dominated by monoaromatic steroid hydrocarbons. In general, where terpanes dominate, the amount of pentacyclic terpanes exceeds that of tricyclic terpanes, although three exceptions are noted, all of which are associated with the Green River Formation in Colorado and Utah: sample 16 (albertite), sample 17 (ingramite) and sample 19 (gilsonite).

Despite the distinctive features of certain of the fingerprints in Fig. 12, it is clear that these distributions cannot be used to uniquely source-correlate the

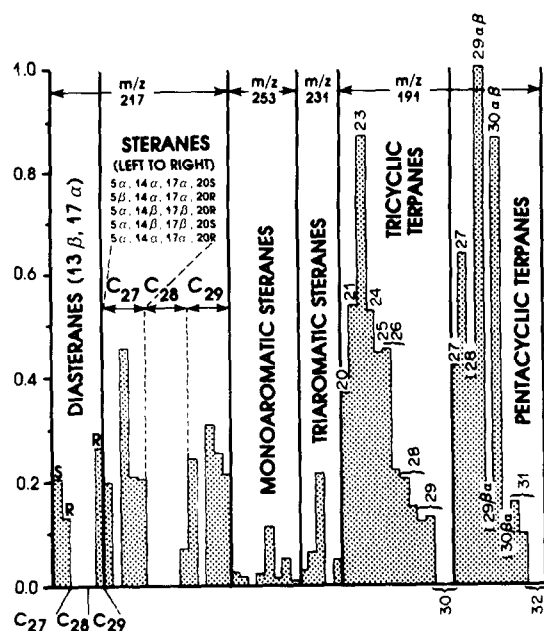


Fig. 11. Histogram ("biomarker fingerprint") showing the relative distribution of fifty-eight biological markers. Within each class, compounds are shown in order of elution (left to right) from a non-polar gas chromatographic column (DB-5). Eight monoaromatic sterane peaks are shown:  $5\beta, 20S-C_{27}$ ,  $5\beta, 20R-C_{27}$ ,  $5\alpha, 20S-C_{27}$ ,  $5\beta, 20S-C_{28}$ ,  $5\alpha, 20R-C_{27} + 5\alpha, 20S-C_{28} + 5\beta, 20R-C_{28} + 5\beta, 20S-C_{29}$ ,  $5\alpha, 20S-C_{29}$ ,  $5\alpha, 20R-C_{28} + 5\beta, 20R-C_{29}$  and  $5\alpha, 20R-C_{29}$ . The five triaromatic steranes peaks are  $20S-C_{26}$ ,  $20R-C_{26} + 20S-C_{27}$ ,  $20S-C_{28}$ ,  $20R-C_{27}$  and  $20R-C_{28}$ . Thirteen tricyclic terpanes ( $C_{20}$ ,  $C_{21}$ ,  $C_{23}$ ,  $C_{24}$ ,  $C_{25}$ , and both epimers of  $C_{26}$ ,  $C_{28}$ ,  $C_{29}$  and  $C_{30}$ ) and eleven pentacyclic terpanes [ $18\alpha(H)-22, 29, 30$ -trishomohopane,  $17\alpha(H)-22, 29, 30$ -trishomohopane,  $17\alpha(H), 21\beta(H)-28, 30$ -bishomohopane,  $17\alpha(H), 21\beta(H)-29$ -norhopane,  $17\beta(H), 21\alpha(H)-29$ -normoretane,  $17\alpha(H), 21\beta(H)$ -hopane,  $17\beta(H), 21\alpha(H)$ -moretane, and the S & R C-22 epimers of  $17\alpha(H), 21\beta(H)$ -homo- and bishomohopane] are also shown. This display shows relative distributions only (see text).

solid bitumens. For example, sample 6, an impsonite from southeastern Oklahoma, almost certainly has a common source with the grahamites from this area (Curiale, 1981, 1983), yet their fingerprints are clearly different. Also, while samples 7 and 22, both Uinta Basin gilsonites, have similar fingerprints, as expected, another gilsonite from the area (sample 19) is distinctly different. It is clear that the fingerprints in Fig. 12 are not entirely a function of source, but also exhibit subsequent migration/alteration overprints.

