

Some Aspects of the Petroleum Geochemistry of Tarsand Deposits in Western Nigeria

V.A. Ndukwe*, B.O. Ogunyinka and S. Abrakasa

Department of Geology, University of Port Harcourt, Rivers State, Nigeria

Accepted 15th October, 2015

The Nigerian tarsand is majorly found in the Western part of Nigeria, the deposits spans a distance of about 120km, the tar deposits occur as heavy oil and manifest as seepages at near surface or on the surface and as impregnated sediments at road cuts, cliff faces and river banks and at break of slopes. Samples were collected at Agbabu, Ilubinrin and Loda where open mining is in progress. The asphaltene content was determined and the concentration of a suite of trace metals, mainly the biophiles were determined. The GC-FID (Saturates and Aromatic hydrocarbons) were examined. The objective of this study is to determine the genetic relationship of the tarsand. The results indicate that the sample (A1) obtained from the drilled wellbore showed an outstanding difference from others. The seep samples (A2, A3, A4, and A6) irrespective of the locations showed a close relationship as represented by the ternary plot. Samples with significant sand content (5, 7) also showed similarity. It is suggested that since the samples (A2, A3, A4, and A6) were seeped, they could have migrated via structural permeability e.g. faults and fractures, while samples 5, 7 could have migrated via a pore network in the trapless reservoir sandbody. The % Asphaltene versus Co/Ni ratio and Pr/Ph versus Pr+Ph/(nC17+nC18) plots discriminates the samples into families.

Key words: Genetic origins, petroleum geochemistry, tarsand, trace metals.

INTRODUCTION

Tarsands are unconventional hydrocarbon resource. Tarsand, bitumen and/or heavy oil are formed by low temperature alteration of crude oil, these processes includes biodegradation, water washing or light-hydrocarbon volatilization, which results in concentration of high molecular weight hydrocarbons and heteroatomic compounds of resins and asphaltenes. Tarsand often exists at the edge, and within shallow layers of a basin, and may be exposed at the surface by tectonic uplift. Tarsand and tar deposits all originate from conventional hydrocarbon sources, when organic matter in the source rock is matured, the rock matrix starts to generate oil, the oil generated is expelled and eventually commences primary migration. After which, the generated hydrocarbon finds its way into a carrier bed/pathway and commences

secondary migration. Migration may be hindered by a trap which provides the configuration on which the accumulation sits and grows. However, where the trap is not in place at the time of hydrocarbon emplacement in the reservoir, the migrating oil will migrate out possibly into the surfaces where it is known as seeps (figure 1), the eventual exposure to oxidative condition results biodegradation formation of tarsand. Figure 1, shows an idealized Foreland basin petroleum system, it also shows the reservoir grading into shallow depth where the oil migrates to and remains exposed to oxidation and biodegradation with increasing loss of lighter molecular weight fractions of the hydrocarbon, the heavier ends are left behind as tarsand which is rich in asphaltene.

