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Characterization of Source Rocks from Off-shore Niger Delta Basin, Nigeria

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ABSTRACT: Rock samples from the offshore Niger Delta basin, Nigeria were characterized by the predominance of C_{26} 20R + C_{27} 20S TAS peak using GC-MS. Among the compounds identified in m/z 245 mass chromatograms, C_{21} methyltriaromatic steroids, C_{22} methyltriaromatic steroids and C_{27}, 4-methyltriaromatic steroid + C_{29}, 4-methyl-, 24-ethyltriaromatic steroid were the dominant compounds in the rock samples from MJI oilfield while the rock samples from MJO oilfield were characterized by higher abundance of aromatic dinosteroids. All the compounds identified in the m/z 245 mass chromatograms of rock extracts from OKN were relatively low compared to the rock samples from MJI and MJO oilfields. The source rocks were found to be formed from mixed origin (terrestrial and marine) but with significant contribution of dinoflagellates to the organic matter and deposited in freshwater-brackish/saline lacustrine environment. The source rocks were found to have immature to early oil window maturity status based on the distributions and abundance of triaromatic steroids in the source rocks and this was further supported by well-established maturity parameters based on the saturate and aromatic biomarkers. This study showed that the abundance and distribution of triaromatic steroids and triaromatic dinosteroids can be used to assess the origin, depositional environments and thermal maturity of source rocks in the Niger Delta Basin.

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Biological markers, or ‘‘molecular fossils”, which can be identified in extracts of ancient sediments and in crude oils, are routinely used to infer organic facies, depositional environment and thermal history of the host rock or, in the case of petroleum, the source rock(s). Particular classes of molecular fossils in petroleum have found increasing application as age diagnostic markers (Peters *et al.,* 2005). Steranes with 27, 28 and 29 carbons and conventional side chains are important biomarkers for eukaryotic life. Furthermore, those with unconventional side chains offer opportunities for making more specific genetic links between families of organisms and mature sediments and oils (Moldowan *et al.,* 1991).

Triaromatic steroids (TAS) may originate by aromatization and loss of a methyl group (–CH_3) from monoaromatic steroids (Peters et al., 2005). The C_{26}, C_{27}, C_{28} triaromatic steroids potentially retain genetic information about petroleum and source rocks similar to C_{27}, C_{28} and C_{29} regular steranes. 2005). The cross plot of C_{26}/C_{28} 20S versus C_{27}/C_{28} 20R triaromatic steroid ratios have been used to distinguish petroleum systems (Peters et al., 2005). Zhang et al., (2002) and Mi et al., (2007) reported relatively higher abundances of C_{26} 20S, C_{26} 20R + C_{27} 20S and C_{27} 20R TAS in oils derived from Cambrian source rocks, whereas C_{28} 20S and C_{28} 20R TAS are relatively abundant in oils which originated from Middle–Upper Ordovician carbonate source rocks in the Lunnan oil field, Tarim Basin. Also, triaromatic steroids have been successfully applied to thermal maturity assessment of crude oils and source rocks (Xiangchun et al., 2011; Asif and Fazeelat, 2012).

Triaromatic dinosteroids are important molecular fossil groups derived from dinosterols, compounds known to be the almost exclusive, widely occurring natural products of dinoflagellates (Moldowan and Talyzina, 1998; Wang et al., 2008). The highest concentrations of these compounds are typically found in strata deposited since the beginning of the Mesozoic. However, Moldowan and Talyzina (1998) concluded that dinoflagellate ancestors may date back to the Early Cambrian on the basis of biomarker evidence. Zhang et al. (2002) reported the wide occurrence of 24-norcholestane, dinosteranes and triaromatic dinosteroids with relatively high abundance in extracts from organic rich sediments in Cambrian and Precambrian (Sinian) rocks of the Tarim Basin. Biogeochemical evidence for dinoflagellate ancestors were reported in the Early Cambrian (Withers, 1987) and molecular evidence has provided a link of cyst-forming dinoflagellates with pre-Triassic ancestors (Moldowan and Talyzina,

1998). These studies suggest that planktonic algae such as dinoflagellates and diatoms may have originated earlier than the Mesozoic.

