



## Generic Aspects of Petroleum Geochemistry of Bitumen Deposits in Western Nigeria

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**Abstract:** In Nigerian, bitumen is majorly found in the Southwestern part, the deposits span a distance of about 120km, the bitumen 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 riverbanks 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) was examined. The objective of this study is to determine the generic characteristics of bitumen. 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 (samples 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 through a network of pores in the matrix of the trapless reservoir sandbody. The % Asphaltene versus Co/Ni ratio and Pr/Ph versus Pr+Ph/ (nC17+nC18) plots discriminates the samples into families.

**Keywords:** Bitumen, generic origins, petroleum geochemistry, trace metals.

### 1. Introduction

Bitumen are unconventional hydrocarbon resources. Bitumen and/or heavy oils are formed by low temperature alteration of crude oil, these processes include biodegradation, water washing or light-hydrocarbon volatilization, which results in the increase in concentration of high molecular weight hydrocarbons and heteroatomic compounds of resins and asphaltenes. Bitumen often exists at the edge, and within shallow layers of a basin, and may be exposed at the surface by tectonic uplift. Bitumen 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), where biodegradation is high in the reservoir, the lighter fractions are used up remaining the intermediates and heavier molecular weight fractions that constitutes bitumen's, the eventual exposure to oxidative condition and impregnation of the sand at the surface results to 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.



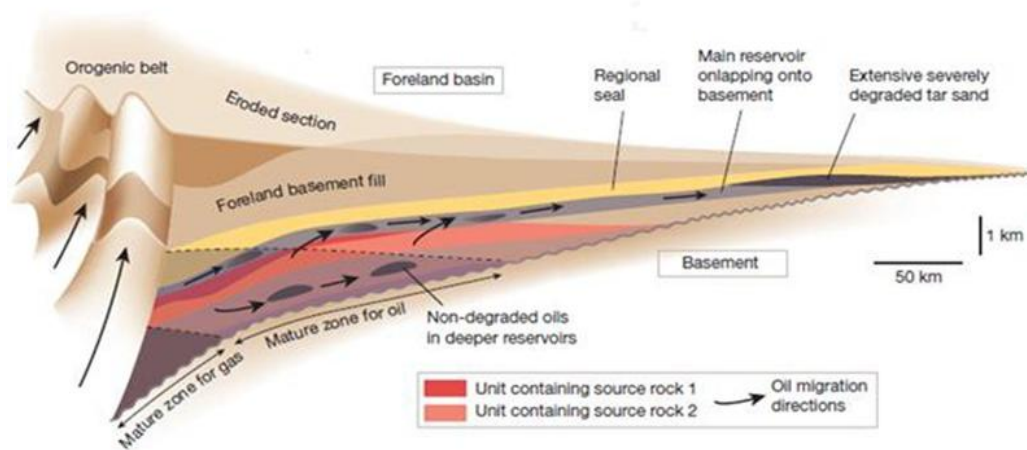


Figure 1: An idealized Foreland basin petroleum system, showing oil migrating into more shallow depths where there is no effective seal, and it becomes biodegraded and exists as tarsands. (Head et al., 2003)

### Location of Study Area

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

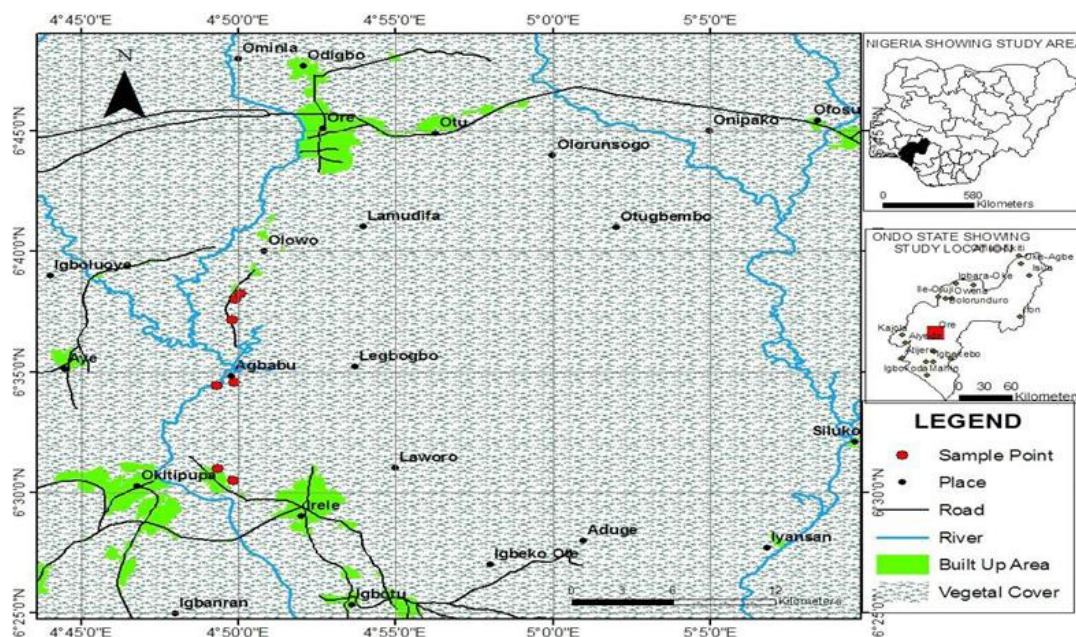


Figure 2: Map of study location showing sample points, insert is map of Nigeria showing the location of Ondo state

