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Carboxylic acids of marine evaporitic oils from Sergipe-Alagoas Basin, Brazil

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Abstract

A suite of 10 different marine evaporitic oil samples from Sergipe-Alagoas Basin, Brazil was studied for its biomarker content, in particular its acidic constituents. The oils showed different molecular distributions and relative abundances of *n*-alkanoic, isoprenoid and hopanoic acids. The observed differences were assigned to the incorporation of immature organic matter in the oils and fractionation along the migration pathway. The diagenetic precursor functionality (alcohol/ether or acid) was proposed based on the comparison of the relative abundances of the neutral and acidic biomarkers (hopanoids, isoprenoids, alkyl-steranes, monoaromatic alkyl-steroids). In the acidic fraction, 3 series of steroid-alkanoic acids and monoaromatic steroid-alkanoic acids (steroid-methanoic, ethanoic and propanoic acids and monoaromatic steroid-methanoic, ethanoic and propanoic acids) were detected, while in the neutral fraction only 2 series of each corresponding class could be observed (methyl and ethyl-steranes and monoaromatic methyl and ethyl-steroids). These carbon shifts suggest that decarboxylation is an important process in the formation of the alkyl-steranes and monoaromatic alkyl-steroids, and we infer that carboxylic acids are the diagenetic precursors of these classes of compounds. When alcohol or ether are the diagenetic precursors (isoprenoids and hopanoids), no significant differences in the molecular distributions between neutral and acidic fractions were observed.

Keywords: Sergipe-Alagoas Basin; Brazil; Carmópolis oil field; Marine evaporitic petroleum; Acidic biomakers; Steroid-alkanoic acids; C-25 regular isoprenoid acid

1. Introduction

In order to establish the thermal evolution and migration history of crude oils, geologists and geochemists primarily use information from hydrocarbon biomarkers (Trindade and Brassell, 1992; Peters and Moldowan, 1993). In recent years, however, an increasing amount of research using carboxylic acids, and nitrogen- and sulphur-containing compounds has shown that these biomarkers provide complementary information allowing a better understanding of the geological history and evolution of a sedimentary basin (Mackenzie et al., 1982; Behar and Albrecht, 1984; Quirk et al., 1984; Jaffé et al., 1988a, b; Sinninghe Damsté et al., 1989; Barakat and Yen, 1990; Jaffé and Gardinali, 1990; Sinninghe Damsté and de Leeuw, 1990; Jaffé and Gallardo, 1993; Schaeffer et al., 1993; Barakat and Rullkötter, 1994;

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Maowen Li et al., 1995; Yamamoto, 1992). The present study is focused on the polar fractions, in which carboxylic acids have been investigated in greater detail. These biomarkers are not routinely analysed in petroleum exploration studies, but they may contribute to the understanding of the evolution of sedimentary basins because their structures and distributions record much information that is lost in the hydrocarbon fractions (Jaffé et al., 1988a,b; Barakat and Yen, 1990; Jaffé and Gardinali, 1990; Koike et al., 1992; Jaffé and Gallardo, 1993; Lopes et al., 1997, 1999; Nascimento et al., 1999). Ten oils recovered from the Carmópolis field in the Sergipe-Alagoas Basin were studied. This basin is one of the most prolific Brazilian basins, producing around 65,000 bbl/day (Aquino and Lana, 1990).

1.1. Geological setting

The Sergipe-Alagoas basin is located on the Sergipana microplate and includes a complex series of tectonic compartments bounded by large faults that are associated with the rifting process and with the counterclockwise movement of the African continent in relation to the South American continent simultaneous to a smaller angle movement of the Sergipana microplate (Lana and Milani, 1986; Lana, 1990). Although two source rocks have been identified in the basin only oils from Carmopolis field, derived from source rocks belonging to Muribeca Formation (Aptian, 113–119 Ma, marine evaporitic shales and marls), were examined in the present study. The Muribeca formation is distributed along extensional faults with a main orientation of N 60° W, N 43° W, N 30° E and N-S. The most important fault system for oil migration seems to be the N 30° E trend. Regional structural highs were also formed during the rift phase and the Muribeca-Carmópolis oil field is located on one of these highs (Mello et al., 1994). Detailed geochemical studies have revealed that the oil window is offshore to the southeast, where the source rock is buried deeper than 2500 m. The onshore oil fields are shallower than the oil window, whereas the source rock is within the oil window offshore. Petroleum migrates for 40 km (approximately 20 km underwater) or more along unconformities and major faults from the pod of the active source rock kitchen to the oil fields (Mello et al., 1994). The oil accumulated in the fractured Pre-Cambrian (700–600 Ma) basement, in Jurassic (144–206 Ma) pre-rift fluvial sandstones and also in sandstone and coquina reservoirs of the rift sequence.

Trindade and Brassell (1992) studied the oil migration from the Sergipe-Alagoas basin and observed no significant modification in the hydrocarbon biomarker compositions assignable to migration processes. The knowledge of the successful use of carboxylic acid biomarkers as indicators of oil migration (Jaffé et al., 1988a, b; Jaffé and Gallardo, 1993) made this previous investigation a challenging theme for the study of acidic biomarkers from Sergipe-Alagoas basin.

2. Experimental

The 10 oil samples from Muribeca-Carmopolis formation from the Sergipe-Alagoas basin studied, were sampled and supplied by Petrobrás. The origins, maturity and degree of biodegradation of oils from this basin have been described in detail by Trindade and Brassell (1992).

The source rock of this basin has a TOC content of up to 12 wt.% with an average of 3.5 wt.%. In the richest intervals, the hydrocarbon source potential exceeds 9 mg HC/g rock and HI averages 300 mg HC/g TOC, indicating that the organic matter is type II kerogen (Trindade and Brassell, 1992; Mello et al., 1994). The geochemical data show that the organic-rich rock located onshore is thermally immature ($Ro < 0.6\%$; Mello et al., 1994).

2.1. Isolation of the carboxylic acids

Typically, the carboxylic acids were isolated using the method of McCarthy and Duthie (1962) adapted by Ramijak et al. (1977) and Schmitter et al. (1978). Crude oil (20 g) was extracted in a glass continuous extractor, constructed following Ramijak et al. (1977) (column 6×50 cm), containing silica gel 60 Merck (200 g, activated at 400°C), treated with a mixture of isopropanol (400 ml) and KOH (25 g) at 50°C for 1 h and then transferred to the column and sequentially washed with diethyl ether and dichloromethane. Hydrocarbons were extracted with dry dichloromethane (500 ml, 4 h reflux). The carboxylic acids were extracted with diethyl ether:-formic acid (8:2, 1000 ml, 8 h reflux).

