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Occurrence and Distribution of Carbazoles and Benzocarbazoles in Tertiary Niger Delta Source Rocks

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The distributions of carbazoles and benzocarbazoles in source rocks from the Northern depobelt of the Tertiary Niger Delta, Nigeria, have been investigated by gas chromatography-mass spectrometry (GC-MS). Biomarker compositions of the source rocks indicate that the source rocks were formed from organic matter of mixed origin (terrestrial and marine) and are either immature or at early maturity stage. The carbazoles distributions in the source rocks are dominated by C_0-C_2-carbazoles and strong variation was observed in their distributions with increasing maturity. Among the C_1-carbazoles, 1-methylcarbazole shows a decrease trend at the immature stage and an increase trend at higher maturity levels. 2- and 3-methylcarbazoles display an increasing trend with increasing maturity while 4-methylcarbazole exhibits a decreasing pattern with increasing maturity. Within the C_2-carbazoles isomers, 1,8- and 2,7-dimethylcarbazoles, show an increasing trend with increasing maturity while the partially exposed isomers 1,3- and 1,6-dimethylcarbazoles decrease with increasing maturity. The ratio of benzo[a]carbazole/benzo[a]carbazole +benzo[c]carbazole varies significantly from 0.36 to 0.55 in the entire maturity range, indicating a strong maturity dependence. These results show that maturity will have great effect on the use of carbazoles and benzocarbazoles distributions as oil migration parameter in the Niger Delta.

Keywords: carbazole, benzocarbazoles, source rocks, Niger delta, gas chromatography-mass spectrometry

1. INTRODUCTION

Organic nitrogen compounds are constituents of nonhydrocarbon fractions of crude oils, present in small amounts and mostly in form of heterocyclic aromatic structures (Tissot and Welte, 1984). These compounds can be classified into two major types: basic (pyridinic nitrogen compounds) and nonbasic (pyrrolic nitrogen compounds). The pyrrolic type is the most abundant in most crude oils (Li et al., 1995). Pyrrolic nitrogen compounds such as carbazole and its derivatives and benzocarbazoles have recently received attention from organic geochemist because of their potential use as secondary migration markers in petroleum exploration (Li et al., 1995; Larter et al., 1996). These compounds have the capacity to interact with the surrounding environments via hydrogen

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and/or ionic bonding (Li et al., 1995). The resultant effect is the differential fractionation of these compounds within the geosphere. The pyrrolic nitrogen compounds often show an overall decrease in concentration with increasing oil migration distance. This is usually accompanied by enrichment of N–H shielded isomers relative to N–H exposed isomers, higher to lower molecular weight homologues, alkylcarbazoles to alkylbenzocarbazoles, and benzo[c]carbazole to benzo[a]carbazole. Recent studies have shown that the distributions of carbazoles and benzocarbazoles in oils and rock extracts can also be influenced by source facies (Bakr and Wilkes, 2002; Bennett and Olsen, 2007), thermal maturity (Stoddart et al., 1995; Clegg et al., 1997; Li et al., 1997; Clegg et al., 1998a; Clegg et al., 1998b; Horsfield et al., 1998; Zhang et al., 2011), biodegradation and water washing (Huang et al., 2003). The origin of carbazole and its derivatives/isomers still remains controversial (Synder, 1965; Li et al., 1995). Synder (1965) proposed that many of the alkylcarbazoles and alkylbenzocarbazoles in petroleum may be derived from alkaloids with an indole nucleus, often present in higher plants and also in blue-green algae. In contrast, Li et al. (1995) argued that plant alkaloids could not be the major source of petroleum carbazoles. They asserted that nitrogen compounds in high wax oils from higher plant material did not show a significant difference from oils from lacustrine and marine origins.

Carbazoles distributions have been used to differentiate two different facies of transgressive and regressive events in the carbonate source rocks of the Lower and Upper Keg River Formations (Clegg et al. (1997). The predominance of low molecular weight homologues (C_1- and C_2-carbazoles) relative to the high molecular weight compounds (C_3–C_5-carbazoles) have been reported in the source rock from nonmarine depositional environments in Qaidam and Turpan basin, Northwest China (Zhang et al., 2008). The influence of maturity on carbazoles distributions has also been reported by Li et al. (1997) in a series of marine carbonate source rocks from a natural maturity sequence (0.45–1.30% Ro). They opined that the variation was due to selective release of different pyrrolic compounds as a result of decrease in the efficiency of bitumen trapping by the kerogen matrix associated with increasing thermal maturation. However, subsequent studies of natural maturity influence on sequences of rocks revealed that maturation did have a strong influence on the distributions of pyrrolic compounds (Clegg et al., 1997; Clegg et al., 1998a; Clegg et al., 1998b; Zhang et al., 2011).

Carbazole and its derivatives have not been reported before in Niger Delta source rock. In this study, the occurrence and distribution of carbazoles and benzocarbazoles were investigated in the Niger Delta source rock by gas chromatography-mass spectrometry.

