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Hydrous pyrolysis of Monterey asphaltenes*

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Abstract—Hydrous pyrolysis of asphaltenes has been tested as a method to reconstruct the chemical composition of biodegraded oils and oil seeps. The asphaltenes of three oils (a nondegraded oil, a biodegraded oil, and a biodegraded oil seep) from the Monterey Formation were studied. Results show that the aliphatic fraction generated by hydrous pyrolysis is very similar in chemical composition to the nondegraded oil. This makes the method very useful in correlation studies of biodegraded and nondegraded oils. It also allows to roughly estimate the maturity of the source of the biodegraded oil or oil seep.

Key words: hydrous pyrolysis, asphaltenes, biomarkers, biodegradation, carbon isotopes, Monterey Formation

INTRODUCITON

Hydrous pyrolysis has become widely accepted in recent years as a tool for understanding the molecular structure of kerogen and for kerogen–crude oil correlation studies (Lewan *et al.*, 1979; Schiefelbein 1983). Rubinstein *et al.* (1979) have shown that unhydrous pyrolysis of asphaltenes from crude oils have yielded significant amounts of crude oil-like material that in some aspects was similar to the parent oil. A major dissimilarity to the parent oil was evident in the presence of unsaturated hydrocarbons (which are also generated in unhydrous pyrolysis of kerogen). Behar *et al.* (1984) and Huc *et al.* (1984) pyrolyzed at high temperatures (450–550°C) and under a flow of argon gas the asphaltic fractions of genetically related biodegraded and nondegraded oil pairs. Their results show that the distributions of the generated *n*-alkanes and *n*-alkenes are similar for each pair. In a study by Telnaes *et al.* (1985) it was demonstrated that hydrous pyrolysis of the asphaltic fraction of biodegraded and nondegraded oils results in the formation of hydrocarbons which may be similar in composition to the hydrocarbons in the original oil and at the same time prevents the formation of unsaturated compounds. The *n*-alkanes and steranes generated by pyrolysis at various temperatures were compared in that study to those present in the oils prior to pyrolysis. Their results show a somewhat complex situation: at relatively low pyrolysis temperatures (300–310°C) the steranes generated from a Green River Formation Gilsonite and from a nondegraded North Sea oil are very similar in composition to the steranes present in these samples prior to pyrolysis. Results also show that at low temperatures the *n*-alkanes generated from the asphaltenes of the nondegraded oil are very similar to the original *n*-alkanes. However, the *n*-alkanes and steranes in the pyrolysis products of a slightly biodegraded North Sea oil (this oil is genetically-related to the other North Sea oil) were significantly different from the *n*-alkanes and steranes of the nondegraded oil.

Although these results may suggest that hydrous pyrolysis (HP) of aspaltenes cannot be applied in correlation studies of biodegraded oils, examination of other genetically related biodegraded and nondegraded oils is necessary before the final conclusion is drawn. Analyzing the isotropic composition of the oil fractions before and after HP and other biomarkers besides steranes (such as tricyclic and pentacyclic terpanes) may also be helpful in establishing the applicability of the hydrous pyrolysis method to correlation studies as well as to the understanding of the molecular structure of asphaltenes.

The study presented here describes the results from the hydrous pyrolysis (HP) of the asphaltic fraction of three Monterey Formation oil samples. One sample (collected by Susan E. Palmer) is a severely biodegraded oil seep Point Arena Cove in Northern California (the asphaltenes of two subsamples—T4 and T5 were combined for HP). The other two samples are from the Santa Maria Basin in California and represent a nondegraded oil (Bell 24) and a biodegraded oil (Bell 92). Both samples are genetically related. Also the asphaltic fractions of the Bell 24 and Bell 92 oils were hydrous pyrolyzed in the presence of sodium montmorillonite to test the effect of mineral matter on the products. The Monterey Formation oils were selected for this study mainly because of the presence of a particular pentacyclic terpane [17α(H),18α(H),21β(H)-28,30-bisnorhopane] which is absent in the pyrolysis products of Monterey Formation kerogen (Tannenbaum *et al.*, 1986a; Palmer, personal communication). The disappearance of 17α(H),18α(H),21β(H)-28,30-bisnorhopane from the pyrolysis products of the asphaltenes would indicate that the asphaltenes act like soluble fragments of

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kerogen, while its presence would indicate that the released hydrocarbons are occluded in the asphaltic structure.