2.2. Derivatisation

Crude carboxylic acid-containing fractions were esterified with diazomethane, reduced with $LiAlH_4$, mesylated with mesyl chloride and divided into two fractions which were reduced with either $LiAlH_4$ or $LiAlD_4$ leading to the corresponding hydrocarbons or to deuterium-labelled hydrocarbons respectively (Koike et al., 1992). The functional group conversions were verified by infrared spectroscopy. The details of this procedure have been described previously by Behar and Albrecht (1984) and Koike et al. (1992).

The methyl esters, hydrocarbons and deuterium labelled hydrocarbons (Table 2), were purified by column chromatography and analysed by gas chromatography/mass spectrometry (GC/MS).

GC/MS analyses were performed on a Hewlett-Packard (HP) 5890 MSD system equipped with a J & W

Scientific DB-5 fused capillary silica column (30 m×0.25 mm×0.25 μm), using helium as carrier gas (ca. 1 ml.min^{-1}). The oven temperature programs were 90°C (1 min hold) to 300°C (15 min hold) at 3°C/min^{-1} for hydrocarbons and 100°C (1 min hold) to 320°C (30 min hold) at 2.5°C/min^{-1} for methyl esters.

The instrument was operated in either full data collection or selective ion monitoring modes. Detection limits range from 10^{-8} g (splitless mode) to 10^{-7} g (split mode). Blanks were run throughout the procedure and no significant contamination was observed. For the calculation of relative ratios between different compounds, quantification was made from reconstructed ion chromatograms (RIC) using HP Chemstation software. Esters were characterised by their relative retention indices using the van den Dool and Kratz equation (van den Dool and Kratz, 1963) but using the methyl *n*-alkanoic acid series in place of the *n*-alkane series first proposed. Mass spectra were compared to those reported previously. The hydrocarbons from the neutral fractions and those obtained by derivatisation from the acidic fractions were identified by their relative retention indices (van den Dool and Kratz, 1963) and their mass spectra compared to those available in the literature. No enolisable ketones were detected. Coelution with authentic reference compounds was also used for the identification of some compounds (compounds 2H1, 2H2, 2H6, 2H7, 2H12 and 2H13, Fig. 2A, and compounds 2N1, 2N2, 2N8, and 2N9, Fig. 2B).

3. Results and discussion

3.1. Hydrocarbons

Although the neutral fraction of the oils studied herein had already been reported (Mello et al., 1993) we have collected our own data in order to establish a good comparison between the neutral and the carboxylic acid biomarkers (analysed as methyl esters, their corresponding hydrocarbons and deuterium-labelled hydrocarbon derivatives).

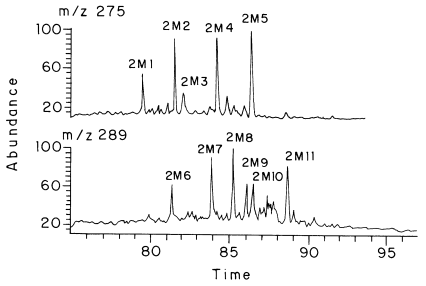

Fig. 1. Typical RICs of the methylated acidic fraction — *m/z* 275 and 289 corresponding to 3-steroid-methanoic and ethanoic acid methyl esters, respectively. Labelled peaks are identified in Table 4.

The hydrocarbon biological marker data of the neutral fractions recovered from the 10 oils of Muribeca-Carmópolis field selected for this study show that the oils are similar in terms of their biodegradation histories, maturity and thermal evolution. Table 3 shows the molecular parameters used to characterise the samples. The presence of C_{30} steranes, the fact that phytane is more is abundant than pristane; the odd over even *n*-alkane predominance; the presence of β-carotane and the high gammacerane index are all diagnostic of oils of marine evaporitic origin (Mello et al., 1993). The higher values of the ratio βα moretane/(αβ hopane + βα moretane) and lower values of the ratios αββ/(αββ + ααα) C_{29} steranes, 20*S*/(20*S* + 20*R*) ααα C_{29} steranes, Ts/(Ts + Tm) and TA/(TA + MA), show that these oils have low thermal maturities. The oils show similar degrees of biodegradation (they have been only slightly altered), and this is confirmed by the presence of large amounts of *n*-alkanes and few demethylated hopanes. A more detailed study of the oils from this basin is reported by Trindade and Brassell (1992).

Beyond the traditional biomarkers detected in this preliminary analysis we have focused our attention on isoprenoids, hopanes, and on the unusual 3-alkyl-steranes and 3-alkyl-monoaromatic steroids. These data are discussed in conjunction with their acidic equivalents in the following section.

3.2. Carboxylic acids

3.2.1. Acyclic carboxylic acids

The major acidic components found in the Muribeca-Carmópolis oils were acyclic acids. A wide range of *n*-alkanoic acids (C_{10}–C_{32}) was observed and in all the cases the most abundant were the *n*-hexadecanoic (C_{16}) and the *n*-octadecanoic (C_{18}) acids. A secondary maximum was observed among the higher molecular weight *n*-acids, mainly between acids with C_{23} and C_{29} carbon atoms.

A series of regular isoprenoid acids (C_{17}–C_{27}) (structure 1A, Appendix) was also detected and among them, phytanoic (C_{20}) and 3,7,11,15,19 pentamethylicosanoic acid (C_{25}) were the most abundant. The corresponding hydrocarbon of the latter acid has been detected in neutral fractions (Mello et al., 1988) and its application, together with squalane, as an indicator of hypersaline environments has been suggested by several authors (Chappe et al., 1979; Brassell et al., 1981; Mello et al., 1988). The origin of the C_{25} isoprenoid has been attributed to inputs of lipids of certain archaebacteria which might be expected to be more abundant in extreme environments like hypersaline waters (Chappe et al., 1979; Brassell et al., 1981). Recent work has shown that archaebacteria were predominant during the Mesozoic

