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Oil residue in exhumed fractured Precambrian basement rock of the Northern Benue Trough, Nigeria: Implication for oil exploration in the Northern Benue Trough

By

Timothy Bata[1], M.B. Abubakar[1 & 2], A.S. Maigari[1], Nuhu K. Samaila[1], Ahmed Isah Haruna[1], Babangida M. Sarki Yandoka[2], Bappah Adamu Umar[2], Nuru Nabage[1], Umar Sambo Umar[1], Simon Y. Ikyoive[1], Ezekiel H. Elijah[3], Mustapha Aliyu[1], Abdulmajid Isah[1], Yusuf Abdulmumin[1], Abdulkarim Haruna Aliyu[2], Idris Ismail Kariya[1], Mohammed Rabiu[1], Ameh Daniel Peter[1], Jabbo Josiah Nuhu[4]

Abstract
This study presents for the first-time field, petrographic and geochemical evidence of oil residue in exhumed fractured Precambrian basement rocks of the Northern Benue Trough. The studied oil residues which are brittle solids, are believed to have been emplaced into fractures of the basement rocks as conventional light oils, but have been degraded. Pyrite crystals are closely associated with the fractured basement reservoir. These pyrite crystals are inferred to have a biogenic origin attributed to microbial activity as part of the biodegradation processes. Total ion current (TIC) fragmentogram of the saturate fractions of the studied oil residue shows progressive depletion of chromatographically resolved hydrocarbons relative to the unresolved hydrocarbon mixture, forming an unresolved complex mixture (UCM) hump consistent with oils that have undergone biodegradation. Pristane (Pr) and Phytane (Ph) are present on the m/z 85 fragmentogram in abundance lower than those of the adjacent n-alkanes, resulting in Pr/nC17, Ph/nC18 and Pr/Ph ratios < 1.0, suggesting suboxic to anoxic depositional environment for the source of the oil. Sterane maturity parameters, ααα C_{27}20S/(20S+20R), ααα C_{28}20S/(20S+20R), and ααα C_{29}20S/(20S+20R), are 0.50, 0.47, and 0.35, respectively, for the studied oil residue, consistent with oils derived from source rocks that have thermal maturities equivalent to early and peak oil generation. The trisnorhopane thermal indicators (Ts:Tm ratio) of 1.08, and 22S/(22R+22S) C_{32} homohopane isomerization ratio of 0.61 agrees with the sterane maturity parameters of the oil residue which implies that the source rock for the oil residue is within the oil window. Sterane distribution for the oil residue shows strong resemblance to the strerane distribution of extracts of Bima Shales, implying that the oil was sourced from shales of the Bima Formation. The basement rocks occur below a regional plane of unconformity which is inferred to have acted as an important migration pathway for the oil residue. Occurrence of oil residue in fractures of the exhumed Precambrian basement rocks of the Northern Benue Trough implies that the fractured Precambrian basement rocks are important petroleum reservoir rocks in the region.

Keywords: Basement Petroleum Reservoirs; Northern Benue Trough; Biodegradation; Pyrite Crystals; Oil Residue.

[1] Department of Applied Geology, Abubakar Tafawa Balewa University, Bauchi, Nigeria
[2]National Centre for Petroleum Research and Development, A.T.B.U., Bauchi, Nigeria
[3]National Productivity Center Bauchi
[4]Department of Geological Technology, Abubakar Tatari Ali Polytechnic Bauchi, Nigeria
*Corresponding Author: e-mail: t.p.bata00@aberdeen.ac.uk

Highlights:

- We present for the first time, field, petrographic and geochemical evidences of oil residue in Precambrian basement rocks of the Northern Benue Trough Nigeria.
- Sterane data presented suggests that the studied oil was sourced from shales of the Bima Formation.
- The studied basement rocks occur below a regional plane of unconformity which is inferred to have acted as an important migration pathway for the studied oil.

1.0 Introduction

It has long been known that oil occur in fractured basement rocks globally such as in Venezuela, Argentina, Brazil, China, Egypt, Angola, Morocco, Libya, Yugoslavia, Hungary, Romania, USSR and the USA[2]. Recent interest in unconventional reservoirs includes a focus on the potential of fractured basement reservoirs. Initially, petroleum basement reservoirs were discovered by accident at the bottom of wells, but drilling into the basement is now a deliberate plan in several oilfields.

Sedimentary source feeds basement petroleum reservoirs rocks, but differ from many sedimentary reservoirs in that the source rocks do not lie underneath. It is not strictly essential that a source rock underlies a reservoir rock, and hydrocarbons may migrate downwards due to compactional squeezing of the source rock above a porous reservoir[3]. Basement rocks can function as reservoirs where they form topographic highs on the basement surface, flanked by sedimentary rocks. Granites, form such highs. In most oilfields of this type, the source rocks overlap the high in which the oil is reservoir. Commonly, the overlapping sedimentary rocks function as a cap to the reservoir.

Many basement reservoirs occur below regional unconformities[4], which have a two-fold significance. Palaeo-exposure of the basement allows the alteration and leaching of unstable minerals and the enlargement of fractures to increase porosity and permeability; and a regional unconformity can be a major pathway for hydrocarbon migration[5]. Fracture porosity is often very significant in basement rocks, as evidenced by the worldwide function of basement rocks as aquifers. Where fractured basement rocks are connected to active petroleum source rocks, the fracture porosity can be 'prolifically productive'[6]. In this study, we present for the first-time

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[2] Tong, K., Zhao, C., 2012. Reservoir evaluation and fracture characterization of the metamorphic buried hill reservoir in Bohai Bay Basin. Petroleum Exploration and Development, 39, 62–69.; Trice, R. 2014. Basement exploration, West of Shetlands: progress in opening a new play on the UKCS. In: Cannon, S.J.C. & Ellis, D. (eds) **Hydrocarbon Exploration to Exploitation West of Shetlands**. Geological Society, London, Special Publications, 397, 81–105, https://doi.org/10.1144/SP397.3; Parnell, J., Baba, M., Bowden, S., Muirhead, D., 2017. Subsurface biodegradation of crude oil in a fractured basement reservoir, Shropshire, UK. **Journal of Geological Society**, 174, pp 655 -666.

[3] Parnell, J. 1987. The occurrence of hydrocarbons in Cambrian sandstones of the Welsh Borderland. **Geological Journal, 22**, 173–190.

[4] Chung-Hsiang, P., 1982. Petroleum in basement rocks Bull. **Am. Assoc. Petrol GeoL Bull. 66**, 1597-1643.

[5] Halbouty, M. T., 1972. Rationale for deliberate pursuit of stratigraphic, unconformity, and paleogeomorphic traps Bull. **Am. Assoc. Petrol GeoL Bull 56**, 537-541.

[6] Parnell, J. 1987. The occurrence of hydrocarbons in Cambrian sandstones of the Welsh Borderland. **Geological Journal, 22,** 173–190.

field, petrographic and geochemical evidence of oil residue in exhumed fractured Precambrian basement rocks of the Northern Benue Trough.