EXPERIMENTAL

The asphaltic fraction was isolated from the oils by precipitation in cold pentane overnight followed by thoroughly rinsing the precipitate in cold pentane to remove all hydrocarbons and NSO compounds. For the asphaltene–montmorillonite experiment, a portion of the isolated asphaltenes (pure asphaltenes) was dissolved in CCl_4 and mixed with sodium montmorillonite at a weight ratio of 1:20 (asph:mont). CCl_4 was then thoroughly evaporated. Both pure asphaltenes and asphaltenes–montmorillonite mixtures were subjected to hydrous pyrolysis for three days at 300°C in Pyrex-lined Parr bombs. About 500 mg of asphaltenes were pyrolyzed in excess distilled water. Experiments were rendered successful if some water was present in the bomb at the end of the experiment. Following pyrolysis, the products were dried and soxhlet-extracted with a 9:1 chloroform:methanol mixture. The organic extracts were deasphalted in cold pentane overnight and then separated into the three standard C_{15+} fractions (aliphatic, aromatic and NSO) by alumina/silca column chromatography (*n*-pentane, toluene and methanol were used to elute the respective fractions). The quantity of each fraction was determined gravimetrically. Stable carbon isotopic compositions of all four fractions were determined using the combustion method of Sofer (1980) with subsequent analysis on a VG Micromass 602D. All values were reported relative to the PDB standard and were corrected for ^{17}O contributions. Capillary gas chromatographic separations of the aliphatic fraction were accomplished on a Hewlett–Packard 5880 gas chromatograph fitted with a 15 m × 0.25 mm fused silica column coated with SP2100. Combined gas chromatography–mass spectrometry was performed using a Kratos MS25 GC/MS/DS equipped with a SE54 30 m × 0.25 mm fused silica capillary column. GC/MS data were collected using the selective ion monitoring mode. Masses $m/z = 217$ (for steranes) and $m/z = 191$ (for terpanes) were monitored during the elution of the aliphatic fraction.

RESULTS AND DISCUSSION

Results for gross C_{15+} oil compositions and stable carbon isotopic compositions before and after pyrolysis are given in Table 1. Table 1 also contains isoprenoid ratios, carbon preference indexes (CPI's) and C_{29} 20S/20R sterane ratios. Gross composition results show that between 6 and 14% of the asphaltenes can be converted to some aliphatic and mostly aromatic hydrocarbons and NDO compounds. The results also show that the addition of montmorillonite enhances the formation of these compound groups. A similar enhanced formation has also been observed in pyrolysis of Monterey kerogen (Tannenbaum *et al.*, 1986b).

Gas chromatograms (GCs) of the C_{15+} aliphatic fraction and terpane and sterane mass chromatograms before and after HP, with and without montmorillonite, are shown in Figs 1–3. The *n*-alkanes of the Bell 92 oil have been affected by biodegradation (Fig. 2). After pyrolysis results show that the *n*-alkanes generated from pure asphaltenes of both the nondegraded and biodegraded oils (Figs 1 and 2, respectively) exhibit patterns very similar to the original *n*-alkanes of the nondegraded oil (Fig. 1) as well as to *n*-alkanes generated by dry pyrolysis of Monterey kerogen (Huizinga *et al.*, 1987). Pristane/phytane (Pr/Ph) ratios increase, however, from 0.5 to approximately 2.0. This is a common phenomenon in kerogen HP experiments where the pyrolysis products are compared to the original organic extract associated with the kerogen. The addition of montmorillonite produces *n*-alkanes distributions with lower even-over-odd-carbon predominances relative to the pure asphaltenes experiments (CPI values for the Bell 24 pyrolysate with and without montmorillonite are 0.915 and 0.976 respectively, and for the Bell 92 CPI values are 0.945 and 0.982 respectively). Also, Pr and Ph become less abundant and the Pr/Ph ratio increases to only 1.3–1.4 when montmorillonite is present.