2. GEOLOGICAL AND STRATIGRAPHIC SETTING

The Niger delta is one of the world's largest Tertiary deltaic systems (Tuttle et al., 1999). The delta is bounded in the west by Benin Flank, in the east by Calabar Flanks. The northern boundary is high marked by Anambra and Abakaliki basins while the delta is bounded in the south by the Gulf of Guinea. The Niger delta basin covers an area of about 75,000 km^2 and consists of 9–12 km total thickness of regressive clastic sequences. The stratigraphy (Figure 1) of the thick sedimentary sequence is divided into three lithostratigraphic units, namely: the Akata, Agbada, and Benin Formations (Short and Stauble, 1967). The Akata Formation, ranging in age from Paleocene to Miocene, consists mainly of overpressure shale deposited under fully marine conditions. This formation underlies the entire delta and has not been drilled in most parts of the delta, except at the continental margin. It is estimated at about 7000 m thick (Doust and Omatsola, 1990). On top of the Akata Formation is the Agbada Formation, which is composed of a paralic sequence consisting of interbedded sands and shales. Hydrocarbons are found within the sandstone reservoir of the Agbada Formation where oil and gas are usually trapped in rollover anticlines associated with growth faults. The thickness and age of the reservoir range from 10 to 20 m and Eocene to recent, respectively (Ejedawe, 1986). It is about 4000 m thick in the central part, thinning
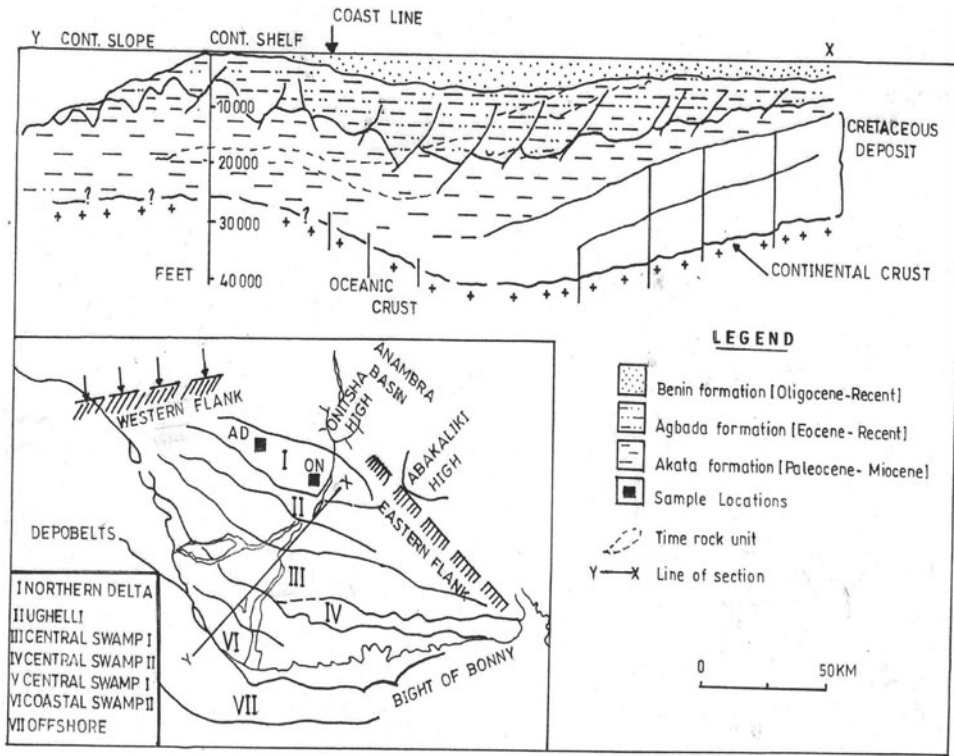
FIGURE 1   Niger delta: stratigraphy, depobelts, and sample locations (after Ekweozor and Daukoru, 1994).

seaward and toward the delta margin and represents the actual deltaic portion of the sequence. The Benin Formation, which is the youngest (Oligocene to recent), is composed of mainly fluviatile gravels and sands. It is up to 2000 m thick in the central onshore part and thins toward the delta margin.

Studies have revealed that available source rocks in the basin exist mainly in the lower parts of the paralic sequence (Agbada Formation) and uppermost strata of the continuous marine shale (Akata Formation) (Ekweozor and Daukoru, 1994). The basin is partitioned into 6–7 east–west bound blocks corresponding to depositional belts or depobelts (Figure 1). These depobelts correspond to discrete periods of the deltas evolutionary history starting from the oldest in the north, northern delta to the youngest, offshore in the south (Ekweozor and Daukoru, 1984; Doust and Omatsola, 1990). It is generally believed that each depobelt constitutes a more or less independent unit with respect to sedimentation, structural deformation and hydrocarbon generation and accumulation (Evamy et al., 1978).

3. SAMPLES AND EXPERIMENTAL

3.1 Samples

A total of 73 rock cuttings from two wells located in the Northern Niger Delta depobelt were analyzed. The samples locations are shown in Figure 1.

3.2 Rock-Eval Analyses

Rock-Eval pyrolysis was conducted using a Rock-Eval 6 analyzer at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, China. 50 mg of powdered rock sample was progressively heated to 850°C using a special temperature program. The computerized system output the pyrograms as well as the calculated parameters. Hydrocarbon extracts were monitored by a FID and recorded as S_1 (thermally extracted free hydrocarbon) and S_2 (hydrocarbon from cracking of organic matter). CO and CO_2 released during pyrolysis were quantified in real time by means of an IR cell, which provided information on the oxidation state of organic matter and allowed the determination of total organic carbon (TOC) and mineral carbon content of the samples. Hydrogen (HI) and oxygen (OI) indices were calculated by normalizing S_2 and S_3 yields to TOC (mg/g TOC). Standards were run in between samples to ensure reproducibility and accuracy of the data generated. Data were acquired using OPTKIN software.

3.3 Extraction

The rock samples were ground into a fine powder and extracted with azeotropic mixture of dichloromethane/methanol (93/7, v/v) in a Soxhlet apparatus for 72 h. The extracts were fractionated by column chromatography on neutral alumina. The saturated, aromatics and polar compounds were eluted using n-hexane (50 mL), toluene (50 mL), and DCM/methanol (99:1, 70 mL) respectively. The polar fraction was further fractionated on 2 g of silicic acid column by elution with n-hexane/toluene (1:1, 50 mL) to obtain the pyrrolic nitrogen compounds (Li et al., 1995).

3.4 GC-MS and GC-MS-MS Analyses

Gas chromatography-mass spectrometry (GC-MS) analyses of the saturated fractions was performed with Thermo Scientific Trace GC Ultra gas chromatography fitted with a HP-5MS fused silica capillary column (60 m × 0.32 mm i.d. × 0.25 μm film thickness) and coupled to a Thermo Scientific Trace DSQ II mass spectrometer. The GC oven was held isothermally at 80°C for 4 min and programmed from 80°C to 285°C at 4°C/min; and a final hold time of 30 min. Helium was used as carrier gas with a constant flow rate of 1.2 mL/min. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 250°C, and injector temperature of 285°C.