2. **Geological Setting**

The Benue Trough is a sediment-filled northeast trending rift basin in Nigeria that stretches for about 800 km in length and about150 km in width. It is believed to have developed from incipient rifting that occurred during the Cretaceous breakaway of South America from Africa and the opening of the South Atlantic Ocean (Whiteman, 1982). The outcropping stretch of the Benue Trough borders Chad Basin to the north, and the Niger Delta to the south and is geographically divided into southern, central and northern sectors. Sediment thickness attains 6000 m in places and is exclusively Cretaceous in age (Fig. 1; Nwajide, 2013).

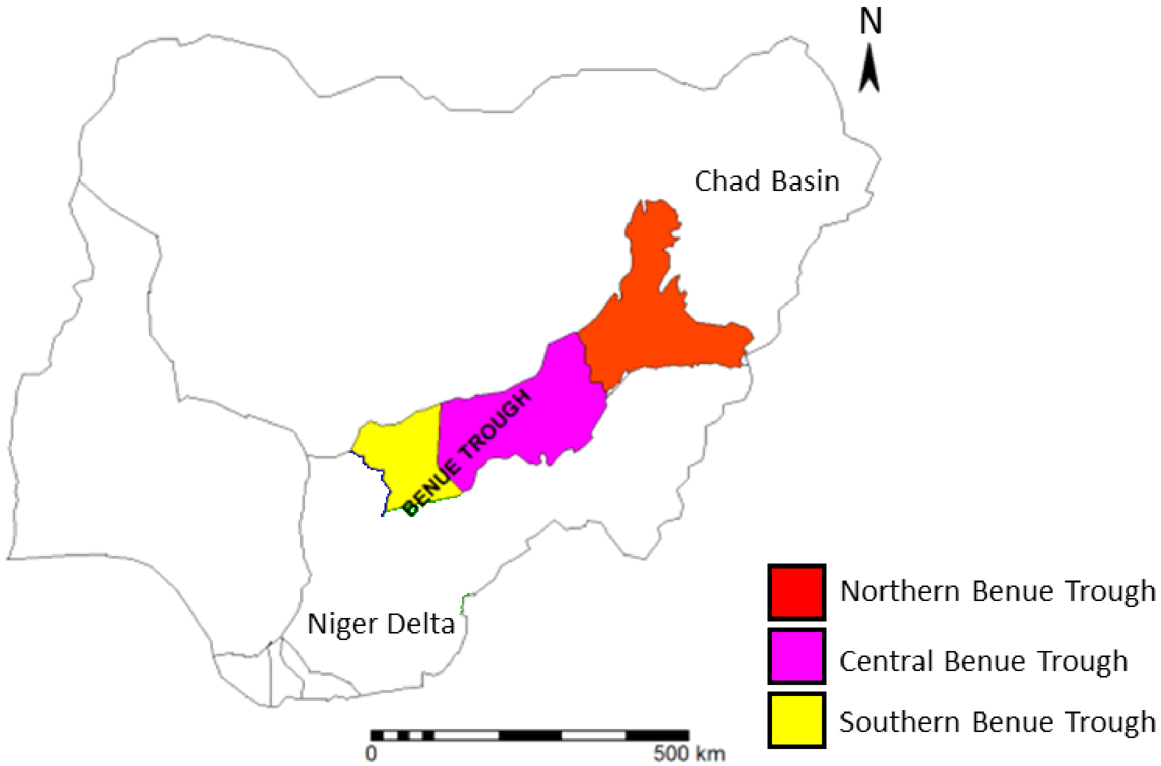

Figure 1: Outline map of Nigeria, showing the Benue Trough.

The Benue Trough has been a subject of several academic discussions especially as regards palaeogeography, sedimentology, structural geology, mineral and hydrocarbon explorations[7].

[7] Samaila, N.K., Dike, E.F.C., Obaje, N.G., 2008. Microstructures in the Cretaceous Bima Sandstone, Upper Benue Trough, NE Nigeria: Implication for hydrocarbon migration. **J. Afr. Earth Sci. 50**, 6–15.; Abubakar, M.B., 2014. Petroleum potentials of the Nigerian Benue Trough and Anambra basin: a regional synthesis. **Nat. Resour. 5** (1), 25-58.; Akande, S.O., Egenhoff, S.O., Obaje, N.G., Ojo, O.J., Adekeye, O.A., Erdtmann, B.D., 2012. Hydrocarbon potential of Cretaceous sediments in the Lower and Middle Benue Trough, Nigeria: Insights from new source rock facies evaluation. **J. Afr. Earth Sci. 64,** 34–47.

At its northern end, the Benue Trough is divided into two arms: the Gongola Sub-Basin which runs northwards into the Chad Basin, and the Yola Sub Basin which runs eastwards, terminating against the Cameroon basement rocks. In both basins, Precambrian basement rocks are overlain by the Bima Formation which is the oldest sedimentary succession in the region (Fig 2). Again, in both basins, the Bima Formation is conformably overlain by the transitional/coastal marine Yolde Formation (Cenomanian) which marks the onset of marine incursion into the Northern Benue Trough. In the Gongola Sub-Basin, the Pindiga Formation conformably over lies the Yolde Formation. The Pindiga Formation is believed to have been deposited by a major marine incursion that occurred during the late Cenomanian to early Santonian[8]. Lateral equivalents of the Pindiga Formation in the Yola Sub-Basin of the Northern Benue Trough are the the Dukul, the Jessu, the Sekuliye, the Numanha and the Lamja Formations (Fig, 3).

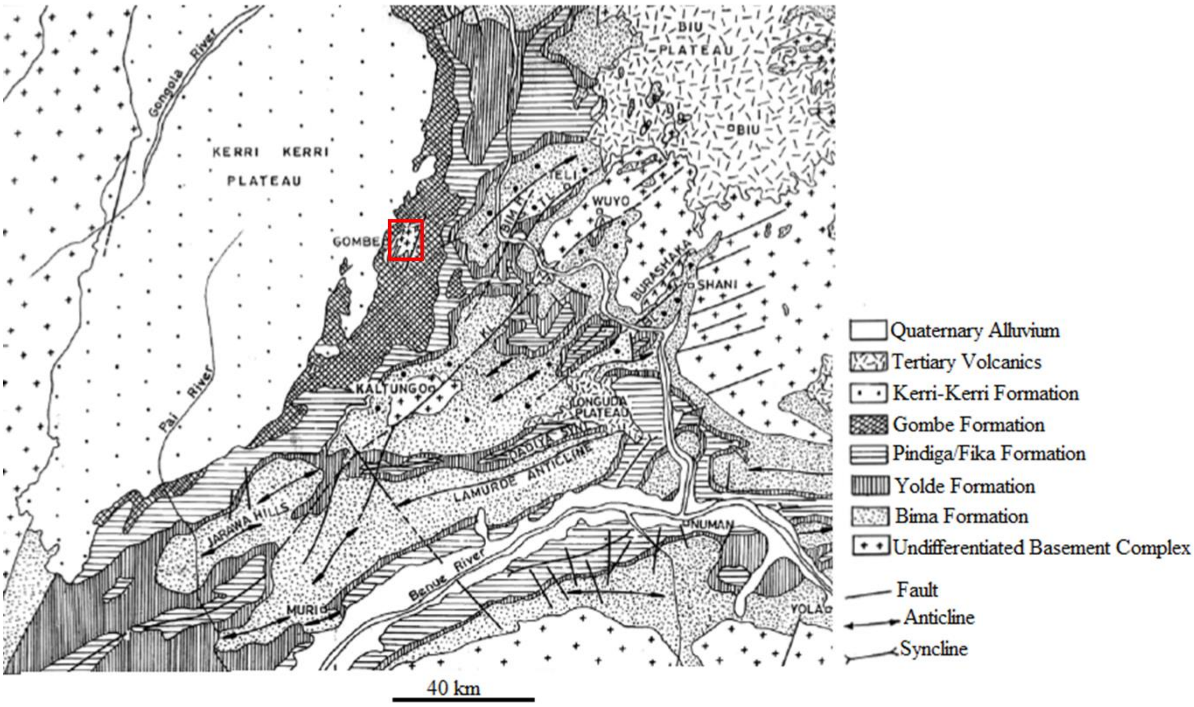

Figure 2 Geologic map of the Northern Benue Trough (modified from Benkhelil, 1989[9]), showing studied locality (red box)