One biomarker parameter commonly invoked as a source-related indicator is the carbon number distribution of the  $5\alpha, 14\alpha, 17\alpha, 20R$ -steranes (Mackenzie *et al.*, 1983). For the solid bitumen extracts of the present study, it is clear (Fig. 13) that the commonly-sourced character of the grahamites from southeastern Oklahoma (Curiale, 1983) support the utility of this indicator. However, three solid bitumens associated with, and most probably sourced from the Green River Formation (Hunt, 1963; circled points in Fig. 13) have widely differing carbon number

distributions. Several explanations are possible, including different organic facies within the Green River (sample 17 is from the lowermost Green River, while samples 22 and 7 are from the uppermost Green River), alteration during migration and/or maturation, biodegradation subsequent to sourcing, etc. It is apparent that this most commonly used biomarker source indicator is of limited use as such for bitumen extracts.

One possible explanation for both the wide variation in solid bitumen biomarker fingerprints (Fig. 12) and the Green River bitumen carbon number distributions (Fig. 13) is variability in the extent of thermal maturation, either of the sourcing unit or the reservoir rock. It is apparent from H/C atomic ratios and carbon aromaticities that wide maturity ranges exist in these samples (Tables 3 and 5). That these parameters do indeed reflect maturity variation (rather than facies or alteration differences) is supported by their good correlation with conventional biomarker maturation parameters (Table 6). The plot in Fig. 14 shows the relationship between H/C atomic ratios of the total solid bitumen, and the 20S/20R ratio of  $5\alpha, 14\alpha, 17\alpha$ -24-ethylcholestanes in the extractable hydrocarbons. A clear correlation ( $r = 0.77$ , excluding sample 20—see caption to Fig. 14) is evident, with 20S/20R ratios approaching an equilibrium value of 1.1–1.2 in the Canadian albertite and Oklahoma grahamites.

It is apparent that the sterane carbon number distribution trends for the three solid bitumens associated with the Green River Formation are consistent with changes in H/C ratios and biomarker maturity parameters. The trend to increasing  $5\alpha, 14\alpha, 17\alpha, 20R$ -methylcholestane content shown in

Table 6. Maturity-related biological marker ratios

Sample	a	b	c
1	ND	ND	ND
2	0.69	0.50	0.15
3	1.01	0.48	0.12
4	1.14	0.55	0.07
5	0.91	0.45	0.10
6	ND	ND	ND
7	0.53	0.19	0.18
13	ND	ND	ND
14	0.84	0.61	0.09
15	ND	ND	ND
16	ND	ND	ND
17	0.18	ND	0.24
18	1.08	0.39	0.10
19	ND	ND	ND
20	0.68	0.32	0.08
21	ND	ND	ND
22	0.43	0.23	0.20
23	0.83	0.50	ND
24	ND	ND	ND
25	0.88	0.46	0.09
26	ND	ND	ND
27	0.66	0.59	ND

(a)  $20S/20R-5\alpha, 14\alpha, 17\alpha$ -ethyl-cholestane.

(b)  $(14\beta, 17\beta, 20R + S)/(14\beta, 17\beta, 20R + S + 14\alpha, 17\alpha, 20R + S)$ -ethylcholestane.

(c)  $(17\beta, 21\alpha)/(17\beta, 21\alpha + 17\alpha, 21\beta)$ -hopanes ( $C_{29}, C_{30}$ ).