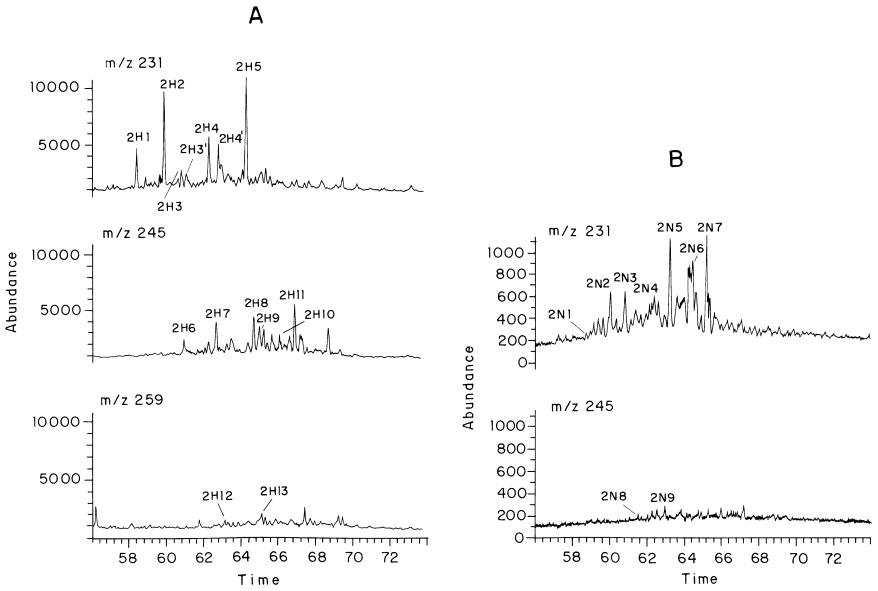

Fig. 2. A — Typical RICs of the hydrocarbon derivatives of the acidic fraction — *m*/*z* 231, 245 and 259 corresponding to methyl, ethyl and propyl-steranes respectively, derivatised from the acidic fractions. Labelled peaks are identified in Table 4. Compounds **2H**1, **2H**2, **2H**6, **2H**7, **2H**12 and **2H**13 (Table 4, Appendix) were identified by coinjection with authentic reference compounds. B — Typical RICs of hydrocarbon fraction — *m*/*z* 231, 245, corresponding to methyl and ethyl-steranes respectively. Labelled peaks are identified in Table 5. Compounds **2N**1, **2N**2, **2N**8 and **2N**9 (Table 5, Appendix) were identified by coinjection with authentic reference compounds.

(Wang, 1998) and their membrane lipids consist of 80–95% of ether-linked condensations of glycerol (or more complex polyols) with isoprenoid alcohols with 20, 25 or 40 carbon atoms (Sprott, 1992).

From our own experimental results the presence of both the C_{25} regular isoprenoid hydrocarbon and the acid strongly suggest that the common precursor is a C_{25} isoprenoid alcohol or ether from the archaebacteria core membrane lipids. Had the precursor of the hydrocarbon been a C_{25} isoprenoid acid, a carbon number shift to C_{24} would be expected upon conversion of the carboxylic acid to the hydrocarbon by decarboxylation.

An analogous rationale can be applied to the presence and relative high abundance of the phytane (Pris/Phy ratio <1; Table 1) and phytanoic acid (Fig. 5), in the neutral and acidic fractions respectively.

3.2.2. Steroid-alkanoic acids

Steroid-alkanoic acids (e.g. structure **2A**, Appendix), were observed in all the oils analysed. Reconstructed ion chromatograms (RIC) of *m*/*z* 275, 289 and 303 were used to detect the presence of the methyl derivatives of steroid-methanoic, steroid-ethanoic and steroid-propanoic acids, respectively. These series of compounds were also analysed by mass chromatography of the key ions at *m*/*z* 231, 245 and 259 and *m*/*z* 232, 246 and 260 for the hydrocarbons and deuterium labelled hydrocarbons, respectively. Fig. 1 shows the RIC for the ions *m*/*z* 275 and 289 of the steroid-methanoic and ethanoic acid methyl ester series, 2M, respectively, and Fig. 2A shows the RIC for the ions *m*/*z* 231, 245 and 259 for the hydrocarbon derivatives, **2H**. Comparison of the mass spectra of these compounds with those reported previously (Lopes et al., 1997, 1999) showed that the alkanoic group is at the 3β position. In order to have precise structural information concerning the position of alkanoic chain and the stereochemistry at position C-5, we have used synthetic 3α-methyl-5β(H),14α(H),17α(H), (20*R**)-cholestane *2H*1, 3β-methyl-5α(H),14α(H),17α(H), (20*R**)-cholestane **2H**2, 3α-ethyl-5β(H),14α(H),17α(20*R**)-cholestane **2H**6, 3β-ethyl-5α(H),14α(H),17α(H), (20*R**)-cholestane **2H**7, 3α-propyl-5β(H),14α(H),17α(H), (20*R**)-cholestane **2H**12 and 3β-propyl-5α(H),14α(H),17α(H), (20*R**)-cholestane **2H**13, as reference compounds (Lopes et al., 1997, 1999), for coinjection experiments using the ester fractions reduced to hydrocarbons (Fig. 2A, Table 4). It is worthwhile pointing out that compound **2M**3, in the ester fraction of all oils, (Fig. 1), corresponds to two compounds that are not separated as esters but which do have different retention times as hydrocarbons (Fig. 2A, compounds **2H**3 and **2H**3′). The same is true for compound **2M**4 which corresponds to a coelution of two compounds that appear as **2H**4 and **2H**4′ in the hydrocarbon fractions. Compounds **2H**3, **2H**3′, **2H**4 and **2H**4′ are isomers of the 3-methyl-24-methylcholestane and 3-methyl-24-ethylcholestane.

Isomerisation during derivatisation at position 3 was not considered important, because this isomerisation did not occur in the cholestane derivatives **2H**1, **2H**2.

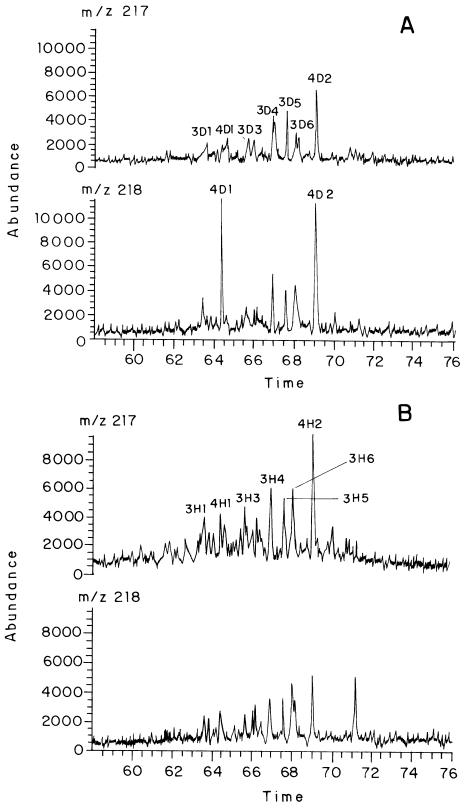

Fig. 3. A — Typical RIC of the deuterium labelled hydrocarbon derivatives of the acidic fraction — *m/z* 217 and 218 corresponding to the labelled sterane derivatives of the steroid acids. B — A typical RIC of the hydrocarbon derivatives of the acidic fraction — *m/z* 217 and 218 corresponding to the sterane derivatives of the steroid acids.