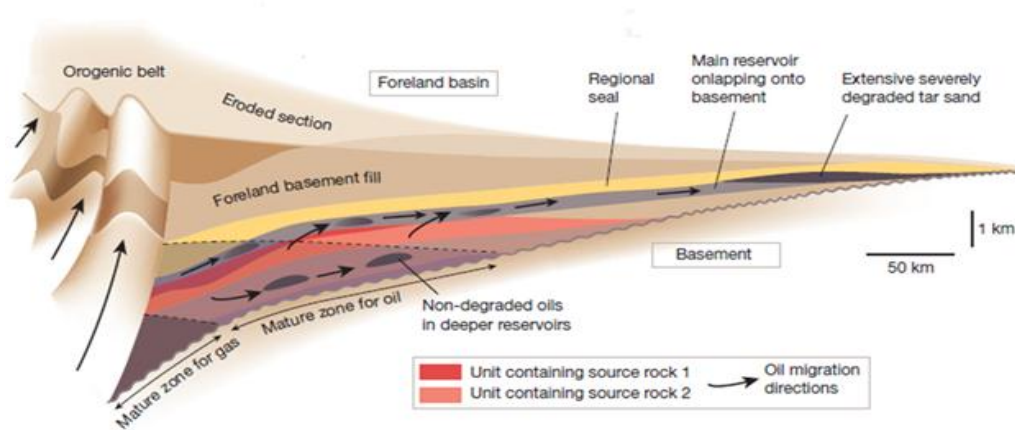


Figure 1: An idealized Foreland basin petroleum system, showing oil migrating into more shallow depths where there is no effective seal and it becomes biodegraded and exists as tarsands. (Head *et al.*, 2003)

Location of study area

The study area is located in Ondo State in Western Nigeria. It spans an area between latitudes 6° 25' N to 6° 45' N and longitudes 4° 45'E to 5° 5' E (figure 2)

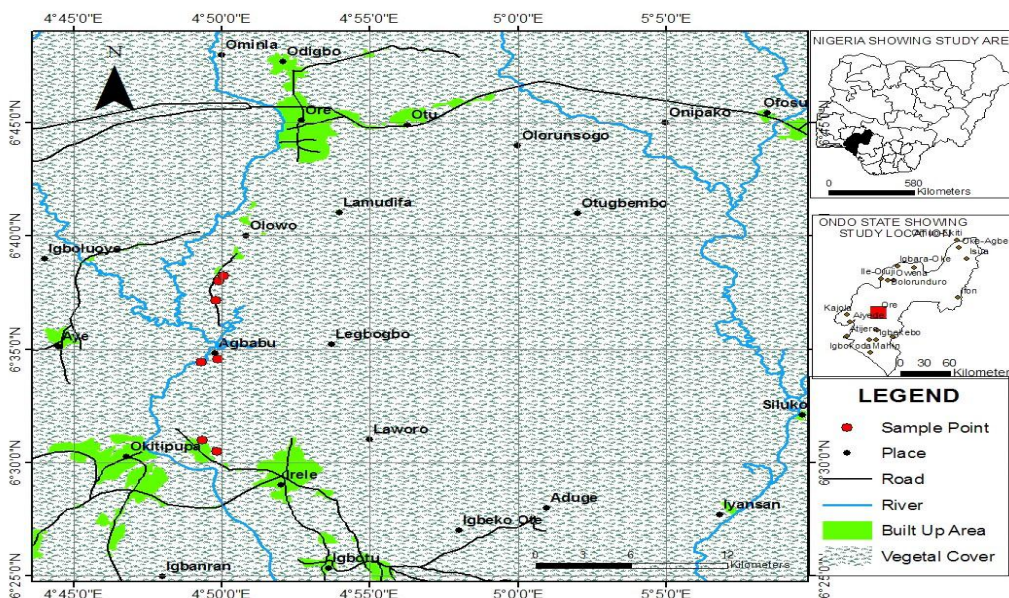


Figure 2: Map of study location showing sample points, insert is map of Nigeria showing the location of Ondo state

METHODOLOGY

Samples were collected from outcrops at sample points indicated in figure 2. The sample points are Agbabu, Ilubbinrin, and Loda all around Ore town in Ondo State. Samples A1 and A2 were collected from Agbabu, they are both pure tar/heavy oil, though sample A1 is from a wellbore. Samples A3, A4 and 5 were collected from Ilubbinrin while samples A6 and 7 were collected from Loda. Samples were deasphalted as explained in Udo *et al.*, (1988). Briefly, the tarsand (5gms) was first dissolved in DCM (dichloromethane) (200mls) to remove the sand, clay and debris which are insoluble in DCM, the solution was filtered separating the sand and clay out. The resultant solution was left in a fume chamber to evaporate. The tar was dissolved in 200mls of pentane (AnalaR Grade) while stirring

and continued for 1hr. The solution was allowed to cool in a freezer for 2hrs at 5°C. The precipitated asphaltene were filtered off and washed with cold n-pentane till the wash solution is colorless and dried in a dessicators, then weighed and scraped off into sample vials. The obtained asphaltene was then presented for Atomic Absorption Spectrophotometry (AAS) analysis of a suite of trace metals and Gas Chromatography–Flame Ionization Detector (GC–FID) analysis of the saturates and aromatic hydrocarbons in the maltenes. The metals were mainly the biophiles (Udo *et al.*, 1992). The GC–FID analysis was carried out with Agilent 6890 GC, the column used was HP–5, 30m in length, and carrier gas was nitrogen, while the AAS analysis was carried out with Agilent Spectraa 55A. Analysis was done by Jawara Analytical Services in Port Harcourt, River State, Nigeria.

