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Evidence for euphotic zone anoxia during the deposition of Aptian source rocks based on aryl isoprenoids in petroleum, Sergipe–Alagoas Basin, northeastern Brazil

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ABSTRACT

Four crude oil samples from the Sergipe–Alagoas Basin, northeastern Brazil, were analyzed using full scan gas chromatography–quadrupole mass spectrometry (GC–qMS) for biomarkers, in order to correlate them using aromatic carotenoids thereby enhancing knowledge about the depositional environment of their source rocks. The geochemical parameters derived from saturated fractions of the oils show evidence of little or no biodegradation and similar thermal maturation ($Ts/(Ts + Tm)$ for terpanes, C_{29} $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$, C_{27}, and C_{29} 20S/(20S + 20R) for steranes). Low pristane/phytane ratios and the abundance of gammacerane and β-carotane are indicative of an anoxic and saline depositional environment for the source rocks. Moreover, we identified a large range of diagenetic and catagenetic products of the aromatic carotenoid isorenieratene, including C_{40}, C_{33}, and C_{32} diaryl isoprenoids and aryl isoprenoid derivatives with short side chains and/or additional rings. These results indicate anoxia in the photic zone during the deposition of the source rocks.

1. Introduction

Several biomarkers in crude oil can be used to reconstruct conditions in the depositional environment of source rocks, including the aromatic carotenoids. Such compounds have been used as proxies for anoxic conditions in the photic zone during source rock deposition (Koopmans et al., 1996; Schaeffer et al., 1997; Clifford et al., 1998). Aromatic carotenoids and their diagenetic derivatives are commonly interpreted as biomarkers produced by green sulfur bacteria (GSB) (*Chlorobiaceae*) and purple sulfur bacteria (PSB) (*Chromatiaceae*) (Schaeffer et al., 1997; Clifford et al., 1998; Brocks and Schaeffer, 2008). The biomarker derivatives of the compounds biosynthesized by these microorganisms suggest that these bacteria were important primary producers during deposition of organic rich sediments.

The Sergipe–Alagoas Basin is located in northeast Brazil and part of it extends onto the continental margin (Fig. 1). Today, the areas onshore and offshore in the Sergipe–Alagoas Basin are mature oil provinces. The current reserves represent 40 million m^3 of oil and 11.5 billion m^3 of gas. This basin has preserved the most complete sedimentary record among the Brazilian marginal basins, resulting in many geological and geochemical surveys. Previous geochemical studies focused on neutral (Trindade and Brassell, 1992; Mello et al., 1993; Machado, 1995; Alves, 1997) or acidic biomarkers (Rodrigues et al., 2000, 2005; Cruz, 2005) rather than the aromatic fraction of oils and their potential as paleoenvironmental indicators.

The first report of isorenieratane and its diagenetic derivatives in rock samples from the Araripe Basin, Brazil (Heimhofer et al., 2008) led us to carry out the analysis of its oils using classical biomarkers and aromatic carotenoids, and to use them as indicators of depositional conditions of their source rocks. In the present study our focus was the full scan gas chromatography–quadrupole mass spectrometry (GC–qMS) analysis of aromatic fractions in order to determine the presence and distribution of aromatic carotenoids and their diagenetic derivatives (Hartgers et al., 1994; Brocks and Schaeffer, 2008).

2. Geological setting

The Sergipe–Alagoas Basin (Fig. 1) is located in northeast Brazil covering an area of about 44,000 km^2. This basin evolved as part of

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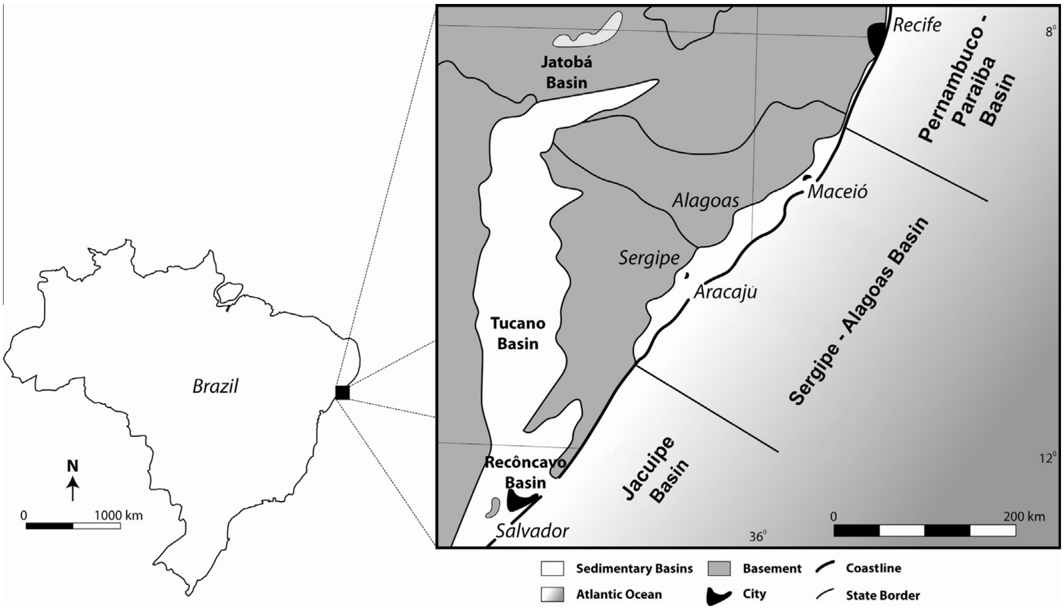


Fig. 1. Location of the Sergipe–Alagoas Basin.

the classic divergent, rifted continental margin that originated during opening of the South Atlantic (Lana, 1990).

The sedimentary record of the Sergipe–Alagoas Basin can be divided into three main stages (pre-rift, rift and post-rift), including transitional and oceanic phases (Fig. 2), according to Ponte and Asmus (1978) and Ojeda and Ojeda (1982). The pre-rift stage, Upper Paleozoic to Jurassic, is represented by Permo-Carboniferous fluvial, glacial and shallow marine sediments. These sediments are separated by an unconformity from overlying fine to coarse clastics deposited under fluvial, eolian and shallow lacustrine conditions (Lana, 1990). During Neocomian to Early Aptian rift stage, clastics comprised of lacustrine, organic rich, mostly freshwater shales (one of the main source rocks) were deposited. The lacustrine shales are interbedded with deltaic progradational sediments and bordered by alluvial plain and fan delta deposits. Fluvial progradation culminates this sedimentary sequence (Lana, 1990). The post-rift stage is represented by two major phases. The Aptian–Albian transitional phase has a wide variety of sediments including carbonates, evaporites, shales and marls that have organic rich intervals with excellent hydrocarbon source potential. These sediments were deposited within a confined water body with stratification, anoxia and salinity enhancement due to the warm and dry climate. Episodic marine incursions flooded the proto-oceanic gulf (Koutsoukos et al., 1991a, 1991b). The oceanic phase (drift) was established in Albian time. The oceanic phase coincides with seafloor spreading together with continuous subsidence culminating with the establishment of oceanic conditions. Initially shelf carbonates and transgressive shales were deposited from the Albian to the Upper Cretaceous, and were followed by the deposition of progradational coarse siliciclastic sediments, shallow shelf carbonates and shallow to deep marine fine clastics and turbidites from Late Cretaceous onwards (Lana, 1990).

2.1. Source rocks

Each tectono-stratigraphic sequence deposited during the evolution of the South Atlantic Margin contains petroleum source rocks (Katz and Mello, 2000). The rift phase source rocks are composed of Neocomian to Barremian (Lower Cretaceous) black shales deposited under lacustrine conditions with variable degrees of salinity. Organic rich shales, carbonates and marls deposited under marine evaporitic conditions during the Aptian (Cretaceous) represent the source rocks of the transitional phase. Aptian–Albian source rocks of the drift phase are represented by marls and calcareous black shales, while the Cenomanian–Turonian source rocks are black shales.

Most of the oil found in the basin is related to the lacustrine and marine evaporitic source rocks. In the Brazilian margin few significant oil accumulations are related to the marine source rocks. New prospects targeting appropriate conditions of overburden can change this scenario. More details about the geochemical characterization of oils in the South Atlantic Margin Basin can be found in Mello et al. (1988a, 1988b) and Katz and Mello (2000).

