Source rock geochemistry of shale samples from Ege-1 and Ege-2 wells, Niger Delta, Nigeria

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Abstract
Selected shale samples within the middle Miocene Agbada Formation of Ege-1 and Ege-2 wells, Niger Delta Basin, Nigeria, were evaluated using total organic carbon content (TOC) and Rock–Eval pyrolysis examination with the aim of determining their hydrocarbon potential. The results obtained reveal TOC values varying from 1.64 to 2.77 wt% with an average value of 2.29 wt% for Ege-1 well, while Ege-2 well TOC values ranged from 1.27 to 3.28 wt% (average of 2.27 wt%) values which both fall above the minimum threshold (0.5%) for hydrocarbon generation potential in the Niger Delta. Rock–Eval pyrolysis data revealed that the shale source rock samples from Ege-1 well are characterized by Type II–Type III kerogens which are thermally mature to generate oil or gas/oil. The Ege-2 well pyrolysis result showed that some of the ditch cutting samples are comprised of Type II (oil prone) and Type III (gas-prone kerogen) which are thermally immature to marginal maturity (Tmax 346–439 °C). This study concludes that the shale intercalations between reservoir sands of the Agbada Formation are good source rocks in early maturity and also must have contributed to the vast petroleum reserve in the Niger Delta Basin because of the subsidence of the basin.

Keywords Agbada Formation · Niger Delta · Hydrocarbon potential · Total organic carbon · Rock–Eval

Introduction
The geochemistry of sedimentary rocks is vital to deduce factors that control sediment characteristics during and after their deposition and also to describe the relationship between specific units of both elastic and carbonate strata (Nagarajan et al. 2007; Madhavaraju and Lee 2009). The significance of geochemistry in describing the origin of sedimentary rocks, paleo-weathering conditions as well as tectonic evolutions of sedimentary basins is recognized in many studies (Cullers et al. 1988; Nagarajan et al. 2007; Frimmel 2009). Organic geochemical analyses are unique in determining the hydrocarbon potential of sedimentary rocks as well as playing a pivotal role in the continued development of oil and gas exploration and production (Philp 2014). These analyses have been a significant tool in determining the hydrocarbon prospectivity of the Niger Delta.

The Niger Delta is located on the western coast of Africa between Latitudes 3°50′ and 6°50′ North and Longitudes 3°25′ and 8°50′ (Fig. 1; Akinsanpe and Benjamin 2018). The delta is one of the world’s largest complexes and a prolific hydrocarbon province with estimated hydrocarbon reserves of about 36.2 billion barrels (EIA 2008). The origin of this hydrocarbon is a controversial subject as some published researches believed that the hydrocarbons are sourced from the Akata Formation, while others alleged Agbada Formation (Weber and Daukoru 1975; Short and Stauble 1967). Weber and Daukoru (1975) and Ekweozor and Daukoru (1984) believed that the source of hydrocarbon was only from the Akata Shales, while Short and Stauble (1967) assumed that the shale intercalations between reservoir sands of the Agbada Formation are the main contributor to the hydrocarbon deposit in the basin.

The organic geochemistry of the sediments of the Niger Delta petroleum province has been fairly studied (Ekweozor and Okoye 1980; Nwachukwu and Chukwura 1986; Akaegbobi 2000; Akinlua and Torto 2010; Akinsanpe and Benjamin 2018). Akinlua et al. (2006) studied some shale...
Geochemical information (TOC and Rock–Eval pyrolysis data) on the shales from the Agbada Formation of the basin, however, remains scanty, hence this study. Attempt is made by this study to determine the hydrocarbon potential of the shales from the Agbada section of the Niger Delta Basin using organic matter and Rock–Eval pyrolysis data. This will further shed more light on the origin, environment of deposition and thermal maturity of this section of Niger Delta sequence and also increase the existing organic geochemistry knowledge in the basin.

