The microbial input in carbonate–anhydrite facies of a sabkha palaeoenvironment from Guatemala: A molecular approach

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Abstract—Nine representative rock samples including four anhydrites, an oil-stained dolomite and a laminated mudstone (source rock) from a sabkha-type palaeoenvironment (La Felicidad 1 well, Guatemala) have been compared in order to tentatively characterize each facies by a geochemical signature.

Each sample has been studied by using basic parameters (TOC, Rock–Eval pyrolysis yields) and analyses of alkanes and aromatics by computerized GC–MS. The following families of compounds have been reviewed: n-alkanes, branched and cyclic alkanes, n-alkylbenzenes, benzohopanes, monoaromatic steroids, D-ring aromatic 8,14-secohopanoids, alkylnaphthalenes, alkylphenanthrenes, alkyldibenzo-thiophenes and triaromatic steroids. Despite close geochemical relationships of all the samples, a more in-depth investigation taking into account molecular patterns and semi-quantitative data reveals significant differences among the samples. Anhydrites may be differentiated from carbonates which illustrates the efficiency of organic geochemistry in environmental palaeoreconstruction even in organic-carbon-lean sediments (TOC = 0.04–0.08% in anhydrites). In these anoxic, marginally mature sediments the strong predominance of triterpanes over steranes (TT to ST > 20) associated with other molecular features leads to the conclusion that the main contribution to the organic matter of all facies is by bacteria. Several prominent components including novel families (iso-C_{23} and iso-C_{27} alkanes, tetracyclic terpanes, D-ring aromatic 8-14-secohopanoids, 1-phenylpentadecane, undecylnaphthalene and their mono- and dimethylated counterparts) have been interpreted as derived from halophilic bacteria. These conclusions may be extended to all crude oils from the same area which may be considered as true bacterially-derived petroleums.

The La Felicidad 1 well data are discussed with reference to other palaeosabkha-type sequences from the SW Aquitaine Basin (France) in which the bacterial input is less important. However, in these sabkha sequences 1-phenylpentadecane, undecylnaphthalene and related structures have also been identified.

Key words: bacteria, sabkha, carbonate, anhydrite, iso-alkanes, steranes, terpanes, alkylbenzenes, mono- and triaromatic steroids, D-ring aromatic 8,14-secohopanoids, benzohopanes, palaeoenvironment, maturity assessment

INTRODUCTION

Molecular parameters are being used by petroleum geochemists to solve oil-to-source rock correlations and to appraise maturities of oils and sediments. In addition, organic geochemistry at a molecular level offers new possibilities through specific pattern recognition to help reconstruction of past depositional environments (Didyk et al., 1978; Connan, 1981; Seifert and Moldowan, 1981; Brassell et al., 1981). Most available data on rocks refer to shales from various basins but published studies on carbonate basins (Palacas, 1983; Rullkötter et al., 1984; Demaison and Bourgeois, 1984) still remain limited.

This work had the following two main objectives:

—First, to provide petroleum geochemists with geochemical information on several sedimentary sequences deposited in hypersaline, highly anoxic environments in basins with significant accumulations of commercial oils. Such research is particularly relevant in carbonate basins which do not show obvious organic matter-rich source rocks as described by Palacas (1983).

—Second, to explore the utility of the organic geochemist's approach to recognize or even define facies selected on the basis of sedimentological criteria. Of particular interest in sabkha sequences are the carbonates on one hand and the anhydrites on the other. Even if anhydrites are devoid of petroleum potential, knowledge about them is necessary for a complete appraisal of the sabkha deposits. For these sediments unfavourable for oil generation, it remains interesting to check whether their geochemical signature may provide consistent and reliable results which may be useful to the sedimentologist for palaeoreconstruction of depositional conditions and inference of the organic matter input.

In order to reach our main objectives, nine representative samples of a sabkha-type deposit from the La Felicidad 1 well (Guatemala) were selected as a test series according to sedimentological and geochemical criteria. The series comprises anhydrites (chicken-mesh, nodular and bedded), carbonate-rich sediments including an oil-stained rock, and an argillaceous carbonate (*i.e.* a presumed source rock).

Fig. 1. Location of the various facies in a schematic sedimento-diagenetic sequence.

This reference series has been compared to other sabkha sediments from the Aquitaine Basin and to oils from Guatemala.

SEDIMENTOLOGICAL SETTING

The cores studied (Cenomanian to Barremian, Coban c/γ and β Fm.) correspond to a recurrent sequence evolving from local evaporitic and restricted inner shelf deposits to early diagenetic evaporitic facies (Fig. 1) similar to those in modern sabkha areas. The sedimentary sequence comprises lagoonal bioclastic or bioturbated micrites and dolomicrites with increasing anhydrite nodules towards the top. It is characterized by very poorly laminated stromatolitic developments at tidal levels. This suggests that the lagoon was near to emerging, which permitted the development of the nodular anhydritic texture on one hand and the rapidity of the sequential evolution due to a dynamic geological setting on the other. In that respect, the situation observed herein is slightly different from that encountered in the Mano Formation (Upper Jurassic) in the SW Aquitaine Basin where the stromatolites and the laminated texture are well developed above very restricted lagoonal sediments.

SAMPLES ANALYZED

The nine samples analyzed were collected within the same formation cored in the La Felicidad 1 well (Guatemala). A sedimentological characterization of each sample has been carried out following examination of thin sections (Fig. 1).

Sample 1—Core 1, 11180'1"–11181'8", thin section 1 (TS 1)—Nodular bedded anhydrite with argillaceous joints and occasional argillaceous laminae between the nodules;

chicken-mesh texture in thin section; early diagenetic texture of sabkha-type deposit.

Sample 2—Core 1, 11180'2"–11180'10", TS 6—Nodular anhydrite scattered into dolomicrite; beginning of early diagenetic anhydrite formation; deposit identical to sample 1.

Sample 3—Core 1, 11185', TS 7—Irregular crystalline dolomicrosparite; later filling of dissolution voids by anhydrite; probably lagoonal deposit, fully dolomitized.

Sample 4—Core 2, 13450'6"–13451', TS 9—Nodular anhydrite, more or less scattered into dolomicrosparite; chicken-mesh texture in thin section, early diagenetic texture of sabkha-type deposit.

Sample 5—Core 4, 13491'40", TS 20—Dolomicrosparite to dolosparite with some intercrystalline anhydrite in later filled voids; sub-laminated texture, small intracrystalline anhydrite in later filled voids, scarce deformed Miliolids; lagoonal, infratidal to tidal level; restricted environment shown by poor development of scarce fauna.

Sample 6—Core 7, 13621'11"–13622'3", TS 23—Laminated black mudstone with pellets, ostracods and foraminifera such as Ophtalmididae and some scarce nodular anhydrite and intraclasts; laminated lagoonal deposits, restricted environment, with tendency to anhydrite concentration in upper tidal levels.

, TS 24—Laminated mudstone with dolomicritic beds, micropellets and some argillaceous levels, ostracods, Miliolids; subcoalescent anhydrite nodules; probably ancient stromatolitic texture with beginning of nodular sabkha anhydrite; tidal to supratidal-lagoon border.

Sample 7—Core 7, 13621'11"–13622'3", TS 25—Laminated microsparite and amygdaloid limestone with dolomicrite, argillaceous and organic-matter-rich beds; Miliolids, Lamellibranchia and calcite patches from bioclastic lumps or gastropods; subtidal level of lagoonal environment.

Sample 8—Core 7, 13631'6", TS 28—Dolomicrite to dolomicrosparite with stromatolitic textures and gravels, scarce ostracods; secondary anhydrite voids; intertidal level.

Sample 9—Core 7, 13648'2", TS 29—Chicken-mesh anhydrite texture of gypsum residues between coalescent nodules; supratidal; early diagenetic sabkha anhydrite.

In order to classify the samples analyzed, their various facies have been placed in a virtual diagenetic sequence (Fig. 1) which locates three anhydrites (samples 9, 1, 2) within the supratidal zone, samples 4, 6, 7, 8 in the intertidal environment and samples 3 and 5 within the subtidal/intertidal zone.

RESULTS

Basic geochemical data

Total organic carbon (TOC) is less than 0.08% in anhydrites and ranges between 0.15 and 0.4% in dolomites with the exception of sample 7 which contains 1.2% organic carbon (Table 1).

The organic extract (OE), lower than 400 ppm in anhydrites, increases steadily with TOC and reaches 1300–1800 ppm in the most enriched samples (6, 7). The laminated calcareous dolomite of core 7 (8), chosen as a presumably impregnated reservoir bed, is certainly oil-stained (4400 ppm HC, Table 1, Fig. 2). The OE/TOC ratios are always very high in the non-impregnated samples even at the most organic-carbon-rich level (7, OE/TOC = 0.14). It should be emphasized, however, that the high OE/TOC values may be influenced by analytical errors. The accurate determination of TOC in rocks at the 0.04–0.2% level is difficult using a routine procedure.

Table 1. Basic geochemical data: lithology, TOC, organic chloroform extract (OE), gross composition of the chloroform extract

SAMPLE REFERENCE	SNEA(P) REFERENCE	CORE DEPTH (FEET)	LITHOLOGY			INSOLUBLE RESIDUE IN HCl (%)	TOC %	CHLOROFORM EXTRACT ppm	CHLOROF. EXTRACT / TOC	GROSS COMPOSITION OF THE CHLOR. EXTRACT				
			ANHYDRITE (%)	CALCITE (%)	DOLOMITE (%)					SATURATES (S) (%)	AROMATICS (A) (%)	RESINS (%)	ASPHALTENES	S + A (ppm)
1	1538	K.1 11180' 11181'	98			66.3	0.04	169	0.37	20.6	12.3	47.5	19.6	55
2	1539	K.1 11180'	98			60.4	0.06	810	0.51	16.6	16.1	55.1	12.1	101
3	1540	K.1 11185'	12		88	4.7	0.16	957	0.58	16.5	11.0	44.7	27.7	264
4	1541	K.2 13450' 13451'	88		10	45.0	0.08	313	0.39	33.2	18.9	42.0	5.9	163
5	1542	K.5 13491'		7	93	0.7	0.15	601	0.38	45.9	16.3	31.9	6.0	313
6	1543	K.7 13621' 13622'	25	57	5	3.4	0.42	1344	0.32	28.7	15.6	45.7	10.0	595
7	1544	K.7 13621' 13622'		33	48	16.8	1.23	1797	0.14	21.4	18.2	52.6	7.8	711
8	1545	K.7 13631'	4	13	75	2.8	0.30	7061	2.35	31.6	20.4	30.7	17.2	4441
9	1546	K.7 13648'	98			47.6	0.06	390	0.65	30.0	19.6	41.3	9.1	193

The plot of TOC vs C_{15+} hydrocarbon yields (Fig. 2) allows the differentiation of four groups of samples. Sample 7 (and to some extent the adjacent sample 6) is a good source rock according to classical concepts. Sample 8 is confirmed as obviously oil-stained. Samples 3 and 5 are poor source rocks and may be partly oil-stained. Samples 1, 2, 4 and 9 (anhydrites) are organic-matter-lean and may possibly contain some allochthonous hydrocarbons.

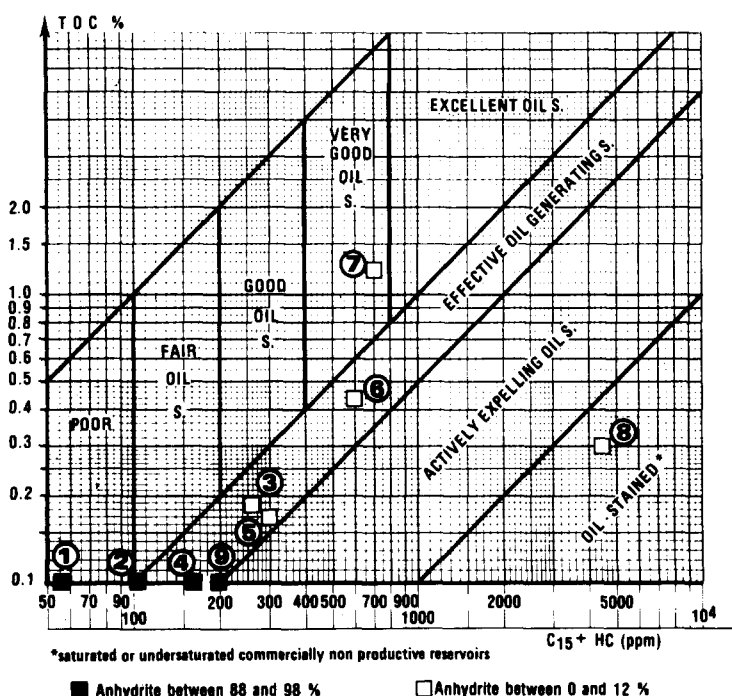Gross compositions of chloroform extracts (Table 1)

Fig. 2. Total organic carbon (TOC, %) vs C_{15+} hydrocarbons (aromatics + saturates, A + S, in ppm) plotted in the Geochem. Lab. diagram.