However, triaromatic steroids and aromatic dinosteroids have not reported or studied in Niger Delta source rocks. This study is conducted to investigate the distributions and geochemical significance of aromatic steroids and aromatic dinosteroids in Niger Delta source rocks.

MATERIALS AND METHODS

*Geological and Stratigraphic Setting***:** Niger delta is a sedimentary basin situated in the re-entrant of the Gulf of Guinea, West Africa. The sub-aerial portion of the Niger Delta covers approximately 75,000 km^2 and stretches about 200 km from apex to mouth. The total sedimentary prism encompasses 140000 km^2, with a maximum stratigraphic thickness of about 12 km (Whiteman, 1982). The stratigraphy of the thick sedimentary sequence is divided into three lithostratigraphic units, namely the Akata, Agbada and Benin Formations (Short and Stauble, 1967). The uppermost unit, the Benin Formation which ranges from Oligocene to recent in age, comprises continental/fluviatile sands, gravels, and backswamp deposits up to 2500 m thick. These are underlain by the Agbada Formation of paralic, brackish to marine, coastal and fluvio-marine deposits. These are mainly interbedded sandstones and shale with minor lignite organized into coarsening upward 'offlap' cycles. Underlying this unit is the Akata Formation, ranging in age from Paleocene to Miocene consists of mainly of overpressure shales deposited under fully marine conditions. The depobelts are partitioned into 6-7east-west bound blocks corresponding to discrete periods of the deltas evolutionary history starting from the oldest in the north, northern delta to the youngest, offshore in the south (Doust and Omatsola, 1990). It is believed that each depobelt constitutes a more or less autonomous unit with respect to sedimentation, structural deformation and hydrocarbon generation and accumulation (Evamy et al., 1978). 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; Evamy et al., 1978; Ekweozor and Daukoru, 1994). The hydrocarbon habitat of the Niger Delta is mostly the sandstone reservoir of the Agbada Formation where oil and gas are usually trapped in rollover anticlines associated with growth faults.

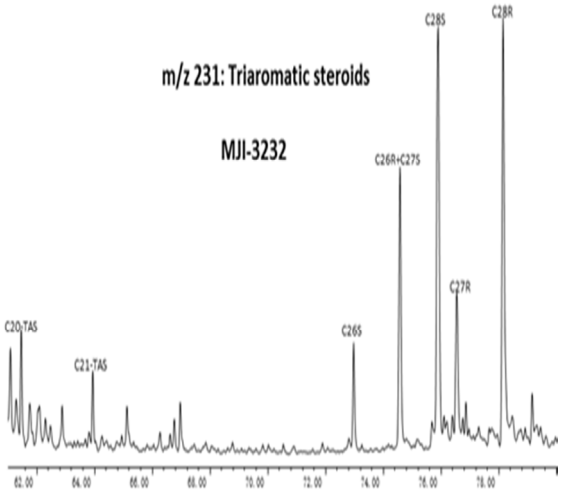
Sampling: Twenty one rock samples from the three wells in three fields in offshore Niger Delta were collected and analyzed.

Extraction and analysis: Rock samples were crushed into powder < 100 mesh and then extracted in batches in a Soxhlet apparatus with 400ml dichloromethane and methanol (93:7, v:v) for 72 h. The rock extracts were separated into saturated and aromatic hydrocarbon fractions using silica gel/alumina chromatography columns eluted with n-hexane and dichloromethane:n-hexane (2:1, v:v), respectively. The GC-MS analyses of the saturate and aromatic fractions were performed on an agilent 5975i gas chromatography (GC) equipped with an HP-5MS (5% phenylmethylpolysiloxane) fused silica capillary column (60m x 0.25mm i.d., x 0.25µm film thickness) coupled to an agilent 5975i mass spectrometry (MS). The GC operating conditions are as follows: the oven temperature was held isothermally at 80˚C for 1 min, ramped to 310˚C at 3˚C/min and held isothermal for 16 min (Li *et al.,* 2012b). Helium was used as the carrier gas with constant flow rate of 1.2 mL/min. The MS was operated in the electron impact (EI) mode at 70eV, an ion source temperature of 250 ^oC and injector temperature of 285^oC. The identification and elution order of fluorene and its derivatives were determined by comparison of their mass spectra and relative retention times in the corresponding mass chromatograms with those reported in literature (Wang *et al.,* 2008a; Li *et al.,* 2012b).