The analysis of pyrrolic nitrogen enriched fractions was carried out on a Thermo Scientific Trace GC Ultra gas chromatography fitted with a 50 m × 0.22 mm i.d. fused silica capillary column coated with BPX5 coupled to a Thermo Scientific Trace TSQ QUANTUM XLS MS-MS. The GC oven was held isothermally at 80°C for 2 min, and then programmed to 290°C at a rate of 3°C/min. Helium was used as carrier gas with a constant flow rate of 1.0 mL/min. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 250°C. Full scan mass spectrometer was recorded over a mass range m/z = 50–600 at a scan rate of 0.5 scans/sec. Carbazoles were detected in selective ion monitoring (SIM) mode, scanning for the following ions: m/z 167 (carbazole), m/z 181 (C_1-carbazoles), m/z 195 (C_2-carbazoles), m/z 209 (C_3-carbazoles), and m/z 217 (benzocarbazoles). Identification of individual carbazoles and benzocarbazoles was based on elution orders from the literatures and comparison of mass spectra data with literature and library data. The relative abundance was calculated from integrated peak areas in the relevant ion chromatograms (Bowler et al., 1997; Clegg et al.,1997).

TABLE 1
Geochemical Data for Rocks Samples From Niger Delta, Nigeria

Sample. No.	Field	Depth, m	TOC, wt%	Tmax, °C	S_1, mg/g	S_2, mg/g	PI	HI	Pr/ Ph	Pr/ C_{17}	Ph/ C_{18}	OI	Ts/ (Ts+Tm)	22S	20S	C_{27}	C_{28}	C_{29}
1	AD	2444–2463	2.32	431	0.04	1.35	0.03	58	1.74	4.15	1.52	0.27	0.34	0.35	0.25	27.20	31.93	40.86
2	AD	2591–2610	0.73	427	0.02	0.85	0.02	116	1.59	4.44	1.25	0.34	0.38	0.41	0.25	23.69	31.62	44.69
3	AD	2792–2810	1.92	433	0.09	2.23	0.04	116	2.13	2.78	0.87	0.58	0.43	0.45	0.29	25.04	28.19	46.76
4	AD	2847–2865	2.76	433	0.08	2.69	0.03	97	3.11	1.74	1.05	0.51	0.39	0.47	0.31	25.58	28.00	46.42
5	AD	2910–2926	2.59	434	0.08	3.83	0.02	148	2.37	3.74	1.24	0.63	0.30	0.48	0.26	24.63	30.20	45.17
6	AD	3017–3035	4.10	436	0.21	7.05	0.03	172	3.73	4.98	1.00	0.70	0.21	0.53	0.28	27.56	27.96	47.48
7	AD	3108–3119	3.19	436	0.18	5.28	0.03	166	4.29	2.73	0.80	0.56	0.30	0.55	0.34	27.72	27.21	45.07
8	ON	2841–2853	3.26	426	1.54	5.62	0.22	172	1.48	5.37	1.24	0.42	0.45	0.50	0.33	32.86	27.26	39.88
9	ON	2938–2957	2.60	424	1.85	6.01	0.24	231	1.56	2.55	0.96	0.37	0.46	0.52	0.41	35.64	28.88	35.48
10	ON	3219–3237	2.11	434	0.39	3.86	0.09	183	1.88	1.97	0.71	0.52	0.40	0.55	0.43	37.68	26.29	36.04
11	ON	3365–3383	2.60	436	0.38	4.36	0.08	168	2.19	2.46	0.98	0.53	0.34	0.56	0.41	35.40	23.60	41.00
12	ON	3463–3481	3.04	438	0.47	5.43	0.08	179	2.61	1.44	0.70	0.50	0.55	0.55	0.43	34.89	26.09	39.02

TOC: total organic carbon (Rock-Eval); S_1: free hydrocarbons (Rock-Eval); S_2: pyrolyzable hydrocarbons (Rock-Eval); PI: $S_1/S_1 + S_2$; HI: S_2/TOC * 100 (mg/g TOC); Pr/Ph: pristane/phytane (m/z 85); Pr/C_{17}: pristane/n-C_{17} alkane (m/z 85); Ph/C18: phytane/n-C_{18} alkane (m/z 85); oleanane index (OI) = 18α(H)-Olenane/17α(H), 21β(H)-hopane (m/z 191); Ts/Ts+Tm: 18a(H)-/(18a(H)- + 17a(H)-trinorhopane) (m/z 191); 22S: C_{31} homohopane 22S/22S + 22R (m/z 191); 20S: C_{29} sterane $\alpha\alpha\alpha$ 20S/20S + 20R (m/z 217); C_{27}, C_{28}, C_{29}: relative abundance of C_{27}, C_{28}, and C_{29} sterane $\alpha\alpha\alpha$ 20R (%).

4. RESULTS AND DISCUSSION

4.1 Geochemical Characteristics of the Source Rock

The results of the geochemical parameters determined for the source rocks are presented in Table 1. The rocks have TOC values ranging from 0.73 to 4.1 wt%. These values exceed the minimum threshold value of 0.5 wt% required for potential petroleum source rocks (Tissot and Welte, 1984). The Tmax values range from 424 to 438°C, indicating immature to early mature source rocks (Peters and Moldowan, 1993). The production (PI) and hydrogen index (HI) of the rocks are very low, ranging from 0.003 to 0.24 and 58 to 231 mg HC/g TOC, respectively. The HI values are comparable to the values reported by other authors for source rocks from the same basin (Udo et. al., 1988; Akinlua and Torto, 2011).