Table 2. Characteristic properties of the total, branched/cyclic and normal alkane fractions analyzed by capillary GC. The ratios listed for total and branched/cyclic alkanes have been obtained by peak height measurements. Data related to n-alkanes are derived from peak area determination

SAMPLE REFERENCE	SNEA(P) REFERENCE	C15+ ALKANES				BRANCHED AND CYCLIC C15+ ALKANES			C15+ N-ALKANE DISTRIBUTION													
									ISOLATED N-ALKANES										MAXIMA (estimated on total alkanes)	$\frac{22}{\sum_x}$ are / $\frac{y}{\sum_{22}}$ are	CPI	$[CPI]_x^{22}$	$[CPI]_{22}^y$
									PREDOMINANCE									MAXIMA					
		PRIST./n-C17	PHYT./n-C18	PRIST./PHYT.	iso C23/n-C22	iso C23/PHYT.	iso C23/HOP.	PRIST./PHYT.	18	20	22	24	26	27	28	30	32						
1	1538	0.59	1.25	0.33	0.32	0.3	1.5	0.32	*	*	*							28	29	0.27	0.96	0.96	0.98
2	1539	0.30	0.52	0.46	1.58	2.1	5.3	0.40	*	*	*	*			*	*		26	24-26-28	0.38	0.84	1.00	0.80
3	1540	0.24	0.27	0.68	0.49	1.1	1.0	0.68				*			*			19-26	18-26	0.62	0.96	1.04	0.92
4	1541	0.22	0.28	0.62	1.06	2.4	1.0	0.63	*	*	*	*			*	*		20	20	0.67	0.93	0.98	0.91
5	1542	0.16	0.17	0.85	0.24	1.8	0.3	0.75		*	*	*						24	24	0.52	0.95	1.00	0.94
6	1543	0.19	0.23	0.73	0.25	1.1	0.6	0.65	*	*	*	*			*	*	*	26	20	0.44	0.90	0.98	0.87
7	1544	0.11	0.16	0.74	0.31	1.4	0.6	0.72	*	*	*	*	*	*	*	*	*	28-18	17-26	0.44	0.94	0.99	0.92
8	1545	0.10	0.14	0.56	0.36	2.5	0.8	0.53		*		*			*	*	*	26	22-26	0.48	0.92	1.02	0.89
9	1546	0.11	0.23	0.53	0.88	2.5	3.1	0.55	*		*	*	*		*	*	*	20	17-20	0.70	0.94	1.04	0.89

CPI : CARBON PREFERENCE INDEX · x - y : CARBON NUMBER RANGE OF THE n- ALKANE DISTRIBUTION
$\sum_x^{22}$ are / $\sum_{22}^y$ are = SUM OF n- ALKANES BETWEEN x AND 22 / SUM OF n- ALKANES BETWEEN 22 AND y

do not separate anhydrites from other samples. Rock Eval pyrolysis has not led to reliable results due to the low level of organic carbon and the type of lithologies including anhydrites and carbonates. The most reliable data were obtained for the source rocks with the following results: $T_{max} = 429\text{--}435°C$, $HI = 107\text{--}118\,mg\ HC/g\ TOC$, $OI = 4\text{--}44\,mg\ CO_2/g\ TOC$.

The organic matter was tentatively studied by microscopy (R. Baranger, C. Boulouard, unpublished results). Due to the lack of vitrinite in all samples, only the palynofacies could be determined. The kerogen is mainly composed of amorphous and colloidal organic matter (algal remains). The thermal alteration index (TAI) was estimated at 2.50–2.75 at 11000'. Therefore, the threshold of intense oil generation is reached in the cores under study.

C_{15+} alkanes

The gas chromatograms of total alkanes from the nine samples display common features: n-alkanes are abundant (pristane/n-C_{17} and phytane n-C_{18} ratios are lower than 0.3 and 0.5, respectively, in most cases; Table 2); strong even predominance (n-C_{20}–n-C_{32}) in the n-alkane distributions (Table 2); pristane/phytane ratios vary between 0.3 and 0.8; occurrence of a prominent peak eluting between n-C_{22} and n-C_{23} (Fig. 3; this peak was identified as the iso-C_{23} alkane by Hussler, 1985).

Although even predominances are recorded in all the samples (CPI = 0.84–0.96), especially within the C_{22}–C_{32} range ($[CPI]_{22}^Y = 0.80$–0.98, $[CPI]_X^{22} = 0.96$–1.04, $X - Y$ = carbon number range of the n-alkanes), bimodal n-alkane distributions (maxima at n-C_{17}–n-C_{19} and n-C_{26}–n-C_{28}) are found in two carbonate samples (3, 7), whereas a unimodal pattern with the maximum around n-C_{24}–n-C_{28} is the most common fingerprint (Table 2).

All four representative GC traces of the C_{15+} branched and cyclic alkanes display similar features reflecting the prevailing hydrocarbon chemistry of the environments studied (Fig. 3): pristane/phytane ratios lower than 1.0, iso- and anteisoalkane series with the iso-C_{23} as a prominent component, large amounts of 17α(H)-hopanes including the high-molecular-weight members (C_{31}–C_{35}). A more detailed investigation at the molecular level, however, shows significant differences among the various facies analyzed. Plotting of several ratios (iso-C_{23}/n-C_{22}, iso-C_{23}/C_{29} 17α(H)-hopane, pristane/phytane; Table 2) in Fig. 4 splits the samples into two main groups: anhydrites (1, 2, 4, 9) and other samples (3, 5, 7, 8).
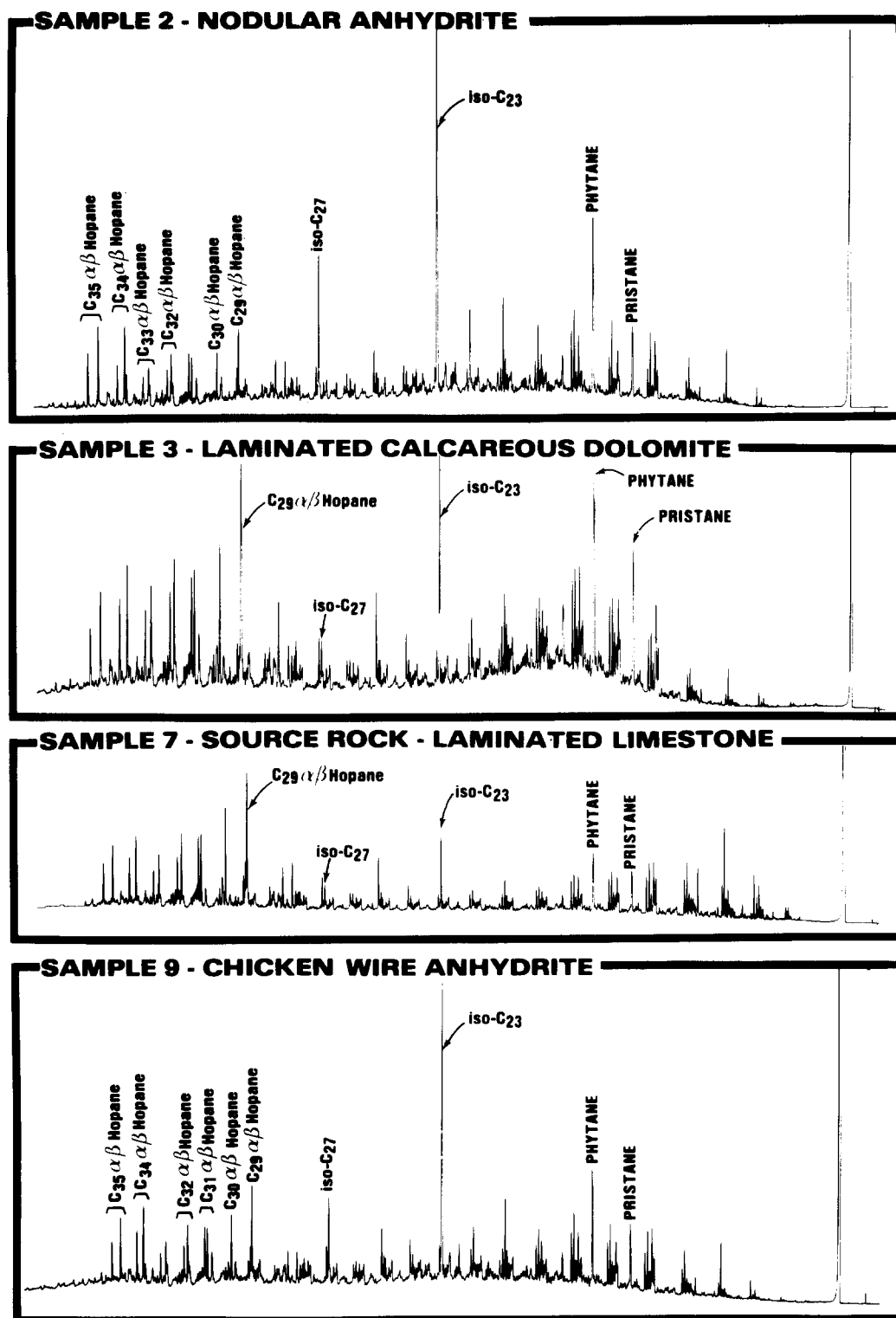
Fig. 3. Gas chromatograms of branched and cyclic alkanes from some representative samples. Intersmat type ICG 120 DLF gas chromatograph, equipped with a 50 m glass capillary column, i.d. 0.25 mm, stationary phase OV 1, split 1/60; temperature programmed from 100 to 300°C at 1.7°C/min.

Anhydrites display lower pristane/phytane ratios but higher iso-C_{23}/n-C_{22} and iso-C_{23}/C_{29} 17α(H)-hopane ratios.

The iso-C_{23} alkane occurrence was carefully checked by recording the mass fragmentogram of m/z

85. Besides the iso-C_{23} alkane, a second prominent peak identified as the iso-C_{27} alkane, was found in the anhydrites (2, 4 and 9; Fig. 3).