**Geological background**

The Tertiary Niger Delta is made of regressive clastic sequences which are stratigraphically divided into three main lithostratigraphic units (Short and Stäuble 1967) (Fig. 2). These units consist of the Akata, Agbada and Benin Formations in ascending order with estimated thickness of about 8535 m at the central part of the basin. The Paleocene Akata Formation is characterized by uniform pro-deltaic, medium to dark gray, fairly hard shale. The shale is under-compacted with thickness greater than 3680 m. The Akata Formation has rich foraminiferal fauna, with planktonic foraminifera constituting more than 50% of the microfauna assemblage.
The Eocene Agbada Formation sits directly above the Akata Formation. The formation consists of alternating cyclic sequence of marine shales and fluvial sandstone deposits (Weber 1971). The sandstones are fairly clean, fine to medium grained, glauconitic and shelly, while the shales are medium to dark gray and fairly consolidated. The thickness of the Agbada Formation at the central part of the basin is 3940 m and overlain by the Benin Formation of Oligocene age. The Benin Formation, a continental latest Eocene to Recent deposit, is predominantly made up of medium to coarse-grained, highly porous, freshwater-bearing sandstones. The maximum thickness recorded for this formation is 1970 m (Doust and Omatsola 1990).

Materials and methods

Fourteen selected ditch cutting shale samples from the Agbada section of Ege-1 and Ege-2 wells offshore Niger Delta, Nigeria, were used in this study (Fig. 1) due to the...
physical observation of their organic matter content. Seven samples each for Ege-1 and Ege-2 wells were selected between depths 1970 m and 3720 m and 1950 m and 3650 m, respectively. These samples are believed to be representative of the whole rock since they are from the same Agbada Formation. The selected samples were then air-dried and crushed in a mortar and pestle treated with 70:30 v/v of dichloromethane/methanol and distilled water. This treatment was carried out to remove any form of contamination. The crushed samples were then stored in well-labeled sample bags for further total organic carbon (TOC) and source rock evaluation (Rock–Eval) pyrolysis experimentations.

The sedimentary source rocks represented by weighted percentage of TOC values contain organic matter capable of generating hydrocarbon. According to Tissot and Welte (1984), the lowest value to admit a sedimentary unit as a source rock is 0.3% for carbonates and 0.5% for clastics. The TOC values and organic matter types were determined by using Rock–Eval II pyrolysis system. The organic matter types were used to assess the shales hydrocarbon potential (Espitalié et al. 1977). The Rock–Eval experimentation was used for appraising the hydrocarbon potential of shale rocks by introducing 100 mg of the crushed samples in a metal crucible which was placed into the Rock–Eval analyzer. The samples were heated in the furnace for 3 min at 300 °C. During this process, free hydrocarbon was released from the sample and measured with the flame ionization detector (FID) and then recorded as S1 peak (mg HC/grock). Further increase in pyrolysis temperature to 600 °C at 25 °C/min and hydrocarbon generated during this period was measured on the FID as S2 peak, and the temperature at which the highest hydrocarbon generation occurs during this process was noted as the Tmax (°C). The hydrocarbon generated over the temperature range of 300–390 °C was split into two portions: one part was passed through a thermal conductivity detector (TCD) to measure CO2 as the S3 peak. The S1 peak then provides a measure of the oxygen content of the organic matter. The parameters listed below were achieved at the end of the pyrolysis process:

- S1—the amount of free hydrocarbons exposed before pyrolysis at 300 °C (mgHC/grock);
- S2—the amount of hydrocarbons exposed by the thermal cracking during programmed temperature increments above 300 °C in pyrolysis (mgHC/grock);
- S3—the amount of CO2 exposed below 300 °C (mgCO2/grock);
- Tmax—the temperature at which the S2 peak is at its maximum (°C);
- Hydrogen index (HI)—(S2/TOC) × 100 (mgHC/gTOC);
- Oxygen index (OI)—(S3/TOC) × 100 (mgCO2/gTOC);
- Potential yield or generation potential (PY)—S1 + S2: (mgHC/grock);
- Production index (PI)—(S1/PY) producible hydrocarbons in a source rock;
- S2/S3—oil and gas generation potential or hydrocarbon type index.

### Results and discussion

#### Organic matter potential and hydrocarbon yield

The results of the organic carbon richness and Rock–Eval pyrolysis in the wells are presented in Table 1. The TOC values in corroboration with the Rock–Eval pyrolysis data were used to evaluate the potential of the shale source rocks. The TOC values of all the samples in both wells vary between 1.27 and 3.28 wt% (with an average of 2.28 wt%, Table 1). These TOC values (0.4–4.4 wt%) are comparable to the Niger Delta source rocks examined by earlier authors (Ekweozor and Okoye 1980; Nwachukwu et al. 2000; Adekoya et al. 2014), and they are capable of generating hydrocarbon. Nwachukwu et al. (2000) suggested that the Niger Delta shales contained an average of 1.2 wt% TOC; with weight percent of the studied samples at 2.28 wt%. Tissot and Welte (1984) reported that clastic source rocks of TOC values greater than 0.5 wt% are capable of generating petroleum. The TOC of Ege-2 well gradually increases with depth (average value of 2.27) as shale source rocks with at least minimum organic matter content are sufficient to generate petroleum provided there were enough heat and depth of burial more than 2 km (Akinsanpe and Benjamin 2018). The depth plots of TOC in both wells (Fig. 3) showed that the organic richness of the shales ranges from low to good.

