



# Geochemical characterization of tarballs on beaches along the California coast. Part I— Shallow seepage impacting the Santa Barbara Channel Islands, Santa Cruz, Santa Rosa and San Miguel

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## Abstract

Tarballs are common along the southern California coastline. This study investigates tarballs from beaches along this coastline, with a focus on Santa Cruz, Santa Rosa, and San Miquel Islands in the Santa Barbara Channel. The tarballs were fingerprinted using biomarker and stable carbon isotope parameters, and then grouped according to genetic similarities. The data show that the tarballs are of natural and not anthropogenic origin and that all originate from source rock within the Miocene Monterey Formation via shallow seeps offshore. Sterane biomarker parameters were found to vary widely in the sample set. Biodegradation, especially of the regular steranes, is the primary process impacting the biomarker distributions in a large group of samples. The most common tarball occurrences appear to come from offshore seepage near the west end of Santa Cruz Island. Another major group most likely was transported north from near Santa Monica Bay. Several individual occurrences of some of these tarball groups also were found on beaches as far north as Pt. Reyes and as far south as San Diego, indicating significant long-distance dispersal by ocean currents. This study begins a library of tarball fingerprints to be used as a database to help distinguish between natural and anthropogenic tar occurrences all along the California coast, and to compare shallow seepage with future samples of deeper production oils from the same area.

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## 1. Introduction

The southern California coastline contains long stretches of sandy beaches, rocky inlets, high cliffs hanging precipitously over crashing waves, and many other scenic wonders. It is also contains some of the most highly productive and biologically diverse marine habitats in the world. Much of the coastline is protected by law in order to preserve its natural beauty and

marine ecosystems. This unparalleled natural resource is, however, continually exposed to contamination from both natural and anthropogenic sources. In particular, the coastline is impacted by petroleum hydrocarbons that occur as tarballs washed up all along the shorelines and as onshore seepages from rocky outcrops and cliff faces. Natural sources for these petroleum hydrocarbons include prolific, frequently chronic, onshore and offshore shallow oil seeps, especially prominent along the southern California coast ([State Lands Commission Staff Report, 1977](#)). Anthropogenic sources include possible accidental oil spills from commercial vessel traffic, from offshore drilling rigs, and from ships

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involved in the processing and transport of oil along the coastal shipping lanes.

Differentiating between natural and anthropogenic petroleum sources and determining specific sources of coastal contamination is essential to evaluate threats to the ecosystems and to limit contaminant impact. This study focuses on tarballs collected on beaches in the southern California borderlands. Although crude oils and source rocks in the California borderland oil fields have been extensively characterized (e.g., Curiale et al., 1985), published geochemical work on the substantial (i.e., approximately 20,000 tonnes/year, as estimated by a US Academy of Sciences report, NAS, 2002) hydrocarbon beach tar accumulations along the California coast is limited. Reed and Kaplan (1977) used stable isotopic ratios of sulfur, nitrogen, and carbon to distinguish seep oils, beach tars, and crude oils from the southern California Borderland. Another early study utilized stable isotopic ratios of carbon and sulfur and total sulfur content of asphaltene fractions to correlate beach tars deposited near Los Angeles with their probable sources, to distinguish natural seep oils from imported tanker crude oils and local production wells, and to evaluate seasonal distribution patterns and transport (Hartman and Hammond, 1981). A more recent study used various molecular parameters of tar residues on beaches within the Monterey Bay National Marine Sanctuary to try to ascertain sources; although widely distributed tarballs could be assigned to specific groups, no local sources within the sanctuary could be identified that would account for the beached tarballs (Kvenvolden et al., 2000). Finally, a preliminary report on coastal tar and oil seeps considers the geologic framework and some potential tarball correlations related to this study (Kvenvolden and Hostettler, 2004).

These works all indicate that much of the tar contamination originated from the Miocene Monterey Formation. Samples generated from source rock in the Monterey Formation share several chemical characteristics, including: (1) unusually “heavy”  $\delta^{13}\text{C}$  (around  $-23\text{‰}$ ); (2) aliphatic biomarker parameters indicating an anoxic marine depositional environment, such as high 28,30-bisnorhopane (Curiale et al., 1985), high  $\text{C}_{35}$   $\alpha\beta$ -hopane 22S and 22R epimers compared to  $\text{C}_{34}$ , and the presence of gammacerane (Peters and Moldowan, 1993); (3) a characteristic value ( $>3$ ) for the biomarker parameter called “the triplet” (Kvenvolden et al., 1995), defined in Appendix I; (4) a small but consistent presence of oleanane; (5) sterane parameters indicating low maturity versus fully mature hopane parameters; (6) very low diasteranes relative to regular steranes, indicating a clastic-poor marine source rock; (7) abundant aromatized steranes, especially monoaromatics relative to triaromatics, indicating low thermal maturity (Curiale et al., 1985); and (8) prominent sulfur-containing PAH, such as dibenzothiophenes.

Although the above chemical components are common to the tarballs, their relative proportions within different tarball sources vary. Fingerprints utilizing ratios of these constituents, plus additional biomarker parameters from both the aliphatic and aromatic hydrocarbon suites, allow discrimination between the different samples, as well as correlation of tarballs that have been transported far from their source by ocean currents.

The chemical composition of the tarballs also sheds light on their geochemical history. Despite the proliferation of offshore shallow hydrocarbon seeps, and the constant impingement of tar onto the shoreline, little is known about the mechanics of the hydrocarbon formation in the shallow seeps, specific sources of tarballs, or their transport from the marine environment onto the shore. There is at present no irrefutable data linking oils on beaches to specific offshore natural seeps (Leifer et al., 2002).

Because many of the tarballs from offshore seeps are transported significant distances from their sources by ocean currents, geochemical assignment of their origin provides insight into the circulation patterns of the coastal currents. The circulation patterns impacting the Santa Barbara Channel have recently been studied (Hickey, 1998; Winant et al., 1999). Persistent cyclonic circulation, upwelling conditions, and wind-relaxing act in different seasons to drive the currents. The net result on drifters in these studies is a combination of in-channel deposition, both on the mainland coast and on the channel islands, with flow predominantly toward the south and east in the spring and summer (California Current) and to the west and north in the late fall and winter (Davidson Current and the Southern California Countercurrent). Mapping deposition sites of tarballs that also drift with these ocean currents, therefore, may further validate past drifter studies, as well as provide information on the fate of these petrogenic contaminants in the coastal environment.

This study examines the possible origins of tars deposited on the beaches of the Channel Islands, Santa Cruz (SCI), Santa Rosa (SRI), and San Miguel (SMI) (Table 1, Fig. 1). These islands are near active offshore oil production and prolific, but only partly mapped natural seeps. The study also includes related tar residues from a larger sample set collected randomly over a five-year period from California beaches from Point Reyes in the north to the Los Angeles shelf in the south. Sources of the Channel Island tarballs are determined as closely as possible. Another aim of this work is to initiate a library of coastal tar fingerprints as a database for future investigations. Future work will expand to include offshore production oils, a broader geographic sampling of tarball incursions, especially coastland beaches near Santa Barbara and Coal Oil Point, and possible specific shallow seep outfalls.

Table 1  
List of samples

Field No.	Type	Location	Field No.	Type	Location
97-10	weathered tar on rock	S. side of Pescadero Creek	00-49	fresh tar on sand	Limintour Beach, mid tide line
97-22	weathered tar on rock	Windansea Beach, San Diego	00-50	fresh tar on sand	Limintour Beach
97-23	weathered tar on rock	Windansea Beach, San Diego	00-65	fresh tar on sand	Fort Funston, surf zone
97-28	weathered tar on granite	Monterey Peninsula, 17 Mile Drive	00-67	fresh offshore seep	3 mi. N. of Anacapa Isl.
98-5	old tar on conglomerate	HTL, Pigeon Pt.	00-102	mixed tar (3 patties)	Santa Rosa I., beach
98-33	fresh tar on rock	Montague State Park	00-103	tar on rock	Santa Rosa I., beach
98-44	fresh tar on rock	Jalama State Beach	00-104	large tarball	Santa Rosa I., beach
98-46	fresh tar on rock	Jalama State Beach	00-105	tar on side of cliff	Santa Rosa I., pocket beach
98-49A	fresh floating tar	Offshore Coal Oil Pt.	00-106	tar on beach	Santa Rosa I., East Point
98-60	fresh tar on sand	Refugio State Beach	00-107	tar on rock	Santa Rosa I., west of East Pt.
L99-2	weathered tar on sand	Sunset Bch., near offshore platform	00-108	true tar ball	Santa Rosa I., marine terrace
L99-3	fresh tar on sand	Manhattan Beach N. by Chevron	00-109	tarball on side of cliff, HTL	Santa Rosa I., marine terrace
L99-4	fresh tar on sand	Manhattan Beach N. by Chevron	00-110	fresh tar on terrace	Santa Rosa I., on terrace
L99-8	fresh tar on sand/cobbles	Redondo Beach, S.	00-111	fresh floating tar mass	Santa Rosa I., Skunk Pt.
L99-9	fresh tar on sand/cobbles	Redondo Beach, S.	00-112	tar on rock	Santa Rosa I., Skunk Pt.
L99-10	fresh tar splotch on rock	Palos Verdes Point	00-113	fresh tar mass on rock terrace	Santa Rosa I., Skunk Pt.
L99-11	fresh tar on rock	Palos Verdes, Vicente Lighthouse	00-114	fresh tar on rock	Santa Rosa I., Skunk Pt.
L99-12	fresh tar on outcrop	Palos Verdes, Whites Point	00-115	fresh tar on sand	Santa Rosa I., Skunk Pt.
L99-13	fresh tar on cobbles	San Pedro, Point Fermin	00-116	fresh tar on sand	Santa Rosa I., Soledad Pt.
L99-25	weathered tar on rock	Catalina Island, Twin Harbor	00-117	tar on rock outcrop	Santa Rosa I., Soledad Pt.
L99-27	weathered tar on rock	Huntington Beach #1	00-118	fresh thick tar on beach	Santa Rosa I., Soledad Pt.
L99-28	fresh tar on sand	Huntington Beach #2	00-119	fresh tar mat, rock outcrop	Santa Rosa I., Soledad Pt.
99-3	fresh tar on sand	Santa Cruz I., Christy Beach	00-120	fresh tar on rock	Santa Rosa I., Soledad Pt.
99-4	fresh tar on sand	Santa Cruz I., Christy Beach, HTL	00-121	tar on rock outcrop	Santa Rosa I., Soledad Pt.
99-5	fresh tar on sand	Santa Cruz I., Christy Beach	00-122	tar on cobbles	Santa Rosa I., Soledad Pt.
99-6	fresh tar on sand	Santa Cruz I., Christy Beach, HTL	00-123	fresh tar on beach	Santa Rosa I., Soledad Pt.
99-7	fresh tar on rock	Santa Cruz I., Christy Beach	00-124	fresh floating tar	Santa Rosa I., Soledad Pt.
99-8	fresh tar on sand	Santa Cruz I., Christy Beach	00-125	tar on terrace	Santa Rosa I., Carrington Pt.
99-9	weathered tar mat on rock	Santa Cruz I., Fraser Pt., N	00-126	fresh thick tar mat on rock	Santa Rosa I., Carrington Pt.
99-10	fresh tar on rock	Santa Cruz I., Fraser Pt., N	00-127	v. weathered tar on rock	Santa Rosa I., Carrington Pt.
99-11	weathered old tar	Santa Cruz I., Fraser Pt., N	00-128	tar on terrace	Santa Rosa I., Lobo Canyon
99-12	weathered old tar mat	Santa Cruz I., Fraser Pt., N	00-129	fresh massive tar	Santa Rosa I., Sandy Pt., HTL
99-13	fresh new tar on mat	Santa Cruz I., Fraser Pt., N	00-130	fresh tar on rock	Santa Rosa I., Sandy Pt.
99-14	fresh tar splotch on rock	Santa Cruz I., Fraser Pt., S	00-131	fresh tar on top of tar mat	Santa Rosa I., Sandy Pt.
99-15	weathered tar splotch on rock	Santa Cruz I., Fraser Pt., S	00-132	tar mat under 00-131	Santa Rosa I., Sandy Pt., intertidal
99-16	fresh tar on rock	Santa Cruz I., Coches Prietos, E	00-133	fresh tar mat	Santa Rosa I., Sandy Pt.
99-17	fresh tar on rock	Santa Cruz I., Coches Prietos, E	00-135	weathered old tar	Santa Rosa I., Sandy Pt., above HTL
99-18	weathered tar on rock	Santa Cruz I., Coches Prietos, W	00-137	fresh tar on beach	Santa Rosa I., Bee Rock West
99-19	weathered tar on rock	Santa Cruz I., Coches Prietos, W	00-146	tar	Santa Rosa I., Cluster Pt.,S
99-20	weathered tar on rock	Santa Cruz I., Coches Prietos, W	00-147	tar on beach	Santa Rosa I., Cluster Pt.