Table 1. Geochemical data for Monterey samples

	Gross C_{15+} Composition				% C_{15+} Hydrocarbons			$\delta^{13}C$ (‰ PDB)						20S/20R Steranes	
Sample name	%Alk	%Aro	%NSO	%Asph	n-Alk	c-Alk	Aro	Alk	Aro	NSO	Asph	Pr/Ph	CPI	C_{27}	C_{28}	C_{29}
Bell 24 oil	21.1	37.2	13.5	28.2	14.4	21.8	63.8	-23.78	-23.55	-22.98	-22.96	0.55	0.876	0.78	0.64	0.80
Bell 24 asph HP	0.7	5.2	3.8	90.3	2.8	9.4	87.8	-24.14	-24.32	-23.01	-23.45	2.00	0.915	0.92	0.63	0.84
Bell 24 asph+mont HP	2.9	10.8	9.5	76.8	4.0	17.1	78.9	-24.42	-23.80	-23.94	-23.41	1.30	0.976	0.84	0.66	0.65
Bell 92 oil	29.1	27.6	24.8	18.5	11.0	40.3	48.7	-23.30	-23.07	-22.32	-22.86	0.85	1.117	0.78	0.40	0.62
Bell 92 asph HP	1.2	8.1	5.2	85.5	2.7	9.9	87.5	-23.92	-24.67	-22.35	-22.89	1.88	0.945	0.77	0.50	0.67
Bell 92 asph+mont HP	3.3	9.6	8.9	78.1	5.1	20.7	74.2	-24.29	-24.60	-24.03	-22.92	1.39	0.982	0.95	0.67	0.55
Monterey seep (T4)	9.5	28.0	25.4	37.2	2.8	22.6	74.7	-23.87	-22.70	-22.76	-22.88		0.865			
Monterey seep (T5)	15.2	26.8	26.7	31.3	2.9	33.2	63.9	-23.26	-22.94	-22.77	-22.52		1.442			
Monterey seep (T4+T5) asph HP	0.9	5.4	19.6	74.1	2.6	11.6	85.8	-23.90	-22.76	-22.23	-23.01	0.89	0.964	0.65	0.35	0.18

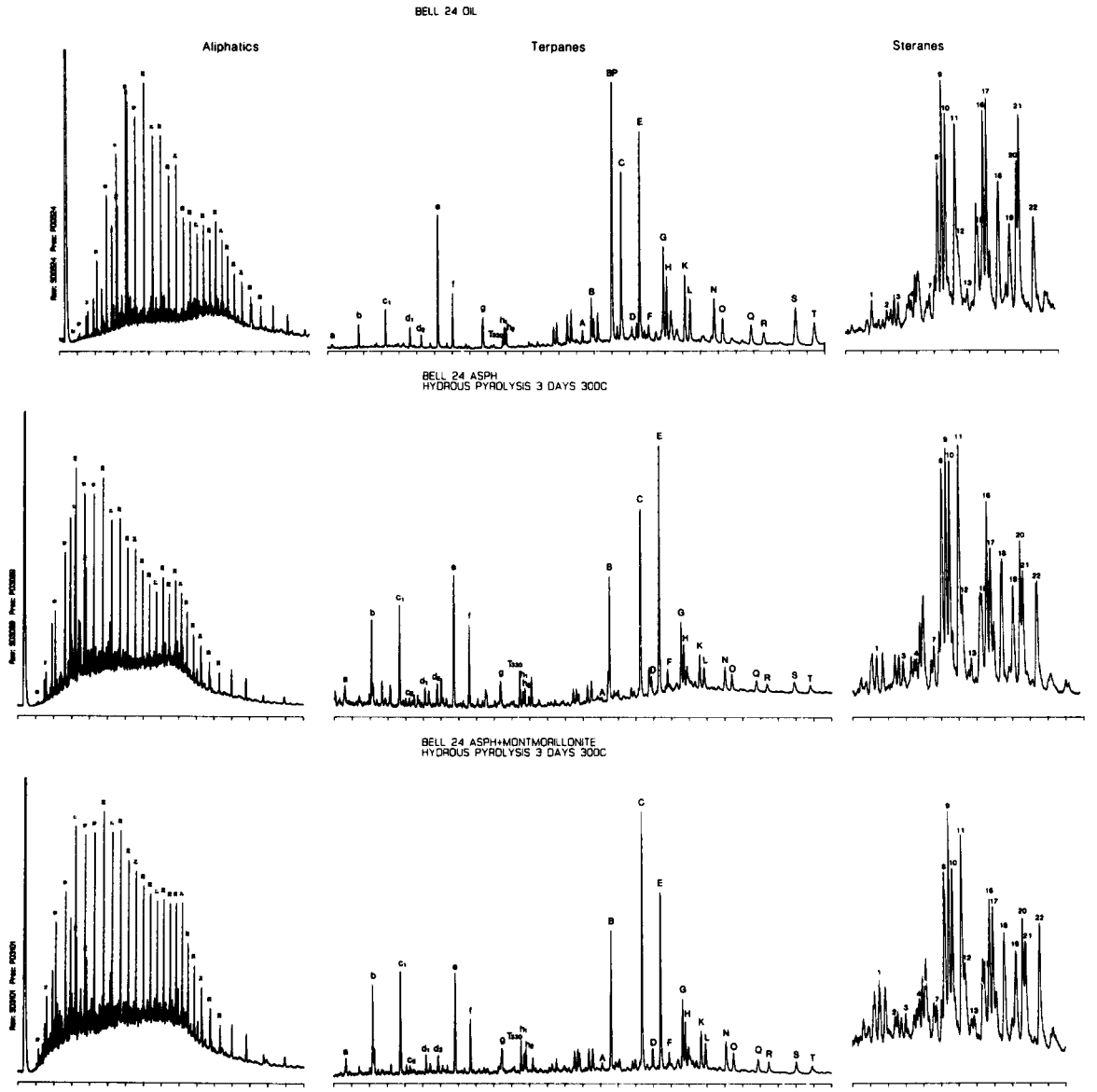

Fig. 1. Aliphatic GCs and terpane and sterane mass chromatograms for the Bell 24 sample.