The Rock–Eval pyrolysis analyses revealed that the samples in the two wells displayed a remarkable difference in free hydrocarbon with S1 varying from < 1.0 in most of the samples to over 8.0 mgHC/g Rock (Table 1). The hydrocarbon (S2) yield generated during pyrolysis was less than 4.0 mgHC/gTOC in all the samples except A3, B5 and B7 shales with S2 values 4.80, 7.72 and 9.71 mgHC/gTOC, respectively. This yield is indicative of source rocks with poor generative potential (Bordenave 1993). This is in agreement with the depth plots of S2 which showed that the hydrocarbon potential of the shales in both wells varies from poor to good (Fig. 3) since the S2 varies between 1.67 and 9.71 mgHC/grock. Recent hydrocarbon exploration researches showed that S2/TOC > 1 is suggestive of the presence of considerable free oils in sample (Li et al. 2018; Adekola and Akinlua 2012) and is considered as oil show (Behar et al. 2003). The ratios of S2/TOC range between 0.30–3.74 in Ege-1 well and 0.19–1.77 in Ege-2 well. The values are typical of source rocks entering the oil window except shale samples A3, A4, A6 and B5 (3.74, 3.78, 2.20 and 1.77) with values exceeding 1.5. This is indicative of a contribution of
nonindigenous oil (Smith 1994). These studied samples (A3, A4 and A6 in Ege-1 well and B5, B7 in Ege-2 well) of greater depth have S1/TOC > 1 and are considered as oil show. This is further corroborated with the depth plots of S2/TOC indicating that samples of Ege-1 well are capable of generating gas as those of Ege-2 mainly produce gas/oil (Fig. 3). Peters (1986) reported that for mature source rock, HI for gas-prone organic matter is less than 150 and that for gas-oil-prone organic matter ranges between 150 and 300, whereas the oil-prone organic matter is more than 300 HI. The result from this study showed that five samples each from Ege-1 well (A1, A2, A5, A6 and A7) and Ege-2 well (B1, B2, B3, B4 and

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Table 1 Results of Rock–Eval pyrolysis of ditch cutting samples from Ege-1 and Ege-2 wells

| Well | Sample laboratory code | Depth (m) | TOC | S1 | S2 | S3 | S2/S3 | HI | OI | PI | Tmax (°C) | S1/TOC | PY |
|------|------------------------|-----------|-----|----|----|----|-------|----|----|----|-----------|--------|-----|
| Ege-1 | A1 | 1970 | 2.51 | 0.76 | 2.20 | 2.36 | 0.93 | 88 | 94 | 0.26 | 433 | 0.30 | 3.27 |
|      | A2 | 2180 | 2.22 | 0.88 | 2.90 | 1.55 | 1.87 | 131 | 70 | 0.23 | 432 | 0.40 | 3.10 |
|      | A3 | 2350 | 2.40 | 8.97 | 4.80 | 1.27 | 3.78 | 200 | 53 | 0.65 | 432 | 3.74 | 11.37 |
|      | A4 | 2500 | 1.64 | 5.55 | 2.85 | 1.28 | 2.23 | 174 | 78 | 0.66 | 433 | 3.38 | 7.19 |
|      | A5 | 2570 | 2.23 | 0.67 | 3.11 | 1.82 | 1.71 | 139 | 82 | 0.18 | 434 | 0.30 | 2.90 |
|      | A6 | 3350 | 2.77 | 6.10 | 3.54 | 1.24 | 2.85 | 128 | 45 | 0.63 | 432 | 2.20 | 8.87 |
|      | A7 | 3720 | 2.25 | 0.83 | 2.32 | 1.68 | 1.38 | 103 | 75 | 0.26 | 439 | 0.37 | 3.08 |
| Ege-2 | B1 | 1950 | 1.42 | 0.45 | 1.87 | 1.21 | 1.55 | 132 | 85 | 0.19 | 433 | 0.32 | 1.87 |
|      | B2 | 2850 | 1.98 | 0.67 | 2.67 | 1.32 | 2.02 | 135 | 67 | 0.20 | 431 | 0.34 | 2.65 |
|      | B3 | 3130 | 2.18 | 0.41 | 1.97 | 3.26 | 0.60 | 90 | 150 | 0.17 | 434 | 0.19 | 2.59 |
|      | B4 | 3160 | 2.47 | 1.65 | 2.44 | 1.89 | 1.29 | 99 | 77 | 0.40 | 432 | 0.67 | 4.12 |
|      | B5 | 3550 | 3.28 | 5.79 | 7.72 | 1.21 | 6.38 | 235 | 37 | 0.43 | 397 | 1.77 | 9.07 |
|      | B6 | 3510 | 1.27 | 0.34 | 1.67 | 2.03 | 0.82 | 131 | 160 | 0.17 | 430 | 0.27 | 1.61 |
|      | B7 | 3650 | 3.27 | 3.62 | 9.71 | 1.18 | 8.23 | 297 | 36 | 0.27 | 396 | 1.11 | 6.89 |