The Benue Trough witnessed tectonic deformation especially folding during the mid-Santonian. Cretaceous sediments which pre-dates the mid-Santonian were folded, faulted and

[8] Abubakar, ibid

[9] Benkhelil, J., 1989. The origin and evolution of the Cretaceous Benue Trough (Nigeria). **Journal of African Earth Sciences 8**, 251–282.

uplifted in several places within the region[10]. This was followed by a compressive phase that occurred at the end of the Maastrichtian which affected the Gombe Formation[11].

Several lines of evidence point to organic-rich sediments with oil-generating capabilities occurring in the Northern Benue Trough. These include the Yolde, Pindiga and Fika Formations in the Gongola Sub-Basin and their lateral equivalents in the Yola Sub-Basin of the basin which includes Yolde, Dukul, Jessu, Sekuliye, Numanha and Lamja Formations[12]. Possible petroleum reservoir rocks occurring in the Northern Benue Trough include sandy units of the Bima, Yolde, Pindiga, Fika and Gombe Formations. Three exploration wells (Kolmani River-1, Kuzari-1 and Nasara -1) drilled into the Gongola Sub-Basin of the Northern Benue Trough showed no significant commercial oil discovery, except in the Kolmani River 1 well, where 33 BCF of gas with associated oils were encountered (Obaje et al., 2004).

[10] Abubakar, M.B., Dike, E.F.C., Obaje, N.G., Wehner, H., Jauro, A., 2008. Petroleum prospectivity of Cretaceous formations in the Gongola Basin, Upper Benue Trough, Nigeria: an organic geochemical perspective on a migrated oil controversy. **J. Petroleum Geol.** 31 (4), 387–408.
[11] Zaborski, P. M., 2003. Guide to the Cretaceous System in the Upper Part of the Upper Benue Trough, Northeastern Nigeria," **African Geosciences Review**, 10, pp. 13-32.
[12] Habib, M., Xie, C., 2012. Nigeria's inland basins: Investment opportunities and environment. **Journal of Petroleum and Gas Exploration Research 2**, 202–211. Akande, S.O., Egenhoff, S.O., Obaje, N.G., Ojo, O.J., Adekeye, O.A., Erdtmann, B.D., 2012. Hydrocarbon potential of Cretaceous sediments in the Lower and Middle Benue Trough, Nigeria: Insights from new source rock facies evaluation. **J. Afr. Earth Sci.** 64, 34–47.; Abubakar, M.B., 2014. Petroleum potentials of the nigerian Benue Trough and anambra basin: a regional synthesis. **Nat. Resour. 5** (1), 25-58.

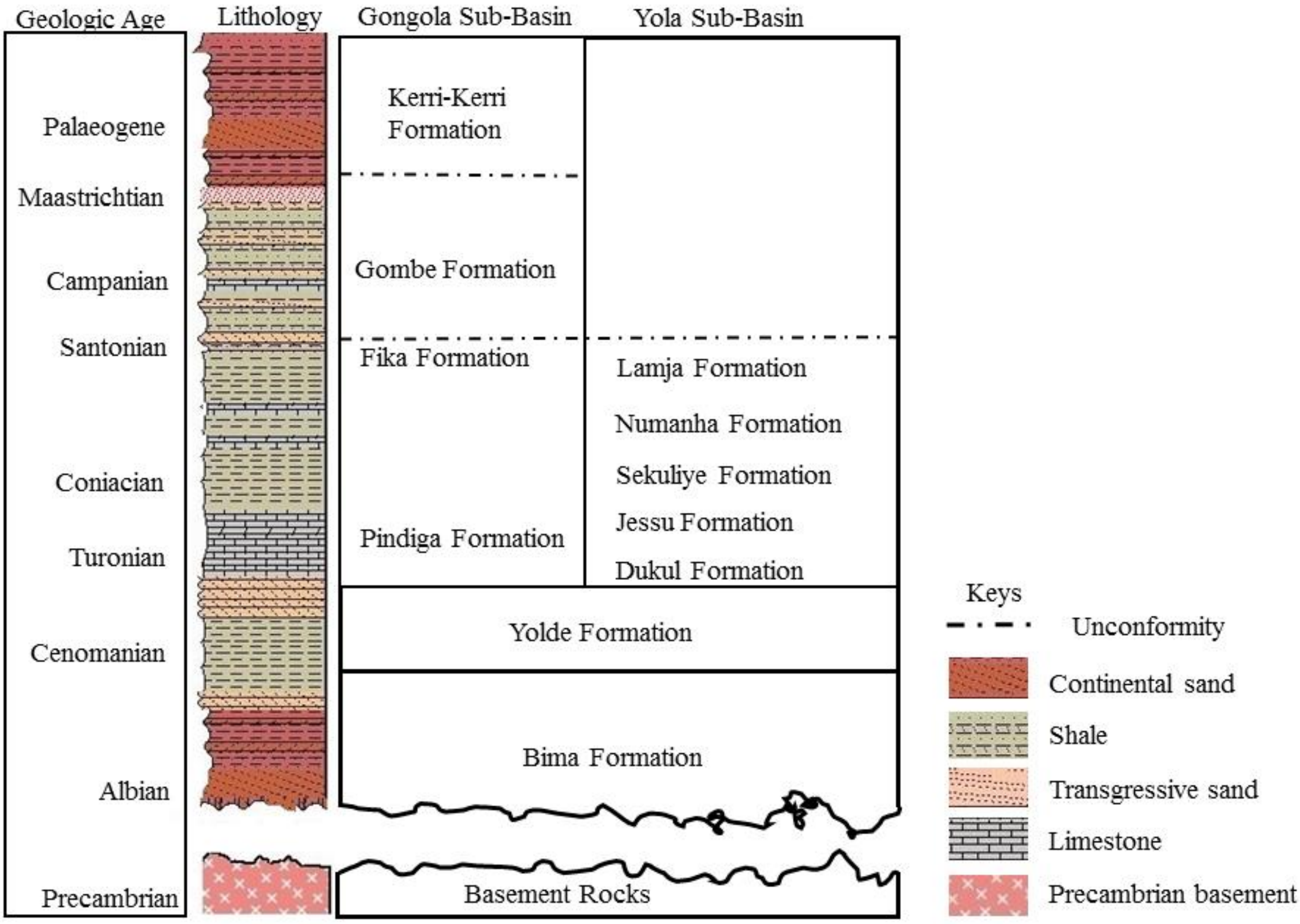

Figure 3 Simplified stratigraphy of the Northern Benue Trough.