(continued on next page)

Table 1 (continued)

Field No.	Type	Location	Field No.	Type	Location
99-21	fresh tar on sand	Santa Cruz I., Coches Prietos	00-148	tar on rock	Santa Rosa I., Ford Pt., E
99-22	fresh tar on sand	Santa Cruz I., Coches Prietos	00-156	tar	Santa Rosa I., South Pt., E
99-23	old bitumen	Santa Cruz I., China Harbor	00-158	tar	Santa Rosa I., Officers' Beach
99-24	fresh tar on rock	Santa Cruz I., China Harbor	00-163	tar on conglomerate	Santa Rosa I., Oat Pt.
99-25	old rock bitumen	Santa Cruz I., China Harbor	SM-1	tar	San Miguel I., Cuyler Harbor
99-26	old bitumen in outcrop	Santa Cruz I., China Harbor	SM-2	tar on beach	San Miguel I., Cuyler Harbor
99-27	fresh tar on rock	Santa Cruz I., China Harbor	SM-3	tar on beach	San Miguel I., Cuyler Harbor
99-28	weathered tar on rock	Santa Cruz I., China Harbor	SM-4	beach tar, on berm	San Miguel I., Cuyler Harbor
99-29	fresh tar on sand	Santa Cruz I., Prisoners' Harbor	SM-5	tar on beach	San Miguel I., Travertine Cove
99-30	fresh tar on sand	Santa Cruz I., Prisoners' Harbor	SM-6	fresh tar on beach	San Miguel I., Travertine Cove
99-31	weathered tar on rock	Santa Cruz I., Prisoners' Harbor	SM-7	tar on beach	San Miguel I., Bowl Cove
99-32	fresh tar on rock	Santa Cruz I., Fraser Pt.	SM-8	fresh tar on older mat	San Miguel I., rock terrace, E of Bowl
99-33	weathered tar on rock	Santa Cruz I., Willows	SM-9	more recent tar patch on rock	San Miguel I., rock terrace, E of Bowl
99-34	weathered tar on rock	Santa Cruz I., Willows	SM-10	tar on beach	San Miguel I., W. Simonton Beach
99-35	weathered tar on rock	Santa Cruz I., Willows	SM-11	tar on beach	San Miguel I., Simonton B., Rangepole
99-36	fresh tar on sand	Santa Cruz I., Willows	SM-12	tar on beach	San Miguel I., Simonton B., Rangepole
99-37	weathered tar on rock	Santa Cruz Isl., Valley Anchorage	SM-13	old tar patch mound	San Miguel I., ter. W. of Peach Rock Cove
99-38	weathered tar on rock	Santa Cruz Isl., Valley Anchorage	SM-14	beach tar, juvenile barnacles	San Miguel I., Peach Rock cove, tide line
99-39	weathered tar on breakwater	Ventura, CA, Channel Isl. Harbor	SM-15	beach tar on berm	San Miguel I., Peach Rock Cove
99-40	fresh tar on swash sand	Ventura, CA, Channel Isl. Harbor	SM-16	tar on rock	San Miguel I., Harris Pt. (D.R.)
99-43	fresh tar on rock	Vandenberg AFB, Minuteman Beach	SM-17	tar on rock, adult barnacles	San Miguel I., Harris Pt. (D.R.)
99-45	fresh tar on rock	Vandenberg AFB, Minuteman Beach	SM-18	older tar on beach	San Miguel I., Cardwell Pt.
00-36	fresh tar on sand	Pt. Reyes, North Beach, surf zone	SM-19	older tar on beach	San Miguel I., Cardwell Pt.
00-39	fresh tar, sand, mussel	Pt. Reyes, South Beach, low surf zone	SM-20	newer tar on beach	San Miguel I., Cardwell Pt.

Abbreviations: AFB = Air Force Base; HTL = high tide line; ter. = terrace; D.R. = samples collected by Dan Richards, Park Ranger; N,S,E,W = north, south, east, or west ends of beaches; bitumen = hydrocarbon residue exuded from onshore rock formations; tar mat = extensive accumulation of tar at shoreline; tar mass = larger than average tarball.

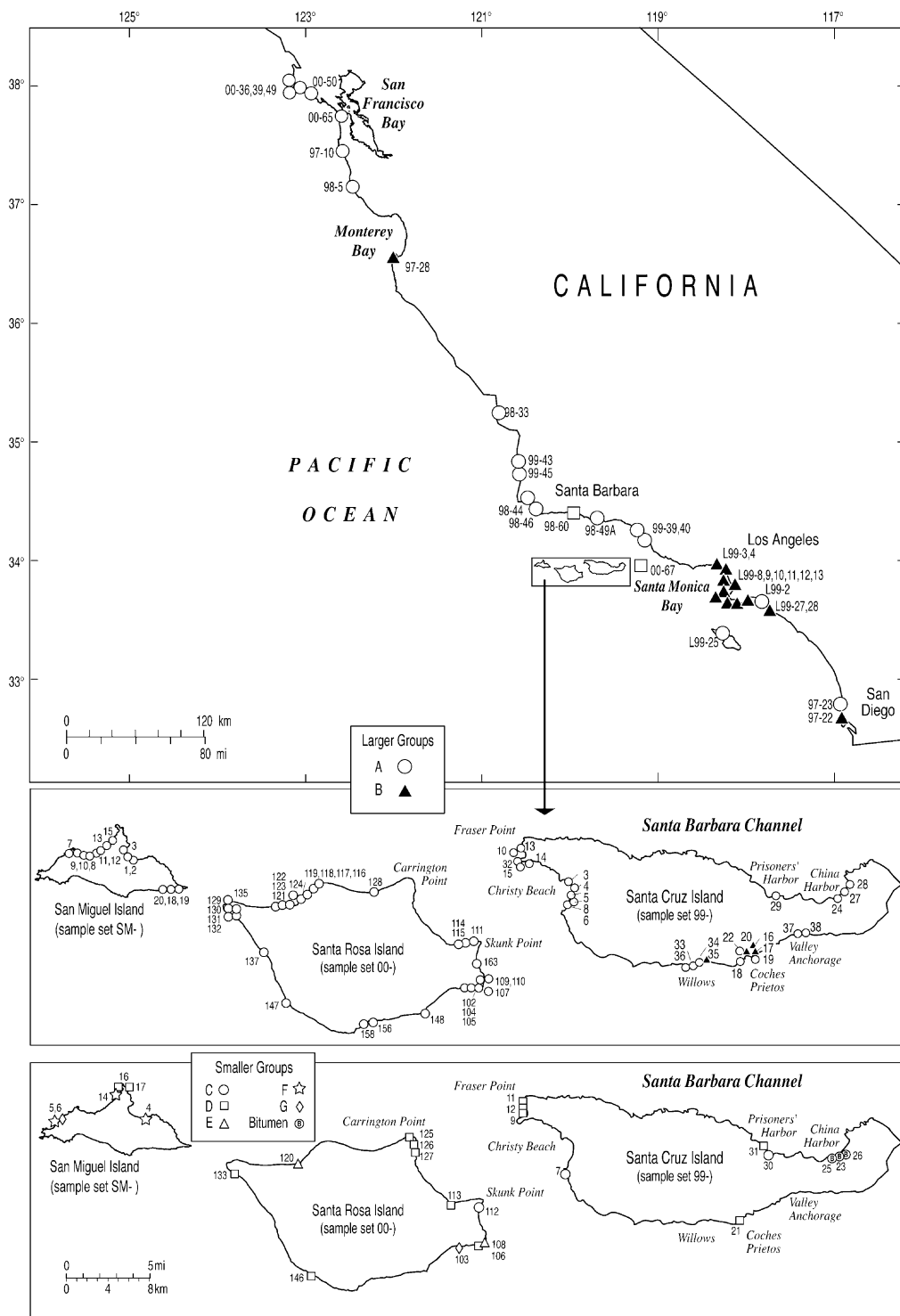


Fig. 1. Locations of coastal tars in this study, with groups designated according to parameter similarities after chemometric analysis.

## 2. Methods

A total of 128 tar balls and tar residues from coastal locations were collected over five years. Tar samples are listed in Table 1 and mapped in Fig. 1, with the first number in the identifier of most samples indicating year collected. SM-samples were collected in 2001. Each tarball was separated from rocks or sand with a clean knife and placed in pre-cleaned glass jars for transport to the laboratory. Tars floating in the salt water were placed in a clean glass jar, and any water was poured off before analysis. Tar samples were dissolved in dichloromethane (DCM), filtered through glass wool to remove particulates, and air-dried under a hood to remove the DCM. After filtration and removal of DCM, a portion of the clean extract was removed to determine bulk stable carbon isotope composition. The results are reported in the

$\delta$  notation in parts per thousand (‰) relative to the Pee Dee Belemnite (PDB) standard.

A second portion of the extract (~25 mg) was dissolved as completely as possible by sonication and mechanical agitation in 5 ml of hexane. This solution was then loaded onto a liquid chromatography column for compound class separation. Each column was layered at the bottom with about 5 mm of activated copper (to remove elemental sulfur), and with 2.5 g of 5% deactivated neutral alumina and 2.5 g and 5.0 g of 62 and 923 silica gels, respectively. Two separate fractions were collected [saturate (hexane eluent) and aromatic (30% DCM eluent)] and analyzed by gas chromatography–mass spectrometry (GC/MS). Compound identifications were made either by comparison with known standards or with published reference spectra. Chromatograms of a typical coastal tar residue,

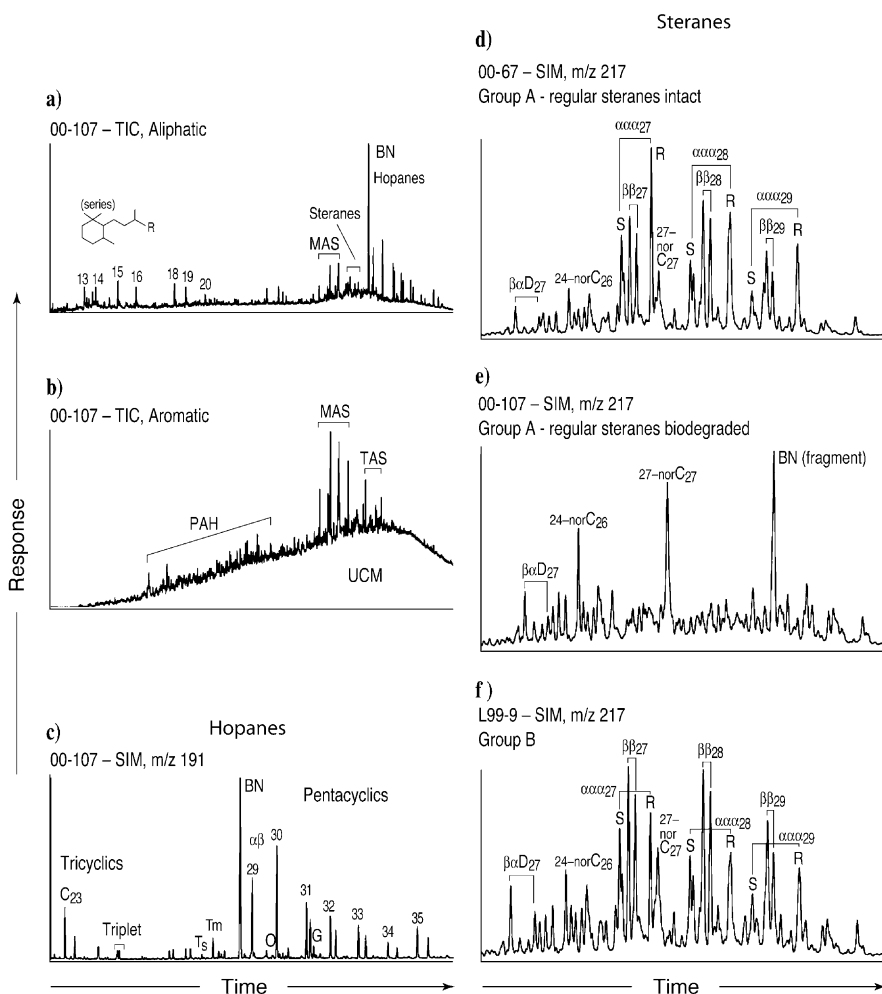


Fig. 2. Chromatograms of representative tarball samples. Total Ion Chromatogram (TIC) of aliphatic (a) and aromatic (b) fractions; Selected Ion Monitoring (SIM) chromatograms of  $m/z$  191, Hopanes (c), and  $m/z$  217, Steranes (d,e,f). Compounds identified in Table 2.

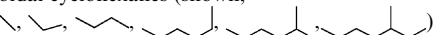
including a total ion chromatogram (TIC) and selected ion monitoring (SIM) mass chromatograms of terpanes (mass/charge,  $m/z$ , 191) and steranes ( $m/z$  217) are in Fig. 2. Compound identifications are in Table 2.

*n*-Alkanes and isoprenoids, and a suite of  $\beta$ -carotenoid-related compounds were profiled with extracted ion (EI) chromatograms ( $m/z$  57 and 125, respectively). Selected biomarker ratios, listed below, were calculated from GC/MS/SIM chromatograms of  $m/z$  191 (terpanes/hopanes) and 217 (steranes) using peak heights. 25,28,30-Trisnorhopane ( $T_{177}$ ) and the presence or absence of a 25-norhopane series was monitored by  $m/z$  177. Extracted ion profiles from TICs of the aliphatic and aromatic hydrocarbon fractions were used for the following ions:  $m/z$  253 for monoaromatic steroids (M, summed from contributions in both the aromatic and aliphatic fractions),  $m/z$  231 for triaromatic steroids (T),  $m/z$  242 for monomethyl chrysenes, and  $m/z$  212 and 206 for dimethyl-, and  $m/z$  226 and 220 for trimethyl-dibenzothiophenes and phenanthrenes, respectively.

Table 2  
Identification of prominent compounds in GC/MS chromatograms

(a) *Saturates*

13,14,15,16,18,19,20: homologs of 1,1,3-trimethyl-2-isoprenoidal cyclohexanes (shown;

R = H, 

MAS: monoaromatic steroid hydrocarbon suite

BN: 28,30-bisnorhopane, common in Monterey oils

Steranes:  $C_{26}$  to  $C_{29}$  steranes as shown in d,e,f

Hopanes:  $C_{29}$  to  $C_{35}$ -pentacyclic triterpanes (hopanes), shown in c.

(b) *Aromatics*

MAS: as above

TAS: triaromatic steroid hydrocarbon suite,  $C_{26}$  to  $C_{28}$

PAH: polycyclic aromatic hydrocarbons, typical of oils

(c) *Hopanes*

$C_{23}$ :  $C_{23}$ -tricyclic terpane

Triplet:  $C_{24}$ -tetracyclic terpane,  $C_{26}$ -tricyclic terpane(S?) +  $C_{26}$ -tricyclic terpane(R?).

Ts: 17 $\alpha$ -22,29,30-trisnorhopane

Tm: 18 $\alpha$ -22,29,30-trisnorhopane

BN: 28,30-bisnorhopane

$\alpha\beta$  29,30,31,32,32,34,35: 17 $\alpha$ ,21 $\beta$ (H)-hopanes,  $C_{31}$ - $C_{35}$ : S + R epimers

O: oleanane

G: gammacerane

(d),(e),(f) *Steranes*

$\beta\alpha D_{27}$ : 13 $\beta$ ,17 $\alpha$ (H)-diacholestane, S + R epimers

24-nor $C_{26}$ : 24-nor-5 $\alpha$ -cholestane

27-nor $C_{27}$ : 27-nor-24-methyl-5 $\alpha$ -cholestane

$\alpha\alpha\alpha_{27}$ , 28, 29: S + R epimers of 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ (H)-cholestane, 24-methyl- and 24-ethyl-

$\beta\beta_{27}$ , $\beta\beta_{28}$ , $\beta\beta_{29}$ : R + S epimers of 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ (H)-cholestane, 24-methyl- and 24-ethyl-

Either summed areas or peak heights (see Appendix I) of the compounds were used to determine the parameter ratios. The biomarker and isotope values were used to correlate the samples and group them according to their probable source locations.

### 2.1. Geochemical parameters

The parameter ratios used in this study are defined in Appendix I, and the values listed in Appendix II. The various parameters were chosen to include as many as possible of the chemical families and constituents common to these tars. This was necessary for the overall geochemical characterization and because, with a common Miocene Monterey source, many of the differences between groups of tarballs are small. The ubiquitous triterpane,  $C_{30}$   $\alpha\beta$ -hopane, was used to normalize seven of the parameters, thus serving as a pseudo conserved-internal-standard (Wang et al., 1998). Ease of measurement was also a factor in choosing parameters in order for this study to be more broadly utilized.