### 2. Materials and Methods

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 bitumen (5gms) was first dissolved in DCM (dichloromethane) (200mls) to remove any sand, clay and debris which are insoluble in DCM, the solution was filtered separating the filtrate and clay out. The resultant solution was left in a fume chamber to evaporate. The bitumen/tar was dissolved in 200mls of pentane (AnalaR Grade), while stirring 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 desiccators, 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.

### 3. Results

**Table 1:** Trace metal concentrations (ppm) in the various asphaltene samples

Samples	Co	Ni	Zn	% Asphaltenes	Bio Status	Co/Ni
A1	37.38	33.08	6.48	37.5	1	1.13
A2	443.57	113.57	70.64	30.0	3	3.91
A3	6595.64	312.08	619.80	21.4	5	21.13
A4	365.68	67.97	31.34	24.4	4	5.38
A5	4427.96	740.67	2945.20	5.0	6	5.98
A6	351.76	92.46	39.12	32.2	2	3.80
A7	353.06	86.86	272.23	5.0	6	4.06

**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

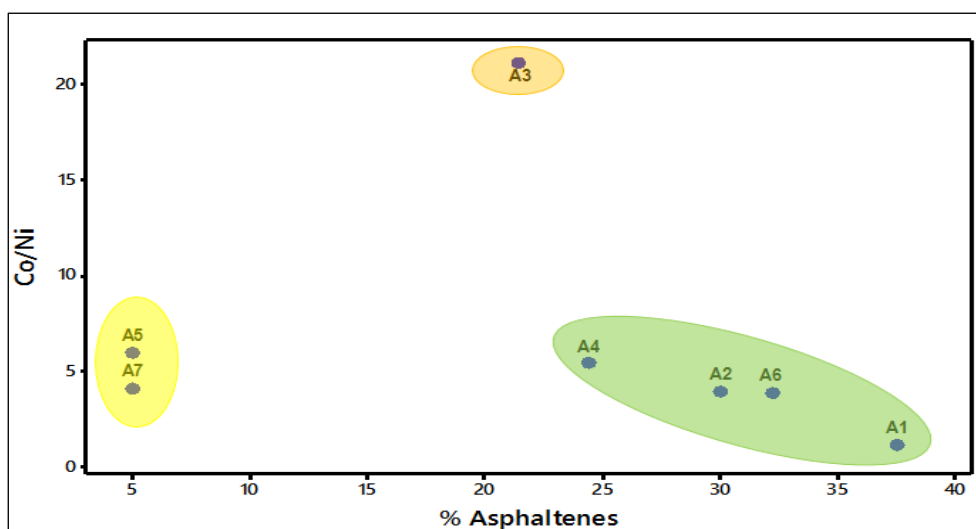


Figure 3: Graph of %asphaltene and Co/Ni ratio, grouping the samples into families