The terpane distribution patterns (m/z 191 mass fragmentograms) show that all samples have a high
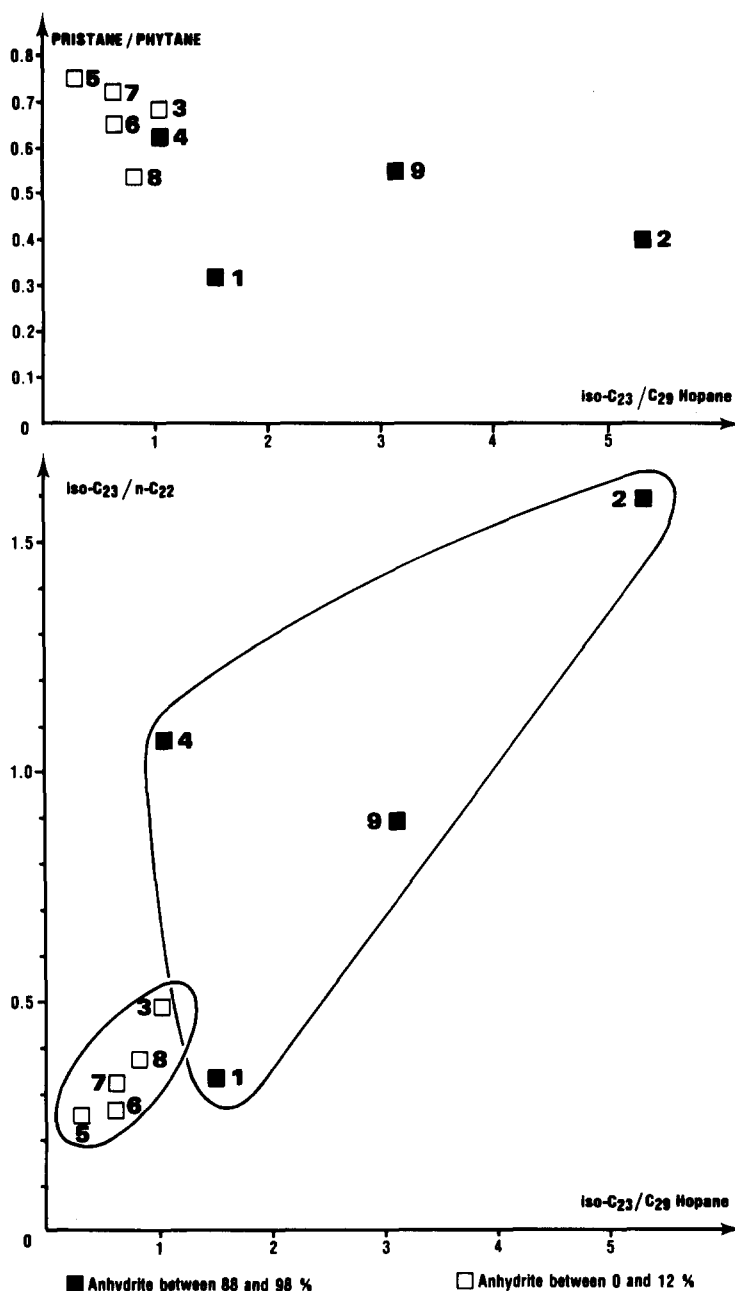
Fig. 4. Variations of some selected ratios with facies changes.

abundance of tetracyclic terpanes (C_{24}, C_{26}, C_{27}) relative to the tricyclic terpanes (C_{23}, C_{24}, etc.) which occur only in trace amounts (C_{23} tricyclic/C_{24} tetracyclic = 0.04–0.15). The major differences among the samples result from the abundance of C_{34}–C_{35} 17α(H)-hopanes relative to C_{29} 17α(H)-hopane. These high-molecular-weight members are very prominent in anhydrites (e.g. 2, 9; Fig. 3). The T_m/T_s ratios are always higher than 1 (1.1–3.6; Table 3) and indicate that the sediments are moderately mature. The moretane series [C_{29} and C_{30} 17β(H), 21α(H)-hopanes], generally abundant in sediments containing terrigenous organic matter, occurs in low concentrations as found elsewhere in

carbonates (Connan et al., 1983; Rullkötter et al., 1984). C_{29}/C_{30} 17α(H)-hopane ratios vary between 1.1 and 1.8 and tend to increase when the C_{29}–C_{35} 17α(H)-hopane series exhibits a C_{29}–C_{30} 17α(H)-hopane enrichment (C_{29}–C_{30} vs $\Sigma C_{34}/C_{29}$; Table 3).

Sample 1 (nodular bedded anhydrite) contains a C_{28} compound of unknown structure which is not present in other samples. Another C_{28} pentacyclic terpane, seen in all samples (lower amounts in anhydrites) has been identified by Schmid (1984, unpublished) as the 17α(H),21β(H)-28, 30-bisnorhopane.

The amounts of steranes are very low relative to the triterpanes (TT/ST ratios between 19 and 144).

Table 3. Sterane and terpane ratios on rock samples

SAMPLE REFERENCE	SNEA(P) REFERENCE	STERANES							TERPANES							
		29ββS/29ααS	29ααS/29ααR	27 S DIA/29ααR	21 ST/22 ST	22 4Me/22 ST	% 20 S C29	%ββ C29	C29H/C30H	ΣC34/C29H	ΣC35/C29H	Tm/Ts	βα/αβ	22 S/22S+22R	TT/ST	23/3 24/4
1	1538	1.2 / 0.9	1.1 / 0.7	0.4 / 0.3	2.5 / 2.4	0.2 / 0.2	52 / 42	58 / 58	1.2 / 1.1	2.1	2.2	1.5 / 1.5	0.08 / 0.09	57 / 57	19	0.4 / 0.4
2	1539	1.4 / 1.2	0.9 / 1.0	1.3 / 1.2	3.0 / 3.0	0.7 / 0.4	47 / 50	60 / 57	1.2 / 1.1	2.6	4.2	1.3 / 1.2	0.07 / 0.10	55 / 56	25	0.1 / 0.1
3	1540	1.0 / 1.1	0.6 / 0.6	0.1 / n.d.	3.6 / 2.8	0.8 / 0.8	39 / 38	57 / 60	1.9 / 1.7	0.8	0.7	2.7 / 2.4	0.10 / 0.07	58 / 58	65	0.1 / 0.1
4	1541	1.3 / 1.1	0.8 / 0.9	n.d. / n.d.	2.5 / 2.9	0.8 / 0.5	46 / 48	62 / 57	1.5 / 1.4	1.2	1.0	2.6 / 2.8	0.09 / 0.07	58 / 58	76	0.05 / 0.04
5	1542	1.4 / 1.4	1.1 / 1.1	n.d. / n.d.	3.7 / 2.5	n.d. / 0.4	55 / 52	59 / 57	1.4 / 2.1	0.2	0.2	3.6 / 3.8	0.07 / 0.06	58 / 58	144	n.d. / 0.06
6	1543	1.2 / 0.9	0.8 / 0.9	n.d. / n.d.	2.7 / n.d.	0.8 / n.d.	46 / 48	58? / 58?	1.3 / 1.4	1.1	0.9	1.1 / 1.1	0.09 / 0.09	55 / 59	139	0.06 / 0.06
7	1544	1.2 / 1.3	0.8 / 0.9	n.d. / n.d.	2.7 / 2.8	0.6 / 0.8	43 / 48	60 / 59	1.6 / 1.2	0.8	0.9	1.1 / 1.1	0.08 / 0.07	56 / 58	161	0.11 / 0.09
8	1545	1.2 / 1.3	0.8 / 0.9	n.d. / n.d.	2.8 / 2.2	0.8 / 0.4	44 / 47	60 / 60	2.0 / 1.2	0.8	0.8	1.8 / 1.9	0.10 / 0.06	57 / 58	69	0.11 / 0.04
9	1546	1.4 / 1.1	0.9 / 0.9	0.3 / 0.3	2.8 / 2.3	0.5 / 0.4	47 / 47	61 / 57	1.7 / 1.2	1.5	1.5	1.3 / 1.3	0.11 / 0.06	48 / 58	45	0.14 / 0.14

(1) — RESULTS ON OV 1 CAPILLARY COLUMN
(2) — RESULTS ON SE 52 CAPILLARY COLUMN

Abbreviations:

$29\beta\beta S/29\alpha\alpha S$: $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$, 20 S-C_{29} sterane/$5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$, 20 S-C_{29} sterane.
$29\alpha\alpha S/29\alpha\alpha R$: $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$, 20 S-C_{29} sterane/$5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$, 20 R-C_{29} sterane.
27 S dia/$29\alpha\alpha R$: 20 S-C_{27} diasterane/$29\alpha\alpha R$.
21 ST/22 ST: C_{21} sterane/C_{22} sterane.
22 4Me/22 ST: C_{22} 4-Me-sterane/C_{22} sterane.
$C_{29}H/C_{30}H$: $17\alpha(H)$, $21\beta(H)$-norhopane/$17\alpha(H)$, 21β (H)-hopane.
Tm/Ts: $17\alpha(H)$-trisnorhopane/18α (H)-trisnorneohopane.
$\beta\alpha/\alpha\beta$: $17\beta(H)$, $21\alpha(H)$-hopane/$17\alpha(H)$, $21\beta(H)$-hopane.
22S/22S + 22R: 22S-$17\alpha(H)$, $21\beta(H)$-bishomohopane/22S-$17\alpha(H)$, $21\beta(H)$-bishomohopane + 22R-$17\alpha(H)$ $21\beta(H)$-bishomohopane (C_{32}).
TT/ST: Triterpane to sterane ratio = ratio of m/z 191 integral to m/z 217 integral for C_{27}–C_{35} terpanes and C_{27}–C_{29} steranes.
23/3/24/4: C_{23} tricyclic terpane/C_{24} tetracyclic terpane.

The sterane/triterpane ratio is generally higher in anhydrites (1, 2, 9; Table 3). The maturity assessment, based on C_{29} $14\alpha(H),17\alpha(H)$-20S/C_{29} $14\alpha(H),17\alpha(H)$-20R and C_{29} $14\beta(H),17\beta(H)$/C_{29} $14\alpha(H)$, $17\alpha(H)$-20S sterane ratios (Seifert and Moldowan, 1978; Mackenzie and Maxwell, 1981), had to be done with care because the presence of coeluting components [e.g. for $14\beta(H),17\beta(H)$ steranes] or interference with abundant compounds with similar retention times [e.g. C_{29} $17\alpha(H)$-hopane elutes just in front of the $C_{29}\alpha\alpha R$ sterane on OV 1 columns] may significantly affect these ratios. In order to better circumvent the effects of coelution and interference, analyses were carried out on two different capillary columns (OV 1 and SE 52). Some characteristic mass fragmentograms (m/z 217) obtained with the SE 52 column are reproduced in Fig. 5. On that column, the disturbing effect of the C_{29} $17\alpha(H)$-hopane on the C_{29} $14\alpha(H),17\alpha(H)$-20R sterane ($C_{29}\alpha\alpha R$ sterane) is