3. Experimental

3.1. Samples

This study includes four oil samples (SEAL 1, 2, 3 and 4) generated predominantly from the marine evaporitic intervals (post-rift Muribeca Formation) (Table 1). Previous studies of Sergipe–Alagoas Basin oils focused on the neutral fractions based mainly on the identification of aliphatic components. In this study, we focused in the aromatic fraction to investigate the presence of arylisoprenoids and their derivatives.

3.2. Preparative thin layer chromatography (PTLC)

The samples were prepared according to the modified methodology of Lopes et al. (1999). About 80 mg of oil were subjected to PTLC on silica gel impregnated with 5% $AgNO_3$ and then the silica was developed using 98:2 (v:v) *n*-hexane:ethyl acetate.

The plates were then selectively scraped and the silica was treated using dichloromethane:methanol 95:5 (v:v) for desorption of the constituents The fractions thus obtained (P1 – saturated and P2 – aromatic) were concentrated in a rotary evaporator and analyzed by GC–qMS.

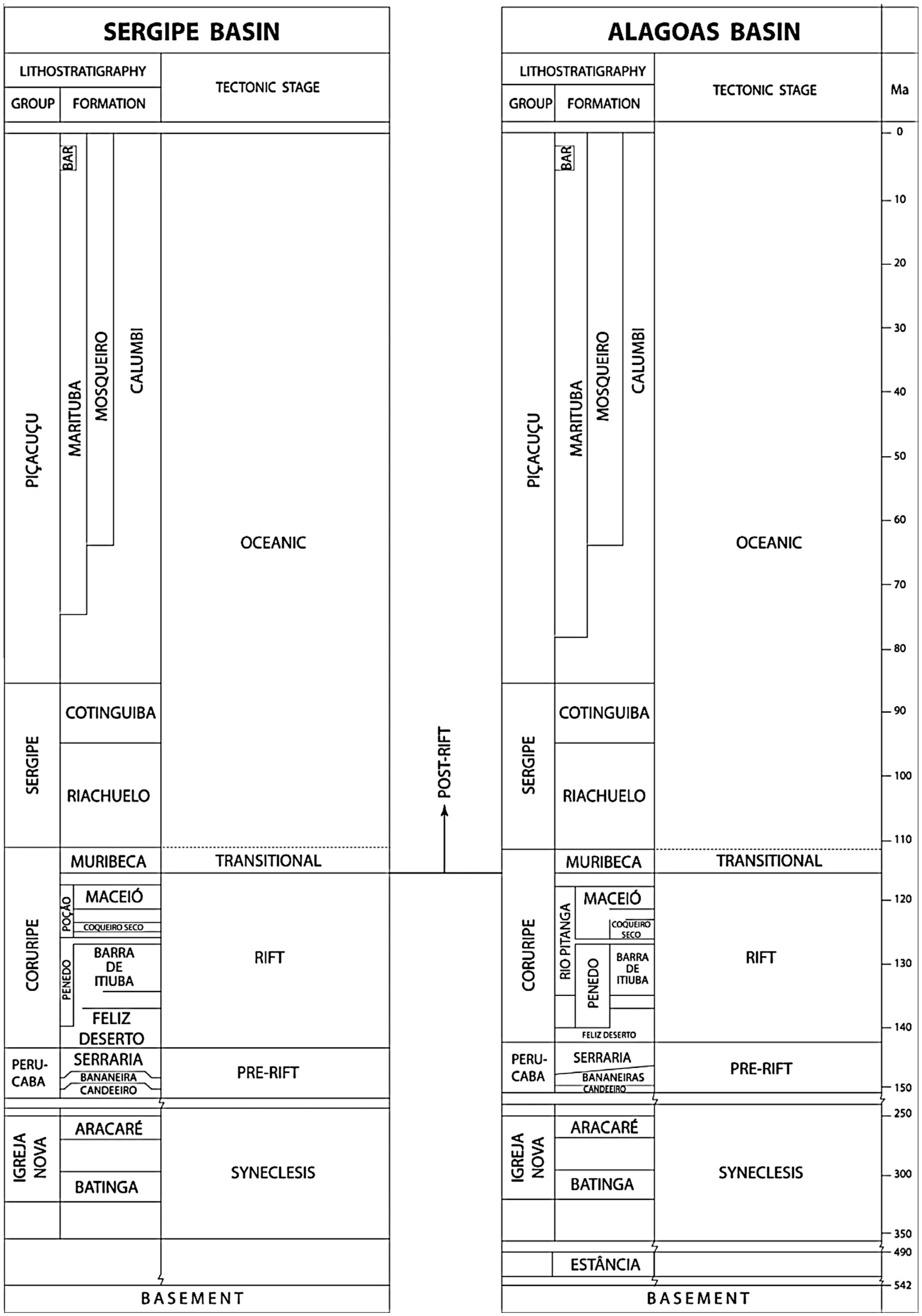


Fig. 2. Schematic stratigraphic chart of the Sergipe–Alagoas Basin.

Table 1
Samples used in this study from the Sergipe–Alagoas Basin.

Sample	Depth (m)	Reservoir (Formation)	Field
SEAL 1	1454	Maceió	Tabuleiro dos Martins
SEAL 2	1178	Muribeca	Angelin
SEAL 3	686	Muribeca	Mato Grosso
SEAL 4	840	Muribeca	Carmópolis

3.3. GC–qMS analysis

The GC–qMS analyses were performed using a Shimadzu GC-17A/MS-QP5050A instrument. Chromatographic separation was achieved using a 30 m × 0.25 mm ID capillary chromatographic column coated with a 0.1 μm film of 5% phenylmethylpolysiloxane (DB-5HT, J&W Scientific). The temperature program for the oven was as follows: an initial temperature of 70 °C (2 min hold), followed by a ramp of 6 °C/min up to a final temperature of 310 °C (10 min hold). The split/splitless (S/SL) injector was used in split mode at the ratio of 10:1 and was set at 300 °C. The carrier gas was helium (99.9999%) at a constant flow rate of 1.0 ml/min. The transfer line temperature was 310 °C. The quadrupole mass spectrometer was operated in full scan mode over the mass range 47–600 Da. The ion source was operated in electron impact (EI) mode at 70 eV. Total scan time for a chromatographic run was 52 min, including a 3 min solvent delay time. The identification of biomarkers was done by comparison of elution order, retention times and mass spectra with literature data (Alves, 1997; Lopes et al., 1999; Peters et al., 2005; Lima et al., 2010).

4. Results and discussion

Saturated hydrocarbons are the main types of biomarkers used in organic geochemistry to characterize sedimentary samples, oils and condensates (Peters et al., 2005) because they are extracted rapidly and analyzed by GC–qMS without need of derivatization. The saturated hydrocarbons are thermal degradation products of many biological precursors. These compounds are used in many geochemical parameters to describe source rock depositional environment, biodegradation, maturation, migration, and correlation. All these issues are thoroughly discussed by Peters et al. (2005).

4.1. General parameters of biomarkers

The total ion chromatogram (TIC, Fig. 3) of the saturated fractions from the four samples show abundant *n*-alkanes ranging from C_{12}–C_{36}. The presence of high molecular weight *n*-alkanes (> 22 carbon atoms) suggest a lacustrine contribution, while pristane/phytane < 1 indicates hypersaline (marine-evaporitic) source rocks (Mello et al., 1988a). Mixing of oil from two sources can explain this apparent contradiction. It is well known linear hydrocarbons undergo the fastest rates of biodegradation in reservoirs (Connan, 1984; Peters et al., 2005). The observed distribution of linear hydrocarbons indicates that the samples are not biodegraded and can be classified as level 0 on the PM biodegradation scale (Peters et al., 2005). However, the prominent UCM in the TIC profiles (Fig. 3) suggests, that reservoirs received more than one pulse of oil at different times. The older oil pulse was biodegraded but was then mixed with younger nondegraded oil.

Values of CPI (carbon preference index) and OEP (odd/even predominance) for the samples decrease with increasing thermal maturity, approaching 1 (Peters et al., 2005). CPI and OEP values obtained for the samples SEAL 1 to 4 (Table 2) suggest that the oils have slightly different degrees of thermal maturity. However the thermal maturity for these samples should be proved using thermally dependent biomarker parameters.