### 2.2. Statistical analysis

A chemometric multivariate statistical approach was applied to the data to sort out the differences in the biomarker ratios, to test for correlations between and within the sample groups, and to attempt to relate the tar residues to possible local sources. We used JMP Statistical Discovery, an interactive statistical and data analysis software package commercially available from the SAS Institute, Inc., Cary, NC (Brand names are used for identification only and do not imply endorsement by the US Geological Survey). Applicable data from Appendix II were subjected to hierarchical cluster analyses (HCA) and principal component analyses (PCA). We chose an incremental hierarchical clustering technique. The data were first standardized by the variable mean and standard deviation. PCA is a tool to reduce the dimensionality of a set of data by depicting relationships among variables and to assess each variable's contribution to the overall variance of the data. PCA uses a separate algorithm and is a visual validation of the clustering based on HCA. The statistical procedure involves a plot of the data in multi-dimensional space, followed by a standardized PCA.

## 3. Results

Biomarker and other constituent ratios are given in Appendix II and summarized according to chemometric groups in Table 3. These parameter ratios show that, except for the three SCI China Harbor bitumen samples, all of the tarball samples in this sample set exhibit all of the characteristics of source rock in the Miocene

Table 3  
Summary (mean values and ranges) of geochemical parameters<sup>a</sup> for sample groups (complete data table in Appendix II)

GROUP	$\delta^{13}\text{C}$	Pr/ Ph	Tm/ Ts	Triplet	23Tri/ C30	23Tri/ 24Tri	C30/ C29	C31 S/ (S+R)	BI	OI	GI	T177/ C30	C29 S/ (S+R)	C28/ C29	Dominant sterane(s)	$\alpha$ 27R/ Hop	nor26&27/ Hop	$\alpha$ 27R/ nor27	PAH-RI	T/ (T+M)	$\Sigma$ C2D/ $\Sigma$ C2P	$\Sigma$ C3D/ $\Sigma$ C3P	Pery/ Chr
A <sup>b</sup>	-23.4± 0.2	nc	4.7± 0.4	3.6± 0.2	0.45± 0.05	2.4± 0.1	1.4± 0.1	0.60± 0.01	1.6± 0.2	0.03	0.11± 0.01	0.08± 0.06	(range)	(range)	(range)	(range)	0.33± 0.01	(range)	56± 10	0.14± 0.02	1.9± 0.2	2.4± 0.2	1.7–31
A-least degraded													0.33± 0.03	1.0± 0.1	$\alpha$ 27R	0.48± 0.04	3.0± 0.3						
A-less degraded													0.34± 0.04	1.0± 0.1	$\alpha$ 27R, $\beta$ 27&28	0.30± 0.05	1.7± 0.3						
A-more degraded													0.30± 0.03(?)	0.92± 0.12(?)	mix of "less" & "most"	0.14± 0.05	0.76± 0.26						
A-most degraded													nc	nc	nor26&27,BN	0.04± 0.01	0.21± 0.08						
<b>B</b>	-23.3± 0.1	nc	4.1± 0.2	5.7± 0.3	0.74± 0.09	2.6± 0.1	1.4± 0.1	0.58± 0.01	0.44± 0.07	0.04	0.07± 0.01	0	0.37± 0.02	1.2± 0.1	$\beta$ 27/28s	0.35± 0.08	0.40± 0.03	1.6± 0.3	155± 12	0.18± 0.05	3.8± 0.2	3.8± 0.1	0.46–3.7
<b>C</b>	-23.4± 0.3	nc	5.0± 0.1	3.6± 0.1	1.1± 0.1	2.4± 0.1	0.71± 0.06	0.60± 0.01	0.88± 0.37	0.06	0.23± 0.03	0.06± 0.02	nc	nc	nor26&27	0.08± 0.05	0.80± 0.01	0.19± 0.10	52± 13	0.16± 0.01	1.2± 0.1	2.3± 0.1	5.3–12
<b>D</b>	-23.5± 0.2	mix	3.4± 0.6	4.7± 0.6	0.48± 0.07	1.9± 0.2	1.5± 0.1	0.58± 0.01	1.1± 0.3	0.05± 0.01	0.09± 0.02	0.05± 0.01	0.34± 0.03	1.1± 0.1	$\alpha$ 27R, $\beta$ 27/28s	0.34± 0.15	0.30± 0.04	1.9± 0.7	26± 11	0.19± 0.04	1.4± 0.3	1.7± 0.4	0.49–7.2
<b>E</b>	-23.5± 0.1	nc	7.1± 0.5	5.5± 0.1	0.37	3.1	1.7± 0.1	0.59	3.0± 0.1	0.02	0.13	0.20	0.39± 0.01	1.1	BN> $\beta$ 27/28s	0.44± 0.01	0.25± 0.01	2.6	53± 4	0.06	4.1± 0.1	8.6	3.1–3.5
<b>F</b>	-22.8± 0.1	nc	4.9± 0.3	3.5± 0.2	1.2± 0.1	3.9± 0.2	1.2± 0.1	0.61	1.1	0.03	0.13	0	0.40± 0.02	1.0	$\beta$ 27/28s, $\alpha$ 27R	0.46± 0.04	0.28± 0.01	3.2± 0.3	138± 18	0.17± 0.04	3.3± 0.1	4.0± 0.1	3.9–4.9
<b>G</b>	-22.7± 0.1	nc	4.8± 0.4	3.0± 0.1	0.67± 0.07	2.8	1.5	0.60± 0.01	0.42± 0.01	0.03± 0.01	0.11± 0.01	0	nc	nc	nor26&27	0.03± 0.01	0.26± 0.01	0.21± 0.08	116± 11	0.27± 0.01	3.3± 0.1	3.9± 0.1	1.7–2.0

Abbreviations: nc = not calculatable due to missing peak(s); (?) = peak assignments questionable due to low levels and overlapping peaks.

<sup>a</sup> Parameter ratios defined in Appendix I. Parameters in bold font are genetic parameters used in HCA. Values are mean ± S.D. except where ranges are more appropriate.

<sup>b</sup> A-group sterane parameters changing due to biodegradation. See Appendix II.



Monterey Formation listed in the Introduction. Particularly notable is the prominence of bisnorhopane (BN) in the saturate fraction, monoaromatic steroids in both fractions, and a prominent but highly variable presence of perylene in the aromatic fraction. One additional common characteristic in the saturate fractions of the tarball samples (see Fig. 2) is a prominent series of 1,1,3-trimethyl-2-isoprenoidal-cyclohexanes ( $C_{13}$ – $C_{16}$ ,  $C_{18}$ – $C_{20}$ ; representative spectrum in Philp, 1985), probably derived from cleavage of  $\beta$ -carotane, a marker for bacterial input and a hypersaline depositional environment (Peters and Moldowan, 1993). Most of the tarball samples lack free  $n$ -alkanes and isoprenoids, although a few contain enough of the isoprenoids to allow calculation of the pristane/phytane (Pr/Ph) ratio, and one sample (00-126) contains low levels of  $n$ -alkanes in an oil-like distribution. Sterane chromatograms contain, in addition to the regular steranes, two unusual steranes that in some samples are the dominant  $m/z$  217 peaks (see Fig. 2e). These compounds are tentatively identified from published spectra and retention times as  $C_{26}$  24-nor-5 $\alpha$ -cholestane (Moldowan et al., 1991) and  $C_{27}$  27-nor-24-methyl-5 $\alpha$ -cholestane (Schouten et al., 1994). The 24-nor-5 $\alpha$ -cholestanes are generally rare but are known to be present in some oils from the Monterey Formation. They have been attributed to widespread Tertiary diatom-rich siliceous sediments, and occur in oils from siliceous source rocks like the Monterey Formation (Holba et al., 1998). The two nor-cholestanes may be related to each other and are reported to co-occur (Schouten et al., 1994). They are ubiquitous in the samples of this study, and the parameter nor26&27/Hop shows that they maintain a very consistent level throughout the sample set when indexed to  $C_{30}$   $\alpha\beta$ -hopane (Table 3), or  $C_{29}$   $\alpha\beta$ -30-norhopane in the few samples where the  $C_{30}$  is degraded.

Samples were correlated and grouped by HCA. Our approach was similar to that used by Kvenvolden et al. (2000), although with an expanded parameter list (Appendix I). Both source and maturity parameters were used. Including maturity parameters with source parameters in the HCA was considered reasonable in the context of this work. For our purposes of correlation, “maturity” parameters essentially become “source” parameters once the oil is released from its reservoir into the environment. At that point thermal maturity is no longer working on the samples to further change the fingerprint. Biodegradation, migration, and physical weathering are the factors that cause changes in parameter values after release. Maturity parameters, however, will be useful in describing the geochemical nature of the different groups.

Two HCAs were determined. The first used 19 parameters from Appendix I and II, excluding the following parameters: Pr/Ph, because the ratio is not available for many samples due to biodegradation,  $C_{31}$  S/(S+R)

hopane parameter, because although it shows that all the tar samples are in the oil window, it is not sufficiently variable to serve as a discriminant, “Dominant sterane”, because it is non-numeric, and Pery/Chry, because its high variability implies extraneous alteration by migration through near-surface sediments. This HCA resulted in a separation of the samples into eight possible groups, with only the three onshore bitumen samples that were unique and did not correlate within groups or with the beached tarballs samples. However, the two largest groups were found to be nearly identical in all parameters except for highly variable sterane parameters. Examples of the sterane profiles are given in the  $m/z$  217 chromatograms, Fig. 2d and e. It seems likely that biodegradation has impacted the steranes in these two groups. Therefore, another HCA, using 15 genetic parameters (shown in bold print in Table 3) and excluding the four regular sterane parameters ( $C_{29}$ S/(S+R),  $C_{28}/C_{29}$ ,  $\alpha$ 27R/Hop, and  $\alpha$ 27R/nor27), was applied to the data set. This resulted in the two large groups collapsing into one very large group (A). In addition there were six other groups (B, C, D, E, F, and G) and the onshore bitumen samples. A dendrogram (Fig. 3) shows relationships among the samples. Shorter lengths of the tie line or linkage indicate closer correlation between samples. Table 3 gives a summary of mean and range of values for each parameter in each group. Fig. 1 shows the location of the samples within these different groupings.

Four Principal Components (PC) accounted for 73 percent of the variance, and seven PC for 91 percent. Values for PC1–4 for each sample are listed in Appendix III, along with the major contributors to each PC.

A further chemometric analysis was applied to group A, using the four previously excluded regular sterane parameters. This resulted in the A-group being divided into four smaller sub-groups, roughly according to the extent of progressive sterane biodegradation. Appendix II lists all the samples according to their HCA groupings, subdividing Group A into the four biodegradation levels. Table 3 includes the means and ranges for group-A parameters within the subgroups.

The statistical ranges for many parameters are not as narrowly constrained as would be expected for a typical anthropogenic oil spill (e.g., Bence et al., 1996), indicating that seep spillage has some natural variability within its constituent concentrations.

## 4. Discussion

### 4.1. Geochemistry of tarball groups

Since all of the beached tarballs in this sample set share characteristics of immature oils from the Miocene Monterey Formation, the tarballs washed up on the

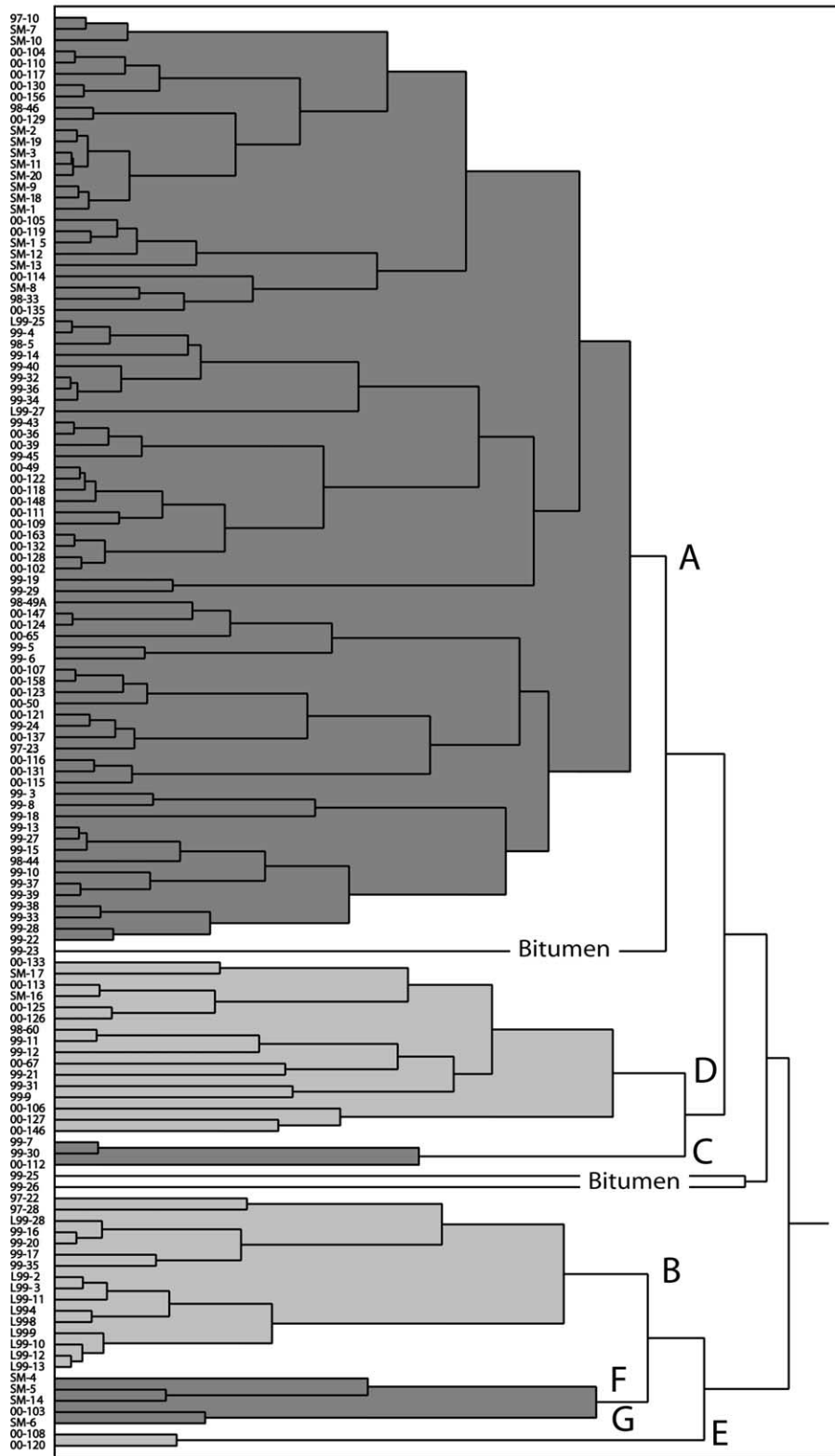


Fig. 3. Chemometric dendrogram of 128 coastal tars grouped by parameter similarities. Samples listed in Table 1.

shores thus appear to be from natural, rather than anthropogenic, sources, most likely from offshore seeps. All of the tars are within the oil window, as seen in the hopane maturity parameter [ $C_{31}S/(S+R)$ ], values at 0.6]. However, such ratios as the immature sterane isomerization values ( $<0.4$ ) and the aromatic steroid parameter  $T/(T+M)$ , with all values  $<0.3$ , indicate that the oils were generated under relatively low thermal stress conditions. Evidence that the depths from which the tarball seepage occurs are shallow includes parameter values such as generally high bisnorhopane ratios and a significant presence of the PAH perylene. It has been reported that bisnorhopane is not generated from kerogen, but is passed on from original free bitumen and diminishes with depth (Peters and Moldowan, 1993). Perylene is frequently found in surface sediments and is attributed to a biogenic source; it has been reported in variable concentrations in surface sediments off Monterey (Kvenvolden et al., 2002). The prominence of both of these compounds in the tarballs implies an origin from relatively shallow depth. Bisnorhopane, however, appears to be incorporated in the tars at the source, since its values are quite constant within the sample groupings. Perylene, in contrast, may be extracted more randomly from Recent sediments as the oil migrates to the surface, accounting for the variation in its range relative to chrysene within sample groups.