RESULTS AND DISCUSSION

Distribution characteristics of triaromatic steroids and aromatic dinosteroids in source rock extracts from Niger Delta Basin: The m/z 231 and 245 mass chromatograms showing the distributions of triaromatic steroids (TAS) and aromatic dinosteroids in the rock samples are shown in Figure 1 and 2, respectively. The peak identities (m/z 245 mass chromatograms) are shown in Table 1. The source rock extracts from MJI oilfield are characterized by higher abundance of C_{28} 20S and C_{28} 20R triaromatic steroids while C_{26} 20S occur as least (Fig. 1). The higher abundance of C_{28} TAS has been reported in a freshwater lacustrine crude oils from Linnan Subsag, Shandong Province, China (Xiangchun et al., 2011) and crude oils from Ordovician reservoirs from the Tahe oil field, Tarim basin, China (Li et al., 2012b). OKN and MJO rock samples are characterized by the predominance of C_{26} 20R + C_{27} 20S TAS peaks while C_{28} 20S and C_{28} 20R TAS and C_{26} 20S occurred relatively low (Fig. 1). Crude oils and source rocks from saline and brackish lacustrine environments have been reported to contain low abundance of C_{26} TAS (Xiangchun et al., 2011). Also, Cambrian and Lower Ordovician source rocks have been shown to be characterized by lower C_{28} 20S and C_{28} 20R TAS and higher C_{26} 20S, C_{27} 20R and C_{26} 20R + C_{27} 20S TAS peaks, which is similar to those reported in the

literature (Zhang *et al*., 2002; Mi *et al*., 2007; Li *et al.,* 2012b). There are appreciable quantities of C_{20} and C_{21} triaromatic steroids in all the rock samples studied in this work (Fig. 1). Among the methyltriaromatic steroids, dimethyltriaromatic steroids, aromatic dinosteroids and C_{29}, 3-Methyl-, 24-ethyltriaromatic steroids identified in m/z 245 mass chromatograms, C_{21} methyltriaromatic steroids, C_{22} methyltriaromatic steroids and C_{27}, 4-methyltriaromatic steroid + C_{29}, 4-methyl-, 24-ethyltriaromatic steroid are the dominant compounds in the rock samples from MJI oilfield while one of the peaks of aromatic dinosteroids occurs as the least (Fig. 2). Rock samples from MJO oilfield are characterized higher abundance of aromatic dinosteroids while C_{21} and C_{22} methyltriaromatic steroids occur very low (Fig. 2). All the compounds identified in the m/z 245 mass chromatograms of rock extracts from OKN are relatively low compared to the rock samples from MJI and MJO oilfields. The low abundance of these compounds in OKN rock samples may be linked to their immaturity status. The significant amounts of aromatic dinosteroids observed in the rock samples indicates significant contributions of dinofilagellates into the organic matter that formed the source rocks (Li *et al*., 2012b; Zhang *et* al., 2002; Wang *et al*., 2008a).