3. **Methodology**

Samples of the exhumed Precambrian basement rocks from the studied locality (Fig. 4) were prepared as polished thin sections using the method described by Reed (2005) and Bata et.al. (2017). The polished thin sections were examined using petrographic microscopes, and photomicrographs were shot. Scraped oil residues from fractures of the exhumed basement rocks were solvent-extracted using 93:7 (v/v) dichloromethane and methanol. The extracted oils were then separated into saturate, aromatics, and polar fractions using thin layer chromatography.

The saturate fraction was then examined by gas chromatography-mass spectrometry (GC-MS). The GC-MS analysis was carried out with an Agilent 6890N GC fitted with a J & W DB-5 phase 50-m-long column that is linked to a 5975 MSD and a quadruple mass spectrometer working in selected-ion monitoring (SIM) mode with ionization energy of 70 eV. Samples were manually injected with a split/splitless injector working in splitless mode (purge 40 ml min^{-1} for 2 min). The temperature ranges of the GC oven varied between 80 and 295 °C. The GC oven was held at the initial temperature of 80 °C for two minutes, increasing by 10 °C min^{-1} for 8 min, then by 3 °C min^{-1}, and finally to the highest temperature of 295 °C for 10 minutes. Compounds were identified by matching retention times to well-characterized materials that served as reference samples.

Quantitative biomarker data were obtained for isoprenoids, steranes, diasteranes, hopanes, and 25-norhopanes by measuring responses of these compounds on m/z 85, 217, 191 and 177mass chromatograms respectively. Thermal maturity was estimated from the Ts/Tm terpanes and 20S/ (20S + 20R) ratio for regular steranes, based on the increasing proportion of the S isomer with maturation[13].

4. Results

The sampling site of the exhumed fractured Precambrian basement considered in this study occurs around the Gombe inlier in Gombe town within the Gongola Sub-Basin of the Northern Benue Trough. The Gombe inlier consists of exhumed rocks of the ‘older granite’ series which are unconformably overlain by the Cretaceous Bima sandstone (Fig. 4). The Gombe inlier is of critical stratigraphic importance because in a narrow area, it shows virtually all of the Cretaceous geology of the Northern Benue Trough through easily accessible, good quality rock exposures[14].

Figure 4: Field photograph showing the studied exhumed Precambrian basement rocks, the plane of unconformity and the Cretaceous Bima Formation above.

[13] Peters, K.E., Moldowan, J.M., 1993. **The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments**. Prentice Hall, Englewood Cliffs, NJ.
[14] Zaborski, P. M., 2003. Guide to the Cretaceous System in the Upper Part of the Upper Benue Trough, Northeastern Nigeria,” **African Geosciences Review, 10**, pp. 13-32.

At the Gombe Inlier, the Gombe fault and the Wuro Ladde – Wurin Dole fault systems show clear evidence of restrictive bends and/or step overs within the inlier thereby offering a rare field opportunity for the study of strike-slip faulting and associated transpressional features. Patches of oil residues were observed within the weathered part of the exhumed basement rocks at the Gombe Inlier (Fig. 5a). Oil residue were also observed within the exposed fractures of the exhumed Precambrian granitic rocks at the study area (Fig. 5b).

Figure 5: Field photographs of the exhumed Precambrian basement rocks at the Gombe Inlier showing: (a) Patches of oil residue (red arrows) within the weathered basement, (b) Oil residue (red arrow) along fractures of exhumed Precambrian basement rocks.

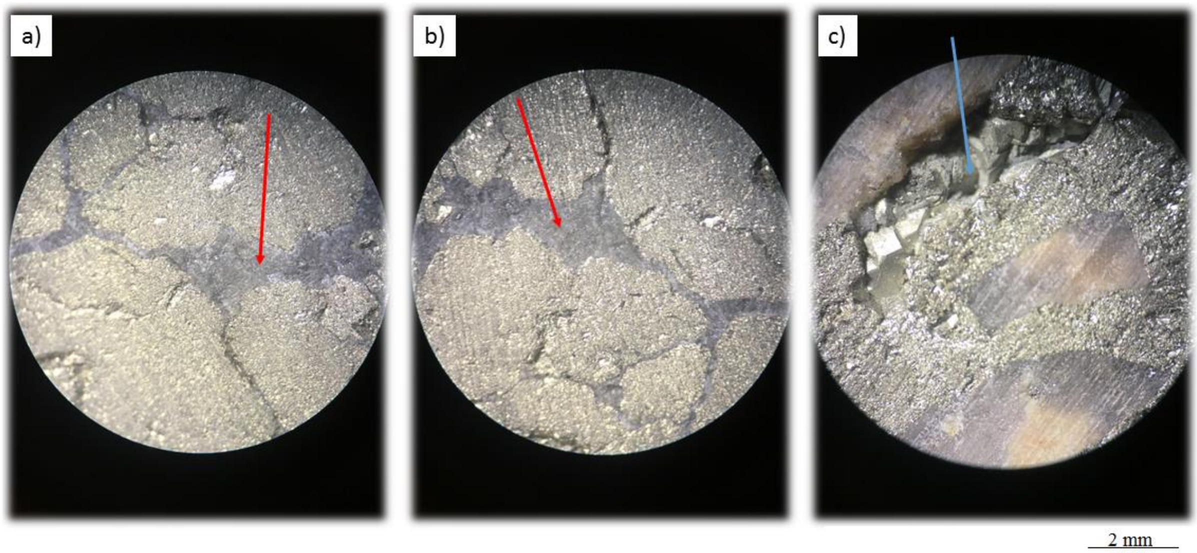

Figure 6: Photomicrographs showing (a & b) Oil residue within fractures of the studied Precambrian rock (c) Pyrite crystals associated with the studied Precambrian reservoir.

Photomicrographs of the studied exhumed basement rock shows evidence of oil residue within the fractures of the studied rock (Fig. 6). The observed fractures range from a few millimeters to about 1 cm in their maximum dimension (Figs. 6 a & b). The oil residue occurring in fractures of the studied basement rock are closely associated with pyrite crystals (Fig. 6c).

Authigenic pyrite crystals are known to be closely associated with oil residues and biodegraded oils[15].

TIC fragmentogram of the saturate fractions of the studied oil residue shows progressive depletion of chromatographically resolved hydrocarbons (e.g. *n*-alkanes, acyclic isoprenoid alkanes; alkyl benzenes, naphthalenes and phenanthrenes) relative to the unresolved hydrocarbon mixture, forming an unresolved complex mixture (UCM) humps (Fig. 7a). UCM is a common characteristic of oils that have undergone biodegradation. *m/z* 85 fragmentogram of the saturate fraction of the studied oil residue showing preserved *n*-alkanes and acyclic isoprenoids (n-C_{16} to n-C_{33}) is presented in Figure 7b. Pristane (Pr) and Phytane (Ph) are present in lower abundance than those of the adjacent n-alkanes, resulting in Pr/nC17 and Ph/nC18 ratios < 1.0. Pr/Ph ratio for the studied oil residue is 0.63, suggesting suboxic to anoxic depositional environment for the source of the oil[16].