By far the largest numbers of beached tarballs in this study are in group A. Group A is characterized by particularly abundant 28,30-bisnorhopane and variable sterane profiles. At first the two end-member distributions of the sterane parameters (described below) were interpreted to indicate two different sources. However, with the close agreement of the non-sterane maturity and source parameters, progressive biodegradation seemed the likely explanation for the differences in the sterane distribution within group A. Biodegradation has already impacted the tarballs (Curiale et al., 1985), removing the *n*-alkanes and isoprenoids from most samples in the sample set. Although more resistant to biodegradation, steranes and then hopanes are known to follow acyclic isoprenoids in the biodegradation continuum outlined in Moldowan et al. (1992).

Within the A-group the least biodegraded samples show sterane profiles ( $m/z$  217) with clearly defined regular  $C_{27}$ – $C_{29}$   $\alpha\alpha\alpha$ - and  $\alpha\beta\beta$ -cholestanes, dominated by the  $C_{27}$  (20R)  $\alpha\alpha\alpha$ -cholestane epimer ( $\alpha 27R$ , which indicates sterane immaturity). A typical chromatogram is in Fig. 2d. The sub-sets of group A show successively less of the regular steranes, until these steranes are almost gone. At this point the sterane chromatograms (Fig. 2e) are dominated by three prominent peaks,  $C_{26}$  24-nor-5 $\alpha$ -cholestane and  $C_{27}$  27-nor-24-methyl-5 $\alpha$ -cholestane and a third peak which is from a non-sterane, the  $m/z$  217 fragment ion of 28,30-bisnorhopane. The degradation can be tracked using several of the sterane

parameters (Table 3). The “Dominant sterane” shows a progression from a dominance of  $\alpha 27R$  with lower  $\beta\beta$ -steranes, to diminishing  $\alpha 27R$  and  $\beta\beta$ 's, to negligible regular steranes. The parameters  $\alpha 27R/Hop$  and  $\alpha 27R/nor27$  follow this change numerically, with diminishing mean values of 0.48, 0.30, 0.14, and 0.04 for the former, and 3.0, 1.7, 0.76, and 0.21 for the latter. These two parameters, then, serve as a rough proxy to follow the biodegradation of the slowly disappearing steranes in the A-grouping. The  $\beta\beta$ -steranes last a little longer than the  $\alpha 27R$  sterane, just as outlined in Moldowan et al. (1992), becoming relatively more prominent in the mid-range group A's. As was noted above, however, the second sterane Index ( $nor26\&27/Hop$ ) is quite consistent throughout these five groups, indicating that the two irregular nor-steranes do not change relative to hopane, even as the regular steranes vary widely. Diasteranes, although they have low relative abundance in the tars, are not impacted within the range of biodegradation in group A, in agreement with the Moldowan et al. (1992) ranking. The group A samples range from 4 to 7 on the biodegradation scale of Peters and Moldowan (1993).

Other evidence that biodegradation impacts the steranes comes from the similar mono- and triaromatic steroid (MAS, TAS) profiles of group A. The  $m/z$  253 (MAS) and 231 (TAS) extracted ion profiles of the group A samples (not shown) are virtually superimposable, and the values of the aromatic steroid parameter,  $T/(T+M)$ , are all in a fairly narrow range. Biogenic sterols are known to undergo diagenesis to form both regular steranes and aromatic steroids (Philp, 1985). If all group A samples have comparable MAS and TAS profiles and abundances, and are alike in other measurable parameters, especially those indicating maturity and thermal stress, it can be assumed that all group A samples at one time had similar regular sterane distributions (Requejo, 1992; Seifert et al., 1984). We postulate that regular steranes have been removed by biodegradation from the group A samples that lack or have very low regular steranes.

There is one additional small group that possibly fits into this degradation progression, although the statistics place it in a separate category. Group C tars occur near the area of heavy group A concentrations, on beaches facing each other across the strait on SCI and SMI (Fig. 1). In group C the sterane profiles resemble the most biodegraded occurrences of group A, except that they are dominated by only the two irregular nor-steranes; the BN-fragment is relatively smaller. In addition, in the  $m/z$  191 chromatograms the  $C_{30}$   $\alpha\beta$ -hopane peak is diminished, as reflected in the only value of  $C_{30}/C_{29}$  in this samples set that is less than unity (Table 3). However, many of the other parameters fall within the same range as those of the above A tars, except those that are indexed to  $C_{30}$   $\alpha\beta$ -hopane. These indices, then, appear

artificially high due to degraded  $\alpha\beta$ -hopane, especially because they are all approximately two times higher than the equivalent ratios in the A group, whereas the  $\alpha\beta$ -hopane is half its regular value in the  $C_{30}/C_{29}$  parameter. The bisnorhopane index is variable in this group. Group C includes samples that have been more biodegraded than those in group A, so that the degradation has progressed beyond removal of regular steranes and has affected the  $C_{30}$   $\alpha\beta$ -hopane and is beginning to impact the BN. It does not appear, however, that the  $C_{29}$   $\alpha\beta$ -30-norhopane (see Seifert et al., 1984), the  $\alpha\beta$ -homohopanes, oleanane, gammacerane, or the tricyclic terpanes have been altered. It is also noteworthy that these three very heavily degraded group-C samples (biodegradation rank of 8) show no evidence of a developing 25-norhopane series, unlike some of the extremely biodegraded Monterey tar samples such as those bubbling up at the onshore Tarwater Creek reported in Kvenvolden et al. (2000).

Unlike groups A and C, group B tarballs are characterized by particularly high levels of the  $C_{28}$  and  $C_{27}$   $\beta\beta$ -steranes and do not show sterane biodegradation. All of these group B samples are at level 5 on the Peters and Moldowan (1993) biodegradation scale. The Triplet and the 23tri/C30 values for group B are somewhat higher than in group A, 28,30-bisnorhopane is not as prominent, and 25,28,30-trisnorhopane ( $T_{177}$ ) is absent or at trace levels. The PAH-RI is the highest in the sample set. Sulfur-containing PAHs are at higher levels, as seen by the higher ratios of C2 and C3 dibenzothiophenes to phenanthrenes. The isoprenoidal cyclohexane series is particularly strong in this group.

Group B tarballs, although found at four locations on the south side of Santa Cruz Island, were found in larger numbers on beaches near Palos Verdes and San Diego, south of Los Angeles. These tarballs likely originated from seepage somewhere near Santa Monica Bay within the Los Angeles Basin, along the northwest-trending Palos Verdes fault where many active seeps are known to occur (Wilkinson, 1971). The dominance of  $\beta\beta$ -steranes within this group also supports this origin.  $\beta\beta$ -Steranes are reported to be particularly prominent in Santa Maria and Los Angeles Basin oils (Curiale et al., 1985). This characteristic, plus the lower BI values and slightly higher  $T/(T+M)$  values of the B-tarballs may reflect oil of higher thermal maturity (Peters and Moldowan, 1993) than that of the A group, and therefore a source somewhat deeper in the Monterey Formation.

The study of Hartman and Hammond (1981) also found that a significant proportion of tar came to the Channel Islands from the region of Santa Monica Bay. The tars then are probably intermittently transported north to the Channel Islands, and occasionally even further north, as shown by the one Group B occurrence (97-28) collected at the edge of Monterey Bay.

Group D tarballs are found mostly in tar mats near a dramatic blowhole in a shoreline outcrop at Carrington Pt. on SRI. There are three other occurrences, 99-9, -11, -12, just across the strait at Fraser Pt., near the group A tarmats. These three D-tarballs, however, appear more physically weathered (Table 1) than the A-tars that underlie them or are nearby, possibly due to across-channel transport of the group D tars. Group D is the only group in the data set with a tar that contains intact *n*-alkanes. A sample from the fresh tar mat at Carrington Pt. (00-126) contains a low level envelope of *n*-alkanes,  $C_{15}$  to  $C_{25}$ , and prominent pristane and phytane. The other samples contain no *n*-alkanes but several have traces of residual pristane and phytane, putting these samples at 3 and 4 on the biodegradation scale. Other distinguishing parameter values include slightly lower  $T_m/T_s$  and BI values, and generally higher  $T/(T+M)$  ratios compared to the A tars, all indicating slightly higher thermal maturity. In addition, group D samples have a fairly low PAH-RI source ratio and low relative levels of perylene.

Just as with group A, the D group shows signs of variable degradation in its regular sterane profiles. The sample with the oil-distribution of *n*-alkanes and prominent isoprenoids (00-126) is part of the fresh tar mat at Carrington Pt. (Table 1) and has a very notable  $\alpha 27R$  dominance on its *m/z* 217 chromatogram. Samples 00-67 and 00-106 also have high  $\alpha 27R$ , and therefore high  $\alpha 27R$  indices. The other D samples are more biodegraded, as shown by their lower  $\alpha 27R$  Index values and chromatograms with  $\beta\beta$ -steranes becoming more prominent relative to  $\alpha 27R$ . One sample (00-133) is highly degraded, based on the loss of regular steranes. This group has a biodegradation rank of 3 to 7, with most samples at the lower end of the range and only one sample at 7.

Other groups in the study, namely Groups E, F and G are very small groups that are found in this data set only on SRI and SMI. Group E is characterized by maturity parameters indicating low thermal maturity, i.e., very high  $T_m/T_s$  and BI, and very low  $T/(T+M)$ , and high values for the dibenzothiophene source parameters. Groups F and G are shown in the dendrogram to be one group, but the tie-lines are long enough, and a few parameters different enough that we consider them to probably be distinct groups. Group F from SMI has a slightly heavier  $\delta^{13}C$  value, with distinguishing source ratios of a high 23Tri/C30, moderate BI, no  $T_{177}$ , regular steranes ( $\beta\beta 27/28$  and  $\alpha 27R$ ) dominant, and a high PAH-RI. Group G, which, like C, has a sterane profile dominated by the two nor-steranes and thus is probably significantly impacted by biodegradation, appears to be a unique group in that source ratios 23Tri/C30, PAH-RI and its DBT parameters are somewhat higher than those of group A. Also, the lower

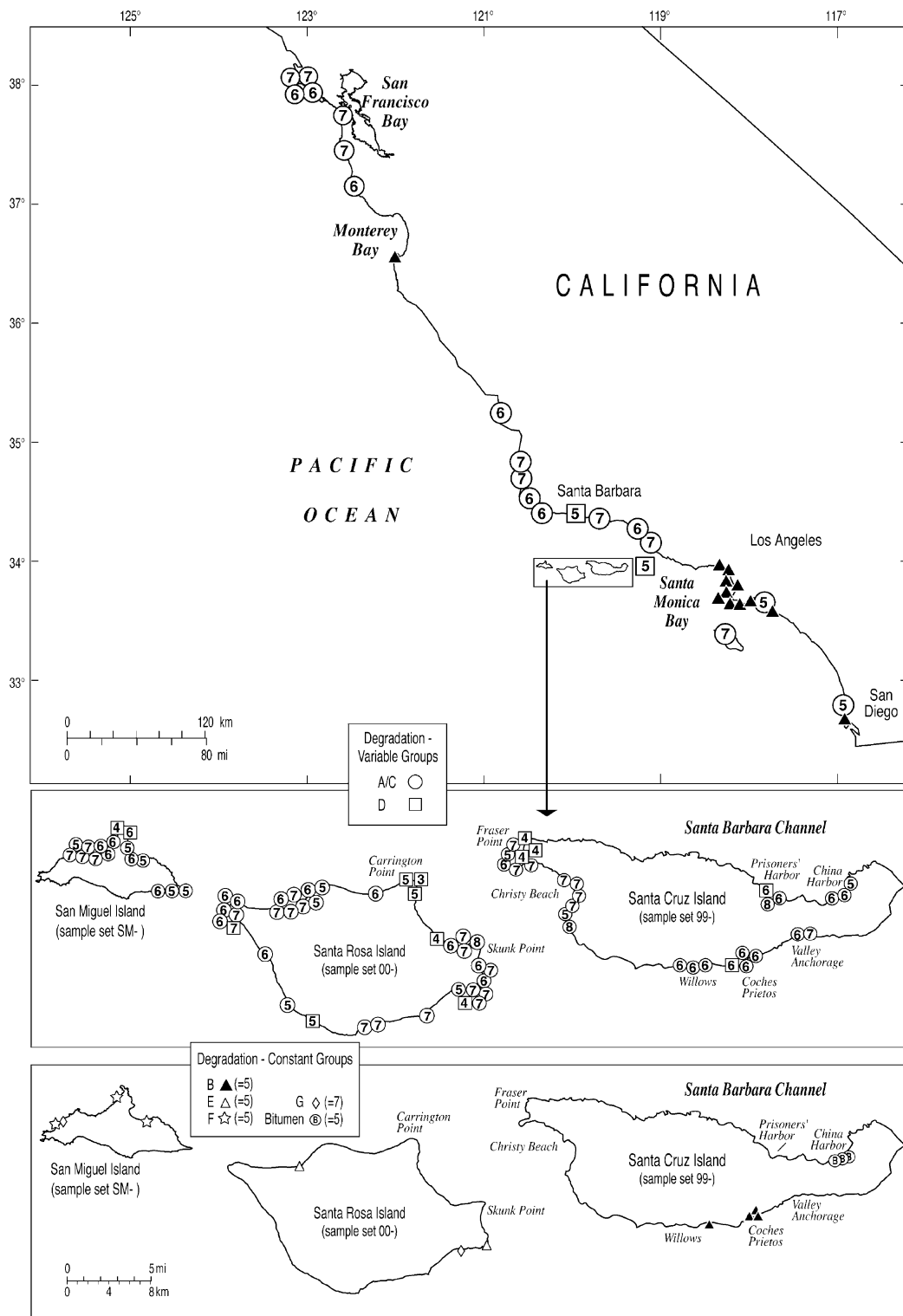


Fig. 4. Map of samples with biodegradation levels assigned as in Peters and Moldowan (1993). Levels in this sample set range from: 3 (only traces of paraffins remain), 4 (no *n*-paraffins, acyclic isoprenoids intact), 5 (acyclic isoprenoids absent), 6 (steranes partly degraded), 7 (steranes degraded, diasteranes intact), and 8 (hopanes partly degraded).