The mass chromatograms m/z 191 (terpanes) and 217 (steranes) of representative rock samples are shown in Figure 2. The Pr/Ph ratios range from 1.48 to 4.29 (Table 1). The high Pr/Ph ratios suggest source rock derived from organic matter with significant terrestrial contribution, deposited in an oxic paleoenvironment (Didyk et al., 1978; Mello and Maxwell, 1990). This observation is consistent with the previously reported studies for source rocks from the Niger Delta (Okoh and Nwachukwu, 1997; Akinlua and Torto, 2007). The presence of oleanane in the samples indicates source rocks that have input of terrestrial higher plants and deposited in a deltaic environment (Whitehead, 1974; Ekweozor et al., 1979; Philip and Gilbert, 1986). The abundance of C_{27}-C_{29} sterane in the source rocks (Table 1) indicates source rocks derived from mixed origin (terrestrial and marine; Huang and Meinschein, 1979).

The assessment of thermal maturity level was based on maturity parameters computed from the terpane and sterane distributions in the source rock. The homohopane (C_{31}) 22S/22S+22R and sterane (C_{29}) 20S/20S+20R range from 0.35 to 0.56 and 0.25 to 0.43, respectively (Table 1), indicating immature to early mature source rock (Seifert and Moldowan, 1978, 1981; Peters and Moldowan, 1993).
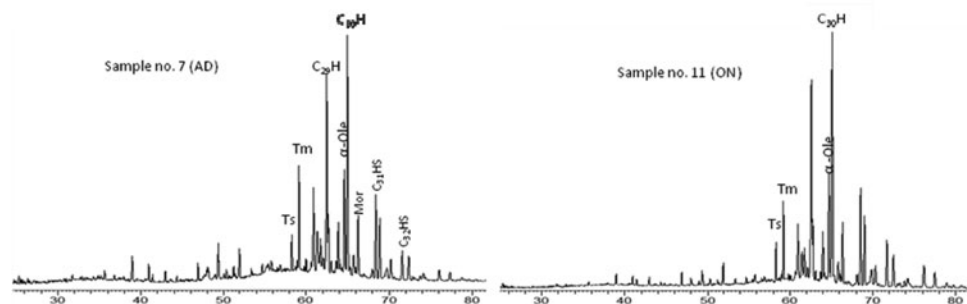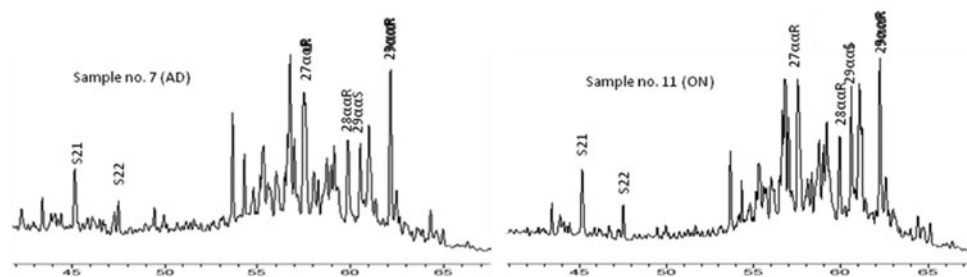
m/z 191: Pentacyclic Terpanes

m/z 217: Steranes

FIGURE 2   Partial m/z 191 (terpanes) and 217 (steranes) mass chromatograms of representative rock samples.

4.2 Occurrence and Distribution of Carbazoles and Benzocarbazoles

The selective ion monitoring (SIM) chromatograms showing the distribution of carbazole and its alkylated derivatives and benzocarbazoles of representative samples are shown in Figure 3. The relative abundances of these compounds are listed in Table 2. The carbazoles are dominated by C_2-carbazoles while 1-methylcarbazole is the most abundant of the C_1 carbazoles. Similar results have been reported for nonmarine source rocks samples from Northwest China (Zhang et al., 2008). Benzocarbazoles are also detected in high abundance in the source rocks (Figure 3). Benzo[b]carbazole is the least abundant isomer among the three isomers of benzocarbazoles. The influence of facies/depositional environments and thermal maturity on the general distributions of carbazoles and benzocarbazoles in the source rock was examined. The C_{0-2}-carbazoles relative abundances show no significant variation that could suggest a strong source facies influence on their distributions (Figure 4a). The cross plot of Pr/Ph and benzocarbazoles ratios do not show much variation to indicate any possible source facies or depositional environment dependent (Figure 4b). However, considerable variations with different maturity levels are observed among the carbazoles and benzocarbazoles.