[15] Fallick, A.E., Boyce, A.J., Mcconville, P., 2012. Sulfur stable isotope systematics in diagenetic pyrite from North Sea hydrocarbon reservoirs revealed by laser combustion analysis. **Isotopes in Environmental and Health Studies**, **48,** 144-165.; Bata, T., Parnell, J., 2014. A Neoproterozoic petroleum system in the Dalradian Supergroup, Scottish Caledonides. **J. Geol. Soc. Lond**. 171, 145–148.; Parnell, J., Bellis, D., Feldmann, J., Bata, T., 2015. Selenium and tellurium enrichment in palaeo-oil reservoirs. **Journal of Geochemical Exploration**, 148, 169-173.; Bata, T., Parnell, J., Bowden, S., Boyce, A., 2016. Origin of Heavy Oil in Cretaceous Petroleum Reservoirs. Accepted manuscript: Bull. **Can. Pet. Geol**.- in press.

[16] Peters, K.E., Moldowan, J.M., 1993. **The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments**. Prentice Hall, Englewood Cliffs, NJ.

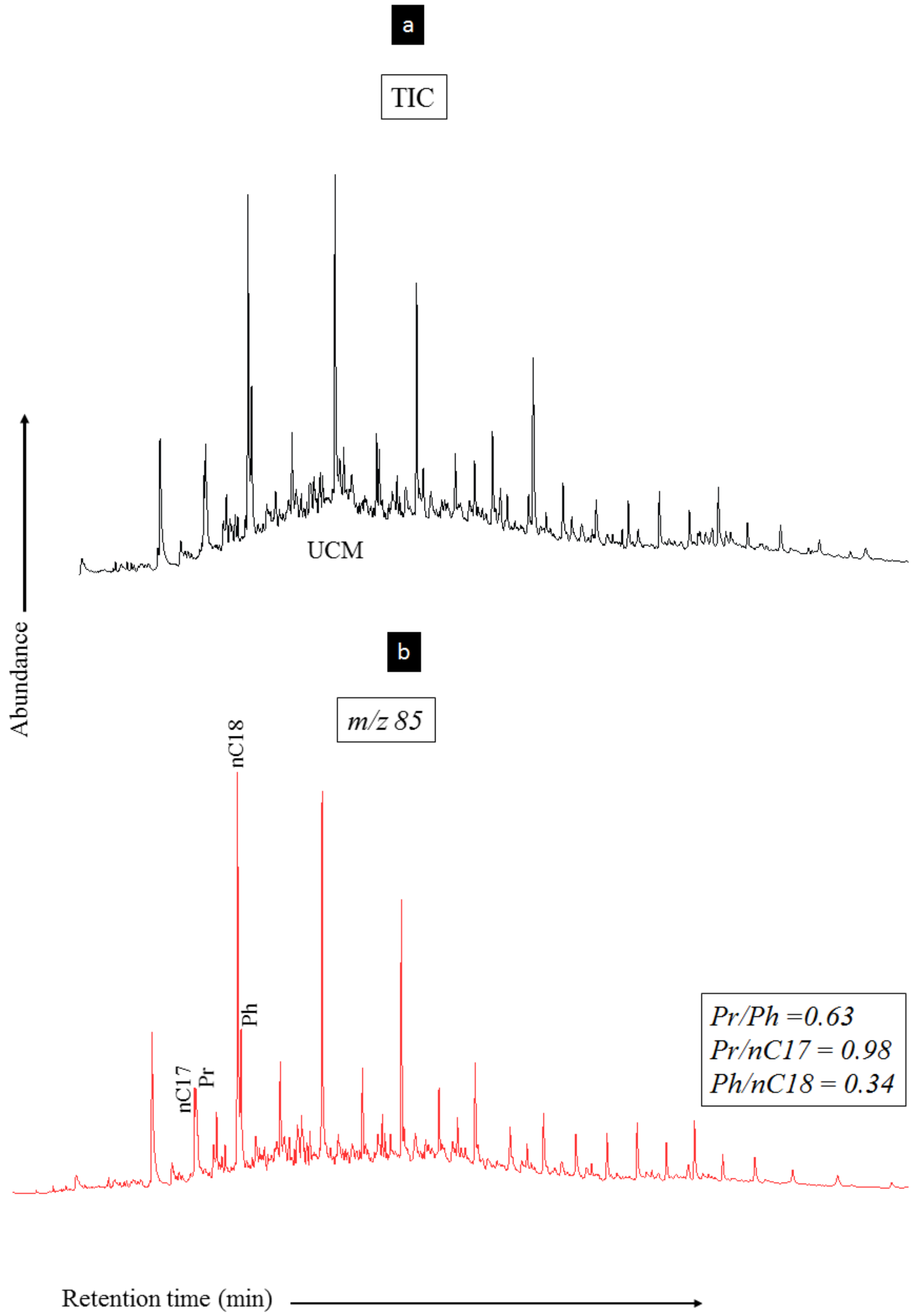

Figure 7: (a) Total ion current (TIC) fragmentogram of the saturate fraction of the studied oil residue showing unresolved complex mixture (UCM) "hump" consistent with oils that have undergone biodegradation (b) m/z 85 fragmentogram of the saturate fraction of the studied oil residue showing preserved n-alkanes and acyclic isoprenoids (n-C_{16} to n-C_{33}). Note that Pristane (Pr) and Phytane (Ph) are present in abundance lower than those of the adjacent n-alkanes, resulting in Pr/nC17 and Ph/nC18 ratios < 1.0, suggesting suboxic to anoxic depositional environment for the source of the oil.

The ternary plot of the relative amounts of C_{27}, C_{28}, and C_{29} regular steranes in the studied oil residue and other closely related oils is presented in Figure 8. *m/z* 217 fragmentogram of the saturate fraction of the oil residue is presented in Figure 8a. The studied oil residue is low in diasteranes relative to regular steranes. The sterane maturity parameters, ααα C_{27}20S/(20S+20R), ααα C_{28}20S/(20S+20R), and ααα C_{29}20S/(20S+20R), are 0.50, 0.47, and 0.35, respectively, for the studied oil residue. These data are consistent with oils derived from source rocks that have thermal maturities equivalent to early and peak oil generation.

Also presented in Figure 8 (b & c) are the *m/z* 217 fragmentogram of oils extracted from shales of the Bima Formation occurring in the Yola Sub-Basin of the Northern Benue Trough. Shales of the Bima Formation are believed to be important petroleum source rocks in the Northern Benue Trough[17]. Sterane distribution data for the Bima Shales adopted and modified from[18] show resemblance to the sterane data of the oil residue, having relatively higher C_{27} regular steranes, followed by C_{29} regular steranes and less C_{28} regular steranes (Fig. 8 a to c).

The hopane characteristic of the studied oil residue is presented in the *m/z* 191 fragmentograms shown in Figure 9a. The hopanes are reasonably well preserved, with all of the C_{31} to C_{35} homohopanes being present. C_{31} to C_{33} homohopanes are relatively more abundant than C_{34} and C_{35}. This can be attributed to the effect of biodegradation. Biodegradation of regular hopanes can result in the production of 25-norhopanes, also known as 10-desmethylhopanes, demethylated hopanes and degraded hopanes. 25-norhopanes are a series of C_{26}-C_{34} compounds that are structurally equivalent to the regular hopanes, except that they lack the methyl group commonly associated with the regular hopanes[19].