reduced because the former elutes after the $C_{29}\alpha\alpha R$ sterane. The most reliable values are probably obtained for anhydrites (1, 2, 9) where the C_{29} $17\alpha(H)$-hopane interference is minimized (Fig. 5). The 20S/(20R + 20S) $C_{29}\alpha\alpha$ sterane ratios (% 20S, Table 3) have not reached the end value of 50–55% (Mackenzie, 1984). Regular steranes (C_{27}–$C_{29}\alpha\alpha,\beta\beta$, R and S) are the dominant components in all samples except in the nodular anhydrite (sample 2) where C_{27} diasteranes are well represented (Fig. 5). C_{27} diasteranes, present in trace amount in all carbonates, are generally more abundant in anhydrites (27 S dia/$C_{29}\alpha\alpha R$ ratio; Table 3). The strong predominance of C_{27}–C_{29} regular steranes is commonly recorded in carbonate source rocks from evaporitic sequences (Aquitaine, Iraq, Connan *et al.*, 1983; La Luna, Colombia, Palacas, 1983; Upper Cretaceous, Ghareb Formation, Israel, Rullkötter *et al.*, 1984). Among the regular steranes, the C_{28} homologs are
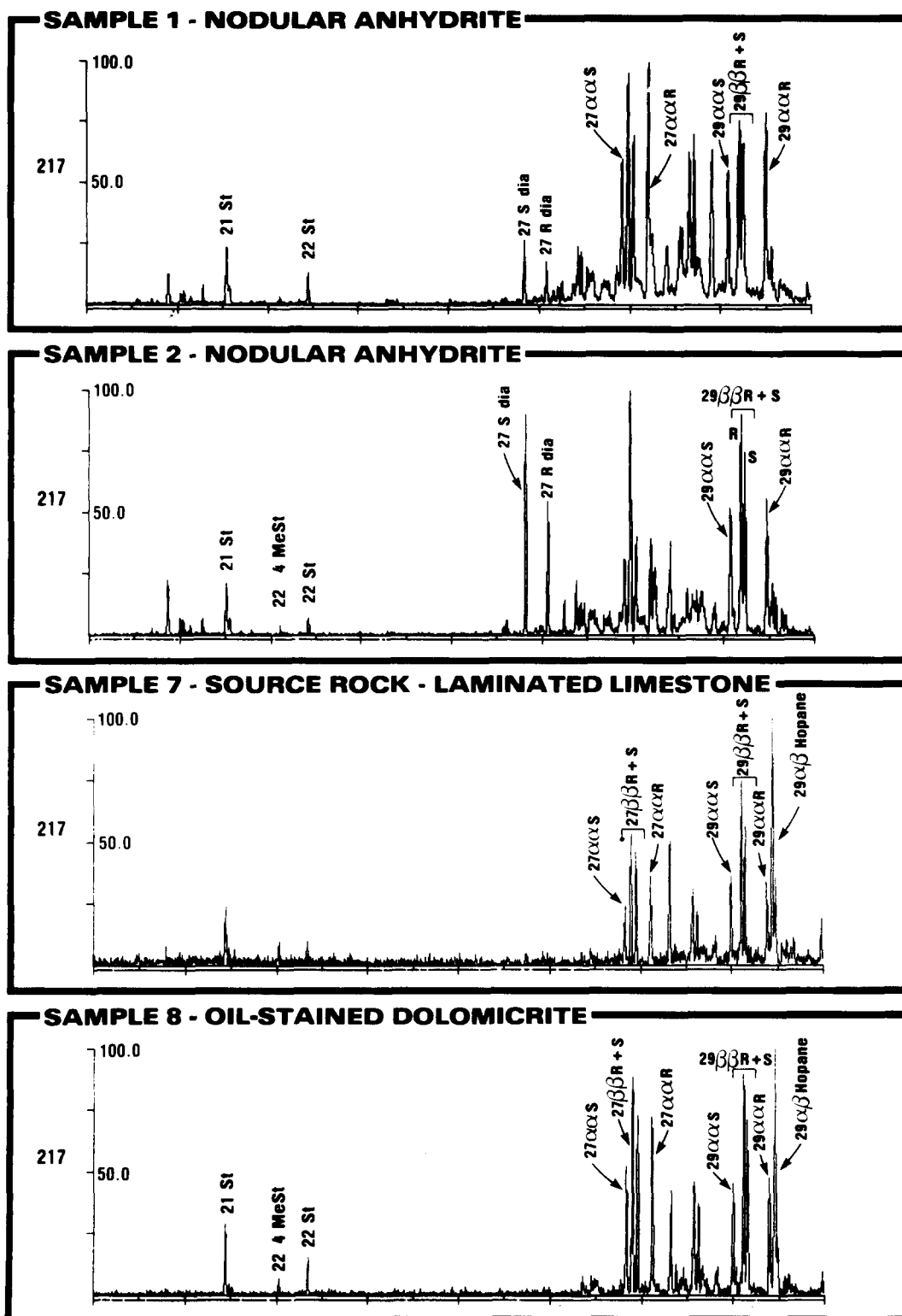
Fig. 5. Mass fragmentograms (m/z 217) showing the sterane distribution pattern of some selected samples including the source rock, the oil-stained dolomicrite and two anhydrites. A Finningan 4500 system was used for the GC–MS analyses. Conditions: fused silica column (50 mm × 0.2 mm i.d.) coated with SE 52; temperature programmed at 2°C/min from 100 to 30°C; electron energy 70 eV; scan speed 1.6 sec/scan; emission current 150 μA; displayed ion source temperature 170°C.
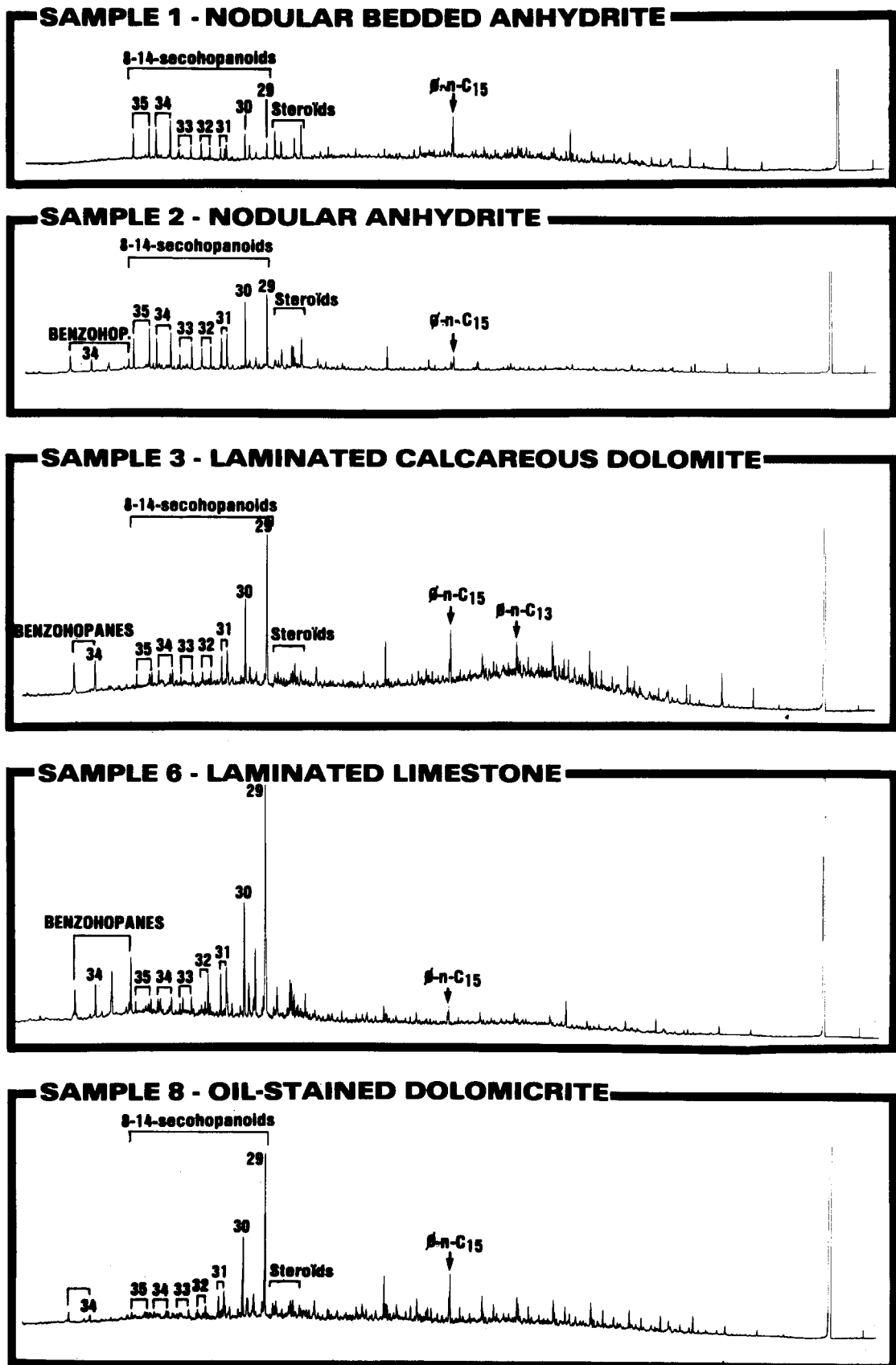
Fig. 6. Gas chromatograms of C_{15+} monoaromatics showing the identification of major components of the main families: benzohopanes (C_{31}–C_{35}), n-alkylbenzenes (1-ϕ-C_8 to 1-ϕ-C_{17}) and aromatic steroids (C_{27}–C_{29}). Same GC conditions as for branched and cyclic alkanes.

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Table 4. Bulk composition of the monoaromatic fraction—evaluation
of some characteristic ratios by computerized GC/MS

SAMPLE NUMBER	SNEA(P) REFERENCE	MAIN FAMILIES [*]				CHARACTERISTIC RATIOS		
		N-ALKYL-BENZENES %	MONO-AROM. STEROIDS %	8,14 SECO-HOPAN. %	BENZO-HOPANES %	8,14 SECOHOP./MONO STER.	1-φ-C15/ALKYL-BZ.TOT	ΣC34 8,14 SECO/C29 8,14 SECO
1	1538	62	98	100	0	1.0	44	6.8
2	1539	11	78	100	8	1.3	50	1.0
3	1540	61	31	100	10	3.2	30	0.2
4	1541	100	7	44	0	6.3	59	0.7
5	1542	95	5	100	10	20	16	0.03
6	1543	20	5	100	18	20	17	0.1
7	1544	34	9	100	4	11	15	0.1
8	1545	100	5	50	2	10	24	0.07
9	1546	47	62	100	10	1.6	29	0.4

* The evaluation has been made by peak area summation of the various
characteristic mass fragmentograms of each family : m/z 92 (n-alkylbenzenes),
m/z 253 (monoaromatic steroids),etc. The relative amount of each family has
been estimated by reference to the prominent one referred as 100%.

Abbreviations:
8,14 secohop./mono. Ster.: D-ring aromatic 8,14-secohopanoids/C-ring monoaromatic steroids.
1-φ-C_{15}/alkyl-bz. tot.: 1-phenylpentadecane/sum of n-alkylbenzenes
ΣC_{34} 8,14-seco./C_{29} 8,14-seco.: ΣC_{34} 8,14-secohopanoids/C_{29} 8,14-secohopanoids.

commonly minor compounds except in sample 1 where they are comparable to the C_{27} and C_{29} steranes.

C_{15+} aromatics

C_{15+} aromatics have been separated into mono-aromatics and polyaromatics (PAH). Mono-aromatics have been studied by computerized GC–MS in order to compare the distribution patterns of n-alkylbenzenes (m/z 92), D-ring aromatic 8,14-secohopanoids (m/z 365, 366, 159), benzo-hopanes (m/z 191) and monoaromatic steroids (m/z 253). Mass spectral characteristics of aromatic 8,14-secohopanoids and benzohopanes are described by Hussler et al. (1983). The four families mentioned above occur in various relative concentrations in the different samples (Fig. 6, Table 4). Anhydrites (1, 2, 9) already characterized as having the lowest triterpane/sterane ratios, also have the lowest 8,14-secohopanoid/monoaromatic steroid ratios (Table 4). This suggests a close genetic relationship between the polycyclic monoaromatic structures (steroids, seco-hopanoids) and the chemically related polycyclic alkanes (steranes and pentacyclic terpanes).

The n-alkylbenzene distributions (m/z 92, Fig. 7) always maximize at 1-phenylpentadecane. This predominance is generally enhanced in anhydrites (1, 2, 4; 1-phenyl-C_{15}/total alkylbenzene ratios = 30–60; Table 4). Apart from this salient feature, the distribution patterns exhibit an odd predominance (1-φ-C_{13}, 1-φ-C_{15} and sometimes 1-φ-C_{11}; 1-φ-C_{17},

1-φ-C_{19}, 1-φ-C_{21}; φ = phenyl-) within the C_{11}–C_{21} range and occasionally an even predominance (1-φ-C_{22}, 1-φ-C_{24}) in the high-molecular-weight range (C_{26}–C_{30}).

The whole D-ring aromatic 8,14-secohopanoid series is always present (C_{27} to C_{35}) although the relative concentration of each compound varies among the samples (Fig. 6). It should be noted that the 8,14-secohopanoid pattern mimics the 17α(H)-hopane distribution. For example, C_{34} and C_{35} members of both 17α(H)-hopane (Fig. 3) and 8,14-secohopanoids (Fig. 6) strongly predominate in the anhydrites (1, 2) from core 1 but are minor structures in the carbonate (3) from the same core.

The benzohopanes have only been detected in trace amounts in two anhydrites (1, 4; Fig. 6). In their distribution pattern the C_{34} and C_{35} members are always present. The lack of the C_{32} and the C_{33} structures in the monoaromatics of some samples (3, 7, 8, 9) has in fact no geochemical significance because both compounds have been identified in the related polyaromatic fraction.