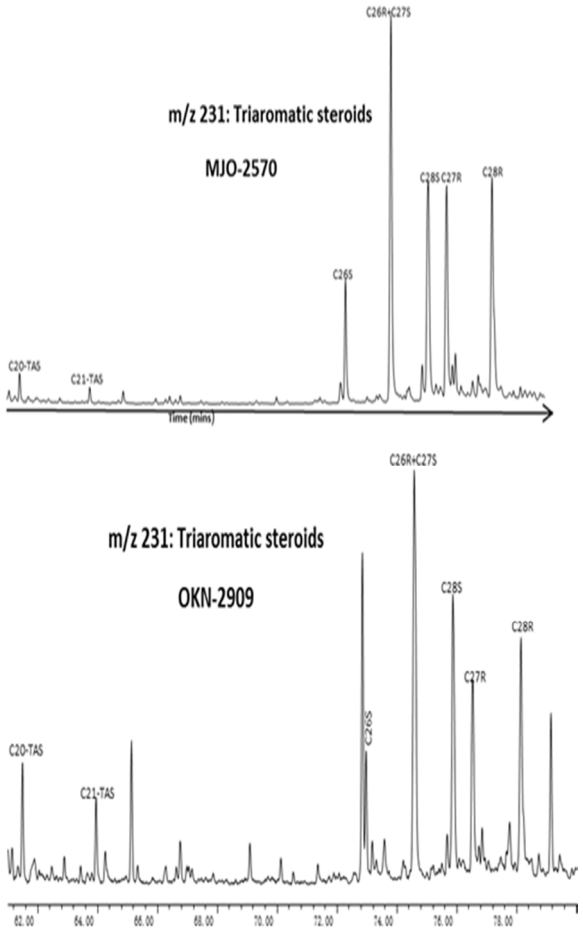
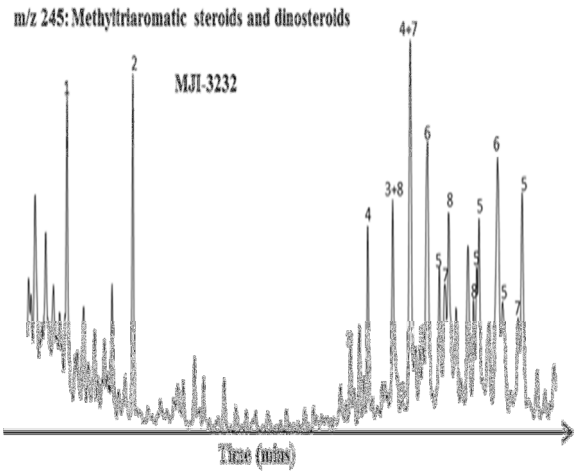


Fig. 1: m/z 231 Mass chromatograms showing the distributions of triaromatic steroids in the source rocks from the Niger Delta



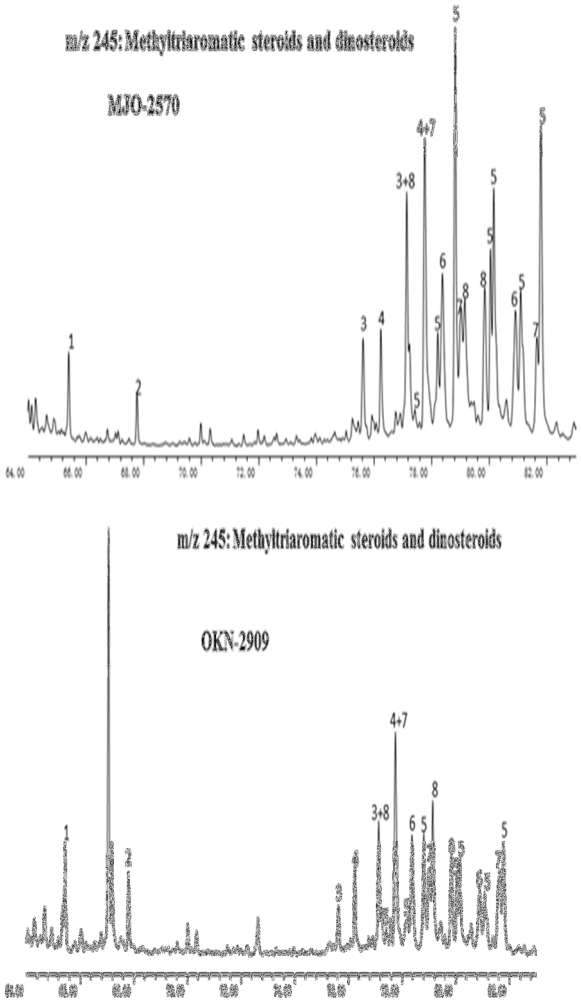


Fig. 2: m/z 245 Mass chromatograms showing the distributions of methyltriaromatic steroids and aromatic dinosteroids in the source rocks from the Niger Delta