The tricyclic and pentacyclic terpanes in the two Bell oils (see Table 2 for peak identification) show some significant changes after HP, however, these changes are similar in both samples. The C_{19}, C_{20}, C_{21} and C_{24} (peaks a, b, c_1 and f) tricyclic terpanes become more abundant relative to the C_{23} (peak e) tricylcic terpane, but the relative abundance of compounds a, b and c_1 and compounds g, h_1 and h_2 remains unchanged. Among the pentacyclic terpanes generated from the pure asphaltenes the 18α(H)-22 29,30-trisnorhopane (peak A) and the 17α(H),18α(H)21β(H)-28,30-bisnorhopane (peak BP) almost completely disappear, while the 17α(H)-22, 29,30-trisnorhopane (peak B) becomes more abundant. The increase in peak B has been observed in pyrolysis experiments of Monterey kerogen (Tannenbaum *et al.*, 1986a). The relationship between 17α(H),21β(H)-30-norhopane (peak C) and 17α(H), 21β(H)-hopane (peak E) remains unchanged, however, (i.e. peak E is larger than peak C).

The pentacyclic terpanes generated from the asphaltenes–montromorillonite experiments again show the absence of 17α(H), 18α(H), 21β(H)-28, 30-bisnorhopane (peak BP) while 17α(H)-22, 29, 30-trisnorhopane (peak B) becomes more abundant. However, a small 18α(H)-22, 29, 30-trisnorhopane (peak A) is present and 17α(H), 21β(H)-30-norhopane (peak C) is larger than 17α(H), 21β(H)-hopane (peak E). The possible significance of these results is discussed below.

17α(H), 18α(H), 21β(H)-28, 30-bisnorhopane (peak BP) and 18α(H)-22, 29, 30-trisnorhopane (peak A) should be present in the pyrolysis products if they were occluded in the asphaltic molecular structure.