The identification of monoaromatic steroids (Riolo et al., 1985; Riolo and Albrecht, 1985) in all samples has been carried out by J. Riolo (personal communication). Distribution patterns (Fig. 8) reveal that the C_{29} homologs are always the dominant structures whereas the C_{28} homologs are generally minor. There is one exception, however, in one anhydrite (sample 1) where the C_{28} isomers are more prominent than the C_{27} compounds (Fig. 8). Changes in patterns
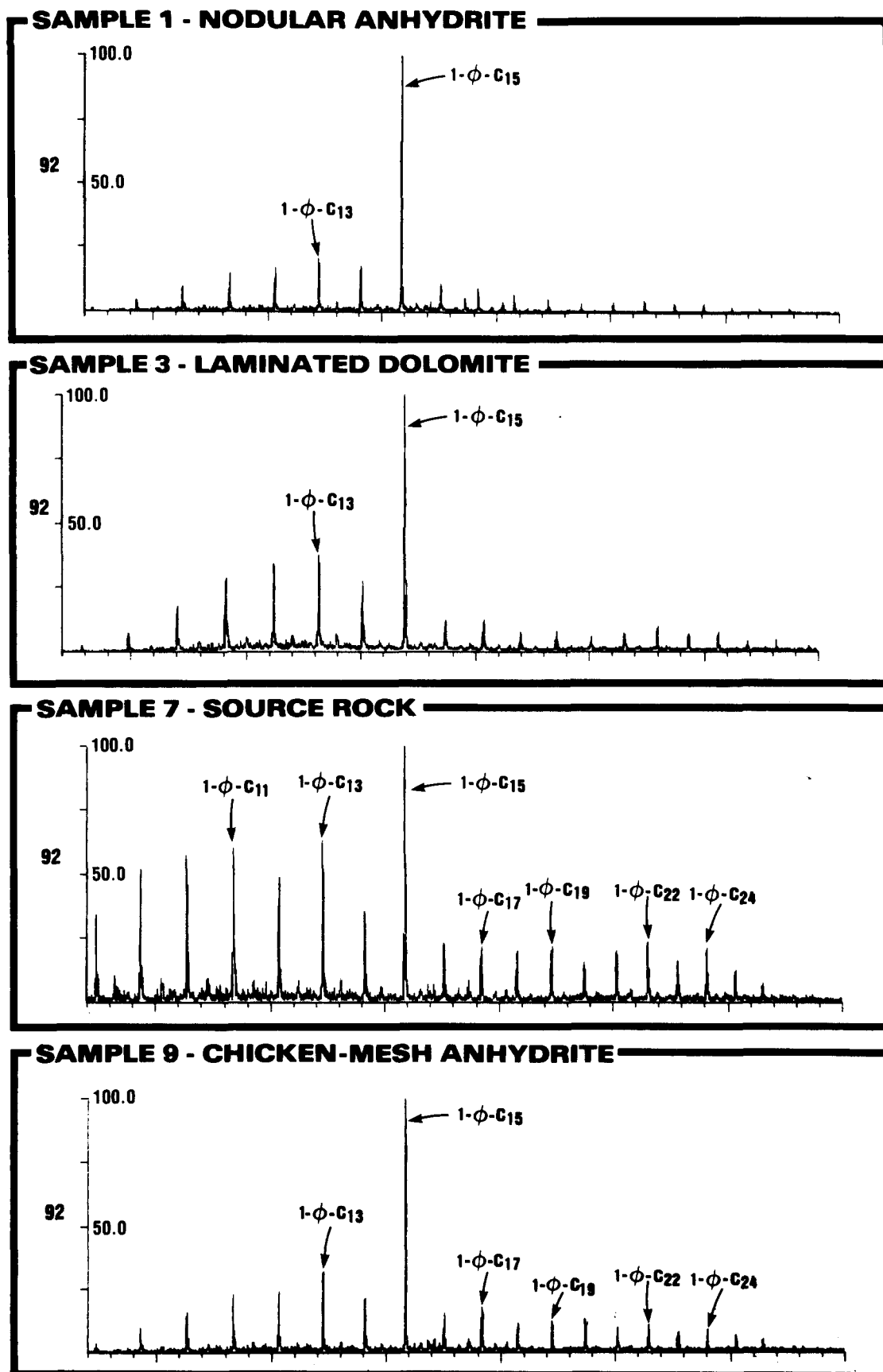
Fig. 7. Mass fragmentograms (m/z 92) showing the n-alkylbenzene distribution of some selected samples. Same GC–MS conditions as for mass fragmentogram m/z 217. Distributions have been normalized to 1-ϕ-C_{15}.
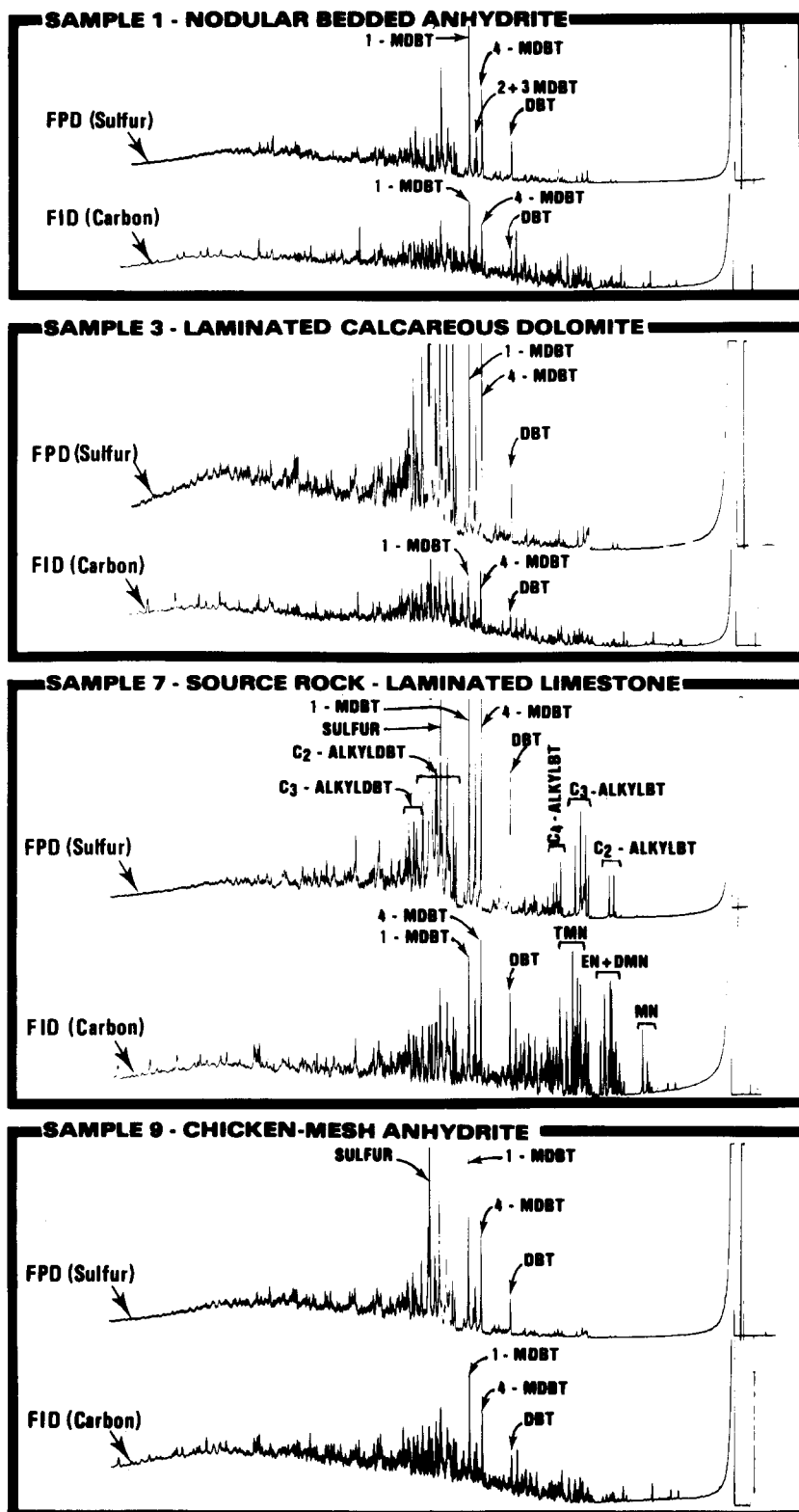
Fig. 8. Partial mass fragmentograms (m/z 253) showing the monoaromatized steroid distributions of some selected samples. Identification of structures performed by J. Riolo (personal communication).

Fig. 9. Gas chromatograms of C_{15+} polyaromatics showing the strong predominance of sulfur-bearing structures, especially dibenzothiophene and methyldibenzothiophenes. The gas chromatogram is obtained by simultaneous FID and FPD detectors. The gas chromatograph is a Tractor 550 A. Gas chromatographic conditions are: 50 m glass capillary column, i.d. 0.25 mm, stationary phase DB 5, split: 1/20. The temperature is programmed from 100 to 300°C at 2°C/min.
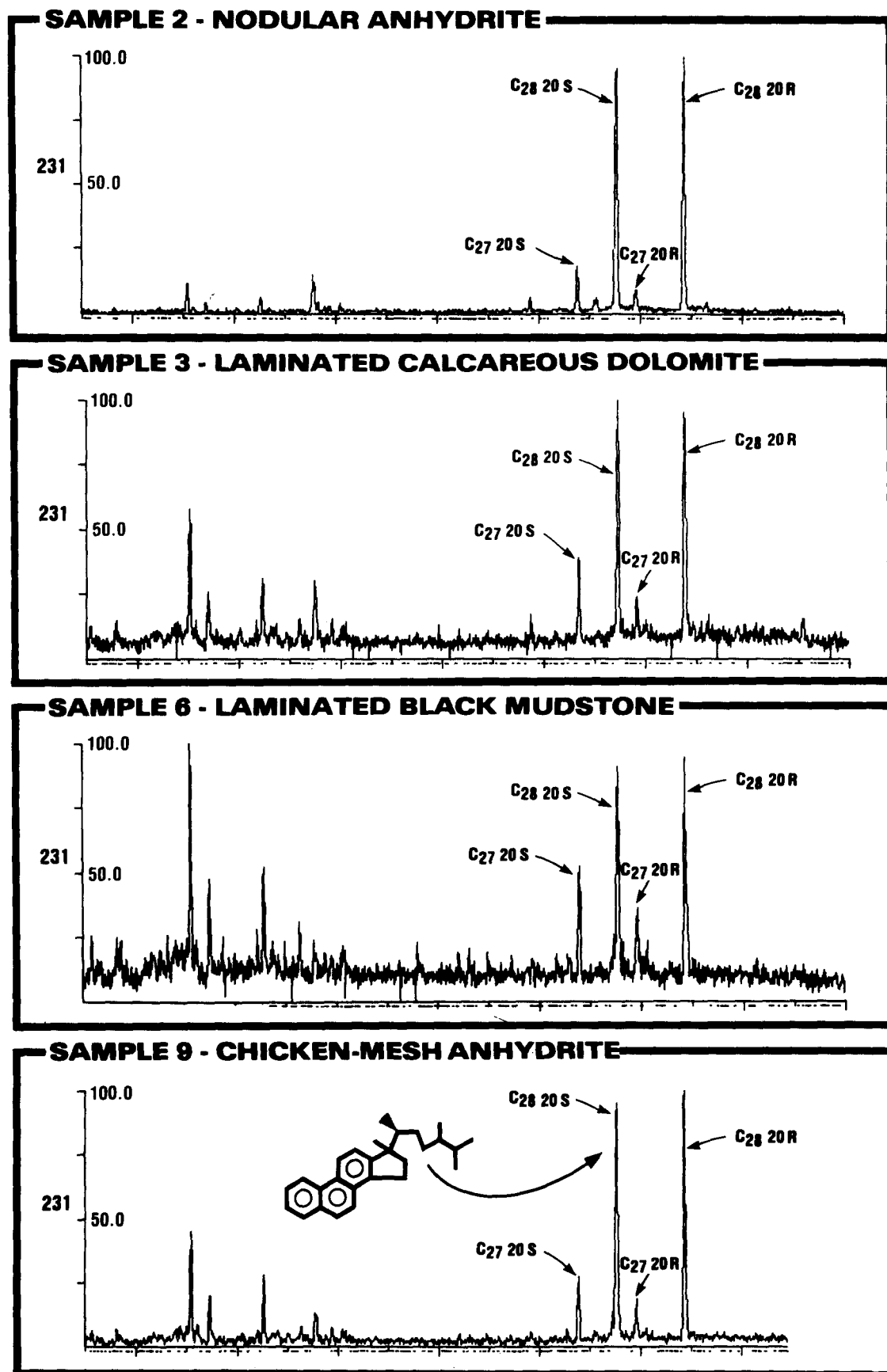
SAMPLE 2 - NODULAR ANHYDRITE

231

100.0

50.0

C$_{28}$ 20 S ← → C$_{28}$ 20 R

C$_{27}$ 20 S → | C$_{27}$ 20 R

SAMPLE 3 - LAMINATED CALCAREOUS DOLOMITE

231

100.0

50.0

C$_{28}$ 20 S → ← C$_{28}$ 20 R

C$_{27}$ 20 S → C$_{27}$ 20 R

SAMPLE 6 - LAMINATED BLACK MUDSTONE

231

100.0

50.0

C$_{28}$ 20 S → ← C$_{28}$ 20 R

C$_{27}$ 20 S → C$_{27}$ 20 R

SAMPLE 9 - CHICKEN-MESH ANHYDRITE

231

100.0

50.0

C$_{28}$ 20 S ← ← C$_{28}$ 20 R

C$_{27}$ 20 S → C$_{27}$ 20 R

Fig. 10. Mass fragmentograms (*m/z* 231) showing the distribution pattern of triaromatic steroids.

of monoaromatized steroids are fully consistent with variations already registered in steranes. Sample 1, a nodular anhydrite, was shown to be noticeably enriched in C_{28} steranes (Fig. 5).