BI and higher T/(T+M) values imply somewhat higher maturity than other groups in the sample set.

The last three samples listed in Table 3 are onshore cliff or rock bitumen from China Harbor on SCI. These onshore bitumen samples are obviously natural and not anthropogenic, but they do not correlate with the tarballs washed onto the shore. They do share some characteristics, namely, a strong dominance of bisnorhopane (but no T<sub>177</sub>, 25,28,30-trisnorhopane, which Peters and Moldowan, 1993, report frequently co-occur), extremely immature sterane profiles, and significant perylene. Otherwise the chemical fingerprints are very different from those of the tarballs, which implies different local sources and geochemical processes, such as thermal maturation, than those giving rise to the offshore tarballs.

#### 4.2. Geographical distribution and potential sources

Two of the major groups in this study have potential sources geographically quite close to each other. These also are the two groups that are impacted by biodegradation, namely the large group A (including C) and group D. Although individual occurrences of group A tarballs cover a wide geographic area, from San Diego in the south to Point Reyes north of San Francisco, the major concentration occurs at Fraser Point on SCI (Fig. 1). Here, very large, dense tar mats dominated by A-tars cover the beach and rock outcrops. There are anecdotal reports of large-scale seepage between SCI and SRI, but no seeps have been mapped in the area. Nonetheless, a source just offshore of Fraser Point, between SCI and SRI, is suggested for the group A tars.

Group D has a major concentration of tars on SRI, at the tarmats on Carrington Point, which also may signal a nearby source. Fraser and Carrington Points are only separated by about 10 kilometers, across the strait between SCI and SRI. Indeed, some of the group D tarballs also have washed onto the shore at Fraser Point. However, sample 00-67, a group D tar from three miles north of Anacapa Island, occurs about 60 kilometers from the other group D occurrences. This tar is the only sample in this data set actually collected from an offshore seep. Thus, with two possible sources for closely correlatable tars (near the blowhole tarmats at Carrington Pt. and to the east near Anacapa Is.), there is a significant spatial range of sources for group D tarballs. The range for group D then is quite close to the area suggested as a source for the A/C tarballs. On the PCA cluster dendrogram (Fig. 3), group D falls very close to A and thus these three groups share some chemical similarities, in line with their spatial proximity.

The question then arises about the variability in the samples in the levels of biodegradation within each group. Fig. 4 shows a map of the tarball groups with each sample labeled according to its level of biodegradation,

using the ranking in Peters and Moldowan (1993). Groups A and D are the only groups with members at varying stages of biodegradation; the other groups, except group B which is noted to come from Santa Monica Bay, near Los Angeles, are very small, so variations may not be represented. Although within groups A and D there is broad areal scatter of the different biodegradation ranks due to ocean circulation, there seem to be more degraded samples (ranks 6, 7, and 8) to the south of the two Points and along the southern coasts of SCI and SRI. The less degraded ranks (3, 4, and 5), on the other hand, cluster at the two Points and north and east. This observation may imply that, although samples within group A and D may originate from different sources or reservoirs, microbial access could be different within different compartments of each of these reservoirs. Perhaps the area between the two islands is shallower and therefore tars seeping from that area are more subject to microbial attack. Tar seeps are known to have many outlets and sources of hydrocarbon emissions even from one localized seep (Leifer, 2002).

Of the other groups, E and G are too small and scattered to infer their sources. Group F, with locations only on the north side of SMI may indicate sources from north in the Santa Barbara Channel, where prolific seepage is known to occur (State Lands Commission Staff Report, 1977). Expanded data sets in future work may pinpoint these sources.

Finally, the locations of the tarballs shown on the map in Fig. 1 indicate that even if they originate in the area of the Channel Islands, tarballs from these groups are occasionally transported by ocean currents out of the area. Scattered occurrences of Group A were found as far north as Point Reyes, north of San Francisco Bay and as far south as San Diego. Group B samples range from Monterey Bay to San Diego. These findings indicate that the sources may be fairly large seepages that have been leaking tar over a long period of time, and that the coastline currents transport the tarballs over long distances. It is important in studying the contaminant record to recognize these specific tars originating from natural sources that may be many hundreds of kilometers away, and not to attribute them to anthropogenic contamination.

## 5. Conclusions

This study provides the following information on the geochemical nature of tarballs common to the Channel Islands:

- All beached tarballs in this sample set share geochemical source characteristics typical of source rock in the Miocene Monterey Formation.

- Differences in relative amounts of constituents reflecting different inputs, levels of thermal maturity, degrees of biodegradation, and probably slightly different depositional facies allow fingerprinting and correlation by chemometric analysis. The range of individual fingerprint parameters within tarball groups, however, is somewhat broad and correlations are not as tight as might be expected from, for example, a spill of a specific crude oil such as the Exxon Valdez. Apparently, seep oil and related shoreline tarballs, even if from the same source, have small local variations in constituent concentrations, giving broader ranges within the chemical signature.
- The tarballs originated from shallow reservoirs, as indicated by their low relative thermal maturity and abundant bisnorhopane. Significant but variable proportions of perylene, a PAH of biogenic origin found in surface marine sediments, implies inclusion by migration through these sediments.
- Biodegradation in these shallow subsurface reservoirs impacts sterane distributions and can cause tars from similar sources to appear different. The largest group of tars, A, represents a continuum of sterane loss, from abundant regular steranes dominated by  $\alpha\alpha\text{C}_{27}\text{R}$  to samples which have lost most of the regular steranes. A small group, C, from the same area as A and probably a subset of group A, is biodegraded even beyond the regular steranes, showing a diminished  $\alpha\beta\text{C}_{30}$ -hopane and, to a lesser extent, bisnorhopane.
- A pair of unusual steranes prominent in this sample set,  $\text{C}_{26}$  24-nor-5 $\alpha$ -cholestane and  $\text{C}_{27}$  27-nor-24-methyl-5 $\alpha$ -cholestane, are not impacted by biodegradation, and maintain a consistent level relative to  $\text{C}_{30}$   $\alpha\beta$ -hopane, throughout the data set.
- The dominant shallow seepage around the Channel Islands seems to originate near Fraser Pt. on Santa Cruz Island and accounts for about 65% of the sample set. The horizontal spatial extent of seepage within grouped samples may be rather large, as implied in the D-group where two possible sources are about 60 kilometers apart.
- Circulation of the coastal currents can transport tarballs hundreds of kilometers north and south along the California coast.
- A library database of the several groups of tarballs from this study can help to differentiate natural from anthropogenic hydrocarbon contamination along the California coast. These data will be used in future studies to compare local offshore production oils, to evaluate how

source parameters change with depth, and to map spatial and temporal tarball distributions.

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## Appendix I. Geochemical parameters

### Whole oil

1.  $\delta^{13}\text{C}$ , the carbon isotopic composition of whole tar residues. These compositions are useful for oil and source rock correlations (Peters and Moldowan, 1993).

### Saturate fraction

2. Pr/Ph, pristane/phytane. This is a widely used source parameter (Peters and Moldowan, 1993) based on two of the most common isoprenoids in crude oils. These compounds are readily lost by degradation, and are not present in most of the tarballs in this study, although they are prominent in unweathered production or crude oils.

### Triterpanes (hopanes), $m/z$ 191 SIM chromatograms

3. Tm/Ts, 17 $\alpha$ -22,29,30-trisnorhopane/18 $\alpha$ -22,29,30-trisnorhopane. This ratio is used as both a source and maturity parameter (Seifert and Moldowan, 1978).

4. Triplet, [ $\text{C}_{26}$ -tricyclic terpane (S?) +  $\text{C}_{26}$ -tricyclic terpane (R?)/ $\text{C}_{24}$ -tetracyclic terpane]. This source parameter was used to distinguish coastal tar residues in Prince William Sound (Kvenvolden et al., 1995).

5. 23T/ $\text{C}_{30}$ ,  $\text{C}_{23}$  tricyclic terpane/17 $\alpha$ ,21 $\beta$ (H)-hopane. This ratio is a source parameter adapted from Peters and Moldowan (1993).

6. 23Tri/24Tri,  $\text{C}_{23}$  tricyclic terpane/ $\text{C}_{24}$  tricyclic terpane. Source parameter.

7.  $\text{C}_{30}/\text{C}_{29}$ , 17 $\alpha$ ,21 $\beta$ (H)-hopane/17 $\alpha$ ,21 $\beta$ (H)-30-norhopane. This ratio was used by Palacas et al. (1984) as a source parameter.

8.  $C_{31}S/(S+R)$ ,  $17\alpha,21\beta(H)$ -homohopane (22S)/ $17\alpha,21\beta(H)$ -homohopane (22S+22R). This epimer ratio is a hopane maturity parameter used extensively in petroleum geochemistry; the equilibrium ratio at full maturity is  $\sim 0.6$  (Ensminger et al., 1974; Mackenzie, 1984).

9. BI, Bisnorhopane Index, 28,30-bisnorhopane/ $17\alpha,21\beta(H)$ -hopane. This source ratio has been used to characterize oils from the Monterey Formation. The presence of 28,30-bisnorhopane, in addition to indicating a marine, highly reducing depositional environment (Curiale et al., 1985), is reported to be passed on from bitumen rather than generated from kerogen and therefore decreases with thermal maturity (Peters and Moldowan, 1993). Therefore, this ratio would be higher in oils sourced from near-surface facies.

10. OI, Oleanane Index,  $18\alpha+\beta(H)$ -oleanane/ $17\alpha,21\beta(H)$ -hopane. This commonly used source parameter indicates a contribution from Cretaceous and younger plant material (Peters and Moldowan, 1993). In the California coastal tars, oleanane is generally present, but in low amounts.

11. GI, Gammacerane Index, gammacerane/ $17\alpha,21\beta(H)$ -hopane. This ratio is used as a source parameter; abundant gammacerane is a carbonate/evaporite facies indicator and a marker for highly reducing, hypersaline depositional environments (Peters and Moldowan, 1993).

12.  $T_{177}/Hop$ , 25,28,30-trisnorhopane/ $17\alpha,21\beta(H)$ -hopane. 25,28,30-trisnorhopane is found in some oils from the Monterey Formation (Curiale et al., 1985) so this index is a possible source indicator.

#### *Steranes, m/z 217 SIM chromatograms*

13.  $C_{29}S/(S+R)$ , 24-ethyl- $5\alpha,14\alpha,17\alpha(H)$ -cholestane (20S)/ 24-ethyl- $5\alpha,14\alpha,17\alpha(H)$ -cholestane (20S+20R). This sterane epimer ratio is commonly used as a maturity parameter; the equilibrium value at full maturity is  $\sim 0.5$  (Mackenzie et al., 1980).

14.  $C_{28}R/C_{29}R$ , 24-methyl- $5\alpha,14\alpha,17\alpha(H)$ -cholestane (20R)/ 24-ethyl- $5\alpha,14\alpha,17\alpha(H)$ -cholestane (20R). This source parameter has been modified from discussions in Grantham and Wakefield (1988) and Waples and Machihara (1991).

15. Dominant sterane(s). This descriptor indicates the sterane(s) that are most prominent in the  $m/z$  217 chromatogram. The  $m/z$  217 chromatogram may also include a fragment of bisnorhopane (BN), which is noted if it is one of the most prominent peaks.

16.  $\alpha 27R/Hop$ , a Sterane Index,  $5\alpha,14\alpha,17\alpha(H)$ -cholestane/ $17\alpha,21\beta(H)$ -hopane. This parameter gives an indication of relative proportions of a common regular sterane to hopane. In this study it helps track sterane biodegradation.

17.  $nor26\&27/Hop$ , another Sterane Index, two tentatively identified steranes,  $C_{26}$  24-nor- $5\alpha$ -cholestane (Moldowan et al., 1991) and  $C_{27}$  27-nor-24-methyl- $5\alpha$ -cholestane (Schouten et al., 1994), indexed to hopane. This is a source parameter and may serve as a maturity parameter, particularly in subsequent studies when deeper production oils are considered.

18.  $\alpha 27R/nor27$ ,  $5\alpha,14\alpha,17\alpha(H)$ -cholestane/ $C_{27}$  27-nor-24-methyl- $5\alpha$ -cholestane. A sterane parameter which also tracks sterane biodegradation.

#### *Aromatic fraction*

19. PAH-RI, Polycyclic Aromatic Hydrocarbon-Refractory Index. This index is a source parameter, the ratio of the second, usually major, peak containing the  $C_{26}R$  and  $C_{27}S$  members in the highly refractory  $C_{26}$  to  $C_{28}$  triaromatic sterane suite ( $m/z$  231) to that of the first, usually dominant, peak in the monomethyl chrysenes ( $m/z$  242) (Hostettler et al., 1999).

20.  $T/(T+M)$ .  $T = \sum$  triaromatic steranes (areas),  $C_{26}$  to  $C_{28}$ ,  $m/z$  231;  $M = \sum$  monoaromatic steranes (areas),  $C_{26}$  to  $C_{28}$ ,  $m/z$  253. Aromatic steroid parameter. This is a thermal maturity and source parameter, widely used, modified from that described in Peters and Moldowan (1993). Low values, reflecting relatively higher levels of the monoaromatic steroids, indicate low thermal maturity.

21.  $\sum C2D/\sum C2P$ ,  $\sum$  dimethyl dibenzothiophenes ( $m/z$  212)/ $\sum$  dimethyl phenanthrenes ( $m/z$  206). Source parameter indicating relative levels of sulfur-containing PAH to regular PAH (Kaplan et al., 1997; Bence et al., 1996).