The analyses of this class of biomarker revealed that the 3-steroid-methanoic acid series was predominant in all oils under study. The origin of the steroid-alkanoic acids is not definitely known but origins from bacterial, microalgal or bacterially-induced transformations of steroids during diagenesis have been suggested (Dahl et al., 1992, 1995; Schaeffer et al., 1993; Lopes et al., 1997,1999). Steroid acids are usually more abundant in oil samples of marine and marine evaporitic origin (Dany et al., 1990; Dahl et al., 1992; Schaeffer et al., 1993; Lopes et al., 1997,1999).

Comparison of the molecular distributions of the steroid-alkanoic acids, derivatised to their corresponding hydrocarbons, and the alkyl-steranes from the neutral fractions (Fig. 2A and B) revealed that there is a carbon number shift between the series. While the acidic fraction showed the presence of three steroid-alkanoic series (steroid-methanoic, ethanoic and propanoic acids), in the hydrocarbon fraction only two series could be detected (methyl and ethyl-steranes). This carbon number shift suggests that the acids may at least partly have generated the alkyl-steranes *via* decarboxylation processes during diagenesis.

Steranes, with no lateral chain at C-3, have not been introduced in the comparison due to the fact that its origin could either arise from the decarboxylation of the 3-steroid-methanoic acid or from sterols.

3.2.3. Steroid acids

During the analyses of the RIC *m/z* 217 and *m/z* 218 of the deuterium labelled hydrocarbon derivatives of the acid fractions we detected the presence of sterane derivatives **4D** (C_{27} and C_{29}) in all oils, possessing~base peak on at *m/z* 218 in the mass spectra (Fig. 3). This could be assigned to the presence of a deuterium atom in rings A, B or C or the presence of 14β(H)-steranes which possess higher a relative abundance of the fragment *m/z* 218 over fragment *m/z* 217 (Tokes et al. 1968).

Table 1
Geological and geochemical data for the oils

Oil	Depth (m)	Lithology	Age	API	Origin	Maturity	Biodegradation level
A	729	Conglomerate	Aptian	22.6	Mar.[a]	e.g.[b]	l.b.[c]
B	789	Conglomerate	Aptian	21.5	Mar.	e.g.	l.b.
C	775	Conglomerate	Aptian	23.3	Mar.	e.g.	l.b.
D	783	Basement	Pre-Cambrian	24.4	Mar.	e.g.	l.b.
E	787	Sandstone	Neocomian	15.8	Mar.	e.g.	l.b.
F	780	Basement	Pre-Cambrian	25.9	Mar.	e.g.	l.b.
G	785	Basement	Pre-Cambrian	23.0	Mar.	e.g.	l.b.
H	756	Conglomerate	Aptian	15.1	Mar.	e.g.	l.b.
I	773	Conglomerate	Aptian	22.0	Mar.	e.g.	l.b.
J	774	Conglomerate	Aptian	23.3	Mar.	e.g.	l.b.

[a] Mar. = Marine hypersaline.
[b] e.g. = Early stage of oil generation.
[c] l.b. = Light level of biodegradation- level 1 according Peters and Moldowan scale (Peters and Moldowan, 1993).

Table 2
Experimental details of the derivatised oils

Oil	Crude oil (g)	Acids (mg)	Methyl esters (mg)	Alcohol (mg)	Mesyl (mg)	Hydrocarbons (mg)	Deuterium labelled hydrocarbons (mg)
A	14.4	424 (2.9%)	420	200	60	4.3	7.5
B	16.6	433 (2.6%)	430	210	90	13.0	16.0
C	22.8	481 (2.1%)	480	250	90	12.0	14.0
D	16.6	297 (1.8%)	300	130	60	4.9	4.6
E	16.7	500 (3.0%)	500	190	100	21.0	16.7
F	14.4	345 (2.4%)	350	130	80	8.0	23.0
G	18.9	370 (2.0%)	370	110	60	5.5	7.1
H	19.7	297 (1.5%)	300	85	50	4.7	4.8
I	18.6	433 (2.3%)	430	110	70	5.4	5.4
J	19.6	322 (1.6%)	320	130	70	9.0	9.0

Table 3
Hydrocarbon molecular parameters used to define the origins and maturities of the crude oils[a]

Molecular parameters	Oil									
	A	B	C	D	E	F	G	H	I	J
Origin										
Abundant *n*-alkanes	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}	C_{15}/C_{17} C_{23}/C_{25}
Pristane/phytane	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Gammacerane index	> 60	> 60	> 60	> 60	> 60	> 60	> 60	> 60	> 60	> 60
β-Carotane	+	+	+	+	+	+	+	+	+	+
Maturity										
αββ/(αββ + ααα) C_{29} steranes	36	31	32	42	36	31	40	34	33	35
20S/(20S + 20R) ααα C_{29} steranes	34	36	42	44	38	40	39	39	41	44
βα moretane/(αβ hopane + βα moretane)	12	15	17	11	18	16	10	15	14	15
Ts/(Ts + Tm)	27	36	46	46	40	38	38	43	41	47
TA/(TA + TM)	n.d.	39	39	n.d.	41	29	34	38	35	n.d.

[a] Gamma. Index = C_{30} gammacerane/ C_{30} αβ hopane; + present; Ts = 18α(H)-22, 29, 30 trisnorneohopane $C_{27}H_{46}$; Tm = 17α(H)-22, 29, 30 trisnorhopane, $C_{27}H_{46}$; αααC_{29} sterane refers to 5α(H), 14α(H), 17α(H)C_{29} sterane mainly 24-ethyl cholestane (20R); αββC_{29} sterane refers to 5α(H), 14β(H), 17β(H)C_{29} sterane; TA = Σ C_{28} triaromatic steroids (20, 24 epimeric compounds), MA = Σ C_{29} monoaromatic steroids; n.d. = not detected.

The latter hypothesis was easily discounted by comparing the RIC of the deuterium labelled (Fig. 3A) and that of the hydrocarbon derivatives (Fig. 3B) obtained from the same acidic fractions. Thus a carboxylic group might have been present at position 18 or 19 or alternatively an enolisable ketone function in any position (preferably at position 3). To confirm the above hypothesis an authentic standard of 5α(H)-cholestan-3-one was submitted to the KOH/silica extraction, but 99.9% of the sample was recovered in the neutral fraction.

Scrutinising the mass spectrum of the hydrocarbon and deuterium labelled hydrocarbon derivatives, we observed that fragment **B** *m/z* 149 (Appendix) did not incorporate deuterium. Therefore we suggest the presence of a C-19-carboxy-steranoic acid in all oils. A synthetic reference compound to confirm the suggested structure was not available.