A more careful examination of various steroid structures occurring in the distribution patterns allows the classification of the samples into two main groups:

—*Group I* (samples 4, 5, 6, 7, 8) exhibits patterns with mainly non-rearranged C_{27} and C_{29} monoaromatized steroids (type I, Fig. 8). Such a pattern is usually seen in carbonates from evaporitic series of the SW Aquitaine Basin.

—*Group II* (samples 1, 2, 3, 9) displays more complex patterns showing all kinds of isomers (type I, non-rearranged; types II and III, rearranged, Fig. 8). Rearranged monoaromatized steroids (II and III) prevail in the three anhydrites (1, 2, 9).

Changes in non-rearranged vs rearranged monoaromatic steroids in the samples closely follow the variations observed in steranes. All these consistent results confirm the close genetic relationship between both steroidal familes and suggest that the aromatization of ring C in both regular and rearranged steroid series is the main pathway which leads to their monoaromatized derivatives.

By referring to De Rycke's thesis (1983), subsequently checked by computerized GC–MS, the main compound families in the polyaromatic fractions have been identified (Fig. 9). As expected for a strongly reducing environment, sulfur-bearing compounds are well represented in the aromatic fraction. True PAH (naphthalene, phenanthrene, and their alkylated analogues) are minor components in most samples including the oil-stained sediment (8). They are, however, recognizable on the GC trace of the source rock (7). In this sediment, mono-, di- and trimethylnaphthalenes represent a significant part of the total aromatic fraction, whereas phenanthrene and methylphenanthrenes occur in minor amounts relative to the methyldibenzothiophenes. Among the sulfur-bearing aromatics, dibenzothiophene structures (dibenzothiophene, C_1-, C_2-, C_3-dibenzothiophenes) are the major ones. Methyldibenzothiophenes (MDBT) normalized to the major component, commonly exhibit a predominance of 4-MDBT in carbonates (Fig. 9). The V-pattern (4-methyl > 2 + 3-methyl- < 1-methyl-) in the methyldibenzothiophenes, considered by Hughes (1984) as generally present in extracts from carbonate source rocks, is indeed observed in samples 3 and 4. However, another V-pattern (1 methyl- > 2 + 3-methyl- < 4-methyl-) is more common in most samples (1, 2, 6, 7, 9). A computerized GC–MS analysis has been carried out to study the distribution patterns of the following families: naphthalene and C_1-, C_2-, C_3-naphthalenes (*m/z* 128, 142, 156, 170), phenanthrene and C_1-, C_2-, C_3-phenanthrenes (*m/z* 178, 192, 206, 220), dibenzothiophene and C_1-, C_2-,

C_3-dibenzothiophenes (*m/z* 184, 198, 212, 226), triaromatic steroids (*m/z* 231), alkylated naphthalenes (*m/z* 141, 155, 169, 183). Alkylfluorenes and naphthobenzothiophenes were also present, but generally in lower abundance. In order to better compare PAH distributions, molecular ions for specific homologous series were summed. This analytical procedure allows the appraisal of the relative concentration of each homologous series, namely alkylnaphthalenes (C_0–C_3), alkyldibenzothiophenes (C_0–C_3), etc. Comparison of distribution patterns shows identical molecular structures in all samples. However, the relative concentration of groups of molecules (e.g. methylnaphthalenes, dimethylnaphthalenes) or of individual compounds (e.g. methyldibenzothiophene isomers) changes from one sample to another. Table 5 summarizes the results of calculations which have been done to evaluate some characteristic ratios on phenanthrenes (Radke *et al.*, 1982a, b, 1983; Garrigues *et al.*, 1983; Garrigues, 1985) and dibenzothiophenes (Radke *et al.*, 1982a).

Distribution patterns of alkylated naphthalenes confirm the enrichment of C_1- and C_2-naphthalenes in the source rock sample (Fig. 9). Although C_2-naphthalenes display similar distributions, C_3-naphthalene distributions vary in the samples investigated. 1-Methylnaphthalene dominating over 2-methylnaphthalene as in sample 3 has been found by Radke *et al.*, (1982b) in coals with ranks lower than 0.8–0.9% R_0. Long-chain alkylated naphthalenes (*m/z* 141, 155, 169) have been recognized as prominent structures in anhydrites (1, 2, 4, 9) and in one carbonate sample (3). Their concentration is low in most carbonates, especially in the source rock sample where it was even difficult to detect the methylated homologues. Examination of mass spectra in the MS data library gave a good match with the following structures: undecylnaphthalene (*m/z* 141), two monomethylundecylnaphthalenes (*m/z* 155), and two dimethylundecylnaphthalenes (*m/z* 169).

High-molecular-weight triaromatic steroids (Ludwig *et al.*, 1981) are limited to C_{27} and C_{28} structures where the C_{28} 20S and 20R homologues, identified by Hussler (1985), are the major compounds (Fig. 10).

DISCUSSION

Representativity of the geochemical signature: indigenous vs migrated hydrocarbons

High OE/TOC ratios (0.12–0.25) are commonly encountered in many carbonate source rocks of the world with rather high TOC values (1.5–10%; Palacas, 1983). Rullkötter *et al.* (1984) report yields close to 20% in organic-matter-rich bituminous chalks with 17–22% organic matter. This study brings consistent data with an OE/TOC of 0.14 in the source rock (7). However, carbonate rocks often act both as source and reservoir (through fracturing), so it is not easy to separate indigenous from migrated hydrocarbons (Hedberg, 1931; Hunt and McNichol, 1984)

especially in organic-carbon-lean sediments. Biomarker chemistry offers a powerful tool to aid in solving this problem.

Despite the fact that the main geochemical properties are similar in all samples, each facies may be differentiated by its detailed biomarker chemistry. Therefore, even if traces of allochthonous hydrocarbons may not be definitely ruled out to be present in the samples analyzed, the striking molecular contrast recorded in anhydrites and laminated dolomites favours the prevailing indigenous origin of the extracts in most samples (except in sample 8 which is obviously oil-stained). This conclusion supports the validity of relating molecular patterns of nearly barren samples as anhydrites to past depositional environments. High bitumen yields (10–25%) in carbonates appear to be related to a characteristic property of their kerogen able to generate appreciable amounts of bitumens in an early stage of catagenesis.

Palaeoreconstruction of the sabkha-type environment in La Felicidad 1 using molecular composition

The La Felicidad 1 sediments: record of an anoxic palaeoenvironment. The environment of deposition, as for modern sabkha deposits, was very restricted. The prevailing strongly reducing conditions are reflected by the very low pristane/phytane ratios which are always lower than 0.75 (cf. Didyk et al., 1978; Connan, 1981). The lowest values (0.3–0.4) are observed in the anhydrite facies (samples 1 and 2, laminated and nodular anhydrites) which arose from gypsum/anhydrite deposition in a hypersaline lagoon under shallow water (few centimeters, submerging facies). A similar result was previously obtained for a carbonate-anhydrite pair in the Mano Dolomite Formation (SW Aquitaine, France) with a pristane/phytane ratio of 0.3 in the anhydrite and 1.2 in the carbonate (Connan, 1981). A more generalized relationship has been established by computing many data (Fig. 11) from the Mano Dolomite Formation (Vic Bilh oil field area). However, if the trend is similar in both sabkha deposits, the variation is less important in the La Felicidad 1 samples where the pristane/phytane ratio never exceeds 0.75 (Fig. 4).

Even-carbon-number preferences for *n*-alkane distributions are commonly found in strongly anoxic environments exhibiting various lithologies (siliceous mudstones, argillaceous shales, dolomites). Examples are the diatomites and organic-matter-rich mudstones of the upper member of the Monterey Formation, and the anhydrite and carbonates of the La Felicidad 1 well. The origin of the even *n*-alkane predominance is not completely understood. Two main explanations are generally proposed. Even-carbon-number preferences are produced either by biosynthetic pathways in some bacteria (e.g. *Sarcina lutea, Desulfovibrio desulfuricans*) or by a secondary process involving thermal decomposition of lipid precursors (*n*-fatty acids, *n*-alcohols, *n*-ketones). Microorganisms contain low amounts of hydro-
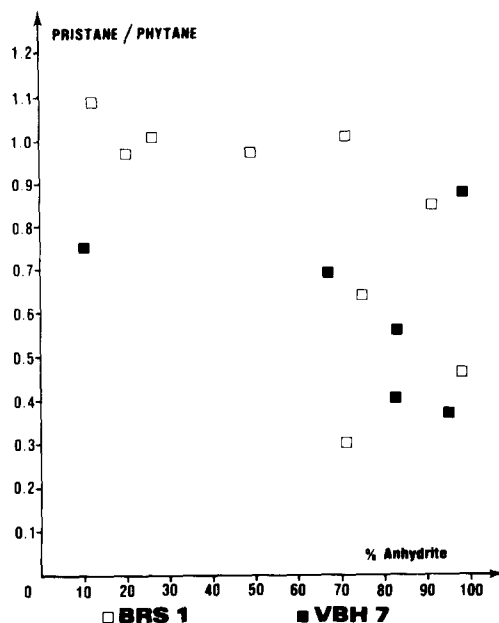

Fig. 11. Pristane/phytane vs % anhydrite in the Aquitaine Basin (BRS 1 and VBH 7 wells, Mano Dolomite Formation, Vic Bilh oil field).

carbons (0.01–0.14% dry wt) within the neutral lipid fraction (Boyd, 1983, unpublished results).

Therefore, the direct formation of abundant quantities of *n*-alkanes with an even predominance by microorganisms is very unlikely. Even-carbon-number preference thus is probably the result of degradation of lipid precursors under anoxic conditions via chemical (Welte and Waples, 1973; Esnault, 1973) or biological processes (Goutx and Saliot, 1980; Grimalt et al., 1985).

Redox conditions probably control the occurrence and distribution patterns of other less well known biomarkers such as *n*-alkylbenzenes, steranes, aromatized steroids, benzohopanes and dibenzothiophenes. The odd predominance (C_{17}, C_{19}, C_{21}) in the *n*-alkylbenzenes has been recorded in sabkha-type deposits (this study; Mano Dolomite Formation, Aquitaine Basin, France) whereas even predominance (1-ϕ-C_{12}, 1-ϕ-C_{16}, 1-ϕ-C_{18}; ϕ = phenyl) is registered in oils from Colombia originating from open-marine source rocks (pristane/phytane = 1.5). The sterane distribution, exclusively composed of regular steranes (C_{27}–C_{29}, $\alpha\alpha$ and $\beta\beta$, R and S), is another typical feature of a very anoxic depositional environment.

The La Felicidad 1 samples: a demonstrative example of strong microbial input. In a recent paper Ourisson et al. (1984) emphasized that many classes of biomarkers (alkanes, aromatics, alcohols, acids) found in sediments, petroleums and coals, have a microbial origin. This thesis, based on molecular palaeontology, needs to be clarified, because the provoking title "The microbial origin of fossil fuels" of the paper has sometimes been misunderstood by earth scientists engaged in coal studies. Geologists,

palynologists and coal petrographers dealing with peats and coals know that most coals are formed from a variety of plant debris (cuticles, spores, woody structures). Consequently, if the microbial activity is an ubiquitous process in various geological environments, its impact on the organic matter incorporated and then preserved in the sediment may be variable.