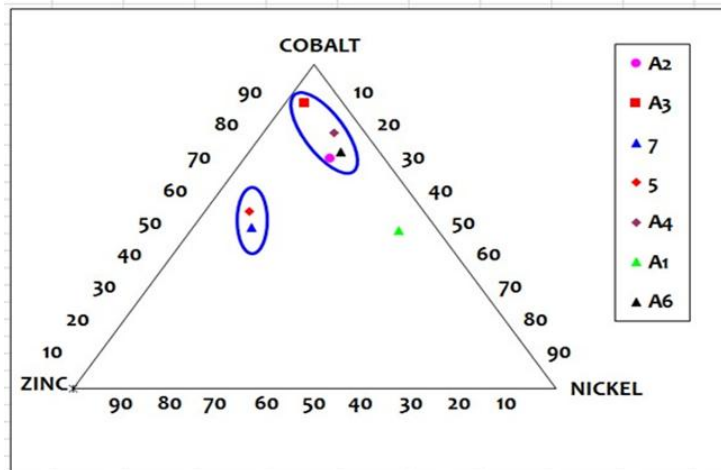


Figure 4: The ternary plot of the biophile metals showing clusters of samples

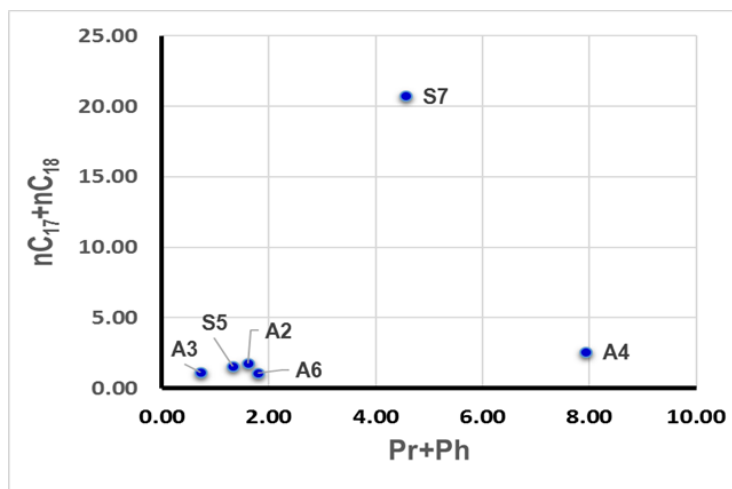


Figure 5: Plot of  $nC_{17}+nC_{18}$  versus  $Pr+Ph$

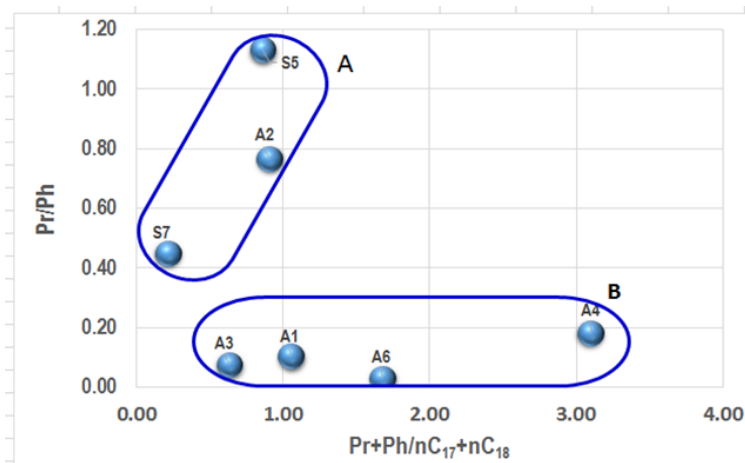


Figure 6: Plot of  $Pr/Ph$  versus  $Pr+Ph/nC_{17}+nC_{18}$

#### 4. Discussion

##### Compositional variations

The results of the AAS analysis (table 1), show that samples A3 and A5 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 A5 and A7 have the lowest percentage composition of asphaltene of 5% each while sample A1 has the highest content of 37.5%. The 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; Barwise, 1990), 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 generic families. Family A consist of samples A5 and A7 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 bitumens with sands 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 (Udoh et al, 1992). Corroborating the generic relationships with their corresponding sample site, it is observed that all samples the were obtained as tarsand (samples A5 and A7) 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 abid 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 consists 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.

### Biodegradation Status

The biodegradation status is critical for any sample, it portrays the fuel value of that sample. When bitumen/tar becomes highly/strongly degraded their value depreciates (Peters et al., 1993; Larter et al., 2003; Head et al., 2003). Figure 7 shows the biodegradation profile of the suite of samples used for his study.

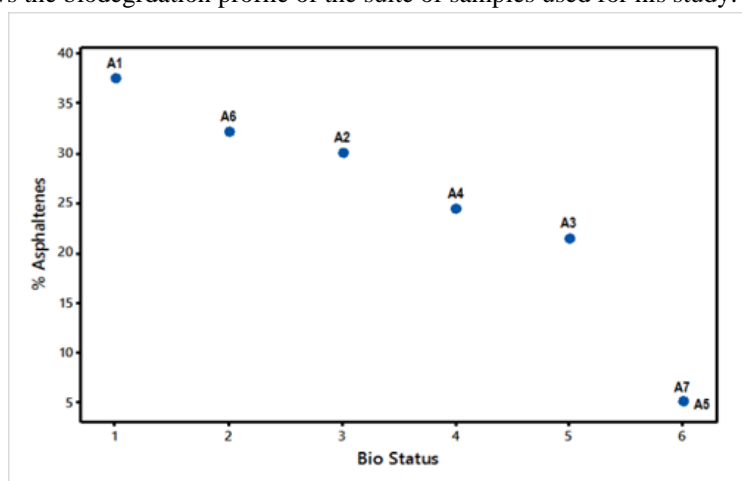


Figure 7: Biodegradation Profile of the bitumen sample



The profile shows that samples A5 and A7 have the same status reference. This observation supports the same origin/source. Thus, samples that migrated through faults/fractures have high asphaltene fraction, while, samples that migrated via network of pores in the matrix of the sandbody have low asphaltene fraction. The most plausible explanation could be that the network of pore in the matrix of the sandbody, serves as a screen to molecules that are larger than the pores.

## 5. Conclusion

The analysis was carried out on the asphaltenes and the maltenes. The premise upon which this study rests 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 the 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 biomarkers 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 A5 and A7 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 A5 and A7 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, which also serves as a screen in the sand body.

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