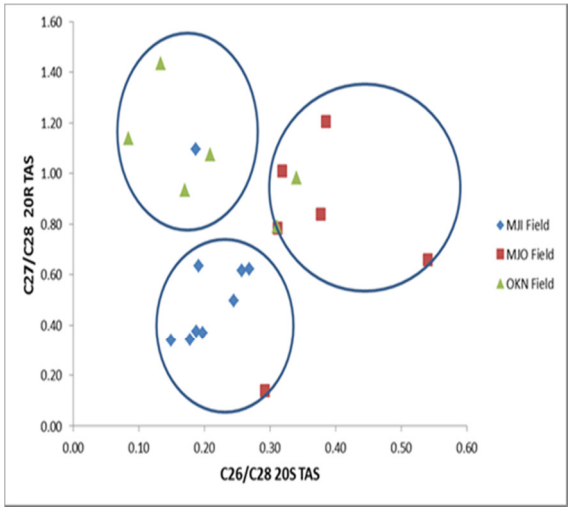


Fig. 3: Cross plots of C_{27}/C_{28} 20R TAS versus C_{26}/C_{28} 20S TAS for Niger Delta rock samples.

Geochemical significance of triaromatic steroids and aromatic dinosteroids in source rock extracts from Niger Delta Basin: The geochemical parameters computed from triaromatic steroids, aromatic dinosteroids and other geochemical parameters are shown in Table 2. The geochemical parameters are used to determine the origin and maturity status of the Niger Delta source rocks. The distributions of aromatic steroids are influenced by multiple factors and thus can be used as indicator of different source inputs and depositional environments. For example, organic matter formed in fresh water environment is abundant with C_{28}-TAS while in saline and brackish water environments it is abundant with C_{26}-TAS (Xiangchun et al., 2011). The C_{26}/C_{28} – 20S TAS and C_{27}/C_{28}- 20R TAS ratios for the rock samples range from 0.08 to 0.54 and 0.14 to 1.43, respectively (Table 2). The low values of C_{26}/C_{28} – 20S TAS recorded in some rock samples indicate source rock formed a freshwater environment while higher values recorded in some samples indicate a lake environment of brackish-saline water (Xiangchun *et al.,* 2011; Li *et al.,* 2012b). These results show that the source rocks studied are formed from the mixed origin (terrestrial and marine) deposited freshwater-brackish/saline lacustrine environments. The cross plots of C_{26}/C_{28} – 20S TAS versus C_{27}/C_{28}- 20R TAS showed that the rock samples from the same field received similar organic material (Fig. 3). The triaromatic dinosteroids are assumed to originate from dinosterol and related sterols, which characterize modern marine dinoflagellates (Moldowan and Talyzina, 1998; Peters *et al.,* 2005). This association suggests that triaromatic dinosteroids are useful biomarkers for improving the recognition of ancient dinoflagellates. The triaromatic dinosteroid hydrocarbon index (TDSI) could be used to reflect the contribution of organic matter from dinoflagellates in the source rocks and crude oils. This parameter has been used to indicate the contribution of dinoflagellates to the oils and source rocks of the Tarim Basin, NW China (Li et al. 2012b) and Paleogene lacustrine sediments from Bohai Bay Basin, China (Wang et al., 2008a). The TDSI values for the rock samples range from 0.53 to 0.79 (Table 2). These values indicate significant contributions of dinoflagellates to the organic matter that formed the source rocks. Progressively more evidence has suggested that dinoflagellates or their ancestors appeared during the Early Cambrian (about 520 Ma, Moldowan and Talyzina, 1998) or even Precambrian (Zhang *et al*., 2002). In this study, the presence of aromatized dinosteroids with extremely high relative concentrations indicates that dinoflagellates or their ancestors lived during the

Cambrian and Early Ordovician in the seas of Niger Delta.

Ratios of C_{26}-TAS 20S/(20S+20R) and C_{28}-TAS 20S/(20S+20R) are mostly used to evaluate thermal maturity (Xiangchun et al., 2011; Asif and Fazeelat, 2012). In the source rocks studied, the ratios are within the range of 0.10 to 0.40 and 0.11 to 0.63 respectively (Table 2), suggesting immature to early mature characteristics. The Methylphenanthrene index (MPI-1) and 20S/(20S+20R) C_{29} steranes for the rock samples range from 0.12 to 0.62 and 0.14 to 0.52 respectively (Table 2), supporting immature to early oil window maturity status (Seifert and Moldowan, 1981; Radke, 1988) already inferred from the from the triaromatic steroids based maturity parameters.

Table 1: The peak identities of the compounds identified in m/z 245 mass chromatograms of aromatic fractions of Niger Delta rock samples.