Generally, the relative abundance of carbazole increases with increasing maturity (Figure 5a). As for C_1-carbazoles, the variation in abundances is within a narrow range and could not allow
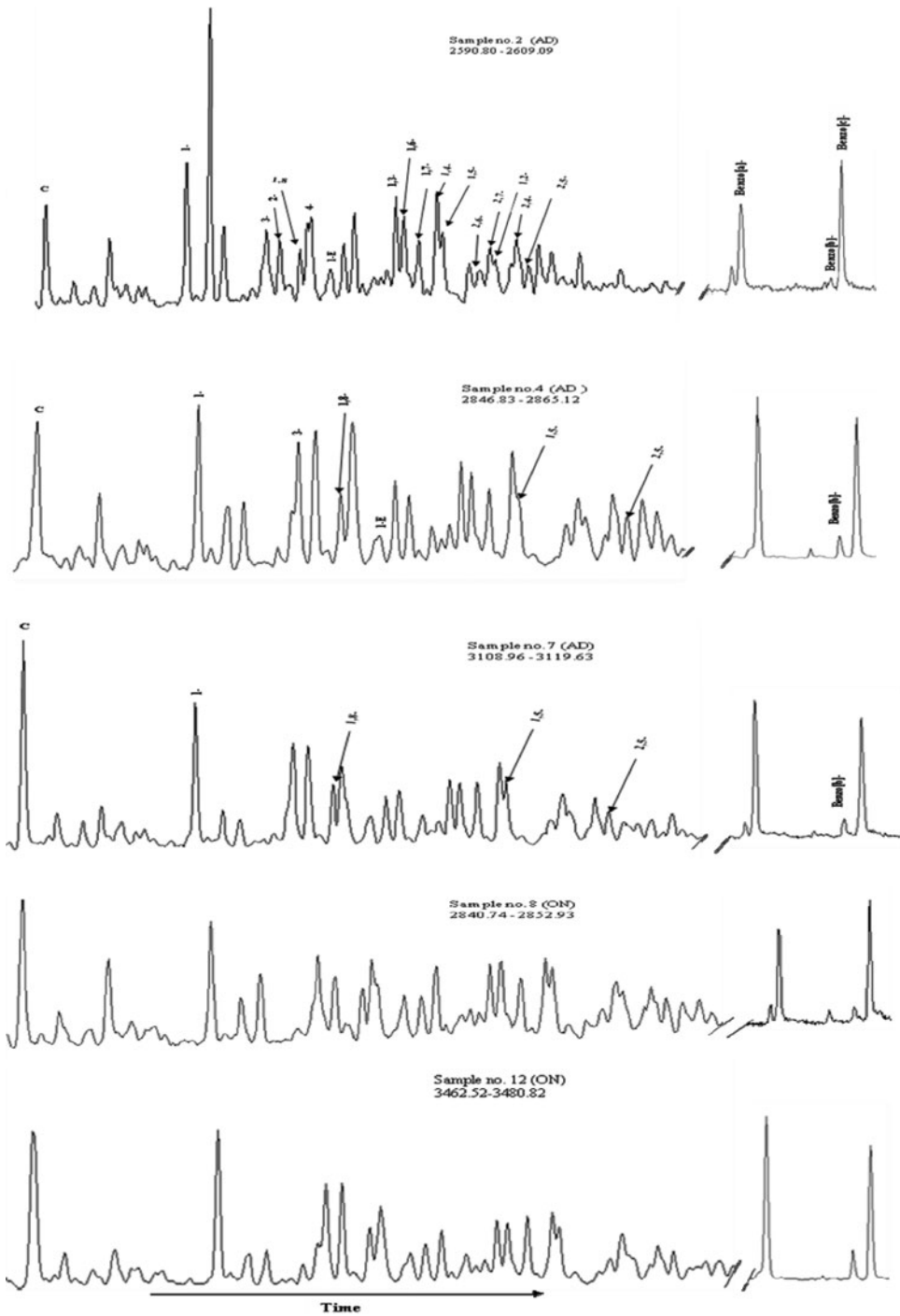
FIGURE 3   Selective ion monitoring (SIM) (m/z 167, 181, 195, and 217) chromatograms showing the distributions of C_{0-2}-carbazoles and benzocarbazoles in source rocks from Niger Delta at different depths.

TABLE 2
Relative Abundance of Pyrrolic Nitrogen Compounds in Rock Extracts From Niger Delta, Nigeria

Sample No.	Field	Depth, m	Carbazoles, %			Methylcarbazoles, %				C_2-Carbazoles, %													
			C_o^a	C_1^b	C_2^c	1-	3-	2-	4-	1,8-^{d}	1-ET^e	1,3-^{d}	1,6-^{d}	1,7-^{d}	1,4-^{d}	1,5-^{d}	2,6-^{d}	2,7-^{d}	1,2-^{d}	2,4-^{d}	2,5-^{d}	a/a+c^f
1	AD	2444–2463	5.3	27.0	67.7	14.2	4.8	5.6	75.4	17.5	8.2	12.0	12.4	14.7	9.4	10.0	1.6	3.5	6.6	2.1	1.8	0.36
2	AD	2591–2610	9.4	28.5	62.1	37.1	11.9	13.6	37.3	8.1	2.8	12.7	11.9	10.1	12.0	9.4	4.9	6.9	6.0	10.3	5.0	0.41
3	AD	2792–2810	10.2	26.9	63.0	32.3	16.0	20.6	31.2	9.5	3.2	10.5	11.3	10.1	10.0	8.5	5.2	9.4	8.5	8.5	5.4	0.45
4	AD	2847–2865	10.4	27.1	62.4	29.2	17.3	18.7	34.7	9.6	4.2	9.6	10.5	9.5	11.6	6.3	6.0	9.9	7.7	9.7	5.4	0.50
5	AD	2910–2926	9.6	31.0	59.4	29.4	18.9	22.0	29.6	10.8	5.2	8.6	9.9	9.1	12.2	6.3	7.2	9.6	8.2	7.6	5.4	0.55
6	AD	3017–3035	13.4	31.7	54.9	31.9	20.3	20.5	27.3	9.7	4.5	9.9	10.3	11.0	9.7	7.8	5.4	9.6	8.0	8.3	5.9	0.47
7	AD	3108–3119	15.7	33.2	51.2	35.3	19.8	19.8	25.1	10.4	5.1	9.3	10.2	10.9	9.3	8.6	5.2	10.2	7.4	7.9	5.4	0.52
8	ON	2841–2853	12.0	26.2	61.8	32.3	19.5	18.0	30.2	8.9	3.9	9.6	11.3	10.5	9.9	10.8	4.7	8.5	7.8	8.2	5.9	0.46
9	ON	2938–2957	12.5	26.8	60.7	36.1	18.5	16.7	28.7	12.9	4.3	8.5	10.5	9.5	10.3	12.3	4.0	7.4	7.2	7.7	5.3	0.44
10	ON	3219–3237	18.6	28.6	52.8	32.4	20.5	20.9	26.3	10.3	4.7	7.6	9.0	11.1	10.8	10.2	5.1	8.8	7.7	8.1	6.6	0.54
11	ON	3365–3383	16.0	31.3	52.7	36.1	22.1	19.7	22.1	10.5	3.5	9.0	10.5	10.6	9.0	10.3	5.0	9.4	8.3	7.7	6.2	0.54
12	ON	3463–3481	14.5	31.6	53.9	38.0	19.8	20.6	21.6	12.0	4.0	9.2	11.5	11.5	9.9	9.1	4.2	9.8	6.6	6.5	5.6	0.55