The $Ts/(Ts + Tm)$, C_{29} 20S/(20S + 20R) sterane and C_{29} $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ sterane ratios (Table 2) suggest that these oils have similar and relatively low thermal maturities, equivalent to the early/middle oil window. The pristane/phytane (Pr/Ph) ratio can be used as an indicator of redox conditions during deposition of the source rock. Values < 1 may indicate reducing environments (sub-oxic or anoxic), while values > 1 indicate oxic conditions (Peters et al., 2005). The range of Pr/Ph between 0.91 and 1.04 (Table 2) is relatively narrow and probably reflects mixing sources with the predominance a saline end member.

Additional proxies for salinity in source rock depositional environments are the concentrations of β-carotane (**1**) and gammacerane (**2**), Fig. 4 (Mello and Maxwell, 1990). In the Sergipe–Alagoas

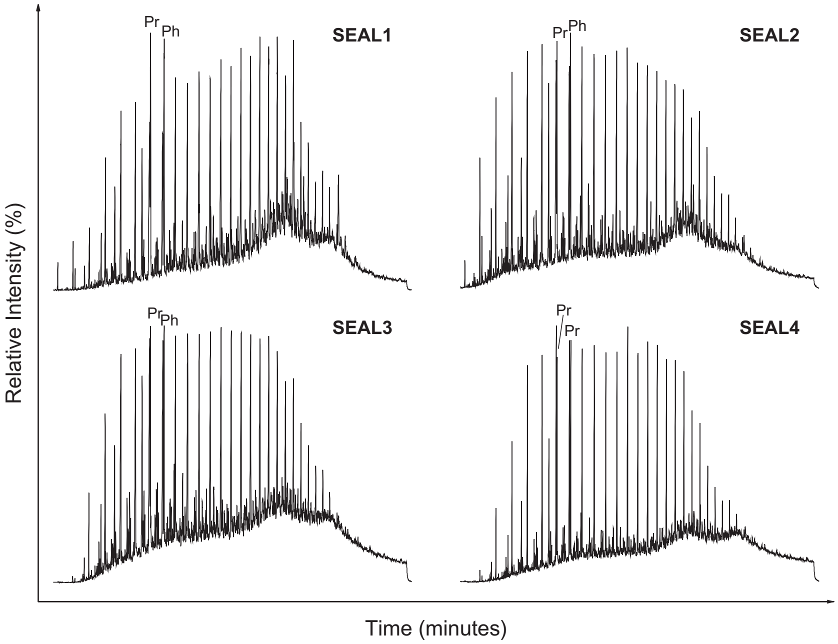


Fig. 3. TIC of the saturate fractions of the four samples.

Table 2
Calculated parameters (based on the peak heights from the chromatogram) for the four samples.

Parameters	Samples			
	SEAL1	SEAL2	SEAL3	SEAL4
CPI[a]	1.17	1.07	1.03	1.06
OEP[b]	1.06	1.04	1.03	1.11
Pr/Ph[c]	1.04	0.93	1.00	0.91
Pr/n-C_{17}[d]	1.59	1.08	1.05	0.85
Ph/n-C_{18}[e]	1.73	1.17	1.07	1.00
Gammacerane index[f]	89.4	63.37	44.53	44.15
β-Carotane index[g]	34.7	19.7	14.7	15.5
Ts/Tm[h]	0.76	0.55	0.72	0.70
C_{27}/C_{29} sterane[i]	1.32	0.81	0.80	1.04
Hopane/Sterane[j]	3.24	1.42	1.97	2.18
C_{34}/C_{35} Hopane[k]	1.88	1.20	1.46	1.68
Bisnorhopane index[l]	10.52	6.39	4.49	3.78
C_{27} 20S/(20S + 20R)[m]	0.25	0.32	0.39	0.31
C_{29} 20S/(20S + 20R)[n]	0.27	0.30	0.36	0.32
C_{29} $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$[o]	0.31	0.24	0.27	0.23
Diasterane index[p]	13.92	22.85	31.26	28.53
Tricyclics index[q]	38.05	61.82	86.77	80.80

[a] CPI: $1/2 \times [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]$ n-alkanes in TIC.

[b] OEP(1): $(C_{21} + 6C_{23} + C_{25})/(4C_{22} + 4C_{24})$ n-alkanes in TIC.

[c] Pristane/Phytane in TIC.

[d] Pristane/n-C_{17} alkane in TIC.

[e] Phytane/n-C_{18} alkane in TIC.

[f] Gammacerane index: 100 × [Gammacerane/C_{30} 17α(H),21β(H)-hopane)] in m/z 191 chromatogram; low < 50, medium 50–60 and high > 60.

[g] β-Carotane index: 100 × [(β-carotane in m/z 125 chromatogram)/(C_{30} 17α(H),21β(H)-hopane in m/z 191 chromatogram)].

[h] C_{27} 18α(H)-22,29,30-trisnorneohopane/C_{27} 17α(H)-22,29,30-trisnorhopane in m/z 191 chromatogram.

[i] C_{27} 20R 5α,14α,17α(H)-cholestane/20R 5α,14α,17α(H)-ethylcholestane] in m/z 217 chromatogram.

[j] (C_{30} 17α,21β-hopane in m/z 191 chromatogram)/(C_{27} 20R and 20S 5α,14α,17α(H)-cholestane in m/z 217 chromatogram); low < 4, medium 4–7, high > 7.

[k] (C_{34} 22R + 22S 17α,21β-hopane)/(C_{35} 22R + 22S 17α,21β-hopane) in m/z 191 chromatogram; low < 1, high > 1.

[l] 100 × (28,30-bisnorhopane)/(C_{30} 17α,21β-hopane) in m/z 191 chromatogram; low < 10, medium 10–50, high > 50.

[m] C_{27} 20S/(20S + 20R): C_{27} 5α,14α,17α(H) 20S/C_{27} 5α,14α,17α(H) 20(S + R) in m/z 217 chromatogram.

[n] C_{29} 20S/(20S + 20R) sterane: C_{29} 5α,14α,17α(H) 20S/C_{29} 5α,14α,17α(H) 20(S + R) in m/z 217 chromatogram.

[o] C_{29} αββ/(αββ + ααα) sterane: C_{29} 5α,14β,17β(H) 20(R + S)/[C_{29} 5α,14β,17β(H) 20(R + S) + C_{29} 5β,14β,17β(H) 20 (R + S)] in m/z 217 chromatogram.

[p] Diasterane index: 100 × [Sum of the peaks C_{27} 20R 13β,17α-diasterane in m/z 217 chromatogram]/[Sum of the peaks C_{27} 20R and 20S 5α,14α,17α-cholestane]; low < 30, medium 30–100, high > 100.

[q] Tricyclic index: C_{24} tricyclic/C_{30} 17α,21β(H)-hopane in m/z 191 chromatogram.

Basin, (Mello et al., 1995) reported a very complex depositional sequence and identified five different facies, including lacustrine fresh water, lacustrine saline water, marine hypersaline, marine carbonate and open marine anoxic. The occurrence of various active petroleum systems in the basin suggests the possibility of oil mixing, especially in shallower reservoirs. The relative abundance or concentration of the isoprenoids i-C_{25} (**3**) and i-C_{30} (**4**) (Fig. 4) is also used to differentiate degrees of salinity; higher concentrations of these compounds are indicative of more saline environments (Mello and Maxwell, 1990). The presence of β-carotane (**1**), gammacerane (**2**), i-C_{25} (**3**) and i-C_{30} (**4**) support the assumption of a saline to hypersaline environment for the source rocks of the studied oils (Fig. 5).

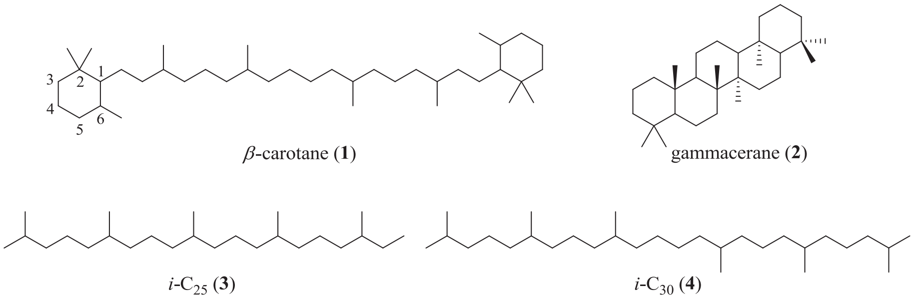
4.2. Distribution of aryl isoprenoids and aromatic carotenoids

The variables controlling organic matter preservation are complex. Factors like primary production rate, water column depth, organic matter sources, sediment transport processes, sediment accumulation rate, oxygen concentration and availability of electron acceptors are critical variables (Tissot and Welte, 1984; Killops and Killops, 2005).