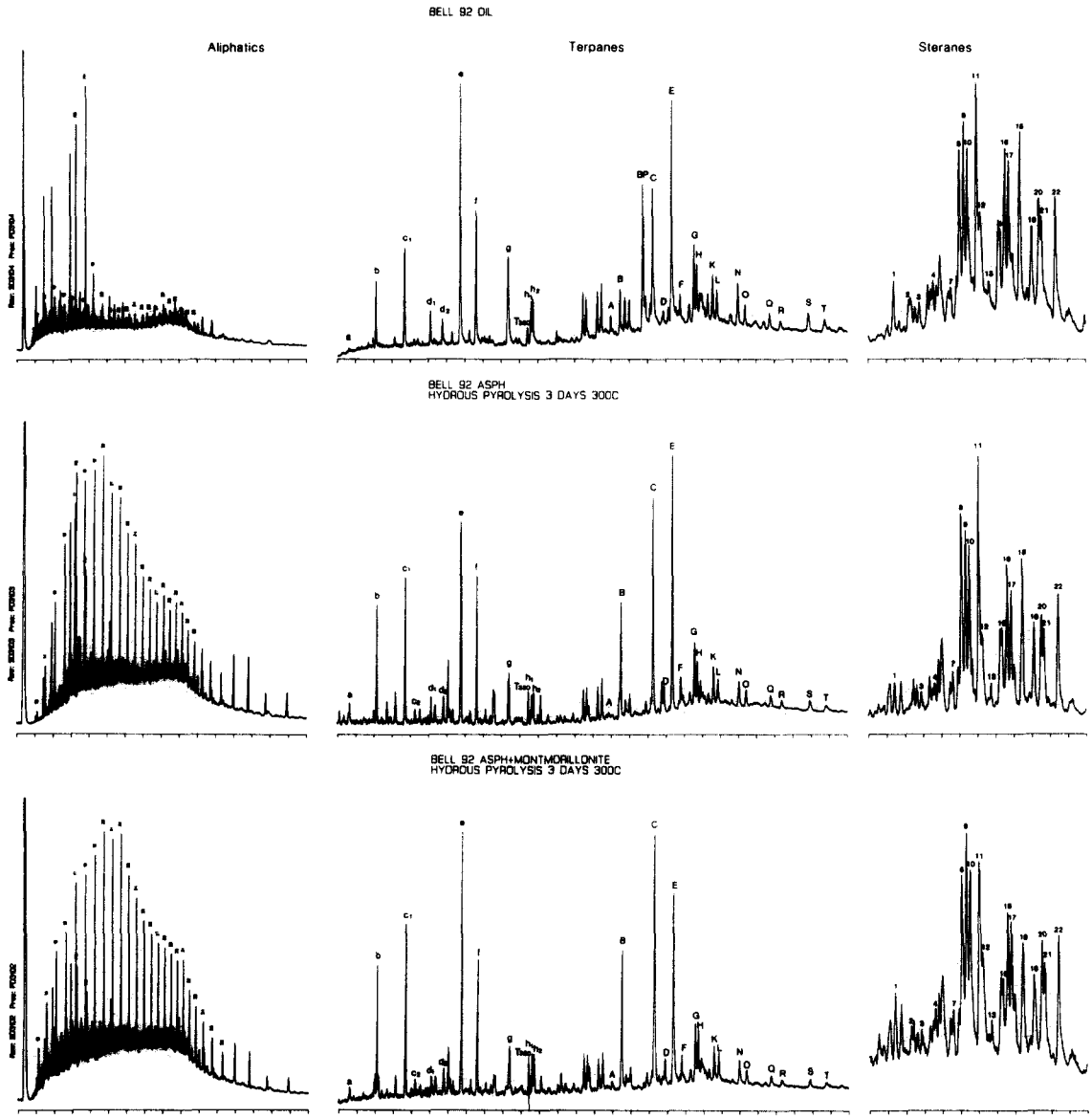

Fig. 2. Aliphatic GCs and terpane and sterane mass chromatograms for the Bell 92 sample.

Their absence indicates that during HP the asphaltic particles of the Monterey oil behave like the Monterey kerogen. The pentacyclic terpanes suggest, therefore, that the hydrocarbons are not occluded in the asphaltic structure but rather that the asphaltenes represent soluble kerogen fragments and the hydrocarbons are released by the breakdown of chemical bonds.

It has been observed by Zumberge (1987) that in oils generated from carbonate source rocks 17α(H), 21β(H)-30-norhopane (peak C) is larger than 17α(H), 21β(H)-hopane (peak E) while in oils generated from clastic source rocks 17α(H), 21β(H)-hopane is larger than 17α(H), 21β(H)-30-norhopane. The increase in 17α(H), 21β(H)-30-norhopane relative to 17α(H), 21β(H)-hopane in the asphaltene–montmorillonite experiments is probably due to an acid catalytic effect by the montmorillonite and perhaps the observation made by Zumberge (1987) may be explained in similar terms. The presence of a small 18α(H)-22, 29, 30-trisnorhopane (peak A), the increase in 17α(H), 21β(H)-30-norhopane (peak C) and the increase in the CPI value in the asphaltene–montmorillonite experiments also suggest that if oils continue to mature in the reservoir, the mineralogical composition of the rock matrix may have an effect on the distribution of the different aliphatic (and aromatic) compounds. This may be significant in particular in cases where low maturity oils, which contain high proportions of asphaltenes, become more mature in the reservoir.

Steranes also show some changes in HP products obtained with and without montmorillonite. Of importance is the change in the ratio of the C_{29} 20S/20R isomers (peaks 19 and 22, respectively) which are