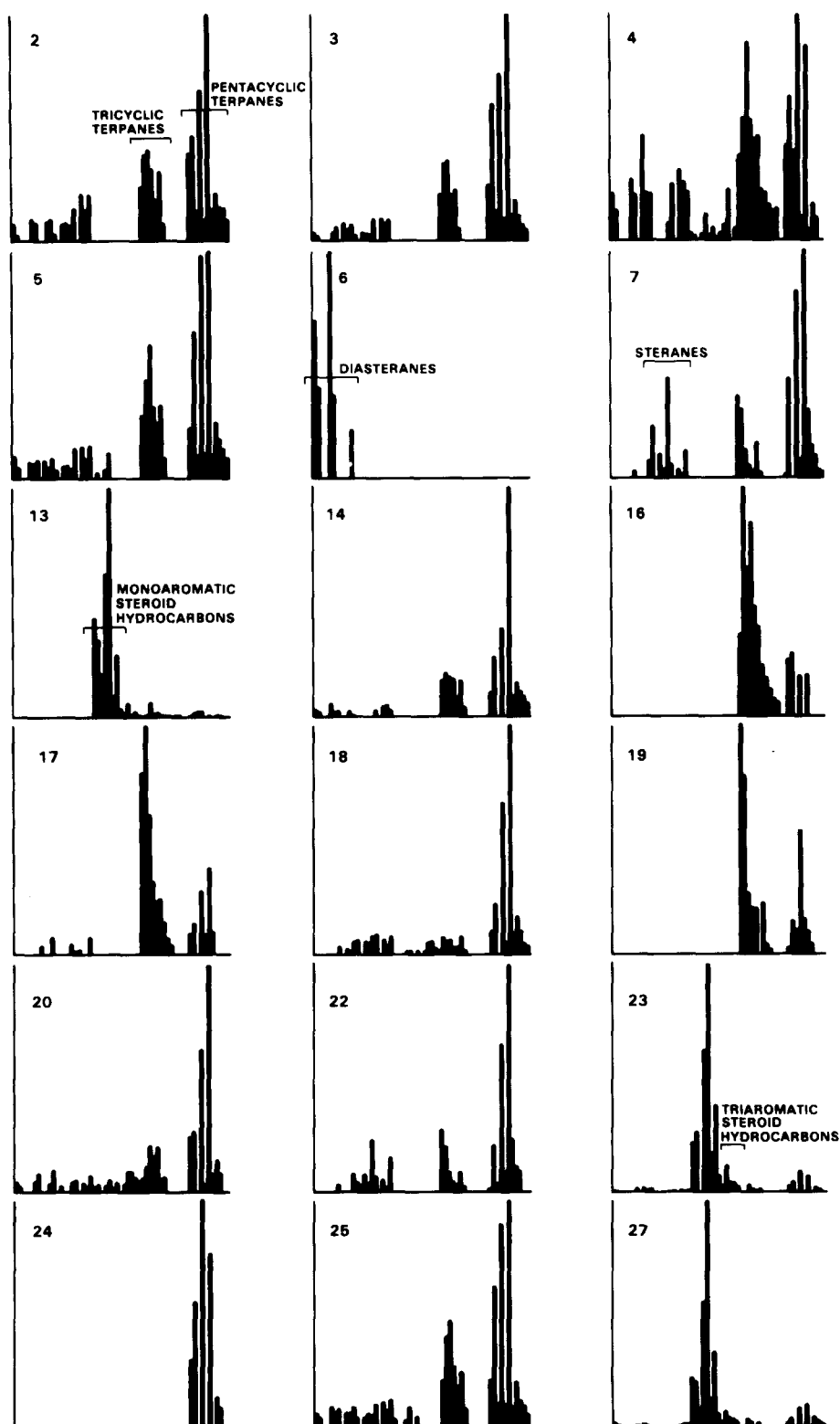


Fig. 12. Biomarker fingerprints for eighteen solid bitumen extracts. Sample numbers correspond to those given in Table 1. See caption to Fig. 11 for a listing of the 58 biological marker compounds shown.

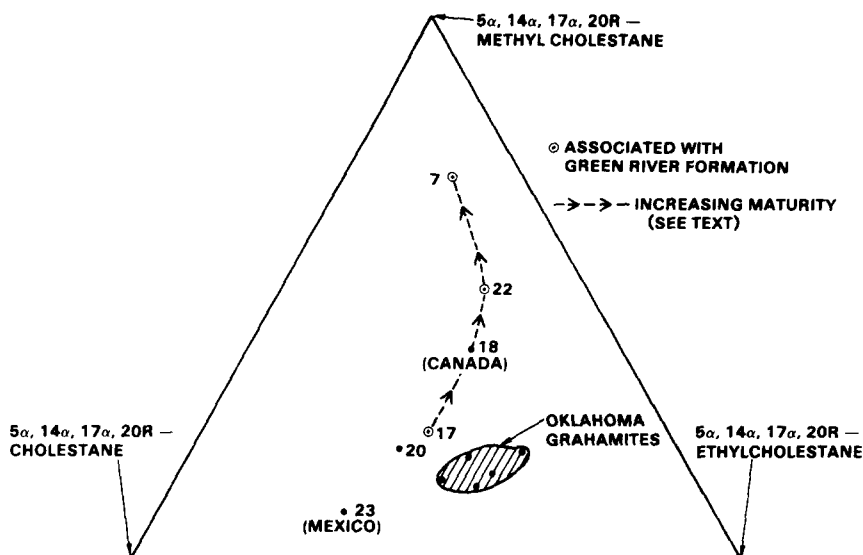


Fig. 13. Ternary diagram showing the distribution of  $5\alpha,14\alpha,17\alpha,20R$ -cholestane (bottom left),  $5\alpha,14\alpha,17\alpha,20R$ -methylcholestane (top) and  $5\alpha,14\alpha,17\alpha,20R$ -ethylcholestane (bottom right) in selected solid bitumen extractable organic matter. Dashed line shows the direction of increasing rank level (as determined by H/C ratios and aromaticities) for samples associated with the Green River Formation of the Uinta Basin (circled). The Oklahoma grahamites fall into a tight cluster, considered to be source-related (Curiale, in prep.). Sample numbers correspond to those in Table 1.