Tissot et al. (1978) described such a case history in the lacustrine Green River Formation (Uinta Basin, U.S.A.). In the upper beds, the organic matter reflects a dominant contribution of algal and higher plant lipids. In the middle and lower part, the intense reworking of the organic matter by bacteria led to the degradation of algal lipids and enhanced the concentration of both higher plant and bacterial lipids. In the underlying formation (Flagstaff member), the biomass mostly originates from microorganisms themselves (no steroids, high amounts of iso- and anteiso-alkanes). More recently, Williams (1984) emphasized that the organic matter of stromatolites in the Monterey Formation of California consists mainly of remnants of colourless, filamentous, sulfur-oxidizing bacteria belonging to the Beggiatoaceae family. Sulfur-oxidizing bacteria may form more than 80% of the biomass accumulated in mats in modern coastal upwelling regions (Peru and Chile, Santa Barbara Basin). These laminated sediments are the modern counterparts of the Monterey Formation. This study provides another demonstrative example of dominant microbial contribution to the dispersed organic matter. The prevailing chemical features, observed both in anhydrites and in carbonates, mainly reflect the heritage of biological markers derived from the bacterial biomass. Among the most specific alkanes found only in microorganisms are the bacteriohopanes (Ourisson et al., 1979). They are particularly prominent in the La Felicidad 1 samples, where the steranes and their related mono- and triaromatic structures are present as minor families (TT/ST ratios = 19–144; Table 3). This characteristic may be extended to most oils from Guatemala (Rubelsanto, Tortugas, W. Chinaya, Terra Blanca, Yalpemech, etc.) which have been generated from the same source rock interval. As reference one may consider a triterpane/sterane ratio of 10 in coals, shales and oils from the Mahakam Delta, i.e. in rock extracts or petroleum derived from type III kerogen rich in components of higher-plant origin (Hoffman et al., 1984). The Guatemala example should be the best example to date for crude oils of mostly bacterial origin.

If the bacterial input prevails in sediments and oils from Guatemala, several chemical features should be examined as possible predictive tools in microbial biochemistry. The terpane distribution pattern shows the microbially derived hopanes as major families. Tetracyclic terpanes (C_{24}, C_{26}, C_{27}) are present, whereas tricyclic terpanes only occur in traces ($C_{23:3}/C_{24:4} = 0.2$–0.4). Such a characteristic, found in the La Felicidad samples, is also encountered in all

the crude oils from Guatemala ($C_{23:3}/C_{24:4} = 0.2$–0.4). Consequently, the fossil bacteria which developed in evaporites from Guatemala did not synthesize significant amounts of a tricyclic terpane precursor, e.g. the tricyclohexaprenol thought to be a stabilising constituent of microorganism membranes (Aquito Neto et al., 1982).

Among other families of bacterially derived biomarkers are iso-alkanes, alkyl-benzenes, alkylated-naphthalenes and n-alkanes. The C_{23} and C_{27} iso-alkanes have probably been released by thermal decomposition of alkyl glyceryl ethers, which play an important role in the membranes of bacteria. Dialkyl-ethers are the only constituents of polar lipids from halophilic bacteria (e.g. Halobacterium halobium, Halobacterium salinarium, Halobacterium volcanii, Halococcus morrhuoe; reviewed by Chappe, 1982) which are the most characteristic organisms of marine hypersaline ecosystems (Larsen, 1980; Cornée, 1983). It is therefore reasonable to assume that the unknown halophilic bacteria which contributed to the La Felicidad 1 sediments may have contained the iso-C_{23} and iso-C_{27} moieties as major alkyl chains in the diethers of their membranes. The predominance of the iso-C_{23} in the branched and cyclic alkanes may be characteristic of certain halophilic bacteria which inhabit hypersaline environments because such a predominance has recently been found in another anhydrite-rich sediment from the Cretaceous of the Aquitaine Basin (Neocomian, more than 70% anhydrite, TOC = 0.07%). In this anhydrite, the prevailing microbial heritage seems also to be responsible for the following molecular features: abundant tetracyclic terpanes relative to tricyclic terpanes ($C_{23:3}/C_{24:4} = 0.39$); occurrence of hopanes including $17\alpha(H),21\beta(H)$-28,30-bisnorhopane; no steranes; marked predominance of the 1-cyclohexyl-pentadecane interpreted as bacterially-derived; n-alkane distribution with a maximum at n-C_{21} and even predominance for n-C_{28} and n-C_{30}.

The alkylbenzene series have not been extensively described in microorganisms, although methyl-branched alkylbenzenes have been identified in Archaebacteria (Holzer et al., 1979). We consider the strong predominance of 1-phenylpentadecane as another salient molecular feature that should be related to the bacterial input. This predominance is particularly enhanced in anhydrite facies either in La Felicidad 1 or in Aquitaine Basin sabkhas. Possible precursors for these compounds should be looked for in halophilic bacteria (membrane components). Undecylnaphthalene and its related methylated structures (C_1- and C_2-undecylnaphthalenes) discovered in anhydrites of La Felicidad 1 (samples 1 and 2), are also well represented in anhydrite-rich sediments of the Aquitaine Basin (Mano Dolomite Formation). Their bacterial origin is again very likely, although their precursor molecules in living microorganisms at present is not known.

The n-alkanes of the La Felicidad 1 sediments

having a maximum between C_{20} and C_{28} (Table 2) and a strong even predominance within the high-molecular-weight range $(C_{20}-C_{32})$ may also be ascribed to a bacterial input. n-Alkane distributions enriched in high-molecular-weight homologues with an even predominance are common in anhydrites of the Mano Dolomite Formation (Connan, 1981). The marked enrichment in high-molecular-weight n-alkanes in the anhydrites of the Aquitaine Basin always correlates with enhanced concentrations of C_{25}, C_{30} and C_{40} isoprenoids, 1-phenylpentadecane and undecylnaphthalene, and a reduction of the pristane/phytane ratio. Aromatic D-ring 8,14-seco-hopanoids whose distribution patterns have been shown to be closely related to the $17\alpha(H)$-hopane spectrum and the benzohopanes complete the inventory of bacterially-derived molecules.

Early formation of petroleum from bacterially-derived kerogen predominant in various environments

The microbial input, variable among sediments of sabkha deposits, may be predominant in some of them as exemplified by the La Felicidad 1 sediments. This more accurate diagnosis of the real biological origin of the kerogen (often referred to as type II or type I-II) in these carbonate–anhydrite sequences forms a key to understand the proposed early generation of oil from carbonates in evaporitic basins (Hunt and McNichol, 1980; Powell, 1984; Palacas, 1983). The same is true for stromatolites in siliceous sediments of the Monterey Formation of California where Petersen and Hickey (1984) claimed that commercial generation of oil has occurred at vitrinite reflectance levels as low as 0.3% R_0. To these two oil-prone environments add phosphorites which display features similar to carbonates (Powell et al., 1975).

The early generation of heavy oils in the Monterey Formation, in phosphorites and in carbonates may be due to a specific character of their kerogens. Consequently, all these kerogens should be chemically related and it appears that they are mostly composed of bacterial remains. Powell et al. (1975) concluded that organic matter of phosphorites derived primarily from microorganisms which accumulated in a euxinic environment. Williams (1984) attributed the peculiar thermal behaviour of the Monterey kerogen to its bacterial origin (filamentous sulfur-oxidizing bacteria) and extended this conclusion to some carbonates (e.g. organic-matter-rich facies of Bear Gulch Limestone, Middle Carboniferous, Montana) where bacterial fossils occur, and some oil shales of the Green River Formation (cyanobacterial mats, type I kerogen with $S_1 = 4.5$ mg HC/g TOC and $S_2 = 167$ mg HC/g TOC).

We conclude that the bacterial biomass (halophilic and methanogenic bacteria, cyanobacteria, etc.) contributes significantly to the kerogen of our sabkha sediments. The occurrence of abundant carbon-sulfur bonds within these kerogens may favour their early thermal degradation (Orr, 1986). The importance of bacterial remains as a source of petroleum was highlighted by Lijmbach (1975) who developed the idea after performing in vitro experiments. By heating bacteria, preextracted with chloroform, he succeeded in totally converting the biomass into petroleum-like material after 8 h at 330°C. He even demonstrated that the oil generation is extremely rapid, because the chloroform extract yield increased from 20 to 64% between 8 and 168 hr of heating at 150°C. He also showed on the basis of other heating experiments that the thermal conversion is much lower for algal cells than for bacteria.

Variations of maturity parameters with facies in the La Felicidad 1 samples

According to the basic data $(TAI = 2.50-2.75$, $T_{max} = 429-435°C)$, the threshold of oil generation should have been reached in the La Felicidad 1 samples. This is supported by data from the geochemical study which showed the presence of an effective source rock (sample 7) and an oil-stained reservoir rock (sample 8). A review of maturity parameters measured on both alkanes and aromatics did not show any downhole relationship in the interval studied. Hence, changes among the so-called maturity parameters reflect facies influences (e.g. lithology, source, geocatalysis) rather than real differences in the thermal stress that affected the sediments. Comparison of the usual maturity parameters (sterane and terpane ratios, methylphenanthrene indices) provides new information on variations in different lithofacies at the same stage of catagenesis.

Isomerization in the hopanes at C-17 and C-22 has reached completion in all the samples (cf. $\beta\alpha$ to $\alpha\beta$ and $22S/(22S + 22R)$ ratios; Table 3). Isomerization in the C_{29} steranes is incomplete for 20S/20R and $\beta\beta/\alpha\alpha$ ratios average 47% and 58%, respectively (Table 3). T_m [$17\alpha(H)$-trisnorhopane] to T_s [$18\alpha(H)$-trisnorneohopane] ratios (Seifert and Moldowan, 1978), vary widely in our set of samples. However, the lowest values never fall below 1.0 as expected in moderately mature sediments. Accurate interpretation of sterane and terpane ratios in terms of maturity is difficult, because there is a lack of published data on sabkha-type deposits. Published results (Mackenzie and Maxwell, 1981) on the Toarcian (Paris Basin) and Pliensbachian shales (NW Germany) provide rough interpretation guidelines. In these basins, the complete isomerization at C-22 in C_{31} $17\alpha(H)$-hopanes occurs at the top of the oil window whereas the complete isomerization at C-20 in steranes is observed at the peak of oil generation. Our samples, located within the zone of hydrocarbon generation, have apparently not reached the maturation stage of maximum oil release. According to sterane and terpane properties, these sediments may be referred to as moderately mature.