Decreased oxygen anoxia and euxinia (high levels of H_2S) contribute to the preservation of organic material (Tissot and Welte, 1984; Killops and Killops, 2005). When the euxinic zone reaches the photic zone in the water column optimal conditions of light and H_2S support the survival of microorganisms such as green and purple sulfur bacteria (*Chlorobiaceae* and *Chromatiaceae*, respectively). These organisms use as photosynthetic pigments aromatic carotenoids, such as isorenieratene (**5**), renieratene (**6**), renierapurpurine (**7**), chlorobactene (**8**) and okenone (**9**) (Fig. 6) (Schaeffer et al., 1997; Brocks and Schaeffer, 2008). Sinninghe Damsté et al. (2001) consider isorenieratene (**5**) to be a "carotenoid uniquely biosynthesized" by green sulfur bacteria (*Chlorobiaceae*) that allows evaluation of the redox conditions in the depositional source rock environments. These aromatic carotenoids can be incorporated into sediments that become petroleum source rocks. Their diagenetic and catagenetic derivatives in crude oils represented biomarkers indicative of euxinic conditions in the photic zone during sedimentation (Fig. 7).

Previous studies of Sergipe–Alagoas Basin oils focused on the saturated fractions, which mainly to the identification of aliphatic components. All of these studies reported high contents of β-carotane (**1**) (Trindade and Brassell, 1992; Mello et al., 1993; Machado, 1995; Alves, 1997; Rodrigues et al., 2000, 2005; Cruz, 2005).

The proposed mass spectral fragmentation schemes that assist in structural determination are in the Appendix A. Table 3 shows the details of the identification of compounds based on the mass spectra data. Reconstructed ion chromatogram (RIC) of ions m/z 133 and m/z 134 (entry A in the Appendix A), clearly show a series of compounds related to carotenoid diagenetic products. The compounds were identified by their respective molecular ions, base peaks at m/z 134 (McLafferty rearrangement) or m/z 133 (tropylium cation). In addition, m/z 119,120, 105, 91 and 77 were used



β-carotane (**1**)

gammacerane (**2**)

i-C_{25} (**3**)

i-C_{30} (**4**)

Fig. 4. Structures for some biomarker indicative of salinity into depositional environment for source rocks.

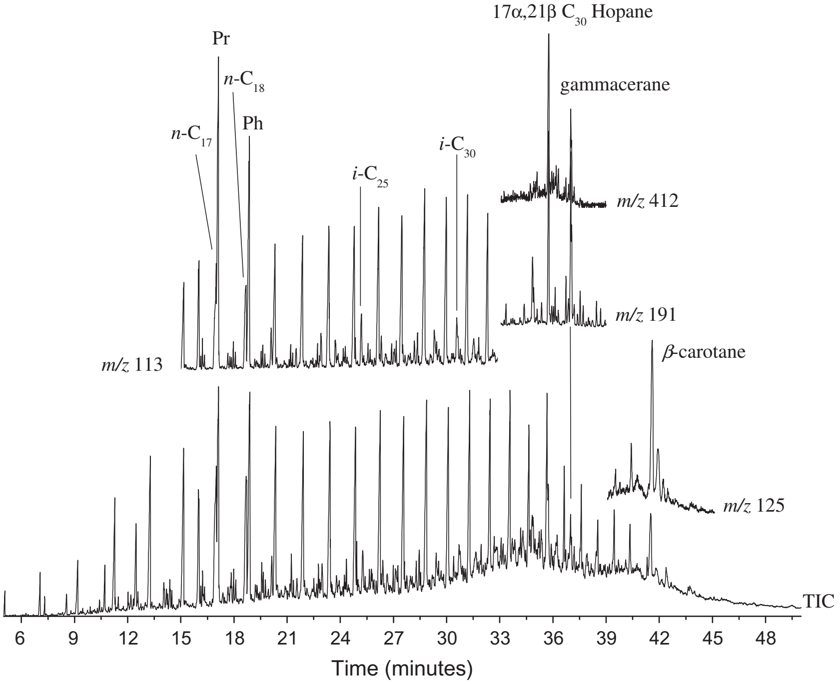


Fig. 5. Composition of TIC and m/z 125, m/z 113, m/z 191, and m/z 412 chromatograms to show the presence of β-carotane, i-C_{25}, i-C_{30}, and gammacerane. Pr = pristane, and Ph = phytane.

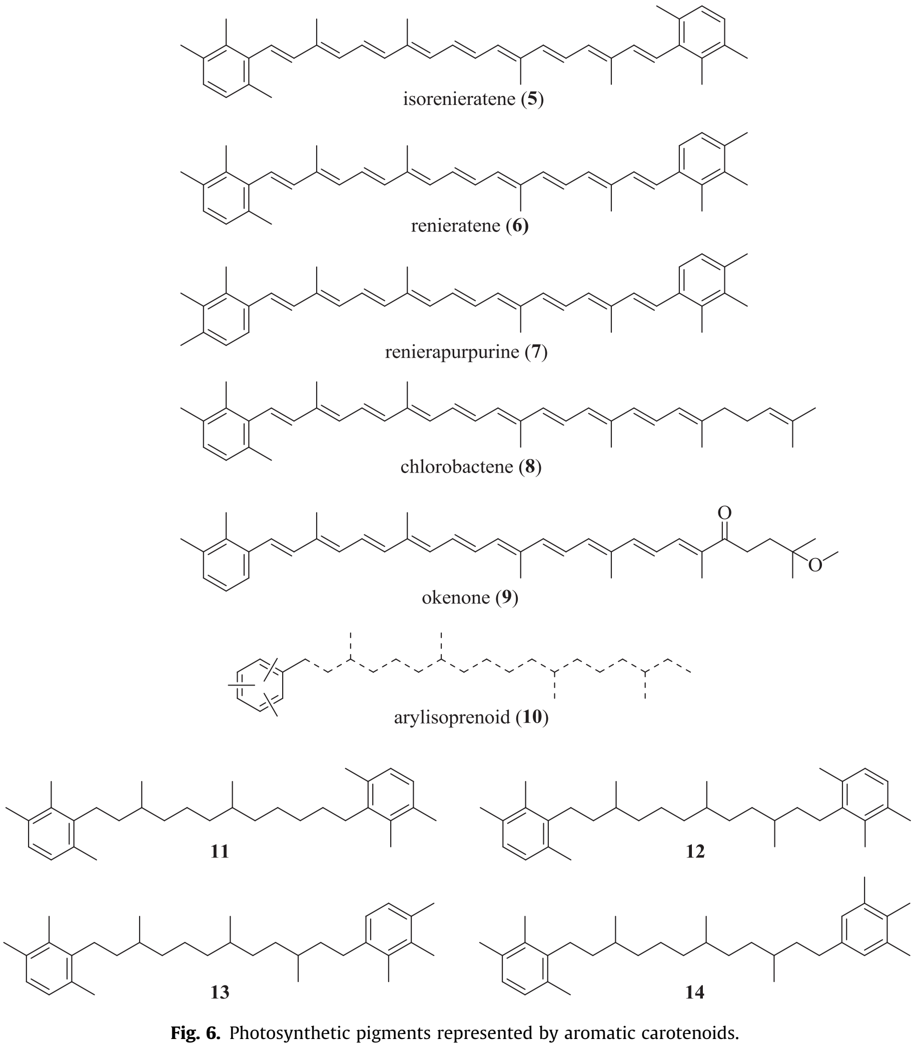


Fig. 6. Photosynthetic pigments represented by aromatic carotenoids.