Fig. 13 for the three Green River-associated bitumens (17—22—7) parallels the trend in increasing maturity for these three samples shown in Fig. 14: the ingramite, 17, is the least mature, while a gilsonite, 7,

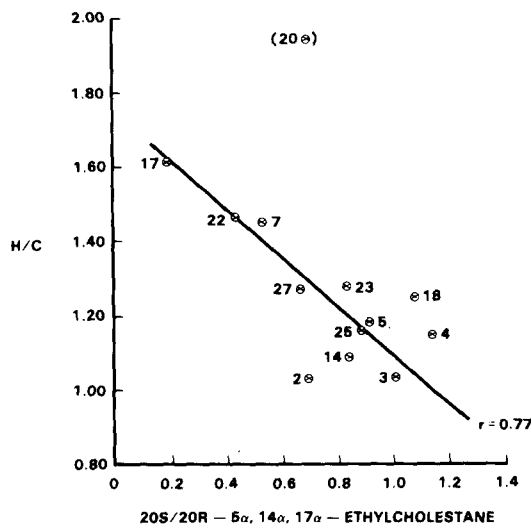


Fig. 14. H/C atomic ratios vs  $20S/20R-5\alpha,14\alpha,17\alpha-24$ -ethylcholestane ratios. Sample numbers correspond to those listed in Table 1. Sample 20 is clearly unrelated to the other solid bitumens; this sample has not been used in the calculation of correlation coefficients in this and subsequent figures. While the highly paraffinic nature of this ozocerite may suggest extensive migration and/or thermal maturation, the H/C ratios and  $f_a$  values indicate extreme immaturity. Most likely, early generation from an unusual source facies is responsible, probably involving the Type III kerogen of the Wasatch Formation (Anders and Gerrild, 1984).

is the most mature. This observation implies that problems may exist in the use of sterane ternary diagrams to assess common source character of immature solid bitumens (H/C greater than 1.3), inasmuch as it appears that sample position on diagrams such as that in Fig. 13 are a partial function of thermal maturity (Mackenzie, 1984, p. 191). It is possible that, for samples sourced from similar organic facies (as is the presumption for the Green River ingramite and gilsonites in Fig. 13), maturity trends are derivable from sterane carbon number plots.

The wide range of maturities for this sample set allows a unique opportunity to compare different sterane-terpane maturity indices (Table 6). The most striking comparison is that between the  $20S/20R$  ethylcholestane epimer ratio and the ratio of moretanes to hopanes (Fig. 15,  $r = 0.95$ , excluding sample 20). As expected, increasing  $20S/20R$  values accompany decreasing moretane/hopane ratios (Schoell *et al.*, 1983), although it is surprising that this relationship holds for a sample set having such obvious source variability. Interestingly, the maturity order of the three Green River-associated samples exhibited by the H/C- $20S/20R$  relationship of Fig. 14 is also clearly apparent in the moretane/hopane ratios of Fig. 15.

In addition to sterane epimerization ( $20S/20R$ ) and moretane  $\rightarrow$  hopane conversion, isomerization of steranes at the C-14 and C-17 positions is often cited as a maturity parameter (Ji-Yang *et al.*, 1982, and references therein). For the present sample set, the ratio  $14\beta,17\beta/(14\alpha,17\alpha + 14\beta,17\beta)$  increases with increasing aromaticity and decreasing H/C ratio (Fig.



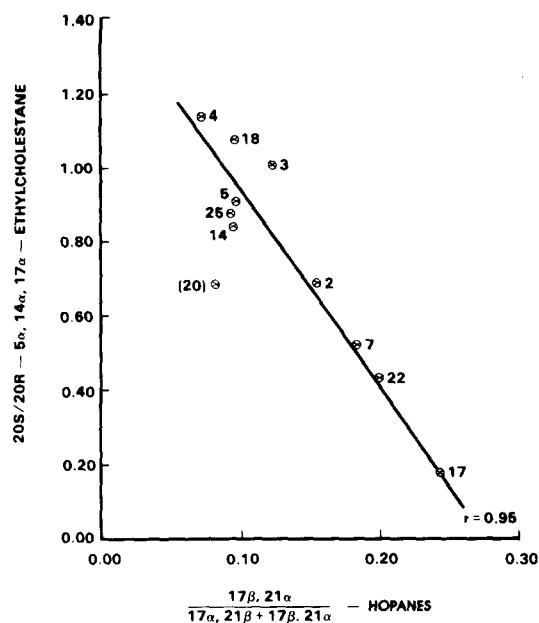


Fig. 15. 20S/20R-5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -24-ethylcholestane vs 17 $\beta$ (H),21 $\alpha$ (H)/(17 $\beta$ (H),21 $\alpha$ (H) + 17 $\alpha$ (H),21 $\beta$ (H)) ratio (moretane/moretane + hopane). See caption to Fig. 14 for a discussion of sample 20. Sample numbers correspond to those listed in Table 1.