[17] Yandoka, B. M. S., Abdullah, W. H., Abubakar, M. B., Adegoke, A. K., Maigari, A. S., Haruna, A. I., Yaro, U. Y., 2017. Hydrocarbon potential of Early Cretaceous lacustrine sediments from Bima Formation, Yola Sub-basin, Northern Benue Trough, NE Nigeria: Insight from organic geochemistry and petrology. **Journal of African Earth Sciences**, 129, 153-164.

[18] Yandoka et al. (2017) ibid

[19] Reed, W. E., 1977. Molecular compositions of weathered petroleum and comparison with its possible source. **Geochimica et Cosmochimica** Acta 41, 237-247.; Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in **Petroleum Exploration and Earth History (Vol. 2).** Cambridge University Press.

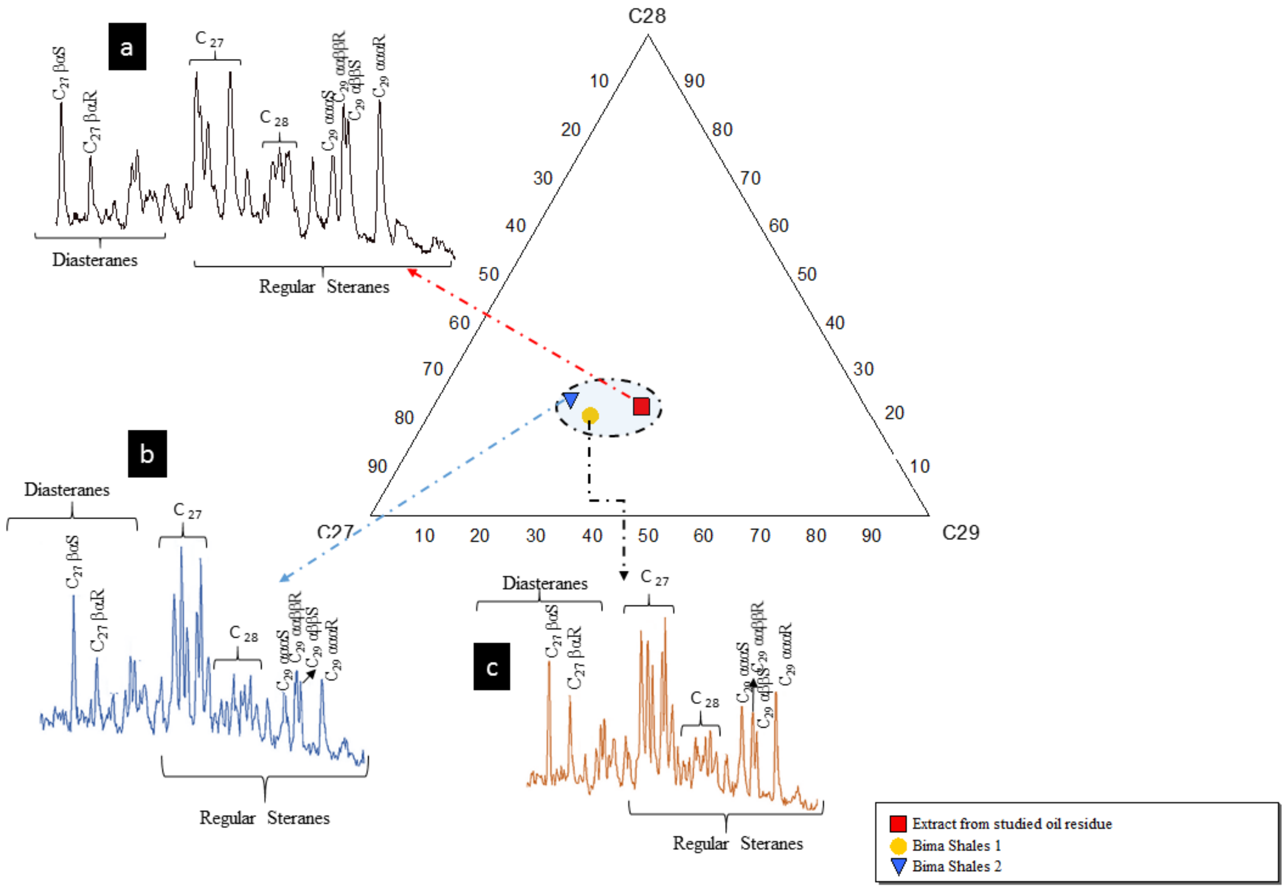

Figure 8: Ternary plot showing the relative amounts of C_{27}, C_{28}, and C_{29} regular steranes in (a) The studied oil residue (b & C) Oil extracted from Shales of Bima Formation. Note similarities in sterane distribution between the studied oil residue and oils extracted from shales of Bima Formation implying that the oils are related, which further suggests that the studied oil residue could have been sourced from shales of the Bima Formation.