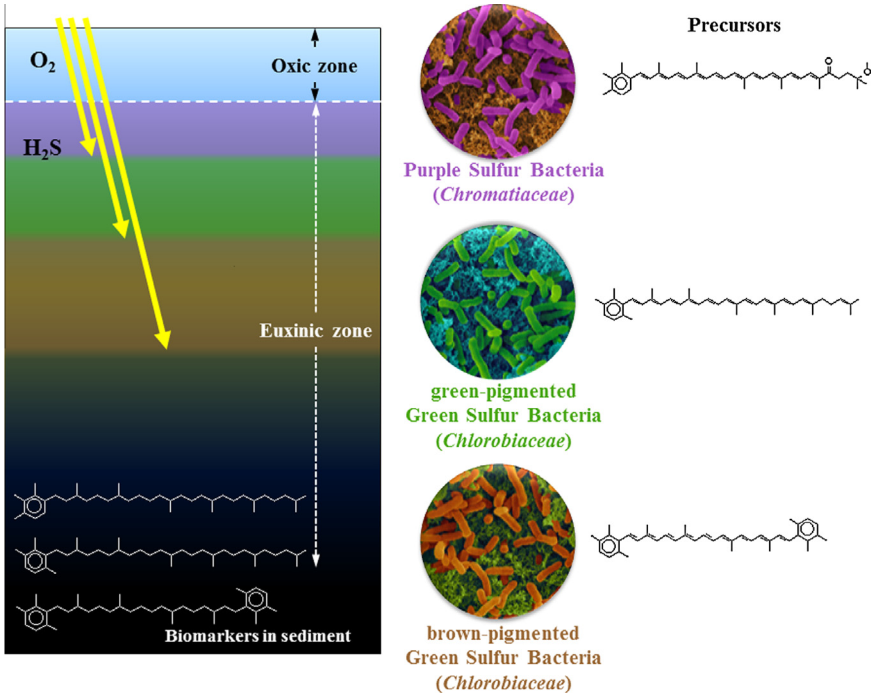


Fig. 7. Simplified profile of a depositional environment showing the intervals where green and purple sulfur bacteria thrive. The carotenoids they synthetize and their corresponding biomarkers.

Table 3
Mass spectral data of aromatic isoprenoids. The path of the fragmentation is indicated in the Appendix A. The structures are indicated in mass chromatogram in Fig. 8 and represented in Fig. 9.

Structure	Formula	$M^{+\cdot}$	Diagnostics fragments	Reference
< C_{32}				
10-C_{10}	$C_{10}H_{14}$	134(40)	119(100), 91(20)	(Summons and Powell, 1987)
10-C_{13}	$C_{13}H_{20}$	176(21)	133(100), 134(20)	(Summons and Powell, 1987)
10-C_{14}	$C_{14}H_{22}$	190(21)	133(100), 134(64)	(Summons and Powell, 1987)
10-C_{15}	$C_{15}H_{24}$	204(15)	133(100), 134(24)	(Summons and Powell, 1987)
10-C_{16}	$C_{16}H_{26}$	218(28)	133(100), 134(83)	(Summons and Powell, 1987)
10-C_{18}	$C_{18}H_{30}$	246(15)	134(100), 133(97)	(Summons and Powell, 1987)
10-C_9	$C_{19}H_{32}$	260(11)	133(100), 134(93)	(Summons and Powell, 1987)
10-C_{20}	$C_{20}H_{34}$	274(16)	134(100), 133(94)	(Summons and Powell, 1987)
10-C_{21}	$C_{21}H_{36}$	288(12)	134(100), 133(80)	(Summons and Powell, 1987)
10-C_{22}	$C_{22}H_{38}$	302(10)	134(100), 133(85)	(Summons and Powell, 1987)
10-C_{24}	$C_{24}H_{42}$	316(20)	133(100), 134(88)	(Summons and Powell, 1987)
10-C_{25}	$C_{25}H_{44}$	344(11)	134(100), 133(81)	(Summons and Powell, 1987)
10-C_{29}	$C_{29}H_{52}$	400(11)	134(100), 133(68)	(Summons and Powell, 1987)
10-C_{30}	$C_{30}H_{54}$	414(7)	134(100), 133(74)	(Summons and Powell, 1987)
10-C_{31}	$C_{31}H_{56}$	428(7)	133(100), 134(62)	(Summons and Powell, 1987)
C_{32}				
11	$C_{32}H_{50}$	434(13)	133(100), 134(81)	(Koopmans et al., 1996)
C_{33}				
12	$C_{33}H_{52}$	448(12)	133(100), 134(87)	(Koopmans et al., 1997)
13	$C_{33}H_{52}$	448(11)	134(100), 133(85)	(Koopmans et al., 1996; Brocks and Schaeffer, 2008)
14	$C_{33}H_{52}$	448(12)	134(100), 133(77)	(Clifford et al., 1998)
15	$C_{33}H_{44}$	440(20)	237(100), 133(63), 134(23), 207(20)	(Grice et al., 1996; Koopmans et al., 1996)
16	$C_{33}H_{44}$	440(34)	237(100), 134(48)	(Grice et al., 1996; Koopmans et al., 1996)
C_{40}				
17	$C_{40}H_{58}$	538(17)	237(100), 133(37), 134(23), 207(23), 222(11)	(Grice et al., 1996; Koopmans et al., 1996)
18	$C_{40}H_{58}$	538(10)	133(100), 134(65), 119(22), 173(12)	(Grice et al., 1996; Koopmans et al., 1997)
19	$C_{40}H_{66}$	546(4)	134(100), 133(93), 119(11)	(Koopmans et al., 1997; Brocks and Schaeffer, 2008)
20	$C_{40}H_{72}$	552(6)	134(100), 133(48)	(Hartgers et al., 1994; Brocks and Schaeffer, 2008)
21	$C_{40}H_{72}$	552(8)	134(100), 133(35)	(Brocks and Schaeffer, 2008)
22	$C_{40}H_{70}$	550(9)	119(100), 120(25), 125(8), 300(7), 370(4)	(Koopmans et al., 1997)
23	$C_{40}H_{70}$	550	243(see entry D in Appendix A)	(Koopmans et al., 1997)
C_{38}				
25	$C_{38}H_{62}$	518(4)	120(100), 119(34)	(Zhang et al., 2011)

ni – ions not identified due to low signal–noise ratio.

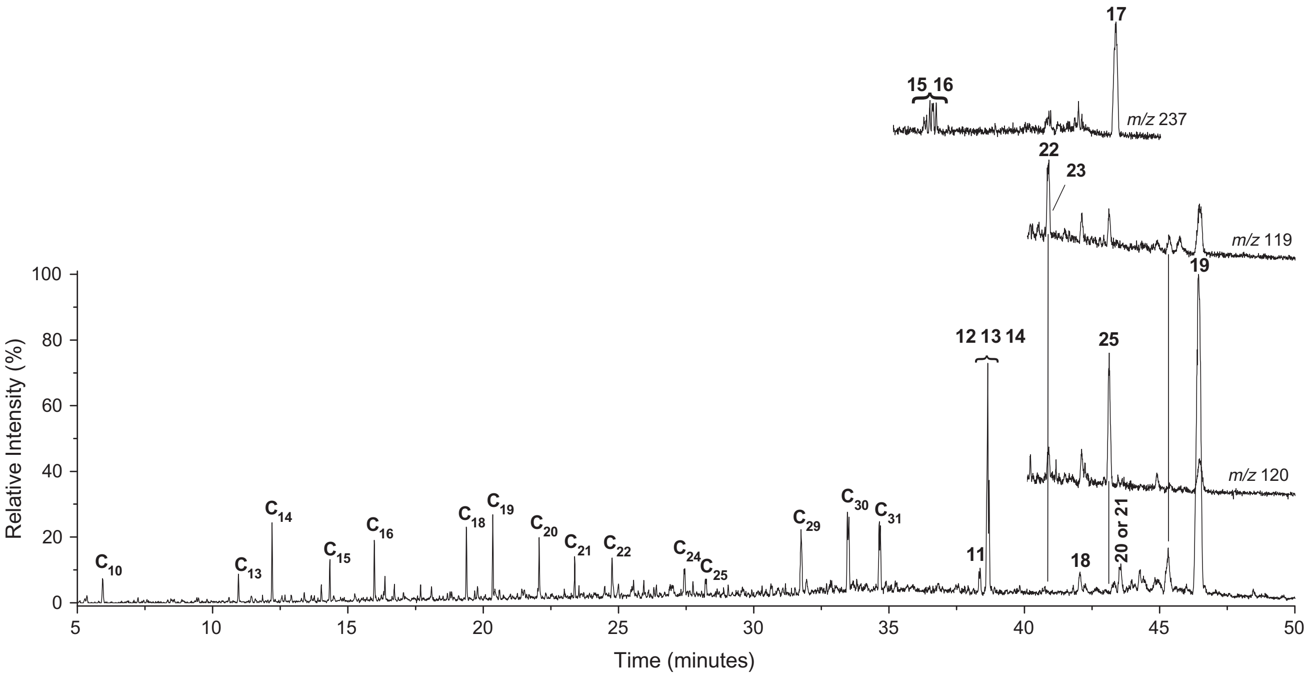


Fig. 8. RIC of m/z 134 and zoom of the region between 35 and 51 min showing the aryl isoprenoids and remaining diagenetic isorenieratane products.

because they are typical of a polysubstituted aromatic structure (see Table 3 and Appendix A).