16). This  $\beta\beta/\alpha\alpha$  ratio (derived for both C-20 epimers of the ethylcholestanes) appears to reach an equilibrium value of 0.60–0.65 at aromaticities and H/C ratios approaching 0.5 and 1.00, respectively. While the correlation coefficients for these relationships ( $r = 0.74$  for both, excluding sample 20) are less than those for maturity relationships involving only bio-

markers (Fig. 15), they are similar to that of the H/C vs 20S/20R plot (Fig. 14).

In general then, three biological marker ratios (Table 6: 20S/20R-ethylcholestanes; moretane/hopane;  $\beta\beta/\alpha\alpha$ -ethylcholestanes), H/C atomic ratios and NMR-derived carbon aromaticities suggest the same approximate maturity ordering for these solid bitumens. Samples associated with the Green River Formation (excluding sample 20) are generally the least mature, whereas the Pennsylvania and Oklahoma grahamites are most mature. It would appear that the ingramite, albertite and gilsonite from the Green River Formation have been sourced at much lower maturity levels than the grahamites, a suggestion that will be pursued in more detail below.

Comparison of data in Tables 4 and 6 reveals curious relationships between two biomarker maturity parameters and the whole bitumen V/(V + Ni) ratio, which are shown in Fig. 17. Correlation coefficients ( $r$ ) for moretane/hopane vs V/(V + Ni), and  $\beta\beta/\alpha\alpha$  vs V/(V + Ni), are 0.71 and 0.87, respectively. While these observations appear to invoke a maturity-dependence for the V/(V + Ni) ratio, the strong bimodal distribution of this ratio (first mode, 0.0–0.2; second mode, 0.5–0.9) suggests that this relationship may be simply fortuitous, as would also be implied by the fact that the low-V/(V + Ni), low-maturity samples are all associated with the Green River Formation. The low V/(V + Ni) ratio of organic matter from this formation has been established (Lewan, 1980, 1984). This would suggest that the V/(V + Ni) ratio is not maturity-dependent, but rather is simply low in the Green River samples, which happen to represent the only low-maturity

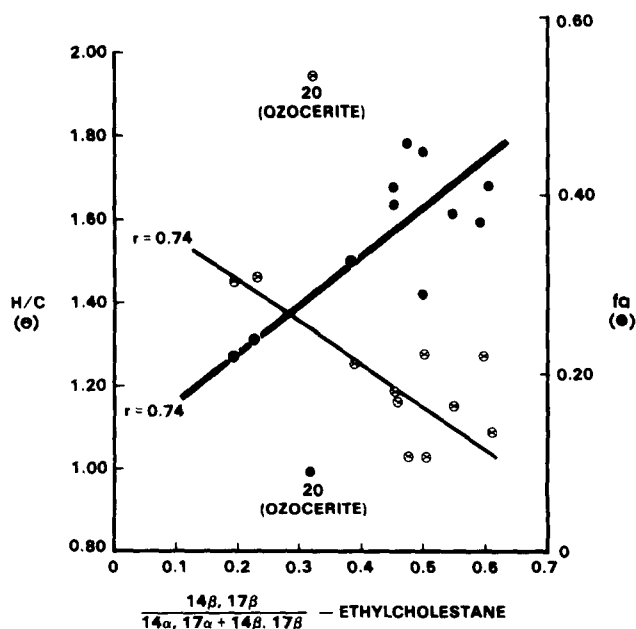


Fig. 16. Rank level (H/C on left,  $f_a$  on right) vs 14 $\beta$ ,17 $\beta$ /(14 $\alpha$ ,17 $\alpha$  + 14 $\beta$ ,17 $\beta$ )-24-ethylcholestane ratios. This sterane isomer ratio increases to an equilibrium value of about 0.6–0.7 with increasing (decreasing)  $f_a$  (H/C). See caption to Fig. 14 for a discussion of sample 20 (ozocerite).