C_o^a, C_1^b, C_2^c: relative percentage of carbazole, methylcarbazoles, and dimethylcarbazoles (m/z 167, 181, and 195) respectively.
(1,8-, 1,3-, 1,6-, 1,7-, 1,4-, 1,5-, 2,6-, 2,7-, 1,2-, 2,4-, and 2,5-)^d: dimethylcarbazoles, ^{e}1-ET: 1-ethylcarbazole (m/z 195).
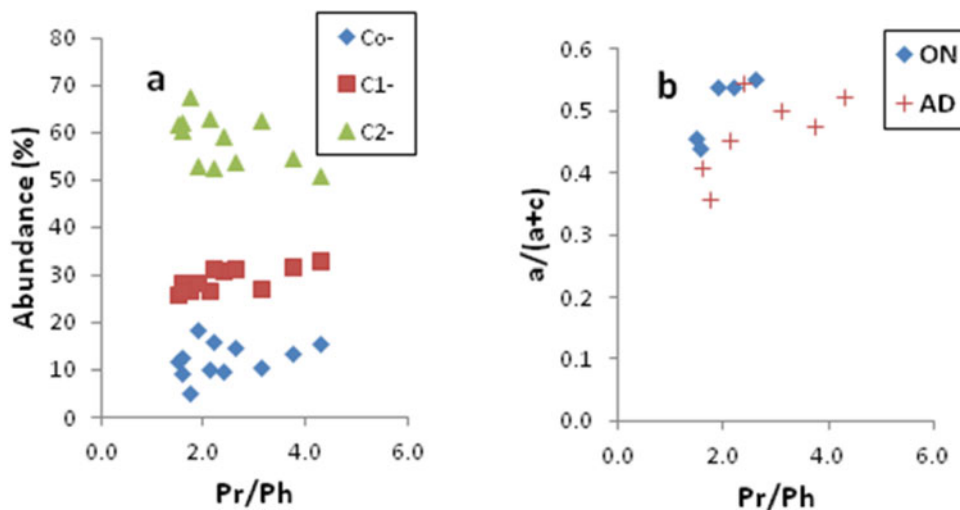a/a+c: benzo[a]carbazole/(benzo[a]carbazole+benzo[c]carbazole) (m/z 217).

FIGURE 4   Cross plots of Pr/Ph vs. (a) relative amounts of C_{0-2}-carbazoles and (b) benzolecarbazole ratio a/a+c.

any pattern to be established. The C_2-carbazoles generally display a downward trend with increasing maturity. The variations between C_1-carbazoles and C_2-carbazoles appear to be controlled by maturity. The plot of C_2-/ C_1-carbazoles and $C_{29}S/S+R$ (maturity assessment parameter) ratios indicates a preferential generation for C_1-carbazoles as maturity increases (Figure 5b). The plot of benzo[a]carbazole/benzo[a]cabazole+benzo[c]cabazole versus $C_{29}S/S+R$ reveals a general increase of benzocarbazoles ratio with increasing maturity (Figure 5c). This observation has been reported by other workers (Clegg et al., 1998a; Clegg et al., 1998b). It has been reported that benzo[c]carbazole is more stable than benzo[a]carbazole based on molecular mechanics of the two benzocarbazoles isomers (Harrison et al., 1997). The influence of maturity on the relative abundances of C_{0-2}-carbazoles and benzocarbazoles was determined based on the ratio of benzo[c]carbazole to carbazole ([c]/C_0). The cross plot reveals a preferential generation of carbazole over benzo[c]carbazole with increasing maturity (Figure 5d). This is in contrast to the observation of Zhang et al. (2011), who reported a preferential generation of benzo[a]carbazoles over carbazole as maturity increases.

