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Research Paper

HopanoidsinNigerian Oilsdiscriminatesonshore and off shorefields

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ABSTRACT:*The hopanoidsin Nigerian oils were investigated for their compositional distribution in some Nigeria oils. Oil samples were obtained from wellheads and whole oil GC–MS analysis was performed. Analytical resultshowed that toils from offshore fieldsexhibit higher* C_{33}–C_{35}/C_{31}–C_{35} *homohopane and higher Oleanane/*C_{30} *hopane ratioscompared to oils from onshore oils. This observation has been accredited to the fact that most offshore oils are sourced from fields that are located on or close to ClayChannels or Canyons. The Clay Channels or Canyons enhances deposition of organic matter from continental runoffs with enriched Oleanane content, while the deep marine environment promotes preservation of* C_{33}–C_{35} *homohopanes which are normally lost in oils sourced from more oxic deltaic environment.These could serve as reliable benchmarks for discriminating the offshore oil from the onshore oils within the Niger Delta Basin.*
KEYWORDS:*offshore, onshore, Niger Delta, Clay Channels and Canyons.*

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I. INTRODUCTION.

The organic matter composition of a source rock largely determines the type of kerogen and invariably the quality of oil generated from the organic matter. The three major input organic matter types are deltaic, lacustrine and marine. The Niger delta basin emerged in the Cretaceous (Tuttle et al, 1999) and the sloppy nature provides that the major input organic matter type is the continental runoffs that is significantly made up terrigenous matter and vascular high land plant materials (Tuttle et al, 1999).

Biomarkers are chemical fossils in oils that has a linkage to the precursor compound and source organism such as algae or bacteria (Peters et al, 2005). In modern petroleum geochemistry, biomarkers serve the basis of correlation studies, spill identification, comingle allocation, migration tracing and caprock integrity evaluations (Peters et al, 2005). Characteristically, the structural development of the Niger delta and the eventual opening of the Southern Atlantic during the Triassic and Jurassic provides that the source rocks which consist those at distal and proximal environment within the Niger delta basin will significantly have different organic input materials due to the mechanism of deposition. The mechanism is such that runoff from continental environment will accumulate and may exceed the sediment angle of repose and will result in the deposits sliding down the slope and eventually deposited at distal part of the delta near deep marine environment. Obviously, sediments in the slope and shoreface and the shelf (offshore) will not have the samecompositional makeup. These characteristic difference will be reflected in the chemical fossil distribution posed by the oils.

Structural Evolution of Niger Delta.

The structural evolution of the Niger delta commenced with the formation of the fractures zone alone the west coast of Africa which were expressed as trenches and ridges in the deep Atlantic (Tuttle et al 1999; Short and Stauble ,1967; Reijers, 2011).This eventually resulted in the different basins and the boundary fault of the Cretaceous Benue–Abakaliki trough. This represents the failed arm of the rift triple junction which is largely associated with the opening of the Southern Atlantic. The rifting commenced in the Late Jurassic, while visible opening of the Southern Atlantic began in the Aptian and was completed in the Albian (Tuttle et al 1999). The deposited shales were noncompacted due to ineffective dewatery of the shales. Shale diapirs were formed due to the deposit of high density sands, the diapirs were not supported with the basinward, lateral pattern of deposition, this resulted in a slope instability resulting in the deposition of the uncompacted shales in distal marine environment (Evamy et al, 1978). The Akata formation was deposited in marine environment during lowstands when terrigenous organic matter and clays were transported into deep water areas characterized by low energy and anoxic conditions. In some areas the tectonic activity of the Santonian created canyons that provided pathway of continental runoffs which were eventually deposited in distal marine waters, providing formarine sourced organic matter to be deposited alongside continental sourced terrigenous vascular land plant organic matter (Short and Stauble, 1967).

The Clay Channels.

The Niger Delta is characterized by clay channels, these are Opuama Clay Channel, the Bonny and Soku Clay Channel and the Qua Ibo Clay Channel (Reijers, 2011).The Channels which are mainly located in the flanks of the Niger Delta are extensive submarine canyons formed by extensive transgressive erosional episodes, their fills are characterized by internal erosional unconformities (Bruso et al, 2004; Short and Stauble, 1967).Geochemically, there should be some compositional variation in the distribution and concentration of organic matter from continental runoff and possibly the incursion of marine waters.