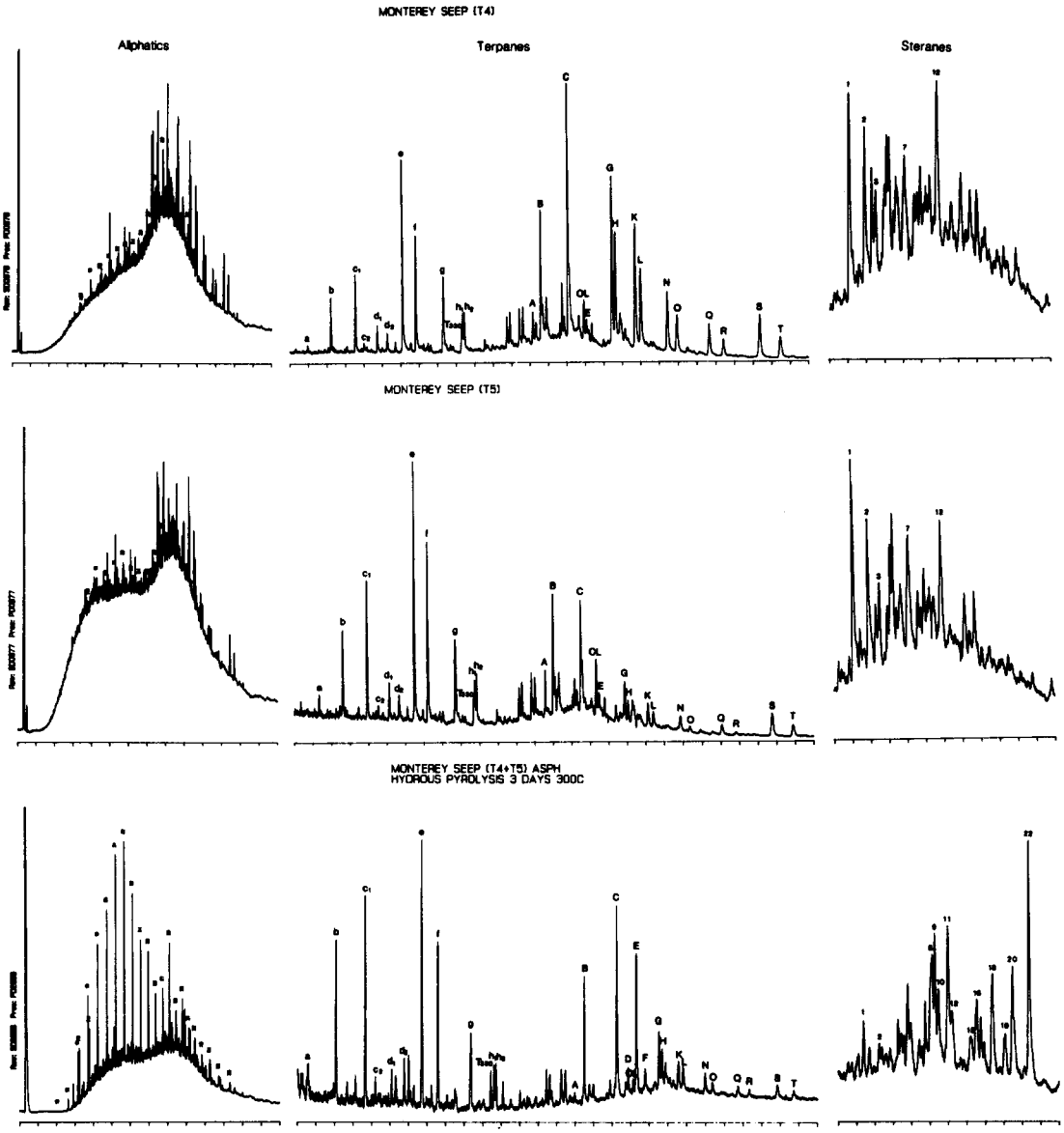

Fig. 3. Aliphatic GCs and terpane and sterane mass chromatograms for the T4 and T5 samples.

often used for maturity evaluation (Seifert and Moldowan, 1978). Relative to the original steranes, the 20S/20R ratio increases for the products from pure asphaltenes and decreases for the products from asphaltene–montmorillonite mixture (Table 1). This is in contrast to the observation made by Telnaes and others (1985) where the ratio in the Green River Gilsonite becomes larger with montmorillonite (due to its acid catalytic effect). The reason for the difference is not well understood but coelution of an unknown compound with the C_{29} 20R isomer of the pyrolysis products of the Monterey oils seems to be the most plausible explanation. Indeed, Table 1 shows that the 20S/20R ratios for the C_{27} and C_{28} steranes (calculated from the hightes of peaks 8, 11, 15 and 18 respectively in Figs 1 and 2) increase as expected in the asphaltene–montmorillonite pyrolysates.

The *n*-alkanes, the steranes, and to some extend the pentacyclic terpanes (as evident by the absence of peak E) of the Monterey seep have been affected by biodegradation (Fig. 3). The tricyclic terpanes on the other hand, are relatively unchanged and have similar distributions as the Bell 24 and Bell 92 oils. After HP the Monterey seep shows the development of *n*-alkanes, terpanes and steranes. Relative to the pyrolysis products of the Bell oils, the Monterey seep pyrolysate shows two major differences in the terpane and sterane mass chromatograms: 17α(H), 21β(H)-30-norhopane (peak C) is larger than 17α(H)-hopane (peak E) and the 20S isomer of 5α(H)stigmastane (peak 19) is much smaller than the 20R isomer (peak 22). The reason for a larger 17α(H), 21β(H)-30-norhopane is not well understood yet (perhaps because the sample is from a different basin). The low 20S/