Analysis of the mass spectra indicates a series of compounds with < 40 carbon atoms. The mass chromatogram (Fig. 8) shows a compound series with mass spectra characterized by a molecular ion having a formula C_nH_{2n-6}, and a base peak ion m/z 133 or 134, indicative of monoaromatic compounds with a terminal trimethylbenzene ring, generically represented by (**10**) (Fig. 7). The absence or low abundance of the C_{12}, C_{17}, C_{23}, and C_{28} members of the series is consistent with the branching pattern of irregular isoprenoid with a tail-to-tail link.

These monoaromatic compounds can be generated by thermal cleavage from carotenoid precursors. They are not generated directly from fossil carotenoids, but from incorporation of the carotenoids into the high molecular weight fractions (e.g., kerogen) and thereafter cleavage of the bond C–C during increase thermal stress (Requejo et al., 1992; Hartgers et al., 1994; Koopmans et al., 1996).

Compound (**11**) (C_{32}) (peak t_R = 38.3 min) with molecular ion m/z 434 and base peak at m/z 133, is consistent with the formula $C_{32}H_{50}$. Comparison with data reported by Koopmans et al. (1996) suggest a 2,3,6-trimethyl substitution pattern for both aromatic ring consistent with structure **11** (Fig. 7). Furthermore a complex signal, which was resolved by GC–qMS and its MS fragmentation allowed the identification of three C_{33} isomeric diaryl isoprenoids (**12**), (**13**), and (**14**). Their fragmentation patterns are similar to those presented by Koopmans et al. (1996) and mentioned by Sinninghe Damsté and Koopmans (1997). Two other C_{33} carotenoids (**15**) and (**16**) were detected with molecular ions m/z 440 and base peak at m/z 237 and fragmentation patterns suggesting a biphenyl, similar to those observed by Koopmans et al. (1996). These compounds can be formed by cyclisation and aromatisation followed by expulsion of toluene (to C_{33}) and *m*-xylene (to C_{32}) from isorenieratene (**5**) (Koopmans et al., 1996; Sinninghe Damsté and Koopmans, 1997; Sinninghe Damsté et al., 2001).

Two diarylisoprenoids (**17**, t_R = 43.3 min and **18** t_R = 45.3 min) with an additional aromatic ring were detected with structures were based on their mass spectra and the literature. Both compounds show molecular ions of m/z 538, consistent with the formula $C_{40}H_{58}$. The MS of **17** shows ions m/z 237 (base peak), m/z 133 and m/z 222. The base peak m/z 237 (entry C in the Appendix A) indicates the presence of a terminal biphenyl system and the remaining fragments are compatible with those observed by Koopmans et al. (1996) and support the proposed structure for (**17**). The mass spectrum of the second product (**18**), shows base peaks at m/z 133 and m/z 134 that are typical of aryl isoprenoids and a peak at m/z 119 (see entry E in the Appendix A) due to an additional aromatic ring. According Koopmans et al. (1996), those compounds formed from isorenieratene (**5**) by a sequence of cyclisation, aromatisation and hydrogenation reactions. Initial cyclisation seems to occur mainly after appropriate *trans–cis* isomerisation at two specific sites, which favours generation of (**17**) and (**18**).

The main component in the mass chromatogram for m/z 134 (**19**, t_R = 46.5 min Fig. 8) was identified as an aromatic carotenoid isorenieratane (**19**, Fig. 9) (M+ m/z 546, base peak m/z 133 and m/z 134 in mass spectrum and comparison to literature). This carotenoid has already been reported and identified using synthetic standards in many studies (Koopmans et al., 1996; Sinninghe Damsté et al., 2001; Brown and Kenig, 2004; Brocks et al., 2005; Brocks and Schaeffer, 2008; Maslen et al., 2009; Zhang et al., 2011). A 2,3,6-trimethyl substitution pattern is present in isorenieratene (**5**), which is specific for photosynthetic green sulfur bacteria (Chlorobium) (Clifford et al., 1998; Sinninghe Damsté et al., 2001; Killops and Killops, 2005). The isorenieratane (**19**) is generated by hydrogenation of the isorenieratene (**5**) isoprenoid chain (Schaefle et al., 1977).

The RIC of ion m/z 134 trace (Fig. 8) shows a broad signal (t_R = 43.5 min) with molecular ions at m/z 552 and base peak at m/z 134 (Table 3) consistent with the formula $C_{40}H_{72}$, suggesting a trimethyl substituted monoaromatic carotenoid structure with a terminal cyclohexane ring. Comparing these data with data reported by Brocks and Schaeffer (2008) it is possible to suggest the structures of β-isorenieratane (**20**) or β-renierapurpurane (**21**, Fig. 9).

Two other minor diagenetic products were also detected and their structures proposed based on data from the mass spectra. Both compounds have molecular ions at m/z 550 and show base

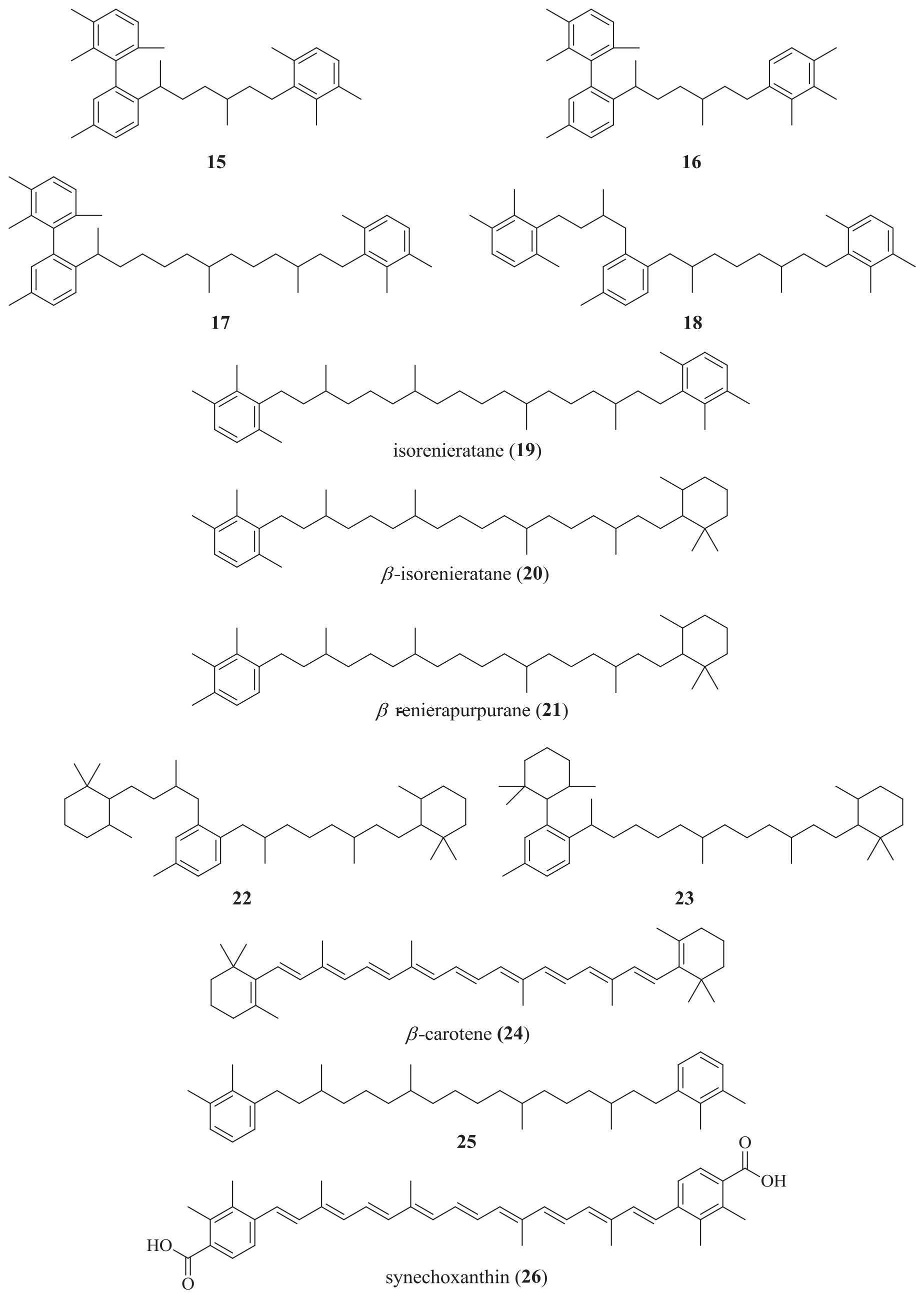


Fig. 9. Biomarker derivatives of aromatic carotenoids identified in the samples.