RESULTS

Table 1: Trace metal concentrations in the various asphaltene samples

Samples	Co	Ni	Zn
A1	37.38	33.08	6.48
A2	443.57	113.57	70.64
A3	6595.64	312.08	619.8
A4	365.68	67.97	31.34
5	4427.96	740.67	2945.2
A6	351.76	92.46	39.12
7	353.06	86.86	272.23

Table 2: Amount of asphaltene present in various tarsand samples

S/N	Samples	Sample Weight (g)	Asphaltene Weight (g)	Percent Asphaltene(%)
1	A1	4.00	1.50	37.5
2	A2	2.00	0.60	30.0
3	A3	2.10	0.45	21.4
4	A4	2.05	0.5	24.4
5	5	2.00	0.10	5.0
6	A6	2.02	0.65	32.2
7	7	2.00	0.10	5.0

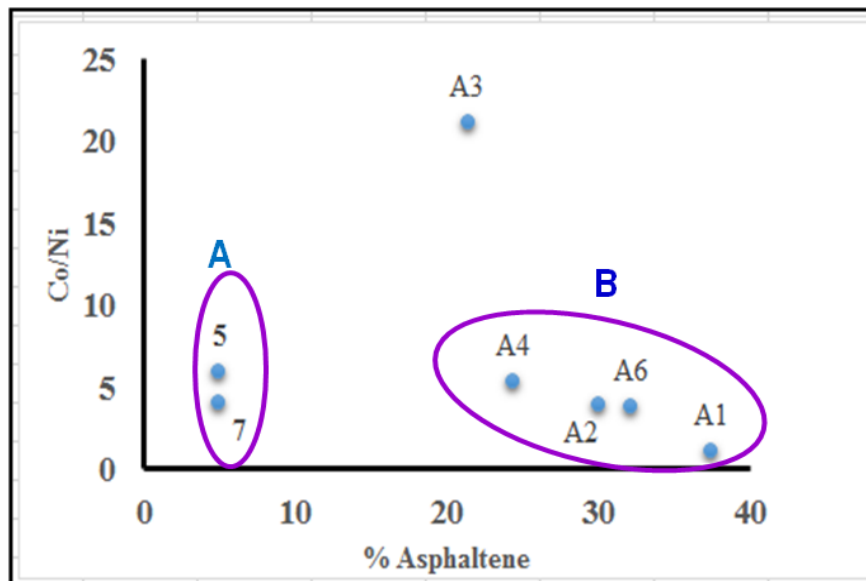


Figure 3: Graph of %asphaltene and Co/Ni ratio, grouping the samples into families