A minor sterane series was detected in the RIC m/z 217 (Figure 3A and 3B) in the hydrocarbon and deuterium labelled hydrocarbon derivatives of the acidic fractions of all oils showing a deuterium atom incorporation in the side chain (molecular ion, M + 1) and fragment *m/z* 217. These compounds were classified as steroid acids **3A** (Appendix) possessing the carboxylic group in the side chain. Overlapping of signals with

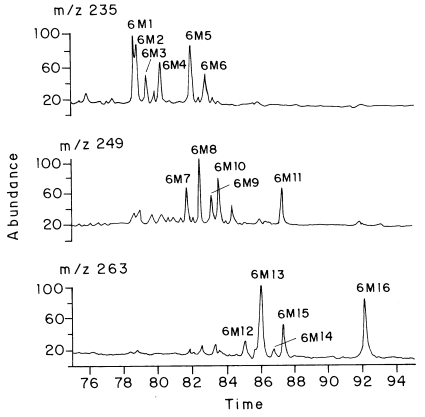

Fig. 4. Typical RICs of C_{30} (m/z 235), C_{31} (m/z 249) and C_{32} (m/z 263) hopanoic acids homologues (as methyl esters). Labelled peaks are identified in Table 4.

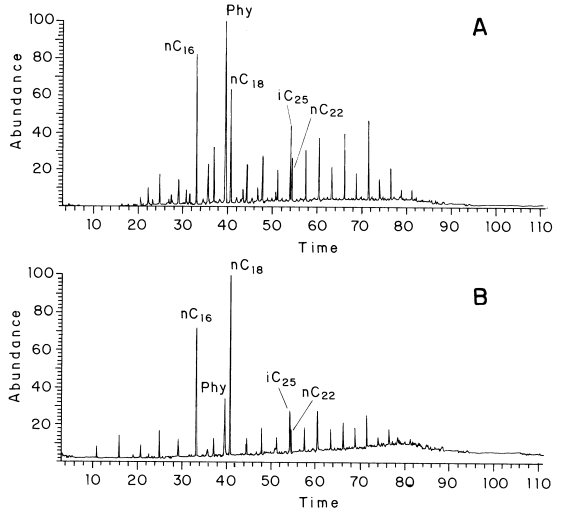

Fig. 5. A — Typical total current chromatogram of the carboxylic acid methyl esters fractions of oils A, B, C, E, G, H, I and J. B — Typical total ion chromatogram of the carboxylic acid methyl ester fractions of oils D and F. nC$_{16}$, nC$_{18}$, nC$_{22}$ = n-alkanoic acid methyl ester derivatives of acids with 16, 18 and 22 carbon atoms, respectively. Phy = phytanic acid, methyl ester. Is.C$_{25}$ = 3,7,11,15,19-pentamethylicosanoic acid, methyl ester.

those of the previous series **4A** prevented the detection of other members of this series. The methyl ester derivatives were also investigated but the findings were not conclusive due to the small amount of compounds.

3.2.4. Monoaromatic steroid-alkanoic acids

The RICs m/z 311, 325 and 339 of the methyl ester derivatives of the carboxylic acids revealed the presence of a series identified as ring-C aromatic steroids with a methanoic, ethanoic and propanoic acid group, respectively attached to ring A. Compounds **5A** were better observed as their hydrocarbon, **5H**, and deuterium labelled hydrocarbon, **5D**, derivatives. Location of the alkanoic acid group at position 3 of the steroidal moiety was the natural choice based on the previous identification of the corresponding non-aromatic derivative **2A** in these oils. The lack of authentic reference compounds prevented a better identification of this series. It should be mentioned that the methanoic acid series was predominant. Monoaromatic steroid-alkanoic acids have been detected in sediments by Schaeffer et al. (1993) and this is the first report of their (albeit tentative) identification in oils.

The corresponding monoaromatic alkyl-steroids, **5N**, were also detected in the neutral fractions of all the oils under investigation and a carbon atom shift detected when comparing the series of the carboxylic acids biomarker and the series of the corresponding hydrocarbons. Three monoaromatic steroid-alkanoic series were detected in the acidic fraction (monoaromatic steroid-methanoic, ethanoic and propanoic acid) but only two monoaromatic alkyl-steroid series (monoaromatic methyl and ethyl-steroids) were found in the neutral fractions, suggesting a decarboxylation process as previously observed for the 3-alkyl-sterane.

3.2.5. Hopanoic acids

Hopanoic acids are widely distributed among oils and sediments and in our analyses they were the most abundant cyclic acidic biomarkers. Three diastereomeric series was identified possessing the 17α(H),21β(H) and 17β(H),21β(H) (hopane skeleton) and 17β(H),21α(H) (moretane skeleton) relative stereochemistries (easily differentiated by their ions at m/z 191/235 + n14 of the methyl esters derivatives **6M**) (Barakat and Yen, 1990). These homologous series range from C_{30} to C_{32}. From a comparison of the RIC m/z 263 (of the methyl ester derivatives of the oils) with those reported by Jaffé and Gallardo (1993) it was evident that 22S* and 22R* C_{30} ββ isomer [17β(H), 21β(H)] was present (Fig. 4).

Comparison of the molecular distribution of hopanoids in the acidic and neutral fraction revealed that C_{30} hopanoid is the most abundant in both cases and there is no carbon number shift by one carbon when comparing the molecular distribution of both acidic and neutral neutral biomarkers.

3.3. Distributions of carboxylic acids

The 10 oils investigated presented two different chromatographic profiles for the linear carboxylic acids (Fig. 5) and hopanoic acids (Fig. 6). The main differences observed were:

(a) In all cases the n-C$_{16}$ and n-C$_{18}$ acids were the most abundant. In the oils D and F, we detected

a preference for short-chain acids (C_{10}–C_{32} with a maximum at C_{24}) and in the remaining oils the *n*-acids ranged from C_{12} to C_{32} with a maximum at C_{28}. The ratios *n*-C_{28}/*n*-C_{18} carboxylic acids were lower in D and F than in the remaining oils (Table 6).

(b) Acyclic isoprenoid acids **1A** in the oils A, B, C, E, G, H, I and J were present in relative higher abundance than in the oils D and F. Of these, phytanic acid and a C_{25} regular isoprenoid acid were the most abundant. The phytanic acid/*n*-C_{18} and pristanic acid/*n*-C_{17} fatty acid ratios were lower for oils D and F (Table 6).

(c) The CPI values of the long and the short chain acids were calculated (Table 6). The values did not show much variation among the 10 oils.