Table 2. List of identified biomarkers

Tricyclic Terpanes

Peak	Molecular Formula	Molecular Weight	R Group
a	$C_{19}H_{34}$	262	$-CH_3$
b	$C_{20}H_{36}$	276	$-C_2H_5$
c_1	$C_{21}H_{38}$	290	$-C_3H_7$
c_2	$C_{21}H_{38}$	290	$-C_3H_7$
c_3	$C_{21}H_{38}$	290	$-C_3H_7$
d_1	$C_{22}H_{40}$	304	$-C_4H_9$
d_2	$C_{22}H_{40}$	304	$-C_4H_9$
e	$C_{23}H_{42}$	318	$-C_5H_{11}$
f	$C_{24}H_{44}$	332	$-C_6H_{13}$
g	$C_{25}H_{44}$	346	$-C_7H_{15}$
h_1	$C_{26}H_{48}$	360	$-C_8H_{17}$
h_2	$C_{26}H_{48}$	360	$-C_8H_{17}$

Tetracyclic Terpane

T_{330}	$C_{24}H_{42}$	330

Pentacyclic Triterpanes

Peak	Molecular Formula	Molecular Weight	Chemical Structure
A	$C_{27}H_{46}$	370	18α(H), 22, 29, 30-trisnorhopane
B	$C_{27}H_{46}$	370	17α(H), 22, 29, 30-trisnorhopane
BP	$C_{28}H_{48}$	384	17α(H), 18α(H), 21β(H)-28, 30-bisnorhopane
C	$C_{29}H_{50}$	398	17α(H), 21β(H)-30-norhopane
D	$C_{29}H_{50}$	398	17β(H), 21α(H)-normoretane
E	$C_{30}H_{52}$	412	17α(H), 21β(H)-hopane
F	$C_{30}H_{52}$	412	17β(H), 21α(H)-moretane
G	$C_{31}H_{54}$	426	17α(H), 21β(H)-30-homohopane (22S)
H	$C_{31}H_{54}$	426	17α(H), 21β(H)-30-homohopane (22R)
K	$C_{32}H_{56}$	440	17α(H), 21β(H)-30, 31-bishomohopane (22S)
L	$C_{32}H_{56}$	440	17α(H), 21β(H)-30, 31-bishomohopane (22R)
N	$C_{33}H_{58}$	454	17α(H), 21β(H)-30, 32, 32-trishomohopane (22S)
O	$C_{33}H_{58}$	454	17α(H), 21β(H)-30, 31, 32-trishomohopane (22R)
Q	$C_{34}H_{60}$	468	17α(H), 21β(H)-30, 31, 32, tetrakishomohopane (22S)
R	$C_{34}H_{60}$	468	17α(H), 21β(H)-30, 31, 32, tetrakishomohopane (22R)
S	$C_{35}H_{62}$	482	17α(H), 21β(H)-30, 31, 32, 33, 34-pentakishomohopane (22S)
T	$C_{35}H_{62}$	482	17α(H), 21β(H)-30, 31, 32, 33, 34-pentakishomohopane (22R)

Steranes

Peak	Molecular Formula	Molecular Weight	Chemical Structure
1	$C_{27}H_{48}$	372	13β(H), 17α(H)-diacholestane (20S)
2	$C_{27}H_{48}$	372	13β(H), 17α(H)-diacholestane (20R)
3	$C_{27}H_{48}$	372	13β(H), 17β(H) diacholestane (20S)
4	$C_{27}H_{48}$	372	13α(H), 17β(H) diachpolestane (20R) + 13β(H)
	$C_{28}H_{50}$	386	17α(H) diaerogostane (20S)
7	$C_{28}H_{50}$	386	13β(H), 17α(H) diaergostane (20R)
8	$C_{27}H_{48}$	372	5α(H) cholestane (20S) + 5β(H) cholestane (20R)
9	$C_{28}H_{48}$	372	5α(H), 14β(H), 17β(H)-cholestane (20R) + 13β(H)
	$C_{29}H_{52}$	400	17α(H) diastigmastane (20S)
10	$C_{27}H_{48}$	372	5α(H) 14β(H), 17β(H)-cholestane (20S)
11	$C_{27}H_{48}$	372	5α(H) cholestane (20R)
12	$C_{29}H_{52}$	400	Rearranged C_{29} sterane
13	$C_{29}H_{52}$	400	Rearranged C_{29} sterane
15	$C_{28}H_{50}$	386	5α(H), ergostane (20S)
16	$C_{28}H_{50}$	386	5α(H), 14β(H), 17β(H)-ergostane (20R) + 5β(H) ergostane (20R)
17	$C_{28}H_{50}$	386	5α(H), 14β(H), 17β(H) ergostane (20S)
18	$C_{28}H_{50}$	386	5α(H) ergostane (20R)
19	$C_{29}H_{52}$	400	5α(H) stigmastane (20S)
20	$C_{29}H_{52}$	400	5α(H), 14β(H), 17β(H) stigmastane (20R) + 5β(H) stigmastane (20R)
21	$C_{29}H_{52}$	400	5α(H), 14β(H), 17β(H) stigmastane (20S)
22	$C_{29}H_{52}$	400	5α(H) stigmastane (20R)