4.2.1 *C_1-carbazoles*

Among the methylcarbazoles, 1-methylcarbazole is the most abundant in the rock samples (Figure 3). The predominance of 1-methylcarbazole in crude oils and source rocks has been previously reported (Clegg et al., 1998b; Zhang et al., 2008). The cross plots of Pr/Ph ratio and the relative abundance of methylcarbazole isomers show no significant trend that could suggest the dependent of these isomers on source depositional environments (Figure 6). Maturity effect seems to be a factor controlling the distributions of these isomers. 1-methylcarbazole shows a decreasing trend at the immature stage and increasing trend at high maturity levels. 2- and 3-methylcarbazoles display an increasing trend with increasing maturity while 4-methylcarbazole exhibits a decreasing pattern with increasing maturity (Figure 7a). The ratio of 3-/4-methylcarbazole increases with increasing maturity. This implies a preferential generation for 3-methylcarbazole over 4-methylcarbazole with increasing maturity (Figure 7b).
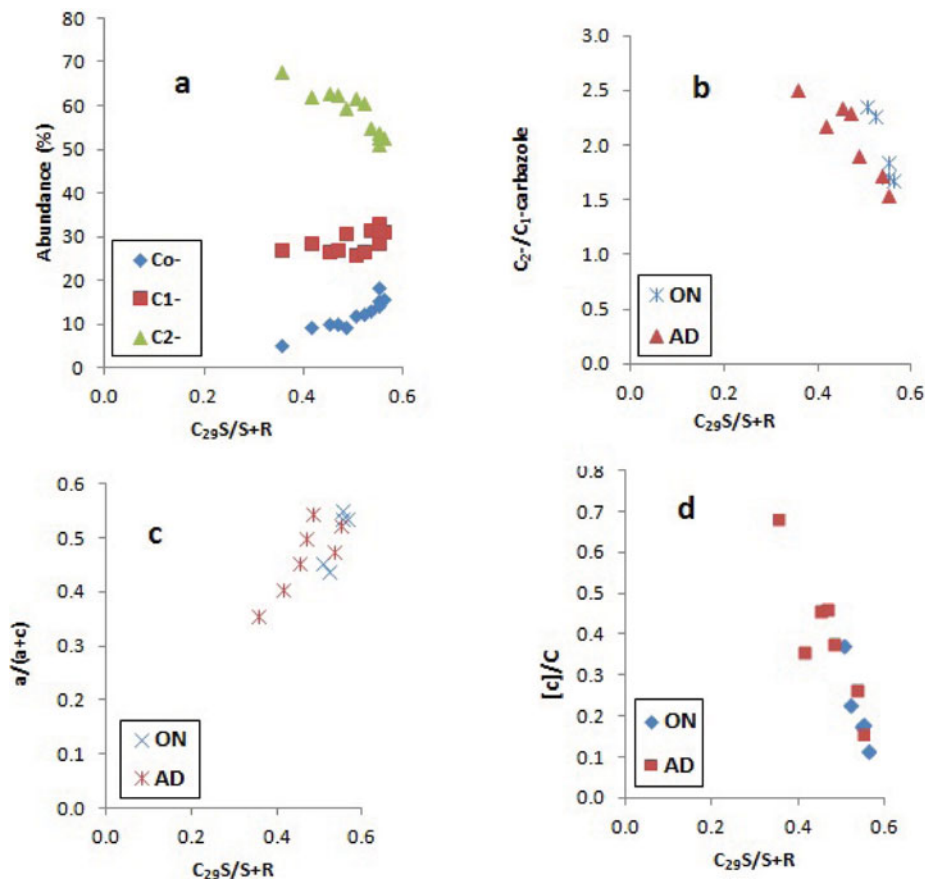
FIGURE 5   Cross plots of sterane $C_{29}S/S+R$ versus (a) relative amounts of C_{0-2}-carbazoles, (b) C_1-/C_2-carbazoles ratio, (c) benzocarbazoles ratio a/a+c, and (d) benzo[c]carbazole/carbazole ratio.

4.2.2 C_2-carbazoles

As for isomers with a methyl group at C-1 (partially shielded), a typical distribution with 1,7-dimethylcarbazole being the most abundant and 1,2-dimethylcarbazole the least abundant was observed. The dominance of 1,6-dimethylcarbazole over 1,3-dimethylcarbazole was observed in most of the source rock. This is contrary to the observation of Zhang et al. (2008), who reported high abundance of 1,3- over 1,6-dimethylcarbazole for source rock from nonmarine depositional environments. Among the exposed isomers, 2,7-dimethylcarbazole is the most abundant and 2,6-dimethylcarbazole is the least abundant.

Cross plots of the relative abundances of some selected dimethylcarbazole isomers and their ratios against Pr/Ph ratio lack significant variations to suggest any effects of facies or depositional environments on the dimethylcarbazoles distributions (Figures 8a and 8b). Maturity effect seems to be more pronounced on the distributions of the dimethylcarbazole isomers. 1,8- and 2,7-dimethylcarbazoles, generally increase with increasing maturity while the partially exposed isomers 1,3- and 1,6-dimethylcarbazoles decrease with increasing maturity
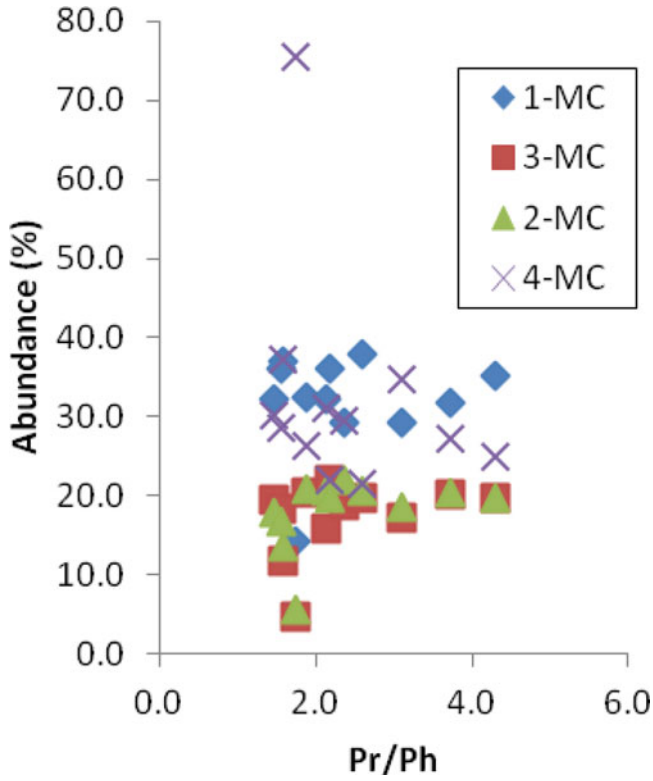
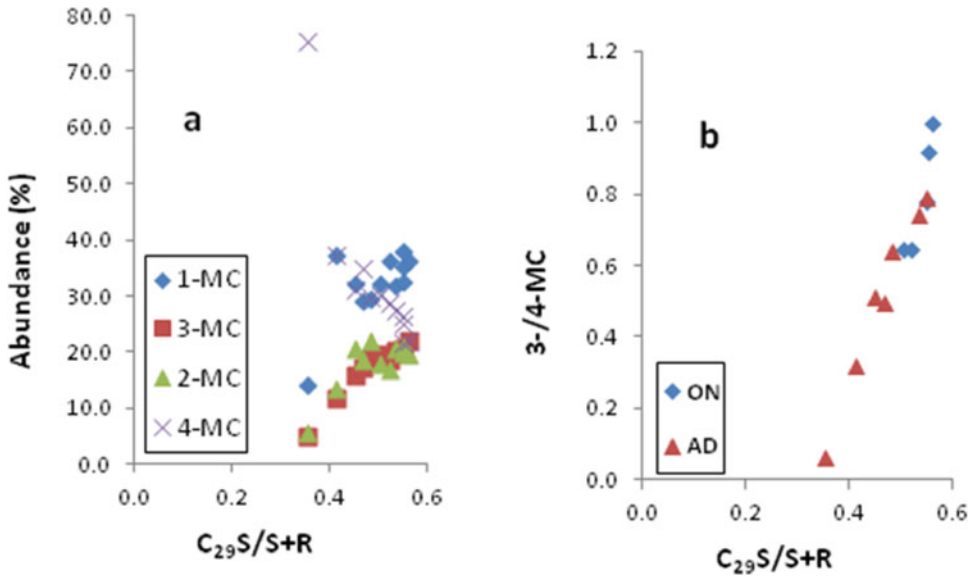FIGURE 6   Cross plots of relative amounts of C_1-carbazoles versus Pr/Ph.