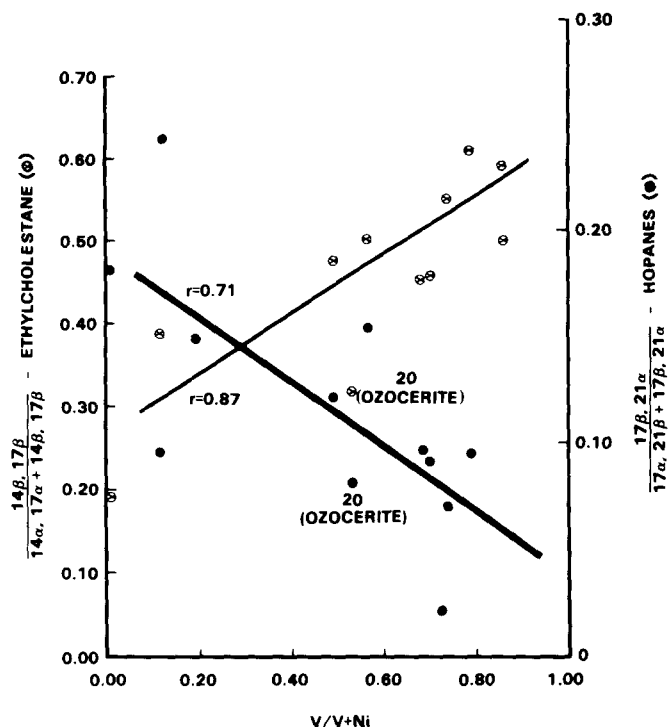


Fig. 17. Biomarker isomer ratios in extractable hydrocarbons vs  $V/(V + Ni)$  ratio in whole solid bitumen. The  $14\beta, 17\beta/(14\alpha, 17\alpha + 14\beta, 17\beta)$  ratio is on the left; the  $17\beta(H), 21\alpha(H)/(17\beta(H), 21\alpha(H) + 17\alpha(H), 21\beta(H))$  ratio is on the right. Note the bimodal  $V/(V + Ni)$  ratio for this sample set. See caption to Fig. 14 for a discussion of sample 20 (ozocerite).

samples studied. These observations point out the pitfalls encountered with limited sample sets.

#### DISCUSSION

The results presented above make it clear that the trivial names assigned to solid bitumens, based upon physical characteristics and H/C ratios (Fig. 1), are inadequate for anything more than a cursory classification of these materials. Further, these names contain little genetic information content. It would be advantageous to petroleum explorationists to abandon this generic classification scheme in favour of a genetic convention, based either on thermal maturity or the related issue of the time of expulsion of the organic matter from the source rock, as with other petroleum products. (Indeed, we do not "name" oils—why should we name solid bitumens?) Such a scheme would fall naturally into the pre-oil vs post-oil dichotomy expressed in the early days by Brooks (1936) and Taff (1909), and touched upon since by Silverman (1964, 1978), Curiale (1981, 1983) and others. The pre-oil vs post-oil nomenclature has intuitive appeal, in that it derives from the field observation that solid bitumens are invariably associated with crude oil and/or crude oil source rocks (Abraham, 1945, and ancient literature cited therein). Under such a scheme (Fig. 18), pre-oil solid bitumens are early-generation products of rich source

rocks, probably extruded from their sources as a very viscous fluid, and migrated the minimum distance necessary to reach fractures and voids in the rock. This appears to correspond to the "explosive" migration discussed by Jones (1984) for carbonate source rocks. In contrast, post-oil solid bitumens are products of the alteration of a once-liquid crude oil, generated and migrated from a conventional oil source rock, and subsequently degraded (Khalimov *et al.*, 1983). The results discussed earlier, particularly those which assess thermal maturity of the source, provide strong evidence for such a genetic classification scheme, structured within a pre-oil vs post-oil framework.

The most immediate difficulty in categorizing specific solid bitumens as pre- vs post-oil involves separating the process of generation from that of alteration which occurs after generation (Fig. 18). This question was addressed earlier in conjunction with categorizing gas chromatographic data based on extent of maturation and biodegradation. The problem of the presence/absence of biodegradation or other forms of alteration can be entirely avoided however, if maturation parameters that are not strongly dependent upon non-thermal secondary alteration are discussed. In conjunction with solid bitumens, these include H/C atomic ratios, NMR-derived carbon aromaticities and biological marker epimerization and (possibly) isomerization. Using