Peak Number	Compound
1	C_{21} Methyltriaromatic steroid
2	C_{22}Methyltriaromatic steroid
3	C_{27},3-Methyltriaromatic steroid
4	C_{27},4-Methyltriaromatic steroid
3+8	C_{27},3-Methyltriaromatic steroid+C_{28},3,24-Dimethyltriaromatic steroid
5	C_{29}Triaromatic dinoflagellates sterane
4+7	C_{27},4-Methyltriaromatic steroid+C_{29},4-Methyl-, 24-Ehytriaromatic steroid
6	C_{29},3-Methyl-, 24-Ethyltriaromatic steroid
7	C_{29},4-Methyl-,24-Ethyltriaromatic steroid
8	C_{28},3,24-Dimethyltriaromatic steroid

Table 2: Source and thermal maturity parameters computed from triaromatic steroids, aromatic dinosteroids and related compounds in Niger Delta source rocks

Field	Depth(m)	C_{26}/C_{28} 20S TAS	C_{27}/C_{28} 20R TAS	TDSI	S/(S+R) C_{26} TAS	S/(S+R) C_{28} TAS	MPI-1	20S/20S+20R C_{29}
MJI	2079-2098	0.19	1.09	0.65	0.10	0.60	0.25	0.15
MJI	2299-2308	0.26	0.62	0.65	0.19	0.51	0.25	0.15
MJI	2637-2655	0.19	0.63	0.64	0.17	0.55	0.22	0.21
MJI	2857-2875	0.27	0.62	0.67	0.21	0.51	0.37	0.29
MJI	2994-3012	0.25	0.50	0.62	0.22	0.52	0.54	0.30
MJI	3085-3104	0.19	0.37	0.61	0.24	0.51	0.36	0.40
MJI	3232-3250	0.18	0.34	0.55	0.24	0.51	0.45	0.46
MJI	3323-3332	0.15	0.34	0.53	0.22	0.51	0.46	0.52
MJI	3405-3424	0.20	0.37	0.57	0.25	0.51	0.62	0.48
MJO	1616-1707	0.32	1.01	0.54	0.20	0.63	0.23	0.16
MJO	1771-1872	0.29	0.14	0.62	0.21	0.59	0.31	0.41
MJO	2091-2101	0.39	1.20	0.67	0.21	0.63	0.21	0.21
MJO	2293-2366	0.54	0.66	0.67	0.28	0.50	0.47	0.13
MJO	2570-2588	0.31	0.78	0.76	0.20	0.51	0.38	0.19
MJO	2808-2817	0.38	0.84	0.78	0.20	0.49	0.35	0.38
OKN	1537-1555	0.21	1.07	0.72	0.40	0.16	0.16	0.18
OKN	1729-1747	0.08	1.14	0.77	0.21	0.31	0.14	0.14
OKN	2625-2643	0.13	1.43	0.63	0.21	0.11	0.12	0.30
OKN	2780-2799	0.17	0.93	0.79	0.17	0.44	0.16	0.24
OKN	2863-2881	0.34	0.98	0.65	0.15	0.59	0.18	0.34
OKN	2909-2927	0.31	0.79	0.67	0.16	0.54	0.22	0.28

C_{26}/C_{28} 20S TAS = triaromatic steroids ratio; C_{27}/C_{28} 20R TAS = triaromatic steroids ratio; TDSI = Triaromatic dinosteroids/(triaromatic dinosteroids + 3-methyl-24-ethyl triaromatic steroids) index; C_{26} TAS S/(S+R) = C_{26} triaromatic steroids maturity parameters; C_{28} TAS S/(S+R) = C_{28} triaromatic steroids maturity parameters, MPI-1 = methylphenanthrene index 1; 20S/(20S+20R) C_{29} = C_{29} steranes maturity parameters.

Conclusion: Rock samples from the offshore Niger Delta basin, Nigeria were characterized by gas chromatography-mass spectrometry (GC-MS). The source rocks were found to be formed from mixed origin (terrestrial and marine) and deposited in freshwater-brackish/saline lacustrine environment within immature to early oil window maturity. This study showed that the abundance and distribution of triaromatic steroids and triaromatic dinosteroids can be used to assess the origin, depositional environments and thermal maturity of source rocks in the Niger Delta Basin.

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