Rank-dependent distribution patterns of phenan-

Table 5. Methylphenanthrene/phenanthrene and methyldibenzothiophene/dibenzothiophene ratios measured by capillary GC and computerized GC–MS

SAMPLE NUMBER	REFERENCE SNEA(p)	PHENANTHRENE AND METHYL PHENANTHRENES												DIBENZOTHIOPHENE AND METHYLDIBENZOTHIOPHENES								
		MP$_1$ GC-MS	MP$_1$ GC*	MP$_3$ GC-MS	MP$_3$ GC*	ΣMP/P GC-MS	ΣMP/P GC*	MDR$_1$ GC-MS	MDR$_1$ GC	MDR$_{2+3}$ GC-MS	MDR$_{2+3}$ GC	MDR$_4$ GC-MS	MDR$_4$ GC	MDBI$_1$ GC-MS	MDBI$_1$ GC	MDBI$_3$ GC-MS	MDBI$_3$ GC	MDR$_{4,1}$ GC-MS	MDR$_{4,1}$ GC	ΣMDBT/DBT GC-MS	ΣMDBT/DBT GC	DBT/P GC-MS
1	1538	0.63	0.72	0.66	0.66	2.9	4.4	1.4	3.6	0.9	1.0	1.1	2.1	0.9	0.8	0.9	0.7	0.8	0.6	3.4	6.6	2.1
2	1539	0.52	0.60	0.56	0.56	2.6	4.0	1.9	3.9	0.8	1.0	1.2	2.2	0.8	0.8	0.7	0.7	0.6	0.6	3.9	6.7	2.0
3	1540	0.77	0.86	0.73	0.73	4.1	6.3	1.1	3.1	1.2	2.0	1.7	5.3	1.3	1.8	1.2	1.4	1.5	1.7	4.1	10.4	1.7
4	1541	0.80	0.91	0.79	0.79	3.8	5.9	1.3	3.5	1.3	1.6	1.5	3.8	1.1	1.3	1.0	1.1	1.1	1.1	4.1	8.9	1.5
5	1542	0.73	0.83	0.75	0.76	3.2	4.9	0.8	1.7	1.2	1.8	1.0	2.7	1.1	1.8	1.1	1.3	1.3	1.8	3.0	6.2	2.6
6	1543	0.77	0.88	0.82	0.82	3.0	4.6	1.3	4.2	1.3	1.7	1.5	3.1	1.1	1.0	1.0	0.8	1.1	0.7	4.1	8.7	1.6
7	1544	0.77	0.89	0.82	0.82	3.1	4.7	0.9	2.0	0.9	1.0	0.9	1.6	0.9	1.0	1.0	0.9	1.0	0.8	2.7	4.6	4.9
8	1545	0.81	0.88	0.70	0.70	5.7	8.7	1.3	3.8	1.3	2.1	1.3	3.8	1.1	1.3	1.0	1.0	1.0	1.0	3.9	9.7	4.8
9	1546	0.62	0.70	0.62	0.62	3.4	5.1	1.2	4.9	0.9	1.3	1.0	2.7	0.9	0.8	0.9	0.6	0.8	0.6	3.1	9.0	3.5

* calculated from GC-MS data after intercalibration on phenanthrene and 2-methylphenanthrene

SIGNIFICANCE OF ABBREVIATIONS:

$$MDR_1 = \frac{1 - MDBT}{DBT} \qquad MDR_{2,3} = \frac{2,3 - MDBT}{DBT} \qquad MDR_4 = \frac{4 - MDBT}{DBT} \qquad MDR_{4,1} = \frac{4 - MDBT}{1 - MDBT} \qquad \Sigma MDBT/DBT = \frac{1 - MDBT + 2 - MDBT + 3 - MDBT + 4 - MDBT}{DBT}$$

$$\Sigma MP/P = \frac{1 - MP + 2 - MP + 3 - MP + 9 - MP}{P} \qquad MP_1 = \frac{1.5(2 - MP + 3 - MP)}{P + 1 - MP + 9 - MP} \qquad MP_3 = \frac{2 - MP + 3 - MP}{1 - MP + 9 - MP} \qquad MDBI_1 = \frac{1.5(4 MDBT + 2,3 MDBT)}{DBT + 2,3 MDBT + 1 MDBT} \qquad MDBI_3 = \frac{4 MDBT + 2,3 MDBT}{2,3 MDBT + 1 MDBT}$$

Abbreviations:
P: Phenanthrene.
MP: Methylphenanthrene.
DBT: Dibenzothiophene.
MDBT: Methyldibenzothiophene.
MDBT: Methyldibenzothiophene.

threne/methylphenanthrenes and dibenzothiophene/ methyldibenzothiophenes have been used to calculate several maturity parameters discussed by Radke et al. (1982a, b) and Garrigues (1985). Unfortunately, interpretation of our data has to be made with caution, because available results (Radke et al., 1982a, b) only refer to typical type II and III kerogens in shales or in coals, and one may expect different reference scales when dealing with sulfur-rich kerogens from hypersaline deposits. Comparison of our methyl-dibenzothiophene ratios (MDR_1, $MDR_{2,3}$, MDR_4; Table 3) with Radke et al.'s (1982a) data supports the assumption by revealing striking differences in range values (0.05, 0.25–1.0, 0.5–3.0 in Radke et al., 1982a; compared to 1.7–4.2, 1–2.1, 1.6–5.3 in this study; Table 5).

Whatever the difficulties may be to convert our maturity measurements to vitrinite reflectance equivalents, it remains of interest to compare these data (e.g. MPI_1, MPI_3) to published ones and to discuss variations of all maturity parameters including new indices ($MDBI_1$, $MDBI_3$) with respect to facies. A review of the available information (Radke et al., 1982a, b, 1983; Garrigues and Ewald, 1983; Garrigues, 1985) provides general maturity trends with the following rules:

(1) Phenanthrene, 9- and 1-methylphenanthrenes

decrease relative to 3- and 2-methylisomers with increasing maturity below 1.3% R_0. Consequently, MPI_1 and MPI_3 increase with maturity.

(2) 1-Methyldibenzothiophene decreases relative to the 4-methylisomer; therefore, the 4- to 1-MDBT ratio ($MDB_{4,1}$) or the methyl-dibenzothiophene indices ($MDBI_1$ and $MDBI_3$; Table 5) should increase with maturity.

According to the above mentioned authors, our data ranges (MPI_1 = 0.6–0.9, $MDR_{2,3}$ = 1.0–2.1, MDR_4 = 0.6–0.7) suggest that the maturation stage of our sediments should roughly be moderate to early mature (i.e. 0.50–0.75% R_0).

The maturity framework of our set of samples being established, it remains to examine whether so-called maturity parameters are changing with lithology and facies. Comparison of some characteristic maturity parameters (MPI_1, $MBD_{4,1}$, MDB_1, etc.; Table 5) leads to the differentiation of three anhydrites (samples 1, 2, and 9) from other samples. Plots of some important ratios (MPI_1, MPI_3, $MDR_{4,1}$, $MDBI_1$) vs pristane/phytane ratios (Fig. 12) show positive correlations which indicate that the so-called maturity parameters are also related to palaeo-environments (or kerogen-type) in our sabkha sequences.
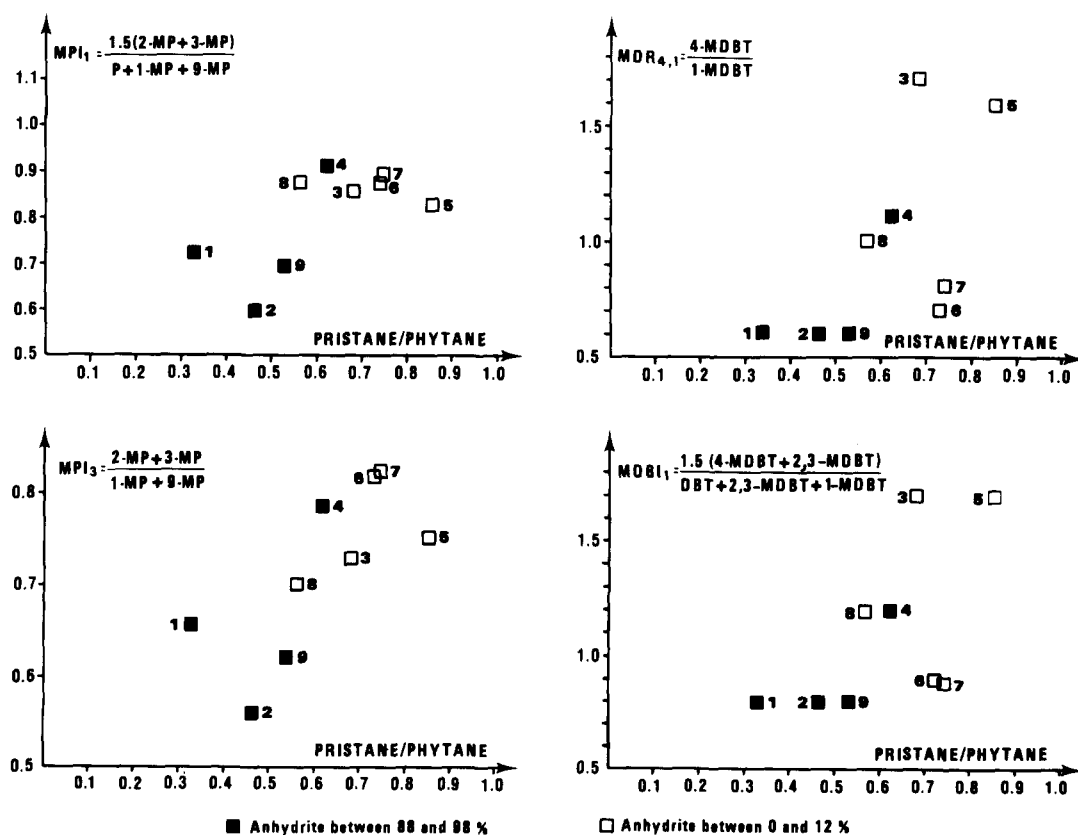

Fig. 12. Influence of the palaeoenvironmental conditions on some maturity parameters measured on C_{15+} polyaromatics: maturity indices vs pristane/phytane.

CONCLUSIONS

Organic geochemistry has proven to be a useful tool to sedimentologists for characterizing facies even when they are practically devoid of organic matter. In the La Felicidad 1 well (Guatemala), anhydrites from the supratidal zone have been differentiated from carbonates and anhydrites in the sub- to intertidal zone. In the La Felicidad 1 well, the classification of samples within a schematic sedimento-diagenetic sequence was fully confirmed by molecular properties. Anhydrites from the supratidal zone exhibit lower pristane/phytane ratios, (reflecting more reducing environments), higher amounts of steranes. In addition, the comparison of the sabkha-type deposits from the La Felicidad 1 well to other sabkhas shows significant differences in the molecular signature. Consequently, the molecular approach leads to promising classifications and reconstructions of sabkha palaeoenvironments and insight into the organic input, especially in organic-matter-lean facies (TOC = 0.04–0.30%).

The palaeosabkha of the La Felicidad 1 well shows molecular patterns mainly ascribed to a bacterial origin [e.g. $17\alpha(H)$-hopane/C_{27}–C_{29} sterane ratios >20]. A similar molecular signature also occurs in carbonates and in anhydrites. A cyanobacterial molecular record has not been registered in carbonate facies which do not exhibit true stromatolitic features. The organic matter of the whole sequence (i.e. algal remains) seems to have been reworked by bacteria. Consequently, the remaining molecular signature should be attributed to the bacterial biomass enriched in the sediments.

Crude oils produced in the vicinity of the La Felicidad 1 well possess molecular properties in good agreement with those of the carbonate source rock extract of this study. They reflect a prevailing bacterial origin.

A review of the detailed chemical record led to some ideas regarding the molecular palaeontology of bacteria in hypersaline environments. Bacteria which contributed to the La Felicidad 1 sediments may have been dominantly halophilic with membranes containing iso-alkanes (iso-C_{23}, iso-C_{27}) as aliphatic chains. The strong predominance of several families of biomarkers in these sabkha-type deposits suggests that they are probably derived from bacterial cells, where they occur as unknown functionalized precursors. The molecules we have selected as bacterially derived are: 1-phenylpentadecane, undecylnaphthalene and methylated homologues, tetracyclic terpanes, aromatized D-ring 8,14-secohopanoids, benzohopanes, iso-C_{23} and iso-C_{27} alkanes.

The assessment of maturity within the La Felicidad sediments is based on intercalibration measurements (e.g. TAI, T_{max}, sterane and terpane ratios, MPI_1, $MDB_{4,1}$) and indicates that the sequence is moderately to early mature ($R_0 \simeq 0.6\%$). No downhole trends were registered in various maturity parameters based on alkanes and aromatics, but it was established that the so-called maturity parameters especially in aromatics are dependent on facies, i.e. palaeoenvironments.

A major conclusion for petroleum geochemists is the interpretation of the early generation of heavy, sulfur-rich oils in carbonates from evaporites. This early generation with high yields, i.e. high OE/TOC and HC/TOC ratios, appears to be a typical property of the bacterially derived organic matter in certain carbonate deposits. This property is also encountered in other palaeoenvironments (siliceous Monterey Formation, phosphorites) where a dominant input of bacterial remains under very anoxic conditions has been recognized. In the Monterey Formation, for instance, a significant oil generation occurs at vitrinite reflectance values as low as 0.3%. High OE/TOC or HC/TOC ratios at a low maturation stage in all the above mentioned environments are the representative properties of bacterial biomass of various origins, preserved under very reducing conditions entailing a significant sulfurization of the primary kerogen. These new data reemphasize the leading role of microorganisms as a source of petroleum in some selected palaeoenvironments. As far as oil potential is concerned bacteria can be considered to be among the most favourable type of organic matter.

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