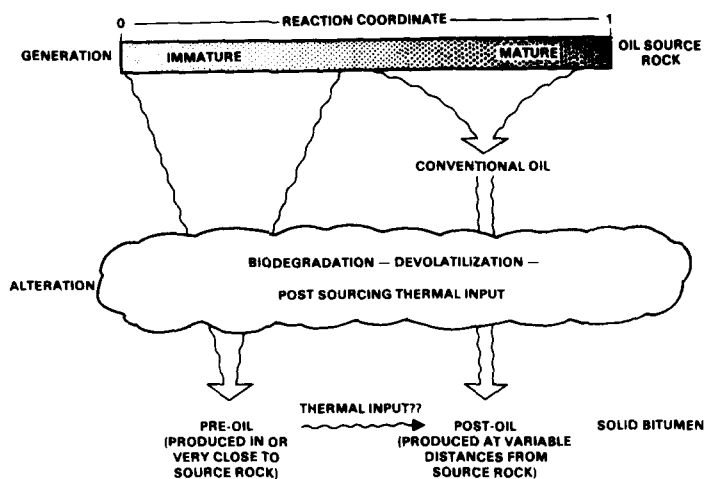


Fig. 18. Schematic drawing showing the mechanism for production of pre-oil and post-oil solid bitumens. Generation occurs in an oil source rock at a particular maturity level, measured by an ideal reaction coordinate ranging from one to zero (Curiale *et al.* In press). Generation from a mature source produces a conventional liquid oil. Both conventional oils and early-generated and expelled source rock organic matter are then subject to the various alterations shown.

these parameters, an assessment of maturity can be made that is independent of subsequent alteration of the organic matter, and thus a pre-oil vs post-oil assignment is possible.

If we recognize solid bitumen (according to our "allochthonous" definition) as being organic matter that has migrated away from a sourcing zone to a fracture/fissure trap, then the biological marker parameters commonly used to assess maturity of crude oils should apply. Specifically, as in the case of crude oils, "maturity" of a solid bitumen will be defined here as the sum of the thermal input to the organic matter that is acquired (a) in the source rock and (b) during and after migration from the source rock. Thus a thermally immature solid bitumen must necessarily have come from a thermally immature source unit. Further, because of the internal consistency among the biomarker maturity parameters, H/C ratios and aromaticities (Figs 14–16), these parameters can be collectively used to support conclusions concerning the maturity of these samples. Once this maturity level is established, the pre-oil vs post-oil question will be resolved, and the question of the nature of subsequent changes in the organic matter can be addressed.

Excellent solid bitumen and extract-derived assessments of solid bitumen maturity can be made from Figs 7 and 15, respectively. The continuity in the H/C vs  $f_a$  relationship shown in Fig. 7 makes it clear that, neglecting post-sourcing maturation and biodegradative effects on these parameters, these solid bitumens have originated from a suite of source rocks having a continuous wide range of maturities, making a pre-oil vs post-oil separation somewhat arbitrary for this sample set. Nevertheless, it is clear from both figures that the solid bitumens group

consistently into two maturity ranges: all Oklahoma, Pennsylvania and Spanish bitumens are consistently of greater maturity than all Utah, Colorado, California, Mexico and Canada bitumens. It is noteworthy that these two maturity-related groups cleanly divide grahamites from gilsonites, even though both are classified together under the generic scheme (Fig. 1). Conversely, the groups do not divide pyrobitumens from other solid bitumens, even though pyrobitumens are distinctly separate in the generic scheme. It is clear that no consistent overlap exists between the classical generic scheme and the proposed genetic scheme.

The continuity of maturation levels among these samples is also recognized from the biological marker maturity parameters (Figs 14–16). However, because of the applicability of biomarker data in assessing the thermal maturity of oils (Philp, 1985), these data may be much more useful than H/C ratios or aromaticities in evaluating the pre-oil vs post-oil genesis of these solid bitumens. It is known that the 20S/20R-ethylcholestane ratio of a crude oil is rarely less than 0.6 (Seifert and Moldowan, 1981; Curiale *et al.*, 1985), providing strong evidence for so-called classically immature oil in such instances. The correlation for solid bitumens shown in Fig. 14 provides an H/C ratio (for this 20S/20R ratio) of about 1.3 which, for source rock kerogens, equates to a vitrinite reflectance (VR) value of about 0.5% for a Type II kerogen (Tissot and Welte, 1978). This VR value is often invoked as presaging the onset of thermal generation of hydrocarbons in oil source rocks, and it is therefore reasonable to assign an "immature" status to solid bitumens falling below this maturity level. On this basis, at least three of the Green River-associated samples, 7, 17 and 22 (Table 1), can

be regarded as immature, and therefore pre-oil, whereas the Oklahoma, Pennsylvania and Canada samples can be considered mature, and therefore post-oil. The two Mexican samples in Fig. 14 appear to be marginally mature. That is, three of the Green River-associated solid bitumens are considered early-generation products of their source, while the grahamites and Canadian albertite appear to have been sourced from a mature source rock. Extrapolating these data to their immature and postmature extremes (Fig. 7), it would then follow that the uraniferous nodules and the two imponsites can be classed as post-oil, while the Monterey asphalt is pre-oil (Curiale *et al.*, 1985).