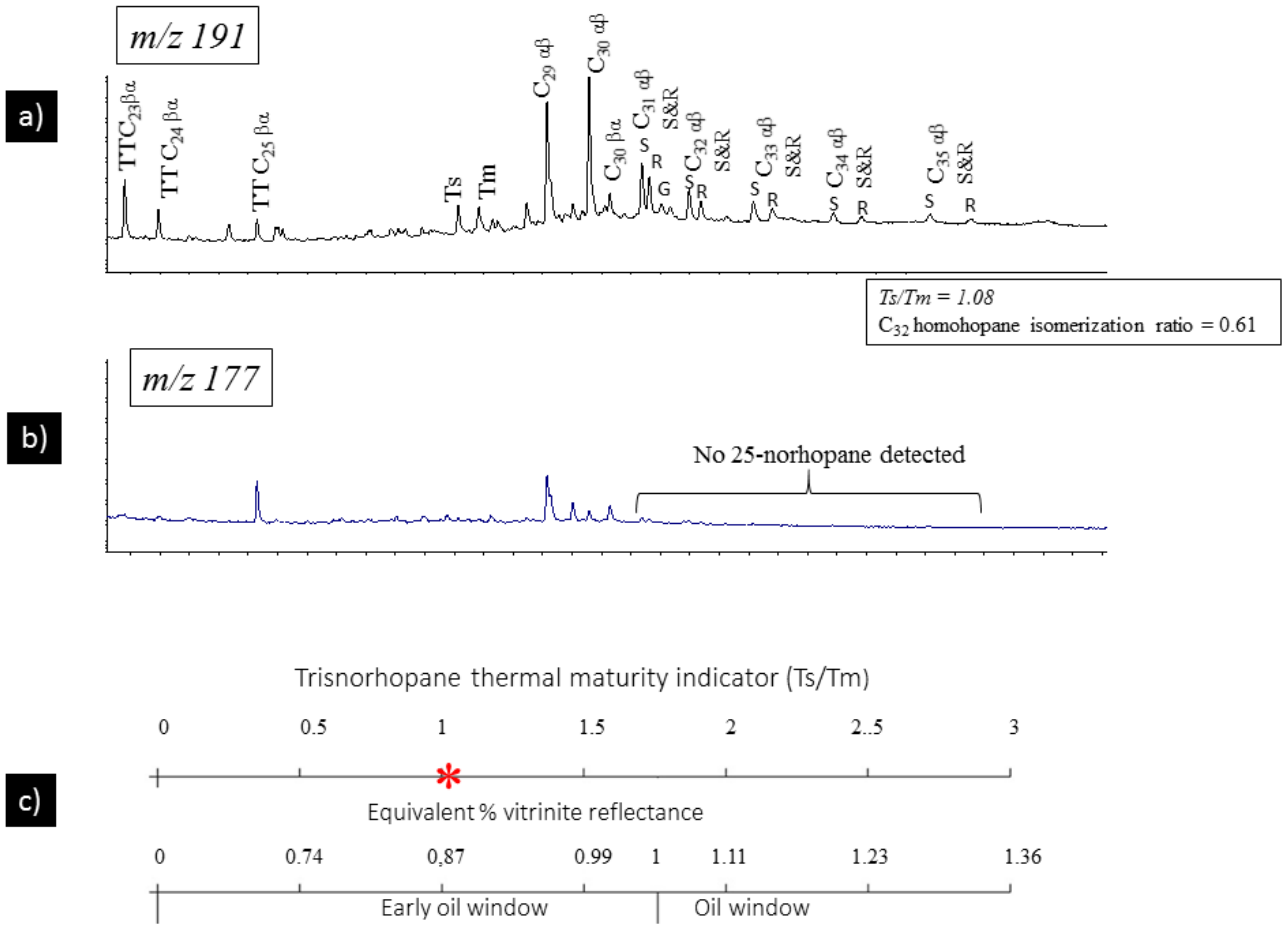

Figure 9: (a) m/z 191 fragmentograms of the studied oil residue showing hopanes. (b) m/z 177 fragmentogram of the studied oil residue. Note that no 25-norhopanes were not detected. This implies that biodegradation occurred at shallow depth. (c) Trisnorhopane thermal indicator (Ts:Tm ratio) for the studied oil residue with equivalent inferred vitrinite reflectance which also suggests that the studied oil residue have thermal maturity level consistent with oils generated within the oil window.

25-norhopanes are usually identified on the *m/z* 177 fragmentogram by having a lower retention time compared to the homohopanes on the *m/z* 191 chromatogram[20]. Peters et al. (2005) also explained that the distribution of 25-norhopanes is similar to that of the hopane series shifted downwards by one carbon number. This implies that the single epimer of C_{30} 17α,21β(H)-hopane on the *m/z* 191 fragmentogram corresponds to C_{29} 25-nor-17α,21β(H)-hopane on the *m/z* 177 fragmentogram. Biodegradation of regular hopanes can result in the production of 25-norhopanes, also known as 10-desmethylhopanes, demethylated hopanes and degraded hopanes. 25-norhopanes are a series of C_{26}-C_{34} compounds that are structurally equivalent to the regular hopanes, except that they lack the methyl group commonly associated with the regular hopanes[21].

25-norhopanes are usually identified on the *m/z* 177 fragmentogram by having a lower retention time compared to the homohopanes on the *m/z* 191 chromatogram (López, 2014). Peters et al. (2005) also explained that the distribution of 25-norhopanes is similar to that of the hopane series shifted downwards by one carbon number. This implies that the single epimer of C_{30} 17α,21β(H)-hopane on the *m/z* 191 fragmentogram corresponds to C_{29} 25-nor-17α,21β(H)-hopane on the *m/z* 177 fragmentogram. It is important to note that all hopanes yield *m/z* 177 ions alongside their base *m/z* 191 ions, so it is possible to observe peaks on the *m/z* 177 fragmentogram even when 25-norhopane is absent. Caution is therefore advised when deducing the presence of 25-norhopanes from this kind of data[22]. The presence of 25-norhopane is commonly used to indicate that biodegradation occurred at depth[23]

No displacement in retention time was observed between the homohopanes on *m/z* 191 and corresponding hopanes on *m/z* 177 the studied oil residue (Figs. 9a & b). This lack of 25-norhopanes implies that biodegradation in the studied oil residue occurred at a shallow depth.

The trisnorhopane thermal indicators (Ts:Tm ratio) for the studied oil residue is 1.08, which again suggests that the studied oil residue have thermal maturity level consistent with oils generated within the oil window (Fig. 9c)[24]. The 22S/(22R+22S) C_{32} homohopane isomerization ratios for the studied oil residue is 0.61. This implies that the source rock for the oils occurring in fractures of the exhumed basement rocks in the Gongola Sub-Basin has attained equilibrium, and it is in the early oil window (Peters et al., 2005), consistent with the Ts/Tm ratio and the sterane maturity data.

Discussion

[20] López, L., 2014. Study of the biodegradation levels of oils from the Orinoco Oil Belt (Junin area) using different biodegradation scales. **Organic Geochemistry**, 66, 60–69.

[21] Reed, W. E., 1977. Molecular compositions of weathered petroleum and comparison with its possible source. **Geochimica et Cosmochimica** Acta 41, 237-247; Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in **Petroleum Exploration and Earth History** (Vol. 2). Cambridge University Press.

[22] Peters and Moldowan, 1993 op. cit; Peters et al., 2005, ibid.

[23] e.g. Peters et al., 2005 op.cit; Bennett, B., Fustic, M., Farrimond, P., Huang, H., Larter, S. R., 2006. 25-Norhopanes: formation during biodegradation of petroleum in the subsurface. **Organic Geochemistry37**, 787- 797; Bata et al., 2015, op.cit; Bata, T., 2016. Geochemical Consequences of Cretaceous Sea Level Rise. **Unpublished PhD Thesis** submitted to the Department of Geology and Petroleum Geology, University of Aberdeen. http://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.690589.

[24] e.g., Bata et al., 2016, ibid

Basement rocks are typically fractured, creating higher permeability than in matrix porosity. Palaeo exposure of basement rocks results in the alteration and leaching of unstable minerals, which subsequently broadens fractures in the basement rock, leading to increase in porosity and permeability. Occurrence of basement rocks as aquifers provides evidence of fracture porosity in basement rocks. Basement rocks of the studied Gongola Sub-Basin are known to be very good aquifers (e.g. Iyioriobtte and Akot, 1986) and so they can also serve as important petroleum reservoir rocks in the region.

Oil residue observed in fractures of the studied Precambrian basement rocks are brittle solids (Figs. 5 & 6). The oil residues are believed to have been emplaced into the fractures of the basement rock as conventional light oils, but are now degraded to bitumen because the studied fractured basement rocks are exposed close to the surface where the fractured basement reservoir forms a favourable habitat for microbial activity. Oil-bearing basement rocks are known to provides a food source for microbes that are capable of degrading hydrocarbon[25].

Pyrite crystals closely associated with the studied fractured basement reservoir (Fig. 6b) are believed to have a biogenic origin attributed to microbial activity. Some specialized chemoorganotropic sulphate-reducing bacteria are known to degrade oil and precipitate pyrite during the biodegradation process[26]. Observed UCM in the TIC fragmentogram presented in Figure 7b agrees that the studied oils that have undergone biodegradation. Oil biodegradation process is mainly a hydrocarbon oxidation process involving the microbial metabolism of several classes of compounds in the oil, which modifies the oil's fluid properties by reducing the saturated and aromatic fractions of the oil relative to polar compounds. This negatively affects the oil's economic value.