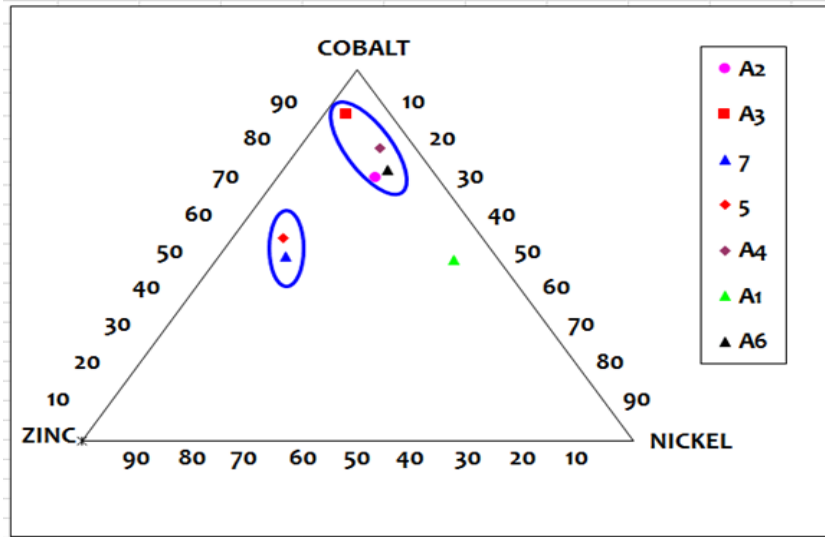


Figure 4: The ternary plot of the biophile metals showing clusters of samples

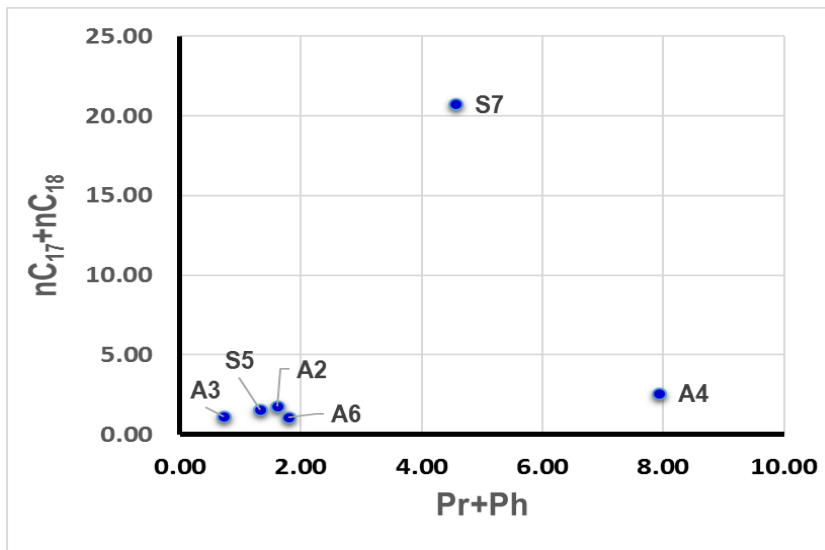


Figure 5: Plot of $nC_{17}+nC_{18}$ versus Pr+Ph

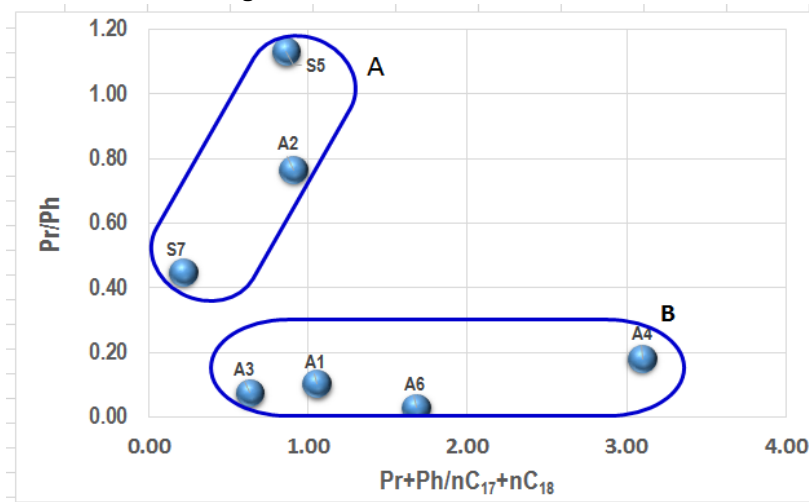


Figure 6: Plot of Pr/Ph versus $Pr+Ph/nC_{17}+nC_{18}$

DISCUSSION

Compositional variations

The results of the AAS analysis (table 1), show that samples A3 and 5 has the highest concentrations of metals, while sample A1 has the lowest concentration of metals. Table 2 shows the asphaltene content of the different samples, samples 5 and 7 has the lowest percentage composition of asphaltene of 5% each while sample A1 has the highest content of 37.5%. Percentage composition of asphaltene ranges from 37.5% to 5%.