FIGURE 7   Cross plots of sterane $C_{29}S/S+R$ versus (a) relative amounts of C_1-carbazoles and (b) 3-/4-methylcarbazole ratio.
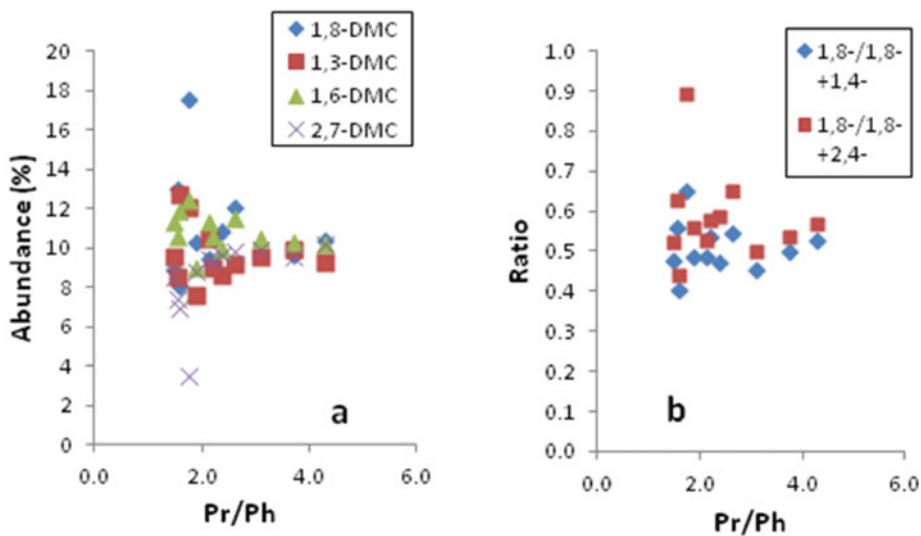
FIGURE 8   Cross plots of Pr/Ph versus (a) relative amounts of C_2-carbazoles and (b) C_2-carbazoles ratios.

(Figure 9a). Also, cross plots between the ratios of shielded isomers to partially exposed iso-mers, and shielded isomers to fully expose isomers reveal an increasing trend with increas-ing maturity (Figure 9b). This variation shows a preferential generation for shielded isomers over both partially and fully exposed isomers of dimethylcarbazoles as maturity increases (Figure 9b).
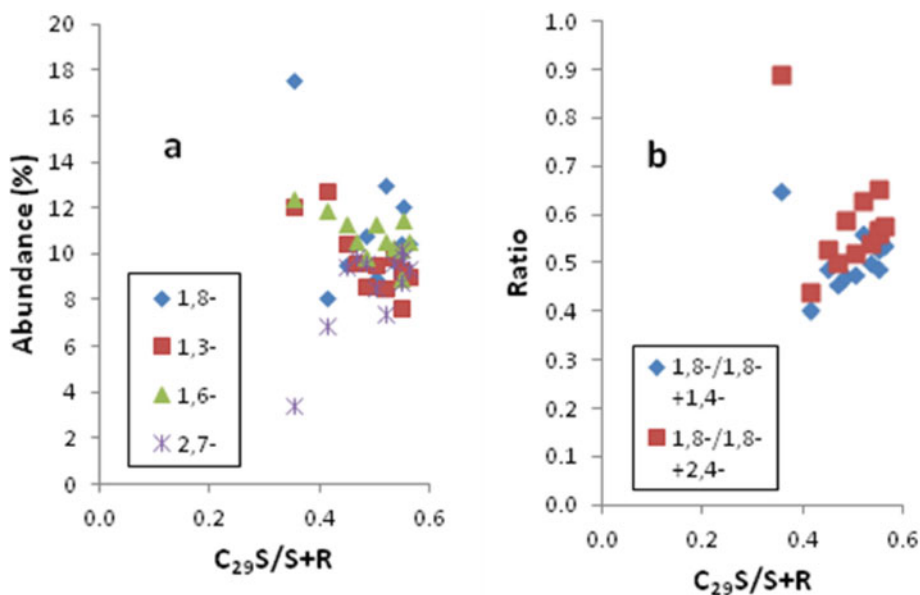

FIGURE 9   Cross plots of sterane $C_{29}S/S+R$ versus (a) relative amounts of C_2-carbazoles and (b) C_2-carbazoles ratios.

5. CONCLUSIONS

The biomarker distributions in the source rocks indicated that they were derived from organic matter of mixed origin (terrestrial and marine) deposited in a deltaic environment. Maturity parameters computed from the biomarker composition indicated a wide range in the source rocks maturity levels. The carbazoles distributions in the source rocks are dominated by C_0-C_2-carbazoles. Strong variation was observed in the distributions of the carbazoles with increasing maturity of the source rock. The ratio of benzo[a]carbazo/benzo[a]cabazole+benzo[c]cabazole varies significantly in the entire maturity range, indicating strong maturity dependence. This results show that maturity has great influence on the distributions of carbazoles and benzocarbazole in the source rocks, suggesting some limitation in their usage as migration parameter.

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