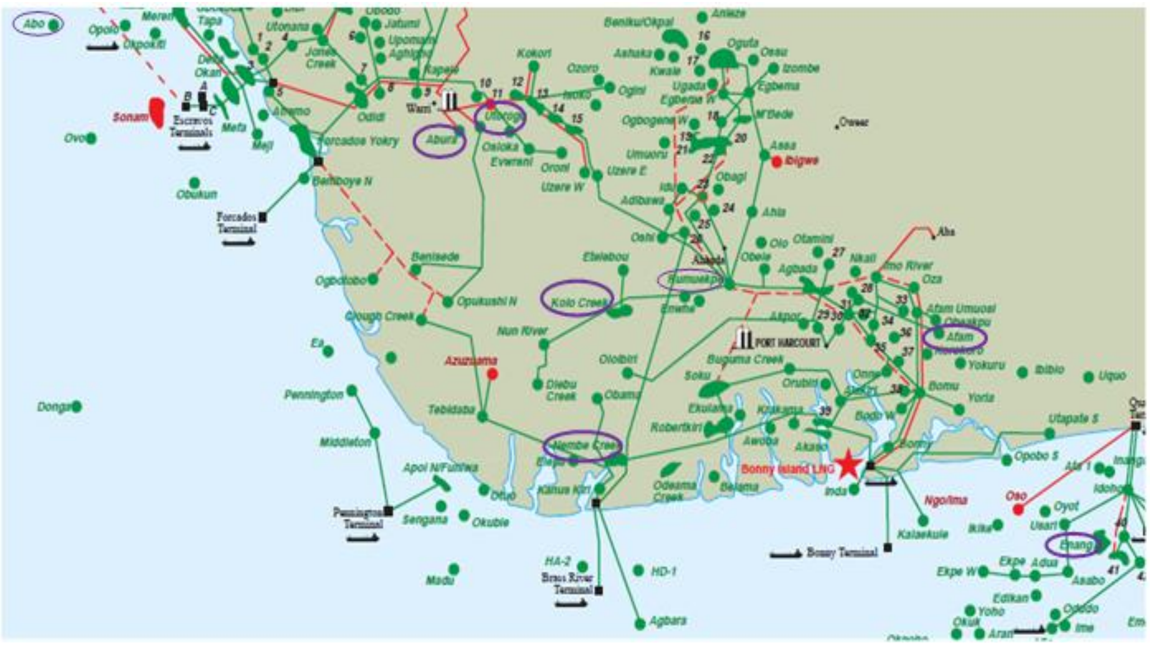

Figure 1. The locations of some oilfields studied are encircled (Bush, 1999)

II. SAMPLES AND METHODS.

Sampling

Samples of oils were obtained from oil wells in fields distributed within the Niger Delta Basin to reflect the distal (offshore) and proximal (onshore) sources facies. Oils were obtained in Teflon capped sample vials, samples were kept in a chest off ice and later transferred to the refrigerator in the laboratory till treatment and analysis were done.

Sample treatment and GC–MS analysis.

Oil samples were diluted with DCM (Dichloromethane) and whole oil analysis was carried out. Peaks were integrated using the RTE integration option, ratios of peak areas were used which were obtained from the percent reports. The integration baseline was at the top of the UCM (unresolved complex mixture). Chromatograms for various ions relevant to the study were extracted uses chemstation software. Ions extracted were m/z=191, m/z=54, m/z =217, m/z=218.

III. RESULTS.

The results for various ratios derived and tabulated.

Wells	C_{33}-C_{35}/C_{31}-C_{35} Hopane	Olean/C_{30} Hopane	$\alpha\beta C_{32}S/(S+R)$Hopane
Usan	0.38	1.44	0.59
Rumuekpe	0.28	0.60	0.59
Enang	0.33	1.31	0.59
Abo	0.28	1.50	0.58
Afam	0.21	0.84	0.58
Kolo	0.16	1.04	0.59
Nembe	0.16	0.96	0.60
Umutu	0.15	0.36	0.58
Abura	0.06	0.35	0.36
Utorugu	0.31	0.85	

The result shows the ratio of the C_{33}–C_{35}homohopanes to C_{31}–C_{35} homohopanes. This ratio is used to indicate extent of influence of anoxic conditions which infer marine environments. The oleanane to C_{30}hopane is also applied, it also infers contributions from terrigenous organic matter relative to the degree of marine influencein the environment of deposition.The $\alpha\beta C_{32}S/(S+R)$ Hopane is the maturity ratio. Maturity of the oils is very consistent, expect for Abura with significantly lower maturity.