22.  $\sum C3D/\sum C3P$ ,  $\sum$  trimethyl dibenzothiophenes ( $m/z$  226)/ $\sum$  trimethyl phenanthrenes ( $m/z$  220). Source parameter as #21.

23. Pery/Chr, a PAH parameter, perylene normalized to chrysene. Perylene helps distinguish shallow-seeping oils from deeper oils. Perylene has a biogenic origin and is associated with near-surface bitumens (Ventkatesan, 1988). It is known to be present in variable amounts in shallow Monterey sediments (Kvenvolden et al., 2002).



Appendix II. Geochemical parameters<sup>a</sup> for samples

Field No.	$\delta^{13}C$	Pr/Ph	Tm/Ts	Triplet	23Tri/C30	23Tri/24Tri	C30/C29	C31 S/(S+R)	BI	OI	GI	T177/C30	C29 S/(S+R)	C28/C29	Dominant sterane (s)	$\alpha$ 27R/Hop	nor26&27/Hop	$\alpha$ 27R/nor27	PAH-RI	T/(T+M)	$\Sigma$ C2D/ $\Sigma$ C2P	$\Sigma$ C3D/ $\Sigma$ C3P	Pery/Chr
<i>GROUP A—least degraded</i>																							
97-23	-23.3	nc	4.6	3.6	0.44	2.5	1.5	0.60	1.7	0.03	0.12	0.19	0.24	0.94	$\alpha$ 27R	0.46	0.31	2.8	78	0.13	2.2	2.5	10
99-10	-23.6	nc	4.6	4.0	0.41	2.1	1.4	0.58	1.5	0.03	0.11	0.07	0.35	1.0	$\alpha$ 27R	0.48	0.28	2.8	47	0.14	2.0	2.4	5.2
99-28	-23.7	nc	4.9	3.7	0.41	2.6	1.4	0.59	1.9	0.03	0.11	0.17	0.31	1.0	$\alpha$ 27R	0.47	0.33	2.6	76	0.11	2.2	2.6	11
00-116	-23.0	nc	4.4	3.6	0.35	2.6	1.6	0.59	2.1	0.03	0.13	0.09	0.36	0.94	$\alpha$ 27R	0.46	0.26	3.2	84	0.12	2.1	2.5	12
00-117	-23.0	nc	4.5	3.5	0.45	2.4	1.6	0.59	1.6	0.03	0.10	0.04	0.35	1.0	$\alpha$ 27R	0.47	0.28	2.8	42	0.14	2.0	2.4	2.0
00-147	-23.1	nc	4.7	3.7	0.41	2.5	1.4	0.59	1.9	0.03	0.12	0.23	0.31	1.0	$\alpha$ 27R	0.58	0.32	3.3	59	0.12	2.0	2.4	9.6
SM-2	-23.2	nc	4.1	3.3	0.51	2.3	1.5	0.61	1.7	0.03	0.11	0.08	0.34	1.1	$\alpha$ 27R	0.46	0.26	3.1	54	0.13	2.0	2.6	4.9
SM-3	-23.2	nc	4.4	3.4	0.51	2.3	1.5	0.60	1.7	0.03	0.12	0.07	0.34	1.1	$\alpha$ 27R	0.47	0.26	3.2	49	0.14	2.1	2.6	5.2
SM-9	-23.2	nc	4.2	3.3	0.49	2.4	1.5	0.60	1.5	0.03	0.11	0.04	0.34	1.0	$\alpha$ 27R	0.48	0.25	3.3	36	0.14	2.0	2.5	2.9
SM-19	-23.2	nc	4.2	3.6	0.46	2.3	1.5	0.61	1.6	0.03	0.12	0.08	0.33	1.0	$\alpha$ 27R	0.50	0.27	3.3	57	0.14	1.9	2.5	5.9
<i>Group A—less degraded</i>																							
98-44	-23.3	nc	4.8	3.8	0.37	2.3	1.4	0.58	1.6	0.03	0.12	0.13	0.32	0.91	$\alpha$ 27R	0.31	0.33	1.6	79	0.16	2.0	2.4	9.6
98-46	-23.3	nc	4.5	3.7	0.38	2.2	1.5	0.57	1.4	0.03	0.11	0.03	0.33	0.97	$\alpha$ 27R	0.34	0.31	1.8	60	0.15	1.8	2.2	4.2
L99-27	-23.3	0.40	5.4	4.0	0.43	2.2	1.3	0.59	1.1	0.03	0.09	0.02	0.34	1.3	$\alpha$ 27R	0.25	0.31	1.4	62	0.23	2.0	2.5	1.7
99-6	-23.6	nc	4.7	3.8	0.41	2.6	1.4	0.60	1.9	0.03	0.11	0.23	0.30	1.0	$\alpha$ 27R	0.35	0.35	1.8	68	0.11	2.0	2.4	12
99-18	-23.6	nc	3.2	3.9	0.34	2.3	1.5	0.59	1.6	0.04	0.10	0.09	0.41	0.96	$\beta\beta$ 28s>27s, $\alpha$ 27R	0.28	0.29	1.7	60	0.13	1.3	1.7	31
99-27	-23.5	nc	5.0	3.7	0.42	2.5	1.4	0.59	1.8	0.03	0.11	0.13	0.30	1.1	$\alpha$ 27R	0.40	0.33	2.2	75	0.13	2.2	2.4	9.2
99-32	-23.4	nc	5.0	3.6	0.43	2.3	1.4	0.60	1.4	0.03	0.10	0.02	0.36	1.1	$\alpha$ 27R	0.31	0.30	1.7	47	0.16	2.0	2.4	3.2
99-33	-23.7	nc	4.8	3.9	0.44	2.3	1.4	0.59	1.7	0.03	0.10	0.15	0.33	1.0	$\alpha$ 27R, $\beta\beta$ 27&28	0.27	0.34	1.4	57	0.14	2.1	2.1	8.0
99-34	-23.6	nc	5.2	3.6	0.41	2.3	1.4	0.59	1.5	0.03	0.10	0.02	0.35	1.0	$\alpha$ 27R	0.31	0.31	1.7	46	0.16	2.0	2.4	3.0
99-39	-23.5	nc	4.9	3.6	0.44	2.3	1.4	0.59	1.7	0.03	0.10	0.09	0.33	1.0	$\alpha$ 27R	0.26	0.32	1.4	58	0.15	2.0	2.4	6.8
00-50	-23.2	nc	5.2	3.5	0.53	2.4	1.4	0.60	1.8	0.03	0.10	0.13	0.28	1.1	$\alpha$ 27R	0.28	0.35	1.5	58	0.10	2.0	2.5	6.9
00-115	-23.1	nc	4.6	3.7	0.37	2.6	1.5	0.60	2.0	0.03	0.14	0.09	0.39	0.79	$\alpha$ 27R, $\beta\beta$ 27&28	0.21	0.27	1.4	59	0.11	2.1	2.8	12
00-128	-23.2	nc	4.4	3.7	0.45	2.3	1.4	0.59	1.6	0.03	0.11	0.04	0.34	0.98	$\alpha$ 27R	0.35	0.30	2.0	53	0.13	2.0	2.4	2.7
00-131	-23.2	nc	4.3	3.6	0.37	2.5	1.6	0.60	2.1	0.03	0.13	0.09	0.40	0.83	$\beta\beta$ 27&28, $\alpha$ 27R	0.23	0.26	1.6	83	0.12	2.2	2.6	11
SM-11	-23.2	nc	4.3	3.4	0.49	2.4	1.5	0.61	1.5	0.03	0.11	0.06	0.33	1.1	$\alpha$ 27R	0.32	0.26	2.2	46	0.14	2.1	2.5	4.6
SM-13	-22.9	nc	3.6	3.6	0.45	2.3	1.6	0.60	1.3	0.03	0.10	0.04	0.30	0.99	$\alpha$ 27R	0.27	0.29	1.7	56	0.14	1.9	2.4	2.9
<i>Group A—more degraded</i>																							
98-5	-23.2	nc	5.0	3.8	0.40	2.3	1.4	0.59	1.5	0.03	0.12	0.02	0.30?	0.91?	"3"> $\alpha$ 27R, $\beta\beta$ 27&28	0.14	0.35	0.74	67	0.16	1.8	2.4	3.4
98-33	-22.9	nc	4.2	3.8	0.41	2.3	1.4	0.61	1.1	0.03	0.11	0.03	0.31?	1.2?	"3"	0.15	0.38	0.72	76	0.16	1.5	2.1	26
99-19	-23.5	nc	4.8	3.7	0.54	2.3	1.1	0.60	1.4	0.04	0.13	0.03	0.25?	0.78?	"3"	0.08	0.40	0.40	47	0.17	1.6	2.1	6.3
99-22	-23.6	nc	5.2	3.7	0.40	2.3	1.4	0.60	1.8	0.03	0.11	0.15	0.30	0.90	"3"> $\beta\beta$ 27&28, $\alpha$ 27R	0.17	0.36	0.87	64	0.12	2.2	2.7	11
99-24	-23.3	nc	4.9	3.6	0.40	2.4	1.4	0.60	1.8	0.03	0.11	0.16	0.28	0.95	"3"> $\alpha$ 27R, $\beta\beta$ 27&28	0.18	0.34	0.92	60	0.14	2.2	2.6	10
99-29	-23.5	nc	5.0	3.6	0.68	2.3	0.97	0.60	1.4	0.04	0.15	0.03	0.32?	1.1?	"3"	0.14	0.53	0.50	41	0.16	1.5	2.2	3.9
99-36	-23.5	nc	5.0	3.6	0.44	2.3	1.4	0.59	1.6	0.03	0.10	0.03	0.32	0.97	$\beta\beta$ 27&28, $\alpha$ 27R	0.18	0.31	0.98	43	0.15	2.1	2.4	3.1
99-37	-23.5	nc	5.1	3.7	0.43	2.4	1.4	0.60	1.7	0.03	0.11	0.09	0.27	0.92	"3"> $\alpha$ 27R, $\beta\beta$ 27&28	0.16	0.33	0.84	56	0.14	2.1	2.7	7.2
00-39	-23.2	nc	5.2	3.4	0.51	2.4	1.4	0.60	1.7	0.03	0.09	0.04	0.25?	0.83?	"3"> $\beta\beta$ 27&28	0.10	0.32	0.55	48	0.12	2.0	2.4	3.0
00-102	-23.3	nc	4.7	3.6	0.43	2.3	1.4	0.59	1.6	0.03	0.11	0.04	0.32	0.87	"3"> $\alpha$ 27R, $\beta\beta$ 27&28	0.17	0.31	0.94	48	0.13	2.0	2.6	3.2
00-109	-23.1	nc	4.6	3.7	0.51	2.3	1.3	0.60	1.6	0.03	0.13	0.04	0.31?	1.1?	"3"	0.09	0.35	0.48	57	0.14	1.6	2.3	3.7
00-119	-22.9	nc	4.3	3.9	0.45	2.3	1.5	0.59	1.5	0.03	0.10	0.04	0.33	0.95	"3"> $\alpha$ 27R, $\beta\beta$ 27&28	0.16	0.31	0.91	37	0.14	1.9	2.3	2.7

(continued on next page)