(d) Oils D, E, F and G had low relative abundances of β,β hopanoic acid in relation to the remaining oils (Fig. 6) depicting a low C_{32} β,β/(αβ + βα)-hopanoic acid ratio (Table 6).

It is generally accepted (Jaffé and Gallardo, 1993) that the molecular distribution of the acids reflects: the incorporation of carboxylic acids from the rock sequence through which the oils have migrated, from the reservoir and from autochthonous carboxylic acids.

Table 4
Structural assignment of acidic biomarkers present in the oils:Steroid alkanoic acids detected as methyl esters (**2M**) and hydrocarbon derivatives (**2H**). Steroid acids detected as deuterium labeled hydrocarbon derivatives (**3D**, **4D**). Hopanoic acids detected as methyl ester derivatives (**6M**)

#	Compound
2M1,**2H**1	[5β(H),14α(H),17α(H)-cholestan-3-yl] methanoic acid (20*R**)
2M2,**2H**2	[5α(H),14α(H),17α(H)-cholestan-3-yl] methanoic acid (20*R**)
2M3,**2H**3	[5β(H),14α(H),17α(H)-24-methylcholestan-3-yl] methanoic acid
2M3,**2H**3′	[5α(H),14α(H),17α(H)-24-methylcholestan-3-yl] methanoic acid
2M4,**2H**4	[5α(H),14α(H),17α(H)-24-methylcholestan-3-yl] methanoic acid
2M4,**2H**4′	[5α(H),14α(H),17α(H)-24-ethylcholestan-3-yl] methanoic acid
2M5,**2H**5	[5α(H),14α(H),17α(H)-24-ethylcholestan-3-yl] methanoic acid
2M6,**2H**6	2-[5β(H),14α(H),17α(H)-cholestan-3-yl] ethanoic acid (20*R**)
2M7,**2H**7	2-[5α(H),14α(H),17α(H)-cholestan-3-yl] ethanoic acid (20*R**)
2M8,**2H**8	2-[5α(H),14α(H),17α(H)-24-methylcholestan-3-yl] ethanoic acid
2M9,**2H**9	2-[5α(H),14α(H),17α(H)-24-methylcholestan-3-yl] ethanoic acid
2M10,**2H**10	2-[5α(H),14α(H),17α(H)-24-ethylcholestan-3-yl] ethanoic acid
2M11,**2H**11	2-[5α(H),14α(H),17α(H)-24-ethylcholestan-3-yl] ethanoic acid
2H12	3-[5β(H),14α(H),17α(H)-cholestan-3-yl] propanoic acid (20*R**)
2H13	3-[5α(H),14α(H),17α(H)-cholestan-3-yl] propanoic acid (20*R**)
3D1	[5α(H),14α(H),17α(H)-cholestanoic] acid
3D2	[5α(H),14α(H),17α(H)-24-methylcholestanoic] acid
3D3	[5α(H),14α(H),17α(H)-24-ethylcholestanoic] acid
3D4	[5α(H),14β(H),17α(H)-24-ethylcholestanoic] acid
3D5	[5α(H),14α(H),17α(H)-24-ethylcholestanoic] acid
4D1	[5α(H),14α(H),17α(H)-cholestan-19-oic] acid
4D2	[5α(H),14α(H),17α(H)-24-ethylcholestan-19-oic] acid
6M1	17α(H), 21β(H)-hopanoic acid 22*S**
6M2	17α(H), 21β(H) hopanoic acid 22*R**
6M3	17β(H), 21α(H) moretanoic acid 22*S**
6M4	17β(H), 21α(H) moretanoic acid 22*R**
6M5	17β(H), 21β(H) hopanoic acid 22*S**
6M6	17β(H), 21β(H) hopanoic acid 22*R**
6M7	17α(H), 21β(H)-30-homohopanoic acid 22*S**
6M8	17α(H), 21β(H)-30-homohopanoic acid 22*R**
6M9	17β(H), 21α(H)-30-homomoretanoic acid 22*S**
6M10	17β(H), 21α(H)-30-homomoretanoic acid 22*R**
6M11	17β(H), 21β(H)-30-homohopanoic acid 22*R**
6M12	17α(H), 21β(H)-30,31-bishomohopanoic acid 22*S**
6M13	17α(H), 21β(H)-30,31-bishomohopanoic acid 22*R**
6M14	17β(H), 21α(H)-30,31-bishomomoretanoic acid 22*S**
6M15	17β(H), 21α(H)-30,31-bishomomoretanoic acid 22*R**
6M16	17β(H), 21β(H)-30,31-bishomohopanoic acid 22*R**