IV. DISCUSSION.

Organic Matter Inputs.

The oils show compositional variation in biomarker distribution that indicates the organic matter. The presence of oleanane infers that the oils originates from a vascular plant material sourced from higher land plants. Hopanes are generally from bacteria which are ubiquitous. The ratio of Oleanane to C_{30}hopane reflects the amount ofthe organic inputs from vascular plant material into the source rock. Table 1 shows that all the oilsfrom offshore fields have higherratios of Oleanane to C_{30}hopane. This implies more input of plant materials relative to bacteria. All the oils from offshore fields e.g. Abo, Enang, Usan show higherOleanane/C_{30} hopane relative to others. Figure 2 show that the oils are grouped into three groups, group1 are oils from fields in the offshore depobelt of the Niger Delta Basin. They also showhigher C_{33}–C_{35} hopane/C_{31}–C_{35} hopane ratio.

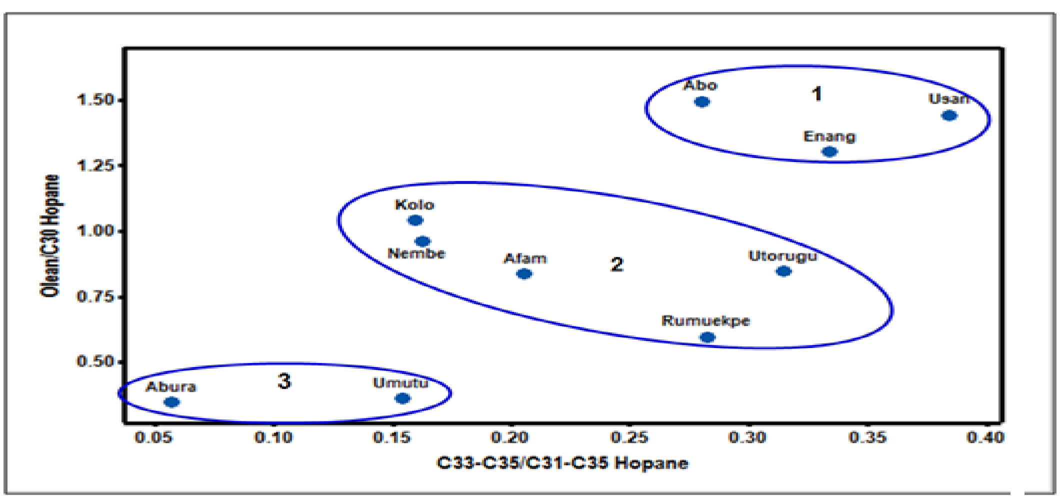

Figure 2. Plot of oleanane/C30hopane Vs C_{33}–C_{35} hopane/C_{31}–C_{35} hopane

This infers that the C_{33}–C_{35} hopane is higher for the offshore fields relative to the onshore fields.Higher oleanane input in the offshore oils could be attributed to their specific locations, the Abo oil field is located close to the Opuama Clay Channel while the Enang and Usan oil fields is located close to the Qua Iboe Clay Channel. These channels are like canyons.Allen (1965) identified the canyons as Avon Canyon, Mahin canyon and Calabar Canyon. The morphology of the canyons provides a depositional mechanism which frequently depends on generated turbidity current that flows through the slopes of the continental margin, once the angle of reposed of the sediment has been exceeded. This could contribute to higher rate of deposition and more anoxic environment relative to areas that do not have canyon like incisions (Allen, 1965; Short and Stauble 1967; Riejers, 2011 and Tuttle et al, 1995).

Environment of Deposition.

The presence of C_{35} hopanes in oils has been attributed to their generation from organic matter in anoxic (marine) environment.The diagenesis of their precursor which is bacteriohopanetetrol or bacteriohopanepentaol which has got four or five (4 or 5) hydroxyl groups may not result in complete oxidation of their functional (hydroxyl) groups. Oils showing high C_{33}–C_{35} homohopanes indicate environment of deposition with no free oxygen, the availability of free oxygen fosters the oxidation the precursor bacteriohopanetetrol and other poly functional C_{35} hopanoids to a C_{33} acid, which might be followed by loss of carboxyl group to C_{32} or preservation of the C_{33} homolog. The environment will vary from suboxic or dysoxic to oxic or suboxic depending on the amount oxygen and its accessibility to the organic matter. The predominance of C_{33} and C_{34}homohopane indicatemild suboxic exposure at the time of deposition followed by partial oxidation of the bacteriohopanetetrol side chain. The implication of this assertion is that all the offshore oils show C_{33} to C_{35} homohopanes and could have been generated by organic matter that were deposited in oxygen deficient environment and for which there were no oxidation of the functional groups.