## Appendix II (continued)

Field No.	$\delta^{13}\text{C}$	Pr/Ph	Tm/Ts	Triplet	23Tri/C30	23Tri/24Tri	C30/C29	C31 S/(S+R)	BI	OI	GI	T177/C30	C29 S/(S+R)	C28/C29	Dominant sterane (s)	$\alpha$ 27R/Hop	nor26&27/Hop	$\alpha$ 27R/nor27	PAH-RI	T/(T+M)	$\Sigma\text{C2D}/\Sigma\text{C2P}$	$\Sigma\text{C3D}/\Sigma\text{C3P}$	Pery/Chr
00-124	-23.1	nc	4.8	3.7	0.42	2.4	1.4	0.59	1.9	0.03	0.11	0.23	0.25?	0.71?	"3"	0.09	0.35	0.45	49	0.11	2.0	2.4	10
00-129	-23.2	nc	4.2	3.9	0.45	2.3	1.5	0.58	1.4	0.03	0.11	0.04	0.32	0.97	$\beta\beta$ 28, $\alpha$ 27R, $\beta\beta$ 27	0.19	0.30	1.2	44	0.14	1.7	2.3	6.2
00-132	-23.2	nc	4.5	3.6	0.45	2.4	1.4	0.59	1.7	0.03	0.11	0.08	0.33	0.98	$\beta\beta$ 28, $\alpha$ 27R, $\beta\beta$ 27	0.20	0.29	1.1	48	0.13	2.0	2.5	7.5
00-135	-23.0	nc	4.5	3.3	0.42	2.2	1.4	0.60	1.5	0.03	0.10	0.05	0.34	0.88	"A" > $\beta\beta$ 28	0.11	0.23	0.74	43	0.16	1.5	1.7	6.0
00-137	-23.2	nc	4.9	3.5	0.41	2.3	1.5	0.59	1.8	0.03	0.11	0.17	0.31	0.87	$\alpha$ 27R, $\beta\beta$ 27&28	0.23	0.33	1.2	52	0.12	2.0	2.4	8.3
SM-1	-23.2	nc	4.2	3.4	0.53	2.3	1.5	0.60	1.5	0.03	0.11	0.03	0.32	0.99	"3", $\beta\beta$ 28/27s, $\alpha$ 27R	0.16	0.29	0.99	67	0.14	2.0	2.5	3.0
SM-15	-22.9	nc	4.1	3.5	0.47	2.4	1.5	0.61	1.5	0.03	0.11	0.05	0.24	0.80	"3" > $\beta\beta$ 28&27	0.08	0.30	0.46	50	0.14	2.0	2.7	4.0
SM-18	-23.2	nc	4.2	3.6	0.48	2.4	1.5	0.61	1.5	0.03	0.12	0.05	0.24?	0.71?	"3"	0.08	0.34	0.43	48	0.14	2.1	2.7	4.3
SM-20	-23.2	nc	4.4	3.4	0.47	2.3	1.5	0.60	1.4	0.03	0.11	0.07	0.30	0.87	"3", $\beta\beta$ 28&27	0.09	0.30	0.54	55	0.15	2.0	2.6	4.7
<i>GROUP A—most degraded</i>																							
97-10	-23.2	nc	4.6	3.4	0.51	2.4	1.5	0.60	1.4	0.03	0.10	0.03	nc	nc	nor26&27,BN (= "3")	0.03	0.33	0.18	47	0.18	2.0	2.4	3.4
98-49A	-23.3	nc	5.0	3.8	0.38	2.3	1.4	0.59	1.5	0.03	0.12	0.25	nc	nc	nor26&27,BN	0.03	0.36	0.14	74	0.14	2.0	2.4	17
L99-25	-23.3	nc	4.7	3.7	0.44	2.3	1.4	0.60	1.4	0.03	0.10	0.02	nc	nc	nor26&27,BN	0.05	0.33	0.31	54	0.16	1.9	2.4	3.3
99-3	-23.6	nc	4.0	3.7	0.35	2.5	1.5	0.60	1.7	0.03	0.07	0.05	nc	nc	nor26&27,BN	0.03	0.40	0.12	54	0.10	1.7	2.4	9.4
99-4	-23.4	nc	4.6	3.8	0.45	2.3	1.4	0.60	1.5	0.03	0.09	0.03	nc	nc	nor26&27,BN	0.05	0.31	0.27	49	0.15	1.9	2.5	3.4
99-5	-23.5	nc	5.2	3.8	0.41	2.4	1.3	0.60	1.9	0.03	0.11	0.23	nc	nc	nor26&27,BN	0.05	0.37	0.23	63	0.12	2.0	2.5	12
99-8	-23.6	nc	3.9	3.7	0.37	2.5	1.4	0.60	1.8	0.03	0.12	0.09	nc	nc	nor26&27,BN	0.03	0.41	0.12	53	0.12	1.8	2.5	10
99-13	-23.5	nc	5.1	3.8	0.39	2.4	1.4	0.58	1.7	0.03	0.11	0.11	nc	nc	nor26&27,BN	0.04	0.36	0.23	64	0.13	2.0	2.5	9.4
99-14	-23.4	nc	4.9	3.6	0.48	2.4	1.3	0.60	1.4	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.37	0.17	45	0.18	1.5	2.1	3.7
99-15	-23.4	nc	5.0	3.8	0.40	2.4	1.4	0.60	1.7	0.03	0.11	0.13	nc	nc	nor26&27,BN	0.04	0.37	0.18	67	0.11	2.0	2.5	11
99-38	-23.7	nc	5.0	3.5	0.43	2.4	1.4	0.60	1.6	0.03	0.10	0.13	nc	nc	nor26&27,BN	0.03	0.34	0.17	55	0.16	2.0	2.4	8.2
99-40	-23.4	nc	5.1	3.6	0.45	2.3	1.4	0.60	1.5	0.03	0.10	0.02	nc	nc	nor26&27,BN	0.04	0.36	0.22	53	0.19	2.0	2.4	4.1
99-43	-23.2	nc	5.0	3.6	0.48	2.3	1.3	0.60	1.6	0.03	0.10	0.04	nc	nc	nor26&27,BN	0.06	0.35	0.29	52	0.12	2.0	2.4	2.8
99-45	-23.5	nc	5.0	3.6	0.48	2.3	1.3	0.61	1.6	0.03	0.10	0.06	nc	nc	nor26&27,BN	0.07	0.33	0.40	50	0.12	2.1	2.5	3.8
00-36	-23.3	nc	5.1	3.6	0.52	2.3	1.3	0.60	1.6	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.05	0.38	0.23	53	0.12	2.0	2.5	3.1
00-49	-23.1	nc	4.6	3.4	0.49	2.3	1.4	0.60	1.5	0.03	0.10	0.03	nc	nc	nor26&27,BN	0.03	0.37	0.14	48	0.14	2.0	2.3	3.5
00-65	-23.2	nc	5.2	3.7	0.49	2.5	1.3	0.60	1.9	0.03	0.11	0.25	nc	nc	nor26&27,BN	0.05	0.42	0.21	67	0.09	2.2	2.5	8.2
00-104	-23.1	nc	4.8	3.5	0.42	2.3	1.5	0.59	1.6	0.03	0.11	0.04	nc	nc	nor26&27,BN	0.07	0.34	0.36	46	0.13	2.0	2.4	2.9
00-105	-22.9	nc	4.0	3.6	0.44	2.3	1.4	0.59	1.5	0.03	0.11	0.04	nc	nc	nor26&27,BN	0.05	0.34	0.24	56	0.13	1.8	2.2	2.4
00-107	-23.2	nc	4.8	3.6	0.47	2.4	1.4	0.60	1.7	0.03	0.11	0.12	nc	nc	nor26&27,BN	0.03	0.32	0.17	66	0.12	2.0	2.4	5.4
00-110	-23.1	nc	4.8	3.5	0.44	2.3	1.5	0.61	1.5	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.34	0.18	52	0.15	1.9	2.4	2.8
00-111	-23.0	nc	5.0	3.6	0.44	2.3	1.4	0.60	1.5	0.03	0.11	0.04	nc	nc	nor26&27,BN	0.03	0.36	0.15	49	0.14	1.5	2.3	3.6
00-114	-23.0	nc	4.6	3.5	0.52	2.4	1.3	0.60	1.5	0.04	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.36	0.16	53	0.14	1.5	2.3	3.2
00-118	-23.2	nc	4.9	3.5	0.43	2.3	1.4	0.59	1.7	0.03	0.10	0.05	nc	nc	nor26&27,BN	0.07	0.32	0.38	46	0.14	2.0	2.4	3.1
00-121	-23.2	nc	4.7	3.7	0.43	2.4	1.4	0.60	1.7	0.03	0.11	0.18	nc	nc	nor26&27,BN	0.03	0.34	0.15	58	0.13	2.0	2.4	7.7
00-122	-23.2	nc	4.8	3.7	0.50	2.3	1.4	0.60	1.6	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.32	0.18	52	0.15	2.0	2.4	2.7
00-123	-23.1	nc	4.5	3.7	0.47	2.5	1.5	0.59	1.8	0.03	0.11	0.13	nc	nc	nor26&27,BN	0.05	0.35	0.27	61	0.11	2.0	2.4	10
00-130	-23.1	nc	4.8	3.6	0.46	2.4	1.5	0.59	1.5	0.03	0.10	0.07	nc	nc	nor26&27,BN	0.03	0.35	0.16	55	0.14	2.0	2.5	4.1
00-148	-23.1	nc	4.9	3.7	0.47	2.4	1.4	0.60	1.4	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.35	0.17	63	0.13	2.0	2.3	2.9
00-156	-23.1	nc	4.7	3.7	0.43	2.3	1.5	0.59	1.6	0.03	0.11	0.09	nc	nc	nor26&27,BN	0.06	0.33	0.21	55	0.12	2.0	2.4	2.7
00-158	-23.1	nc	4.8	3.7	0.44	2.4	1.4	0.60	1.7	0.03	0.12	0.12	nc	nc	nor26&27,BN	0.04	0.35	0.23	55	0.13	2.0	2.5	5.6
00-163	-23.2	nc	4.6	3.8	0.45	2.3	1.4	0.59	1.6	0.03	0.11	0.07	nc	nc	nor26&27,BN	0.04	0.36	0.18	63	0.13	2.0	2.5	3.9
SM-7	-23.2	nc	4.3	3.5	0.50	2.3	1.5	0.61	1.4	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.01	0.31	0.05	48	0.20	1.9	2.5	3.5

(continued on next page)

Appendix II (continued)

Field No.	$\delta^{13}\text{C}$	Pr/Ph	Tm/Ts	Triplet	23Tri/C30	23Tri/24Tri	C30/C29	C31 S/(S+R)	BI	OI	GI	T177/C30	C29 S/(S+R)	C28/C29	Dominant sterane (s)	$\alpha$ 27R/Hop	nor26&27/Hop	$\alpha$ 27R/nor27	PAH-RI	T/(T+M)	$\Sigma$ C2D/ $\Sigma$ C2P	$\Sigma$ C3D/ $\Sigma$ C3P	Pery/Chr
SM-8	-22.8	nc	4.2	3.4	0.51	2.4	1.4	0.60	1.4	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.03	0.33	0.14	49	0.17	1.9	2.4	3.2
SM-10	-23.2	nc	4.4	3.4	0.55	2.4	1.4	0.61	1.6	0.03	0.11	0.03	nc	nc	nor26&27,BN	0.05	0.34	0.28	42	0.17	2.1	2.7	3.1
SM-12	-22.7	nc	4.2	3.4	0.49	2.3	1.5	0.60	1.6	0.03	0.11	0.04	nc	nc	nor26&27,BN	0.03	0.32	0.16	46	0.13	2.1	2.7	3.6
<i>GROUP B</i>																							
97-22	-23.2	nc	3.8	6.6	1.0	2.7	1.5	0.61	0.38	0.04	0.09	0	0.37	1.3	$\beta\beta$ 27/28s	0.48	0.46	1.9	148	0.29	3.7	3.6	0.46
97-28	-23.1	nc	3.8	5.7	0.86	2.7	1.5	0.60	0.39	0.04	0.10	0	0.29	1.2	$\beta\beta$ 27/28s	0.36	0.38	1.8	148	0.25	4.2	4.0	0.64
L99-2	-23.4	nc	4.0	5.5	0.72	2.6	1.4	0.57	0.39	0.04	0.07	0	0.38	1.2	$\beta\beta$ 27/28s	0.42	0.39	1.9	160	0.16	3.8	3.8	1.7
L99-3	-23.4	nc	4.0	5.8	0.71	2.6	1.4	0.57	0.41	0.04	0.07	0	0.38	1.2	$\beta\beta$ 27/28s	0.38	0.41	1.6	146	0.14	3.7	3.7	1.3
L99-4	-23.3	nc	4.2	5.7	0.74	2.7	1.4	0.57	0.43	0.04	0.07	0	0.36	1.2	$\beta\beta$ 27/28s	0.38	0.43	1.6	174	0.15	3.9	4.0	1.7
L99-8	-23.3	nc	4.3	5.5	0.65	2.6	1.4	0.58	0.56	0.04	0.08	0.01	0.36	1.2	$\beta\beta$ 27/28s	0.34	0.39	1.5	163	0.15	3.7	3.7	3.7
L99-9	-23.2	nc	4.3	5.8	0.71	2.6	1.5	0.56	0.43	0.04	0.07	0	0.38	1.1	$\beta\beta$ 27/28s	0.25	0.34	1.3	163	0.12	3.8	4.0	1.1
L99-10	-23.3	nc	4.0	5.7	0.65	2.6	1.5	0.57	0.55	0.04	0.08	0.01	0.37	1.2	$\beta\beta$ 27/28s	0.33	0.37	1.6	163	0.12	3.6	3.7	1.8
L99-11	-23.5	nc	3.9	5.5	0.68	2.5	1.5	0.56	0.40	0.04	0.07	0	0.39	1.2	$\beta\beta$ 27/28s	0.36	0.38	1.7	158	0.14	3.8	3.8	1.0
L99-12	-23.3	nc	4.2	5.8	0.68	2.5	1.5	0.57	0.38	0.04	0.07	0	0.36	1.2	$\beta\beta$ 27/28s	0.41	0.41	1.8	175	0.13	3.7	3.8	2.1
L99-13	-23.3	nc	4.0	5.8	0.68	2.6	1.5	0.57	0.40	0.04	0.07	0	0.38	1.2	$\beta\beta$ 27/28s	0.40	0.39	1.8	165	0.13	3.7	3.8	1.1
L99-28	-23.2	nc	3.9	5.5	0.75	2.6	1.4	0.57	0.42	0.04	0.06	0	0.38	1.3	$\beta\beta$ 27/28s	0.41	0.41	1.8	137	0.22	3.9	3.9	0.78
99-16	-23.4	nc	4.2	5.7	0.75	2.6	1.4	0.58	0.40	0.04	0.06	0	0.38	1.3	$\beta\beta$ 27/28s	0.39	0.40	1.8	144	0.21	3.8	3.9	0.81
99-17	-23.5	nc	4.2	5.8	0.81	2.8	1.4	0.58	0.45	0.03	0.06	0	0.37	1.2	$\beta\beta$ 27/28s	0.27	0.39	1.3	149	0.22	4.0	4.0	1.0
99-20	-23.4	nc	4.3	5.6	0.76	2.6	1.4	0.58	0.41	0.04	0.06	0	0.37	1.2	$\beta\beta$ 27/28s	0.28	0.39	1.3	152	0.23	3.9	4.0	0.95
99-35	-23.4	nc	4.4	5.2	0.72	2.6	1.4	0.59	0.62	0.03	0.07	0.004	0.35	1.1	$\beta\beta$ 27/28s	0.17	0.38	0.82	131	0.22	3.5	3.8	1.5
<i>GROUP C</i>																							
99-7	-23.4	nc	5.0	3.7	0.97	2.3	0.74	0.61	0.67	0.06	0.21	0.05	nc	nc	nor26&27	0.05	0.79	0.13	48	0.16	1.1	2.3	5.6
99-30	-23.6	nc	5.0	3.5	0.98	2.4	0.76	0.60	0.66	0.06	0.21	0.05	nc	nc	nor26&27	0.06	0.80	0.14	42	0.16	1.2	2.3	5.3
00-112	-23.1	nc	4.9	3.7	1.2	2.4	0.64	0.59	1.3	0.07	0.27	0.08	nc	nc	nor26&27	0.14	0.81	0.31	67	0.15	1.2	2.2	12
<i>GROUP D</i>																							
98-60	-23.3	nc	4.1	4.4	0.45	2.1	1.5	0.58	1.1	0.04	0.10	0.04	0.36	1.1	$\alpha$ 27R	0.43	0.27	2.5	37	0.18	1.5	1.9	2.5
99-9	-23.3	0.46	2.9	5.4	0.49	1.6	1.5	0.57	0.90	0.06	0.08	0.05	0.40	1.0	$\alpha$ 27R, $\beta\beta$ 27/28s	0.35	0.29	2.0	10	0.21	1.1	1.4	0.80
99-11	-23.4	0.56	3.7	4.4	0.46	2.0	1.5	0.58	1.1	0.04	0.10	0.04	0.36	1.0	$\alpha$ 27R > $\beta\beta$ 27/28s	0.26	0.29	1.5	30	0.18	1.4	1.7	2.0
99-12	-23.6	0.59	4.4	4.2	0.42	2.1	1.4	0.58	1.4	0.04	0.10	0.07	0.33	1.0	$\alpha$ 27R	0.24	0.33	1.3	40	0.15	1.6	1.9	3.9
99-21	-23.7	nc	4.1	5.3	0.51	1.9	1.5	0.57	1.6	0.04	0.07	0.05	0.37	1.2	$\beta\beta$ 28s > 27s, $\alpha$ 27R	0.34	0.33	1.7	39	0.17	2.0	2.3	5.4
99-31	-23.5	nc	3.7	4.7	0.56	1.9	1.4	0.58	1.0	0.05	0.08	0.04	0.37	1.1	$\beta\beta$ 28s > 27s, $\alpha$ 27R	0.23	0.29	1.3	20	0.23	1.3	1.3	2.8
00-67	-23.4	nc	3.8	5.4	0.59	1.7	1.4	0.59	1.4	0.05	0.07	0.05	0.30	1.3	$\alpha$ 27R	0.70	0.40	3.1	26	0.15	1.9	2.0	3.2
00-106	-22.8	0.45(w)	3.0	5.3	0.47	1.8	1.5	0.57	0.88	0.07	0.10	0.05	0.32	1.1	$\alpha$ 27R	0.52	0.32	2.8	21	0.19	0.93	1.2	0.73
00-113	-23.2	0.57	3.6	4.4	0.51	2.0	1.4	0.58	1.2	0.05	0.11	0.06	0.35	1.0	$\alpha$ 27R	0.30	0.30	1.7	31	0.17	1.4	1.9	1.6
00-125	-23.0	tr	3.2	4.3	0.49	1.8	1.5	0.58	1.1	0.05	0.09	0.05	0.33	1.0	$\beta\beta$ 28s > $\alpha$ 27/28/29Rs	0.27	0.26	1.7	18	0.18	1.3	1.6	2.0
00-126	-23.2	0.67 (&alks)	3.0	4.6	0.45	1.9	1.5	0.58	0.99	0.05	0.09	0.06	0.30	1.1	$\alpha$ 27R	0.49	0.31	2.7	17	0.19	1.3	1.4	1.7
00-127	-22.9	tr	2.5	5.0	0.38	1.6	1.7	0.58	0.64	0.07	0.07	0.04	0.32	0.99	$\alpha$ 27/28/29Rs, $\beta\beta$ 28s	0.27	0.26	1.7	16	0.26	1.1	1.2	1.1
00-133	-23.0	nc	3.1	3.9	0.41	2.2	1.5	0.59	1.4	0.04	0.14	0.06	nc	nc	nor26&27,BN	0.07	0.35	0.38	27	0.14	1.2	1.8	7.2
00-146	-23.9	tr	2.5	5.9	0.53	1.5	1.5	0.57	0.70	0.07	0.08	0.05	0.40	1.1	$\alpha$ 27R, $\beta\beta$ 27/28s	0.42	0.27	2.4	11	0.26	1.1	1.2	4.09
SM-16	-23.2	0.71	3.4	4.2	0.52	2.1	1.5	0.61	1.2	0.05	0.10	0.06	0.32	1.0	$\alpha$ 27R	0.32	0.28	2.1	20	0.17	1.6	1.8	3.1
SM-17	-23.1	nc	3.8	3.7	0.50	2.3	1.5	0.61	1.4	0.04	0.11	0.07	0.31	0.98	$\alpha$ 27R > $\beta\beta$ 28 > 27s	0.25	0.30	1.5	50	0.15	1.8	2.3	3.2