Trace metal geochemistry

The correlation study of the samples based on trace metals and the asphaltene content, indicates that the samples are related and can be grouped into genetic families. Asphaltenes have been redefined as micro kerogens bearing in preserved state the features of the original source of organic matter (Tissot, 1984; Pelet *et al.*, 1986), since the trace metals content was determined from the asphaltene, the established relationships should be a true representation that exists. Figure 3 is a plot of Co/Ni ratio and that of %Asphaltene, the plots discriminates the samples into different genetic families. Family A consist of samples 5 and 7 and are basically the samples that were obtained as tarsand, with a significant amount of sand. While family B are samples that were obtained as seeps of tar or heavy oils. Sample A1 is a live sample that was obtained from the wellbore. The plot distinguishes tarsands from live tars/heavy oils. Figure 4 is a ternary plot using Ni, Co and Zn. The ternary plot also discriminates the samples into genetic families. Corroborating the genetic relationships with their corresponding sample site, it is observed that all samples that were obtained as tarsand (samples 5 and 7) represents samples which migrated via networks of pores embedded in the matrix of the sandstone reservoir. Samples that were obtained as seeps (A2, A3, A4, and A6) represent those that migrated via fractures and faults. Sample A1 is outstanding because it was obtained from a well bore that was drilled into the formation bearing the tar/heavy oil.

Biomarker geochemistry

Biomarker ratios were also employed in order to foster a better understanding of the relationship of the samples, figure 5 is a plot of Pr+Ph versus $nC_{17}+nC_{18}$. These are very sensitive parameters, they both decrease with increasing degradation, Figure 5 show that the samples are heavily degraded with almost complete loss of the medium weight hydrocarbons (nC_{17} and nC_{18}) relative to the isoprenoids (Pr and Ph). Figure 6 is a plot of Pr/Ph versus $Pr+Ph/(nC_{17}+nC_{18})$, the Pr/Ph ratio does not express biodegradation but the environment of deposition, which expresses a genetic relationship and could be used to discriminate the samples into marine and deltaic origins. However, $Pr+Ph/(nC_{17}+nC_{18})$ is a sensitive parameter which increases with biodegradation, since the isoprenoids are more recalcitrant to biodegradation relative to the normal hydrocarbons, the normal hydrocarbons degrades earlier. Figure 6 discriminates the samples into two groups which are A and B respectively. Group A has lower $Pr+Ph/(nC_{17}+nC_{18})$ ratio relative to group B. Group B consist of samples that were obtained as seeps hence may not have been exposed to oxidative conditions that fosters biodegradation. Group A is mainly made up of samples (5 and 7) which were obtained

from outcrops as tarsands, which are exposed to oxidative conditions that enhances biodegradation.

CONCLUSION

The analysis was carried out on the asphaltenes and the maltenes, the premise upon which this study rest is that asphaltenes are micro kerogens and they retain features of the original organic matter (Tissot, 1984; Pelet *et al.*, 1986). The trace metal contents in petroleum are not influenced or contaminated during migration (Barwise (1990); Lewan and Maynard, 1982). Hence results obtained reflect their true genetic state. Figures 3 and 4 showed the use of trace metals to discriminate the samples into families which could be inferred to represent their migratory pattern. Figure 6 showed the use of biomarker to discriminate the samples into similar groups as that of figures 4 and 5. The high degree of similarity shown by samples A2, A3, A4, and A6 indicate that they are genetically related, they are from the same end member formation. Samples 5 and 7 are very similar. Samples A2, A3, A4, and A6 are pure tar/heavy oil, but obtained from different locations as seeps. The state of the samples infers that these samples migrate via structural permeability such as faults and fractures. Samples 5 and 7 are more of tarsand/oilsand obtained as outcrops with high sand content; these samples are suggested to migrate via a network of the pore system in the sand body.

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