TOC total organic carbon (wt%), S1 mgHC/grock, S2 hydrocarbon generated from the thermal breakdown of kerogen (mgHC/grock), S3 CO2 value (mgCO2/gTOC), Tmax the temperature at which the maximum release of hydrocarbons from the cracking of kerogen during pyrolysis (°C), HI Hydrogen index (mgHC/gTOC), OI oxygen index (mgCO2/gTOC), PI production index (mgHC/gTOC), PY(S1 + S2) potential yield (mg HC/grock) and S2/S3 hydrocarbon-type index.

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Fig. 3 Depth plots of S2/TOC, TOC and S2 of a Ege-1 well and b Ege-2 well
have HI values less than 150 mgHC/gTOC. This shows that the organic matter is gas prone. The two other samples in the wells (A3 and A4) and (B5 and B7) have HI ranging between 150 and 300 mgHC/gTOC, which signifies gas-oil-prone organic matter. These results are comparable to the shale samples analyzed from the Agbada Formation by Nyantakyi et al. (2014). Their result showed that most of the samples studied have HI values less than 150 mgHC/gTOC.

Thermal maturity of the organic matter and hydrocarbon yield

The samples studied are associated with low $T_{\text{max}}$ (< 432 °C in Ege-1 well and < 400 °C in Ege-2 well) showing decreasing trend with $T_{\text{max}}$. This is suggestive of an early onset of hydrocarbon generation or an abnormal trend due to influence from in-migrated hydrocarbons (Li et al. 2018). This possibility is corroborated with the plot of HI against $T_{\text{max}}$ and HI against TOC, and the ratios of $S_2/S_3 > 1$ suggest the samples studied as immature to mature Types II to III organic matter capable of generating fair oil to gas/oil (Figs. 4, 5). This plot agreed with the plot of $S_2$ against TOC signifying that the samples are mainly Type II–Type III organic matter (Fig. 4).

The total hydrocarbon yield (PY) determined by the sum of $S_1$ and $S_2$ for the wells showed that PY ranges from 2.96 to 13.77 mgHC/grock in Ege-1 well (average of 6.50 mgHC/grock) indicative of fairly significant amount of hydrocarbon generation in the samples. The highest hydrocarbon yield of 13.77 mgHC/grock was recorded within Ege-1 well section at 2350 m which indicates rich source rock with a TOC value of 2.40 wt% has potential to expel generated hydrocarbon. Ege-2 well section also showed a low PY (< 5.85 mgHC/grock) indicating that the shales within this well generated fairly significant hydrocarbon which is low for expulsion. Rich source rock with potentials to expel...
generated hydrocarbon occurred at 3550 m and 3650 m (PY > 13 mgHC/grock).

**Conclusion**

The TOC and Rock–Eval pyrolysis results from the shale samples of the Agbada Formation in wells Ege-1 and Ege-2 were used to deduce the hydrocarbon potential of selected shale samples from the wells. The results showed that all the shale samples in both wells have high TOC values ranging between 1.27 and 3.28 and Types II and III kerogens capable of generating oil to gas/oil. The plot of the HI against $T_{\text{max}}$ which is indicative of thermal maturity with $S_1$, $S_2$, $S_3$ and OI parameters showed that the samples range from immature to mature Types II–III organic matter capable of generating fair oil to gas/oil.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they do not have conflict of interest.

**Availability of data and material** The data from the work are included in the write-up.

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