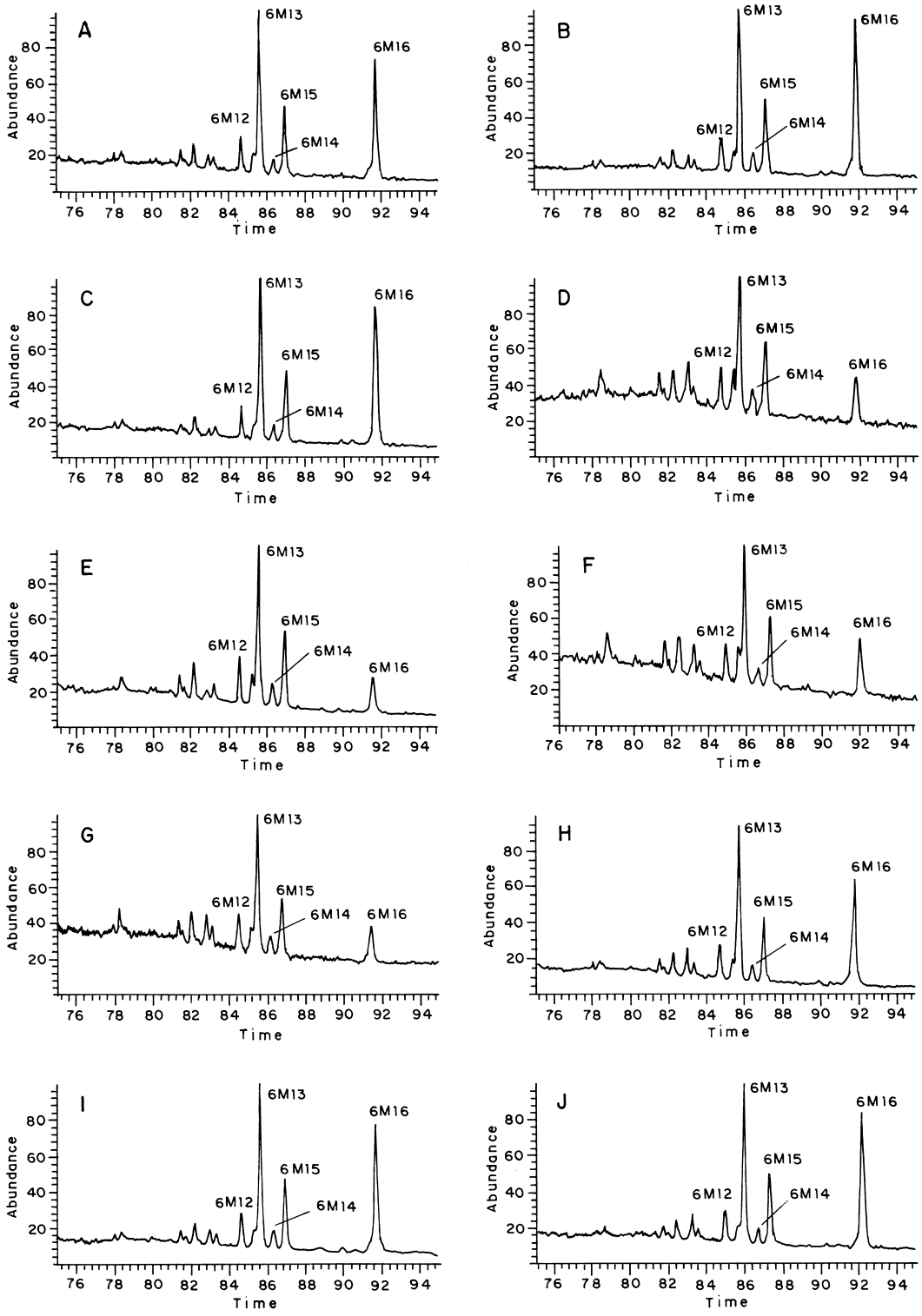

Fig. 6. RIC of C_{32} (m/z 263) hopanoic acid methyl esters of all oils from Carmopolis oil field, Sergipe Alagoas Basin, Brazil. The labelled peaks are identified in Table 4.

Table 5
Structural assignment of 3-alkyl steranes present in the oils

#	Compound
2N1	[5β(H),14α(H),17α(H)-3-methylcholestane (20*R**)
2N2	[5α(H),14α(H),17α(H)-3-methylcholestane (20*R**)
2N3	[5β(H),14α(H),17α(H)-3-methy-24-methylcholestane
2N4	[5α(H),14α(H),17α(H)-3-methyl-24-methylcholestane
2N5	[5α(H),14α(H),17α(H)-3-methyl-24-methylcholestane
2N6	[5α(H),14α(H),17α(H)-3-methyl-24-ethylcholestane
2N7	[5α(H),14α(H),17α(H)-3-methyl-24-ethylcholestane
2N8	[5β(H),14α(H),17α(H)-3-ethylcholestane (20*R**)
2N9	[5α(H),14α(H),17α(H)-3-ethylcholestane (20*R**)

Table 6
Molecular parameters of carboxylic acid biomarkers[a]

Molecular parameters	Oils									
	A	B	C	D	E	F	G	H	I	J
SCA-CPI	1.7	nd	1.7	1.7	1.5	2.1	2.1	1.5	1.5	1.8
LCA-CPI	2.7	2.0	1.5	1.7	2.4	1.5	1.7	1.9	1.7	1.7
Pristane/nC_{17}	2.4	3.1	2.2	0.5	1.0	0.5	2.7	1.6	2.7	2.1
Phytane/nC_{18}	6.2	6.1	4.8	0.7	3.6	0.5	3.9	4.5	7.4	3.1
nC_{28}/nC_{18}	1.4	2.6	1.9	0.5	1.4	0.5	1.4	1.4	2.6	2.4
ββ/(αβ + βα) C_{32} hopane	0.5	0.7	0.7	0.1	0.2	0.2	0.1	0.5	0.6	0.7
*S**/*R** C_{31} αβ hopane	0.5	0.5	0.5	0.7	0.7	0.7	0.6	0.5	0.5	0.5

[a] ββ/(αβ + βα) hopane refers to 17α(H),21β(H) and 17β(H), 21β(H) C_{32} hopane (hopane skeleton) and 17β(H),21α(H) C_{32} hopane (moretane skeleton); S*/R* C_{31} αβhopane refers to 17α (H),21β(H) C_{31} hopane isomers at position C-22 (R* and S*); CPI-LCA = $nC_{24} + nC_{26} + nC_{28}/nC_{25} + nC_{27} + nC_{29}$ and CPI-SCA = $2 \times nC_{14}/nC_{13} + nC_{15}$; CPI = carbon index preference, SCA = short chain acids, LCA = long chain acids, n.d. = not determined.

Though caution is recommended when drawing conclusions based on acidic biomarkers, fractionation processes can be more evident through such parameters than those of the apolar components. However, the concentration of free acids in crude oils is very low, therefore their molecular distribution is more easily altered *via* incorporation of immature organic matter or fractionation along the migration pathway, than the aliphatic fraction, which is much more abundant in oils.

As previously mentioned there is a stronger predominance of longer linear chain and isoprenoid acids in the oils A, B, C, E, G, H, I and J than in the oils D and F. These differences could be assigned to a fractionation along the migration pathway from the source rock and Atalia fault to Carmopolis oil field. Thus, an increase in the relative abundance of the less polar acids (isoprenoid and long chain acids) could be taken as evidence of a longer migration pathway. Alternatively the relative abundance of isoprenoid acids can be assigned to the dichotomy in the source rock organic matter and oil generation produced over a wide stratigraphic interval of the source rock which is not totally homogeneous.

It is noteworthy that the thermal maturity molecular parameter of the neutral biomarkers (Table 3) in all the oils studied are similar while the molecular distributions for the hopanoic acids isomers present in the oils were strikingly different (Fig. 6, Table 6). All the hopanoic acid isomers are present in different relative abundances. The C_{30} components were the most abundant. Among the 17β(H),21β(H) isomers only the C_{30} are present as a pair of diastereoisomers 22*R** and 22*S**. Similar data were also obtained by Jaffé et al. (1988a) and the fact was assigned to the faster rate of epimerization for the C_{30} homologue at position 22 than for C_{31} and C_{32} homologues.

In the oils D, E, F and G the relative abundance of 17β(H), 21β(H) isomers is much lower than in oils A, B, C, H, I and J indicating that these oils have different thermal evolution. These differences were interpreted by invoking incorporation of immature organic matter in the reservoirs and/or during the migration pathway (Jaffé and Gallardo, 1993). Therefore, oils D, F, G located in basements and oil E located in sandstone (little or no organic matter content, Trindade, 1992) (Table 1) have lower relative abundances of ββ hopanoic acid, indicating little or no incorporation of immature organic matter.