(continued on next page)

## Appendix II (continued)

Field No.	$\delta^{13}\text{C}$	Pr/Ph	Tm/Ts	Triplet	23Tri/C30	24Tri/C30	C30/C29	C31S/(S+R)	BI/OI	GI	TI177/C30	C29S/(S+R)	C28/C29	Dominant sterane (s)	Hop/Hop	nor26&27/nor27	$\alpha 27\text{R}/\text{PAH-RI}$	T/(T+M)	$\sum\text{C2D}/\sum\text{C2P}$	$\sum\text{C3D}/\sum\text{C3P}$	Pery/Chr		
<i>GROUP E</i>																							
00-108	-23.4	nc	7.4	5.4	0.37	3.1	1.6	0.59	3.0	0.02	0.13	0.20	0.39	1.1	BN > $\beta\beta 27/28\text{s}$	0.43	0.24	2.6	50	0.06	4.1	8.6	3.5
00-120	-23.6	nc	6.7	5.6	0.37	3.1	1.7	0.59	2.9	0.02	0.13	0.20	0.38	1.1	BN > $\beta\beta 27/28\text{s}$	0.44	0.25	2.6	55	0.06	4.0	8.6	3.1
<i>GROUP F</i>																							
SM-4	-22.7	nc	4.5	3.3	1.2	3.7	1.3	0.61	1.1	0.03	0.12	0	0.42	0.98	$\beta\beta 27/28\text{s}, \alpha 27\text{R}$	0.42	0.29	2.9	159	0.21	3.3	3.9	3.9
SM-5	-22.8	nc	5.1	3.6	1.2	4.1	1.2	0.61	1.1	0.02	0.13	0	0.39	1.0	$\beta\beta 27/28\text{s}, \alpha 27\text{R}$	0.47	0.27	3.2	129	0.14	3.4	4.0	4.9
SM-14	-22.9	nc	5.1	3.6	1.1	3.9	1.2	0.61	1.1	0.03	0.13	0	0.38	1.0	$\beta\beta 27/28\text{s}, \alpha 27\text{R}$	0.50	0.27	3.4	126	0.15	3.3	4.1	4.9
<i>GROUP G</i>																							
00-103	-22.6	nc	5.0	3.0	0.62	2.8	1.5	0.59	0.43	0.03	0.10	0	nc	nc	nor26&27	0.04	0.26	0.15	124	0.26	3.2	3.8	2.0
SM-6	-22.8	nc	4.5	2.9	0.72	2.8	1.5	0.61	0.41	0.02	0.11	0.007	nc	nc	nor26&27	0.02	0.25	0.26	108	0.27	3.3	3.9	1.7
<i>ONSHORE BITUMEN</i>																							
99-23	-23.7	nc	4.9	2.9	0.10	1.5	1.6	0.59	2.9	0.02	0.16	0	0.23	0.62	$\alpha 27\text{R} > \alpha 29\text{R} > >$	0.89	0.34	5.0	nc	0.20	nc	nc	nc
99-25	-24.8	0.31	n.c.	0	0	0	1.3	0.13	9.0	0.07	0	0	0.02	0.47	$\alpha 27\text{R} > \alpha 29\text{R} > >$	66	3.8	32	nc	~0	?1.1	?	nc
99-26	-23.9	nc	6.0	4.3	0.10	2.1	0.92	0.55	8.8	0.02	0.88	0	0.10	0.61	$\alpha 27\text{R} > \alpha 29\text{R} > >$	7.0	0.81	17	135	0.05	nc	nc	nc

<sup>a</sup>Parameter ratios defined in Appendix I. Abbreviations: nc = not calculatable due to missing peak(s); ? = peak assignment questionable; w = weathering-impacted; "3" = 3 peaks characteristic of biodegraded A-group.

Appendix III. First four Principal Components<sup>a</sup>. Samples are ordered as in Fig. 3 Dendrogram

Field No.	PC1	PC2	PC3	PC4
<i>GROUP A</i>				
97-10	0.11	-0.12	-0.67	-0.51
SM-7	0.05	-0.5	-0.71	-0.54
SM-10	0.05	-0.03	-0.11	-0.51
00-104	-0.36	0.53	-0.85	-0.28
00-110	-0.21	0.26	-0.79	-0.46
00-117	-0.03	0.23	-1.38	-0.28
00-130	-0.06	0.57	-0.86	-0.25
00-156	-0.38	0.77	-0.98	-0.11
98-46	-0.54	0.01	-0.85	-0.17
00-129	-0.40	-0.08	-0.86	-0.24
SM-2	-0.41	0.38	-0.84	-0.04
SM-19	-0.39	0.32	-0.88	-0.13
SM-3	-0.25	0.44	-0.73	-0.16
SM-11	-0.15	0.32	-0.81	-0.18
SM-20	-0.21	0.28	-0.86	-0.17
SM-9	-0.24	0.17	-0.82	-0.28
SM-18	-0.13	0.22	-0.62	0.00
SM-1	-0.15	0.00	-0.53	-0.13
00-105	-0.42	-0.09	-0.71	-0.76
00-119	-0.09	-0.10	-1.15	-0.58
SM-15	0.07	0.09	-1.04	-0.49
SM-12	0.11	0.09	-1.13	-0.71
SM-13	-0.07	-0.50	-1.57	-0.22
00-114	-0.42	-0.26	0.16	-1.24
SM-8	0.19	-0.32	-0.65	-1.24
98-33	-0.21	-0.42	-0.70	-1.03
00-135	-0.72	-0.07	-1.03	-1.31
L99-25	-0.27	0.06	-0.23	-0.30
99-4	-0.32	0.13	-0.27	-0.09
98-5	-0.27	0.31	-0.19	-0.52
99-14	-0.49	0.09	0.22	-0.97
99-40	-0.17	0.10	-0.05	-0.34
99-32	-0.32	0.31	-0.17	-0.21
99-36	-0.43	0.49	-0.11	-0.04
99-34	-0.46	0.50	-0.06	-0.04
L99-27	0.37	-0.27	0.08	-0.87
99-43	-0.40	0.71	0.13	-0.52
00-36	-0.40	0.75	0.45	-0.40
00-39	-0.27	0.90	-0.19	-0.35
99-45	-0.57	0.91	0.29	-0.03
00-49	-0.33	0.18	-0.33	-0.50
00-122	-0.15	0.26	-0.17	-0.49
00-118	-0.43	0.59	-0.46	-0.39
00-148	-0.06	0.49	-0.23	-0.55
00-111	-0.41	0.45	-0.58	-1.00
00-109	-0.47	0.28	0.15	-1.03
00-163	-0.36	0.54	-0.33	-0.13
00-132	-0.39	0.68	-0.50	-0.28
00-128	-0.40	0.29	-0.36	-0.26
00-102	-0.47	0.57	-0.27	-0.10
99-19	-0.80	-0.36	1.44	-1.24
99-29	-0.93	-0.17	2.48	-1.54
98-49A	-0.68	1.70	-1.00	0.01
00-147	-0.59	1.76	-1.06	-0.26
00-124	-0.74	1.79	-1.11	-0.16

Field No.	PC1	PC2	PC3	PC4	Field No.	PC1	PC2	PC3	PC4
00-65	-0.60	2.38	-0.31	-0.02	99-11	-0.92	-1.68	-0.83	-0.21
99-5	-0.92	2.07	-0.27	0.18	99-12	-1.18	-0.52	-0.23	0.10
99-6	-0.93	1.99	-0.50	0.69	00-67	-0.79	-2.24	0.07	0.51
00-107	-0.41	1.12	-0.48	-0.22	99-21	-0.54	-1.36	-0.22	1.15
00-158	-0.34	1.05	-0.59	-0.40	99-31	-0.82	-2.92	-0.30	-0.77
00-123	-0.34	1.07	-0.93	0.01	99-9	-1.26	-4.01	-0.96	-0.26
00-50	-0.41	1.55	-0.38	-0.17	00-106	-1.03	-4.19	-1.13	-1.23
00-121	-0.54	1.28	-0.82	-0.16	00-127	-0.91	-5.30	-2.34	-0.75
99-24	-0.48	1.36	-0.62	0.09	00-146	-0.65	-5.53	-1.24	-1.13
00-137	-0.72	1.42	-1.23	0.05					
97-23	-0.36	1.44	-0.92	0.37	<i>GROUP E</i>				
00-116	-0.16	1.06	-1.30	0.08	00-108	3.23	5.94	-0.15	3.44
00-131	-0.33	0.99	-1.09	0.49	00-120	3.05	5.46	-0.38	4.13
00-115	-0.23	1.33	-0.82	-0.02	<i>GROUP F</i>				
99-3	-1.08	0.48	-0.66	1.02	SM-4	4.45	0.07	2.31	-1.48
99-8	-1.15	0.67	-0.16	0.61	SM-5	4.61	1.81	2.77	-1.43
99-18	-1.67	-0.73	-0.90	0.49	SM-14	4.10	1.25	2.74	-1.22
99-13	-0.59	1.26	-0.27	0.23	<i>GROUP G</i>				
99-27	-0.46	1.4	-0.20	0.31	00-103	3.18	-0.42	-0.4	-1.17
99-15	-0.66	1.45	-0.37	0.28	SM-6	3.22	-0.28	-0.29	-0.94
98-44	-0.46	0.84	-0.56	-0.12	<i>ONSHORE BITUMEN</i>				
99-10	-0.80	0.39	-0.28	0.34	99-23	-2.40	0.35	0.37	0.47
99-37	-0.43	1.13	-0.09	0.28	99-25	-14.51	-3.83	3.91	7.84
99-39	-0.58	0.76	-0.28	0.06	99-26	-7.57	5.94	6.74	-2.96
99-38	-0.69	1.05	-0.26	0.29					
99-33	-0.89	1.02	-0.28	0.56					
99-28	-0.70	1.90	-0.12	0.85					
99-22	-0.80	1.67	-0.22	0.71					
<i>GROUP B</i>									
97-22	4.30	-2.97	1.61	0.83					
97-28	4.03	-2.16	1.29	1.13					
L99-28	3.25	-1.90	1.25	1.27					
99-16	3.20	-1.64	1.44	1.47					
99-20	3.39	-1.69	1.52	1.45					
99-17	3.71	-1.13	1.61	1.63					
99-35	2.85	-0.94	1.14	1.11					
L99-2	2.77	-1.22	1.53	1.82					
L99-3	2.62	-1.15	1.46	1.86					
L99-11	2.52	-1.16	1.06	2.25					
L99-4	3.18	-1.00	1.64	1.79					
L99-8	2.65	-0.84	1.27	1.50					
L99-9	3.1	-0.78	0.95	1.86					
L99-10	2.54	-0.84	0.88	1.92					
L99-12	2.74	-1.00	1.08	2.12					
L99-13	2.76	-1.04	1.04	2.11					
<i>GROUP C</i>									
99-7	-0.89	-1.28	4.48	-2.67					
99-30	-0.98	-1.14	4.62	-2.35					
00-112	-0.70	-1.42	5.62	-3.52					
<i>GROUP D</i>									
00-133	-1.27	-1.24	-1.17	-0.75					
SM-17	-0.40	-0.73	-0.82	-0.35					
00-113	-0.90	-1.99	-0.40	-0.68					
SM-16	-0.78	-2.08	-0.85	-0.43					
00-125	-1.01	-2.69	-1.31	-0.84					
00-126	-1.13	-2.84	-1.20	-0.49					
98-60	-0.51	-1.33	-0.88	-0.42					

<sup>a</sup>Principal components: **PC1**— Contains most variables, but dominated by 23Tri/24Tri, BI, 23Tri/C30, and the C2 and C3 D/P ratios (accounts for 30% of variance). **PC2**— Tm/Ts, OI, T/(T+M) are most important, with T177/C30 significant (19% of variance). **PC3**— C30/C29 dominant, with 23Tri/C30, GI, and nor26&27/Hop significant (13% of variance). **PC4**— Dominated by  $\delta^{13}\text{C}$  and the C2 and C3 D/P ratios (11% of variance).

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