peaks at m/z 119 (Table 3). For the first compound the m/z 119 fragment is consistent with β-cleavage (entry E of Appendix A) and agrees with the structure (**22**, Fig. 9) while the fragment m/z 243, in the second compound is consistent with entry D (Appendix A), thus suggesting the structure (**23**, Fig. 9). Just as cyclization of isorenieratene (**5**) generated (**17**) and (**18**) (Koopmans et al., 1996), structures (**22**) and (**23**) formed from β-carotene (**24**) by cyclization of the isoprenoid chain (Koopmans et al., 1997).

The mass spectrum of the component (**25**) is characterized by molecular ion m/z 518 and peak base ion m/z 120, consistent with an aromatic carotenoid C_{38} (Table 3). Zhang et al. (2011) assigned this compound as a diaryl isoprenoid with a 2,3-/2,3-dimethyl substitution pattern. Graham and Bryant (2008) reported a diaromatic carotenoid in cyanobacteria called synechoxanthin (**26**) (Fig. 9) functionalized at C-4, which could generate (**25**) during diagenesis.

The presence of diagenetic and/or catagenetic products of isorenieratane in source rocks and crude oils suggests photic zone anoxia during the deposition of organic-rich sediments. Additional confirmation of the origin of aryl isoprenoids from *Chrobiaceae* can be obtained if these compounds are isotopically heavier ($\delta^{13}C > -15‰$) than their carotane counterparts of algal origin (Koopmans et al., 1996; Sinninghe Damsté et al., 2001).

5. Conclusion

The chromatographic profiles and geochemical parameters from the saturated fractions of four oils from the Sergipe–Alagoas Basin analyzed in this study indicate that they are not biodegraded and achieved similar thermal maturity levels (early to middle oil window) and that their source rocks were deposited in a reducing depositional environment, under different levels of salinity. However, the prominent UCM in the GC profiles suggests at least two oil pulses of oil. The geochemical parameters of the oils are consistent with contribution from two sources: marine evaporitic (predominant) and lacustrine (Mello et al., 1995).

This study identified isorenieratane as the most abundant component within the carotenoid derivatives in these oils. Its presence indicates that euxinia reached the photic zone during the deposition of the organic rich source rocks. We also detected a variety of isorenieratane diagenetic and catagenetic products with broad ranges of structure, including derivatives of C_{40}, C_{33} and C_{32} diaryl isoprenoids and aryl isoprenoids with short chains and/or with additional aromatic rings.

Aryl isoprenoids in the oils are most likely of lacustrine origin and suggest that the Cretaceous paleolakes between Brazil and Africa experienced episodes of increasing salinity. The phenomenon of anoxia increasing during the Cretaceous along the Brazilian Mesozoic basins could have been widespread because aryl isoprenoids have already been recognized in the Araripe Basin (Aptian, Santana Formation) and now in oils from the Sergipe–Alagoas Basin sourced by source rocks of equivalent age.

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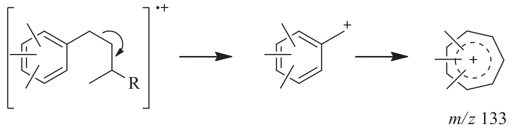
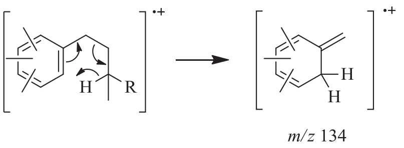
Appendix A

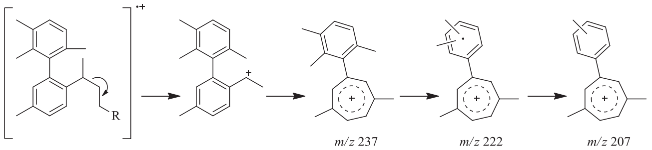
(**A**) β Cleavage.



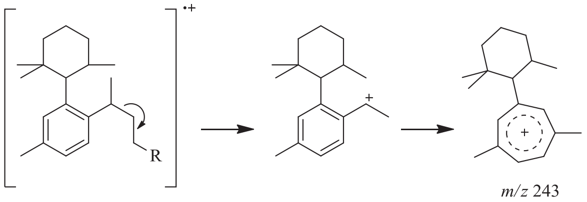
(**B**) McLafferty rearrangement.



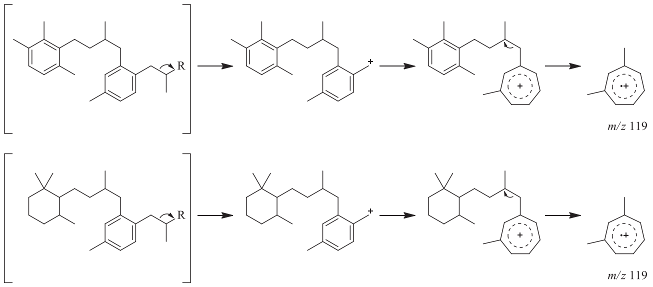
(**C**) Cleavage of the biphenyl moiety.



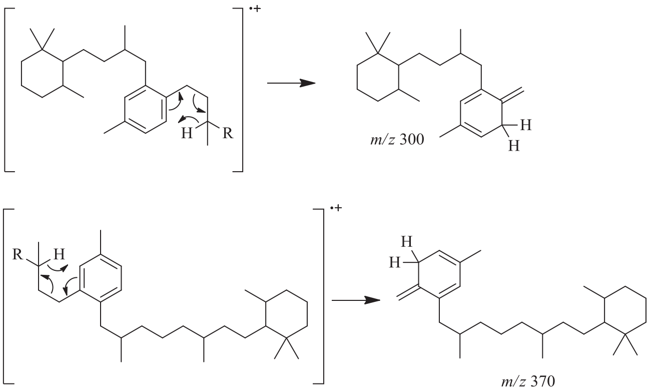
(**D**) Cleavage of the arylcyclohexyl moiety.



(**E**) Cleavage of the both sides of the additional aromatic ring.



(**F**) McLafferty rearrangement for cartotenoid with additional aromatic ring.



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References

Alves, P.B., 1997. Detalhes Sobre a História Geológica da Bacia Sergipe/Alagoas a partir de Biomarcadores Ácidos e Síntese de Biomarcadores. Instituto de Química. Universidade Estadual de Campinas, Campinas, p. 258.

Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A., Bowden, S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. Nature 437, 866–870.

Brocks, J.J., Schaeffer, P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. Geochimica et Cosmochimica Acta 72, 1396–1414.

Brown, T.C., Kenig, F., 2004. Water column structure during deposition of Middle Devonian-Lower Mississippian black and green/gray shales of the Illinois and Michigan Basins: a biomarker approach. Palaeogeography, Palaeoclimatology, Palaeoecology 215, 59–85.

Clifford, D.J., Clayton, J.L., Sinninghe Damsté, J.S., 1998. 2,3,6-/3,4,5-trimethyl substituted diaryl carotenoid derivatives (*Chlorobiaceae*) in petroleums of the Belarussian Pripyat River Basin. Organic Geochemistry 29, 1253–1267.

Connan, J., 1984. Biodegradation of crude oils in reservoirs. In: Brooks, J., Welte, D.H. (Eds.), Advances in Petroleum Geochemistry. Academic Press, London, pp. 299–335.

Cruz, G.F., 2005. Contribuição ao Estudo de Biomarcadores em Óleos da Bacia Sergipe-Alagoas. Departamento de Química. Universidade Federal do Piauí, Teresina, p. 101.