These conclusions, based entirely on H/C ratios, aromaticities and biomarker maturity parameters, are generally consistent with maturation/biodegradation conclusions discussed earlier, derived solely from gas chromatographic (GC) data. For example, based on *n*-hydrocarbon data in whole bitumen pyrolyzates and in aliphatic fractions, Oklahoma, Canada and Pennsylvania samples are considered thermally mature, while the Monterey asphalt and Green River-associated samples are considered immature. The major exception to this consistency is sample 17, listed as immature based on biomarker, H/C and aromaticity data, yet classified as mature based solely upon GC data. Because the distinction between pre-oil vs post-oil solid bitumens is decidedly maturity-related, sample 17 must be considered as immature, suggesting that GC *n*-hydrocarbon data, while usually definitive, cannot be exclusively relied upon.

#### GENERIC VS GENETIC

The genetic classification scheme proposed here, whereby solid bitumens are assigned a position on a continuum between pre-oil and post-oil maturity levels (Fig. 18), has several advantages over the classical generic classification scheme (Fig. 1). Firstly, knowledge of the maturity of a solid bitumen's source rock could be a useful addition to our understanding of a basin. Secondly, because migration distance may be a function of genesis, knowledge of a solid bitumen's origin could provide information useful in source rock identification. And finally, because the proposed genetic classification scheme is phenomenological in nature, the classification of a solid bitumen can now be regarded as a by-product of routine modern organic geochemical analysis, as with any other oil.

A hierarchical description of the proposed genetic scheme is present in Fig. 19. The initial classification is made based on derivation from oil source rocks, followed by a pre-oil vs post-oil split for oil source rock-derived solid bitumens, including inferences concerning migration distance. These inferences are based solely on the notion that organic matter that is generated thermally early from a source rock would

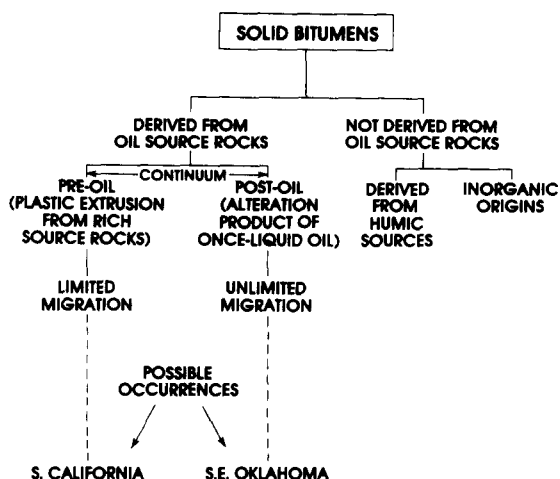


Fig. 19. Proposed genetic classification scheme for solid bitumens, showing the separation of oil source rock-derived solid bitumens into those generated pre-oil and those generated post-oil. The resultant implications for migration distance, as well as the geochemical basis for the distinction, are discussed in the text.

be rich in heteroatom content, viscous, and not susceptible to long flow distances (Welte, 1965; Silverman, 1978; Tannenbaum and Aizenshtat, 1985). This idea has some empirical basis for the samples of this study, inasmuch as (a) the Green River-associated solid bitumens (pre-oil) are all located within the Green River Formation (Hunt, 1963), and the Monterey asphalt (pre-oil) is located within the Monterey Formation (i.e. each in their presumed source rock), whereas (b) the grahamites and imponsites of Oklahoma (post-oil) are reser-voired in Carboniferous rocks, yet sourced from Ordovician rocks (Curiale, 1981, 1983). Thus it seems that pre-oil solid bitumens are found still intimately associated with their source rock, whereas post-oil solids can be reservoired extended distances away from the source rock, being limited only by the migration distance of the oil that eventually altered to produce the solid bitumen.

The generic classification scheme shown in Fig. 1 was derived prior to the advent of modern geochemical analytical methods, such as high resolution gas chromatography and computerized-gas chromatography-mass spectrometry (Abraham, 1945), and is therefore based entirely on elemental analysis, carbon disulfide solubility, and fusibility. It undoubtedly has a certain utility to those interested in the technological uses of solid bitumens (as paving materials, sources of metals, etc.). Such utility is inapplicable to the problems of the petroleum geochemist, who is more often in need of an understanding of the origin and role of these materials in petroliferous basins. The genetic classification scheme proposed here is a preliminary effort in that direction.

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