4. Conclusions

By comparison of both acidic and hydrocarbon biomarkers we have observed that decarboxylation is an important process during the formation of alkyl-steranes and monoaromatic alkyl-steroids, but not for the hopanes and acyclic isoprenoids. Thus, the functionality of the diagenetic precursors was inferred as carboxylic acids for the alkyl-steranes and monoaromatic alkyl-steroids and alcohols or ethers for the hopanes and isoprenoids. A similar situation was observed during the analyses of marine evaporitic oils from Fazenda Belém, Potiguar Basin (Lopes et al., 1997, 1999) when the 3-alkanoic-steroid derivatives (the alkanoic chain varying from 1 to 6 carbon atoms) were identified while alkyl-steranes present in the neutral fractions had side chains composed of 1–5 carbon atoms, once again suggesting a decarboxylation process and a carboxylic acid precursor.

Therefore alkyl steranes and monoaromatic alkyl-steroids, derived from different biological sources, as yet not elucidated (Dany et al, 1990, Dahl et al, 1992, 1995, Schaeffer et al., 1993; Lopes et al., 1997, 1999), ought to have a carboxylic functionality in their diagenetic precursor. This hypothesis could be reinforced with more comparative studies between acidic and neutral biomarkers.

The differences observed in the distribution pattern of hopanoic acids show that although the migration paths (conglomerates or faults) were poor in organic matter, the analysis of the carboxylic acids present in the oils revealed incorporation of immature organic matter (OM) during the migration pathway and/or in the reservoirs Thus, oils A, B, C, H, I and J with higher ββ/(αβ + βα) and lower S^*/R^* hopanoic acid ratios, have undergone more incorporation of immature OM than oils D, E, F and G and [lower ββ/(αβ + βα) and higher S^*/R^* hopanoic acid ratios].

The abundance of isoprenoid acids, with a predominance of C_{25} and C_{20} isoprenoid acids and their correlation to their neutral counterparts without a carbon shift, indicate a major contribution of common precursors. Based on the chemical composition of archaebacterial membranes (Zhang and Poulter, 1993), the C_{25} isoprenoid acid and alkane could derive from membrane glyceryl ethers, bearing saturated isoprenoid side chains, having undergone different diagenetic pathways in the subsurface (oxidation or reduction processes). As archaebacteria are unique organisms that are able to inhabit hostile environments (Zhang and Poulter, 1993) characterised by high salt, low pH, high temperatures or complete lack of oxygen, biomarkers related to their membranes are important molecular parameters of the depositional environment. Finally our data suggest a possible utility for joint parameters arising from neutral and acidic biomarkers as a means of revealing diagenetic precursor functionalities.

The carboxylic acids present in Muribeca-Carmópolis oils allowed conclusions about the origin of the organic matter input which could not have been reached through the neutral fractions and reinforces the idea that the acidic biomarkers retain some details about diagenetic processes and precursors that are not always available in the neutral fractions.

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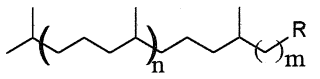
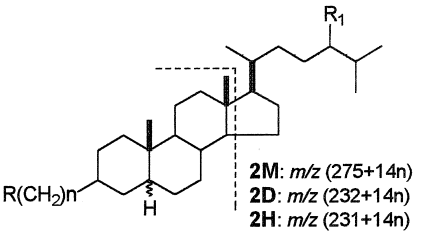
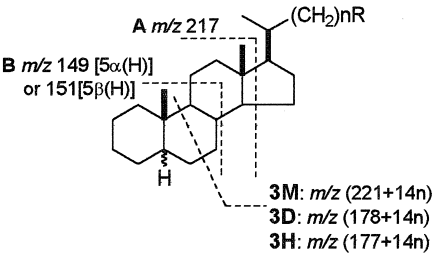
Appendix



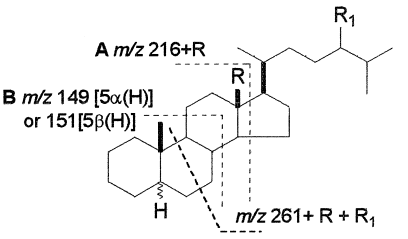
1A: R=COOH
1M: R=COOMe (methyl esters from carboxylic acid)
1D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
1H: R=CH_3 (hydrocarbon from carboxylic acid)
1N: R=CH_3 (hydrocarbon from neutral fraction)
n = 1-3
m = 0-4



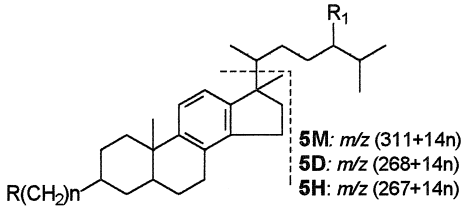
2A: R=COOH
2M: R=COOMe (methyl esters from carboxylic acid)
2D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
2H: R=CH_3 (hydrocarbon from carboxylic acid)
2N: R=CH_3 (hydrocarbon from neutral fraction)
R_1 = H, Me, Et
n = 0, 1, 2



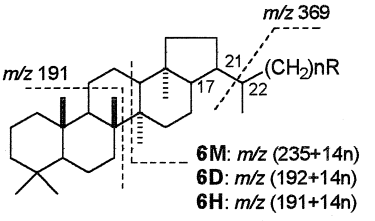
3A: R=COOH
3M: R=COOMe (methyl esters from carboxylic acid)
3D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
3H: R=CH_3 (hydrocarbon from carboxylic acid)
3N: R=CH_3 (hydrocarbon from neutral fraction)
n = 5,6,7



4A: R=COOH
4M: R=COOMe (methyl esters from carboxylic acid)
4D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
4H: R=CH_3 (hydrocarbon from carboxylic acid)
4N: R=CH_3 (hydrocarbon from neutral fraction)
R_1 = H, Et



5A: R=COOH
5M: R=COOMe (methyl esters from carboxylic acid)
5D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
5H: R=CH_3 (hydrocarbon from carboxylic acid)
5N: R=CH_3 (hydrocarbon from neutral fraction)
R_1 = H, Me, Et
n = 0, 1, 2



6A: R=COOH
6M: R=COOMe (methyl esters from carboxylic acid)
6D: R=CH_2D (deuterium labelled hydrocarbon from carboxylic acid)
6H: R=CH_3 (hydrocarbon from carboxylic acid)
6N: R=CH_3 (hydrocarbon from neutral fraction)
n = 0,1,2

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