Assumes 8β(H), 9α(H), 14α(H), 17α(H) unless otherwise stated.
dia = rearranged

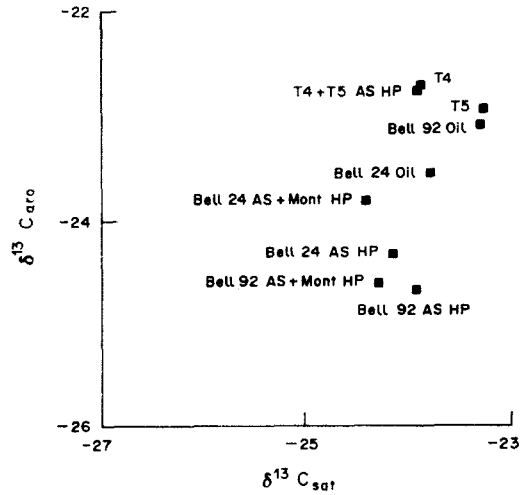

Fig. 4. Isotropic composition of the aliphatic and aromatic fractions.

20R 5α(H) stigmastane ratio (peaks 19/22) suggest that the seep was generated from a source rock that is less mature than the source of the Santa Maria (Bell) oils (this is also reflected perhaps in the lower CPI value shown in Table 1).

The tricyclic terpanes in the pyrolyzed Monterey seep are very similar to those generated by HP of the Bell 24 and Bell 92 pure asphaltenes. This demonstrates the importance and usefulness of these biomarkers as a correlation tool in hydrous pyrolysis of the asphaltenes of biodegraded oils and oil seeps. It seems from the results shown here that hydrous pyrolysis does not regenerate these biomarkers to their exact original composition. However, when the tricyclic terpanes generated during pyrolysis of the asphaltenes of a nondegraded oil are compared to the tricyclic terpanes generated from a biodegraded oil or oil seep, a good correlation can be established.

The isotopic composition of the aliphatic and aromatic fractions before and after pyrolysis are plotted in Fig. 4 (data from Table 1). A shift in the isotopic composition of the pyrolysis products relative to the same fraction before pyrolysis occurs. Also the shift in the isotopic composition is larger for the aromatic fraction than for the aliphatic fraction (in the Santa Maria oils). This may suggest that hydrous pyrolysis does not restore the aromatic fraction as well as it does the aliphatic fraction. The shift in the isotopic composition is toward more negative δ values. However, in HP of other oils and oil seeps (Sofer, unpublished data), shifts in an opposite direction have also been observed. The magnitude of the shift is not uniform but it seems to be small enough so that the genetic relationship between samples before and after pyrolysis is not obscured.

CONCLUSIONS

Based on the data shown here, hydrous pyrolysis of asphaltenes offers a fast and simple method to reconstruct the aliphatic fraction in severely biodegraded oils. The biomarkers generated during hydrous pyrolysis are somewhat different from those

in a nondegraded, genetically-related oil. Yet these differences are small and when the asphaltenes of the nondegraded oil are also hydrous pyrolyzed and compared to the pyrolysate of the biodegraded oil, a high level of similarity is obtained.

Steranes of biodegraded oils and in particular of biodegraded oil seeps are often severely altered. Hydrous pyrolysis regenerates the steranes in proportions that are similar to the proportions in the original oil. This allows to roughly estimate the maturity of the source of biodegraded oil or oil seep.

Data have also shown that montmorillonite changes the chemical composition of the pyrolysis products to a larger extent than when pure asphaltenes are pyrolyzed. It is therefore recommended to use pure asphaltenes in hydrous pyrolysis experiments designed for correlation studies. The observation that montmorillonite (and perhaps other acidic minerals) has an effect on the pyrolysis products may have strong implications regarding the effects that the mineral matrix may have on oils that continue to mature in the reservoir. This in particular may be important in low maturity oils which normally contain high proportions of asphaltenes.

The data shown here indicate that asphaltenes act like fragments of soluble kerogen during hydrous pyrolysis. This means that the release of the hydrocarbons occurs through the breakdown of chemical bonds and not by release of hydrocarbons occluded in the asphaltic molecular structure.

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