Petroleum biodegradation requires conditions that support microbial life. The studied fractured basement occurs at a shallow depth at the studied locality, with temperature obviously below 80 ºC and so is favourable for microbial activity. Furthermore, the fracture system of the studied basement rock provides sufficient porosity and permeability that can allow bacterial mobility and diffusion of nutrients. Biodegradation of oils is known to rapidly remove oil components with the alkyl chains, particularly *n*-alkanes. Indeed, lower molecular *n*-alkanes in the range $< C_{16}$ have been preferentially removed in the studied oil residue (Fig. 7b). This implied that the studied oil residue has been biodegraded corresponding to a minimum Peters-Moldowan (PM) biodegradation level of 5[27].

Both regular steranes and diasteranes are reasonably preserved in the studied oil residue (Fig. 8a). C_{27} regular sterane is observed to be relatively more abundant than C_{28} and C_{29} regular steranes. This could imply a relatively moderate level of biodegradation[28]. Basement petroleum reservoirs are known to be fed by sedimentary petroleum source rocks (e.g. Parnell et al., 2015). Occurrence of diasteranes in the studied oil, with the C_{27} diasterane dominating, could suggests that the studied oil residue was derived from clay-rich source rocks (e.g., Peters et al., 2005; Bata, 2016). Similarities in sterane distribution between the studied oil residue and oils extracted from shales of Bima Formation in Yola Sub-Basin of the Northern Benue Trough

[25] e.g., Parnell et al., 2017, op. cit

[26] e.g. Mason, G. M., Kirchner, G., 1992. Authigenic pyrite: evidence for a microbial origin of tar sand. Fuel, 71,1403-1405; Bata and Parnell, 2014, op. cit.; Parnell et al., 2015, op. cit; Bata et al., 2016, Op. Cit.

[27] Peters and Moldowan, 1993, Op. Cit.

[28] e.g. Peters and Moldowan, 1993, ibid; Peters et al., 2005, Op. Cit.

(Figs. 7a – c) implies that the oils are related, which further suggests that the studied oil residue occurring in fractures of basement rocks in the Gongola Sub-Basin could have been sourced from shales of the Bima Formation.

Such oil-source correlation is based on the concept that the composition parameters of reservoir oils do not differ significantly from those of the bitumens remaining in the source rocks.[29] The slight relative difference in position on the ternary plot between the studied oil residue and extracts of the Bima Shales (Fig. 8) can be attributed to the effect of the difference in the connectivity of the reservoir sands and the source rocks, as well as differences in the effect of biodegradation.

By at least mid-Santonian, when deposition of the Yolde, Pindiga and Fika Formations (in the Gongola Sub-Basin), and their lateral equivalents (Dukul, Jessu, Sekuliye, Numanha and Lamja Formations) in the Yola Sub-Basin was completed, the Bima Formation would have been sufficiently buried to a depth that would have placed it within the oil window. Hence, oil could have been expelled from the Bima Shales by at least the mid-Santonian. The generated oils could have migrated downwards due to compactional squeezing of the source rock, or laterally, since the Bima Formation is known to pinch out against the Precambrian basement rocks in the study area[30].

The basement rocks of the Northern Benue Trough occur below a regional unconformity (e.g., Fig. 4). Planes of unconformities are known to be important pathways for hydrocarbon migration[31]. The generated oils are therefore believed to have been emplaced into fractures of the basement rocks through the plane of unconformity. At the studied locality, biodegradation of the studied oil residue can be inferred to have occurred after exhumation of the basement rocks during the mid-Santonian tectonic events, since the studied oil residue does not contain 25-norhopane (Fig. 9b) suggesting biodegradation at shallow level. Elsewhere in the region, the basement rocks are typically buried to a depth (>5 km). Because microbes that degrade oils do not thrive at such depths[32] it is possible to find non-degraded oils preserved in fractures of the deeply buried basement rocks.

Summary and Conclusion.

This study is the first documented evidence of oil occurring in fractures of Precambrian basement rocks in the Northern Benue Trough. The brittle solid oil residue studied are believed to have been emplaced into the fractures of the basement rock as conventional light oils, but are now degraded to bitumen because the studied fractured basement rocks occur at a shallow depth, forming a conducive habitat for microbial activity. Specifically, this study demonstrates the following:

i. TIC fragmentogram of the saturate fractions of the studied oil residue shows progressive depletion of chromatographically resolved hydrocarbons relative to the unresolved hydrocarbon mixture, forming an unresolved complex mixture (UCM) hump consistent with oils that have undergone biodegradation.

ii. Pristane (Pr) and Phytane (Ph) are present in abundance lower than those of the adjacent n-alkanes in the studied oil residue, resulting in Pr/nC17, Ph/nC18 and Pr/Ph ratios < 1.0, suggesting suboxic to anoxic depositional environment for the source of the oil.

[29] e.g. Peters and Moldowan, 1993 Op. Cit; and Peters et al., 2005, Op. Cit.

[30] e.g. Iyioriobhe, S. E., Ako, B. D., 1986. The hydrogeology of the Gombe subcatchment, Benue Valley, Nigeria. **Journal of African Earth Sciences, 5**, 509-518.

[31] e.g., Bata et al., 2015. 2016; Bata, 2016; Parnell et al., 2017, Op. Cit.

[32] e.g., Bata, 2016, Op. Cit

Sterane distribution for the studied oil residue shows strong resemblance to the strerane distribution of extracts of Bima Shales, implying that the studied oil was sourced from shales of the Bima Formation.

iii. Sterane maturity parameters, ααα C2720S/(20S+20R), ααα C2820S/(20S+20R), and ααα C2920S/(20S+20R), are 0.50, 0.47, and 0.35, respectively, for the studied oil residue, consistent with oils derived from source rocks that have thermal maturities equivalent to early and peak oil generation. The trisnorhopane thermal indicators (Ts:Tm ratio) of 1.08, and 22S/(22R+22S) C32 homohopane isomerization ratios of 0.61 agrees with the sterane maturity parameters of the studied oil residue which implies that the source rock for the oil residue is in within the oil window.

iv. Pyrite crystals closely associated with the studied fractured basement reservoir are believed to have a biogenic origin attributed to microbial activity as part of the biodegradation process.

v. By at least mid-Santonian, when deposition of the Yolde, Pindiga and Fika Formations (in the Gongola Sub-Basin), and their lateral equivalents (Dukul, Jessu, Sekuliye, Numanha and Lamja Formations) in the Yola Sub-Basin was completed, the Bima Formation would have been sufficiently buried to a depth that would have placed it within the oil window. Hence, oil could have expelled from the Bima Shales by at least the mid-Santonian. The generated oils could have migrated downwards due to compactional squeezing of the source rock, or laterally, since the Bima Formation is known to pinch out against the Precambrian basement rocks in the study area

vi. The basement rocks of the Northern Benue Trough occur below a regional unconformity. The generated oils are believed to have been emplaced into fractures of the studied basement rocks through the plane of unconformity.

vii. At the studied locality, biodegradation of the studied oil residue is inferred to have occurred after exhumation of the basement rocks during the mid-Santonian tectonic event. This explains why the studied oil residue does not contain 25-norhopane suggesting biodegradation at shallow level. Elsewhere in the region, the basement rocks are typically buried to a depth (>5 km). Since microbes that degrade oils do not thrive at such depths, it is possible to find non-degraded oils preserved in fractures of the deeply buried basement rocks.

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