Graham, J.E., Bryant, D.A., 2008. The biosynthetic pathway for synechoxanthin, an aromatic carotenoid synthesized by the euryhaline, unicellular cyanobacterium Synechococcus sp. Strain PCC 7002. Journal of Bacteriology 190, 7966–7974.

Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1996. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. Organic Geochemistry 25, 131–147.

Hartgers, W.A., Sinninghe Damsté, J.S., Requejo, A.G., Allan, J., Hayes, J.M., Ling, Y., Xie, T.M., Primack, J., De Leeuw, J.W., 1994. A molecular and carbon isotopic study towards the origin and diagenetic fate of diaromatic carotenoids. Organic Geochemistry 22, 703–725.

Heimhofer, U., Hesselbo, S.P., Pancost, R.D., Martill, D.M., Hochuli, P.A., Guzzo, J.V.P., 2008. Evidence for photic-zone euxinia in the Early Albian Santana Formation (Araripe Basin, NE Brazil). Terra Nova 20, 347–354.

Katz, B.J., Mello, M.R., 2000. Petroleum systems of South Atlantic marginal basins – an overview. In: Mello, M.R., Katz, B.J. (Eds.), American Association of Petroleum Geologists Memoir. Tulsa, OK, pp. 1–13.

Killops, S., Killops, V., 2005. Introduction to Organic Geochemistry, second ed. Blackwell Publishing, Oxford.

Koopmans, M.P., Köster, J., Van Kaam-Peters, H.M.E., Kenig, F., Schouten, S., Hartgers, W.A., De Leeuw, J.W., Sinninghe Damsté, J.S., 1996. Diagenetic and catagenetic products of isorenieratene: molecular indicators for photic zone anoxia. Geochimica et Cosmochimica Acta 60, 4467–4496.

Koopmans, M.P., Leeuw, J.W.D., Sinninghe Damsté, J.S., 1997. Novel cyclised and aromatised diagenetic products of β-carotene in the Green River Shale. Organic Geochemistry 26, 451–466.

Koutsoukos, E.A.M., Mello, M.R., Azambuja Filho, N.C., 1991a. Micropalaeontological and geochemical evidence of mid-Cretaceous dysoxic-anoxic palaeoenvironments in the Sergipe Basin, northeastern Brazil. Geological Society, London, Special Publications 58, 427–447.

Koutsoukos, E.A.M., Mello, M.R., Azambuja Filho, N.C., Hart, M.B., Maxwell, J.R., 1991b. The Upper Aptian-Albian succession of the Sergipe Basin Brazil: an integrated paleoenvironmental assessment. American Association of Petroleum Geologists Bulletin 75, 479–498.

Lana, M.C., 1990. Bacia de Sergipe-Alagoas: uma hipótese de evolução tectonosedimentar. In: Gabaglia, G.P.R., Milani, E.J. (Eds.), Origem e Evolução de Bacias Sedimentares. CENSUD, Rio de Janeiro, pp. 311–332.

Lima, S.G., Steffen, R.A., Reis, F.A.M., Koike, L., Santos Neto, E.V., Cerqueira, J.R., Lopes, J.A.D., 2010. Propylergostanoic acids: possible new indicator for oil biodegradation. Organic Geochemistry 41, 325–339.

Lopes, J.A.D., Santos Neto, E.V., Mello, M.R., Koike, L., Marsaioli, A.J., Reis, F.D.A.M., 1999. 3-Alkyl and 3-carboxyalkyl steranes in marine evaporitic oils of the Potiguar Basin, Brazil. Chemical Geology 158, 1–20.

Machado, S.S., 1995. Aspectos Moleculares das Frações Neutra e Ácida de Petróleos da Bacia de Sergipe-Alagoas: Síntese de Biomarcadores Aromáticos Derivados de Esteróis. Instituto de Química. Universidade Estadual de Campinas, Campinas, p. 258.

Maslen, E., Grice, K., Gale, J.D., Hallmann, C., Horsfield, B., 2009. Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. Organic Geochemistry 40, 1–11.

Mello, M.R., Gaglianone, P.C., Brassell, S.C., Maxwell, J.R., 1988a. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. Marine and Petroleum Geology 5, 205–223.

Mello, M.R., Telnaes, N., Gaglianone, P.C., Chicarelli, M.I., Brassell, S.C., Maxwell, J.R., 1988b. Organic geochemical characterisation of depositional paleoenvironments of source rocks and oils in Brazilian marginal basins. Organic Geochemistry 13, 31–45.

Mello, M.R., Maxwell, J.R., 1990. Organic geochemical and biological marker characterizations of source rocks and oils derived from lacustrine environments in the Brazilian continental margin. In: Katz, B.J. (Ed.), Lacustrine Basin Exploration: Case Studies and Modern Analogs. AAPG Memoir, Tulsa, OK, pp. 77–97.

Mello, M.R., Koutsoukos, E.A.M., Santos Neto, E.V., Telles Jr., A.C.S., 1993. Geochemical and micropaleontological characterization of lacustrine and marine hypersaline environments from Brazilian sedimentary basins. In: Katz, B.J., Pratt, L.M. (Eds.), Source Rocks in a Sequence Stratigraphic Framework. American Association of Petroleum Geologists, Tulsa, OK, pp. 17–34.

Mello, M.R., Telnaes, N., Maxwell, J.R., 1995. The hydrocarbon source potential in the Brazilian marginal basins: a Geochemical an Paleoenvironmental Assessment. In: Huc, A.-Y. (Ed.), Paleogeography, Paleoclimate and Source Rocks. American Association of Petroleum Geologists, Tulsa, OK, pp. 233–272.

Ojeda, H.A., 1982. Structural framework, stratigraphy, and evolution of Brazilian marginal basins. American Association of Petroleum Geologists Bulletin 66, 732–749.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in the Petroleum Exploration and Earth History, second ed. Cambridge University Press, Cambridge.

Ponte, F.C., Asmus, H.E., 1978. Geological framework of the Brazilian continental margin. Geologische Rundschau 67, 201–235.

Requejo, A.G., Allan, J., Creaney, S., Gray, N.R., Cole, K.S., 1992. Aryl isoprenoids and diaromatic carotenoids in Paleozoic source rocks and oils from the Western Canada and Williston basins. Organic Geochemistry 19, 245–264.

Rodrigues, D.C., Koike, L., Reis, F.D.A.M., Alves, H.P., Chang, H.K., Trindade, L.A., Marsaioli, A.J., 2000. Carboxylic acids of marine evaporitic oils from Sergipe-Alagoas Basin, Brazil. Organic Geochemistry 31, 1209–1222.

Rodrigues, D.C., De Vasconcellos, S.P., Alves, P.B., Nascimento, L.R., De Abreu Filho, B.A., De Oliveira, V.M., Manfio, G.P., Dos Santos Neto, E.V., Marsaioli, A.J., 2005. Relationship between cyclohexyl-alkanoic acids and the acidothermophilic bacterium *Alicyclobacillus* spp.: evidence from Brazilian oils. Organic Geochemistry 36, 1443–1453.

Schaeffer, P., Adam, P., Wehrung, P., Albrecht, P., 1997. Novel aromatic carotenoid derivatives from sulfur photosynthetic bacteria in sediments. Tetrahedron Letters 38, 8413–8416.

Schaefle, J., Ludwig, B., Albrecht, P., Ourisson, G., 1977. Hydrocarbures aromatiques d'origine geologique. II: Nouveaux Carotanoïdes Aromatiques Fossiles. Tetrahedron Letters 18, 3673–3676.

Sinninghe Damsté, J.S., Koopmans, M.P., 1997. The fate of carotenoids in sediments: an overview. Pure and Applied Chemistry 69, 2067–2074.

Sinninghe Damsté, J.S., Schouten, S., Van Duin, A.C.T., 2001. Isorenieratene derivatives in sediments: possible controls on their distribution. Geochimica et Cosmochimica Acta 65, 1557–1571.

Summons, R.E., Powell, T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. Geochimica et Cosmochimica Acta 51, 557–566.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, second ed. Springer Verlag, Berlin.

Trindade, L.A.F., Brassell, S.C., 1992. Geochemical assessment of petroleum migrations phenomena on a regional scale: case studies from Brazilian marginal basins. Organic Geochemistry 19, 13–27.

Zhang, C., Zhang, Y., Cai, C., 2011. Aromatic isoprenoids from the 25–65 Ma saline lacustrine formations in the western Qaidam Basin, NW China. Organic Geochemistry 42, 851–855.