The inferences from this study as portrayed from figure 2 show that the Niger Delta oils shows a variation in biomarker distribution that indicates gradual increase in marine contributions across the depobelts to the offshore depobelts. The gradual increase in the presence of the homohopanes from C_{32} in the Umutu and Afam oils to C_{35} in the Abo and Enang oils show increasing prevailing presence of anoxic environment at the time of deposition of the organic matter that generated the oils. This may infer decreasing marine condition with subsequent organic matter that was deposited from the Paleocene to the present in geological time frames. The significant presence of Oleanane as indicated by the Oleanane/C_{30}Hopane ratiowhich discriminates the offshore from onshore oils for the suite of samples studied could be attributed to the geomorphology of the flanks of the continental margin on which the oil fields are located. The presence of canyon like clay channels (Short and Stauble, 1967)which provide the avenue for fast and frequent supply of vascular plant materials from higher land plants in the continental runoffs intothe continental margin explains the high Oleanane/C_{30}Hopane ratios in the offshore oils. These attributes significantly discriminate the oils from the offshore fields from the oils from the onshore fields.

Figure 3, which is aplot of Pr/Ph ratio versus $\alpha\beta C_{31}$RHopane/C_{30}hopane ratio show all the oils except Enang oil have low $\alpha\beta C_{31}$RHopane/C_{30}hopane ratio, this observation corresponds with the fact that most marine oil show high $\alpha\beta C_{31}$RHopane/C_{30}hopane ratio relative to fluvial–deltaic oils (Peters et al, 2005).

Figure 3. Plot of Pr/Ph ratio versus αβC31RHopane/C30hopane ratio

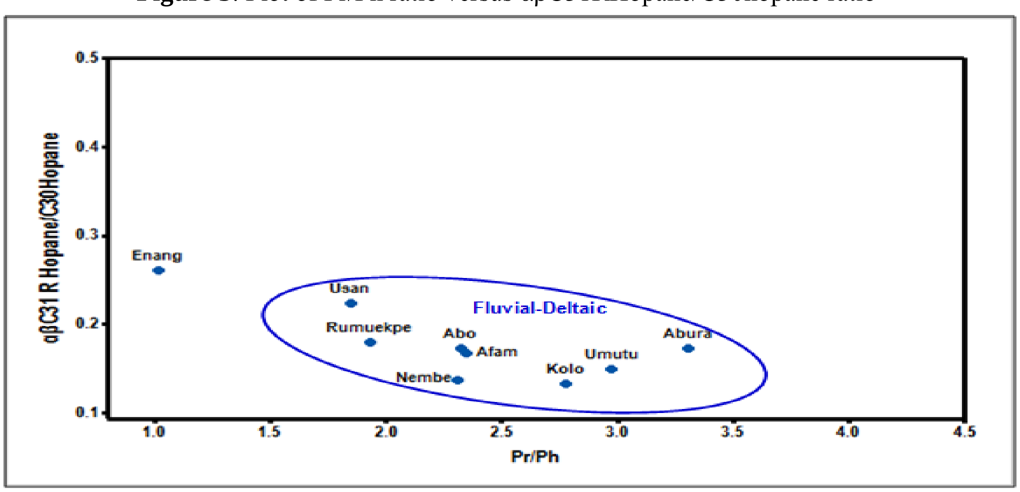

Figure 4 is a plot of Pr/Ph versus C_{33}–C_{35} hopane/C_{31}–C_{35} hopane, the distribution of the oils in the plot reflects a gradual increase in anoxicity of the depositionalenvironment as inferred by the C_{33}–C_{35} hopane/C_{31}–C_{35} hopane ratio. This is based on the fact the precursor compound (bacteriohopanepentaol) will undergo oxidation reducing it to either C_{23} or C_{33} homolog depending on the degree of oxicity of the prevailing environment (Peters et al, 2005). Oils with higher C_{33}–C_{35} hopane/C_{31}–C_{35} hopane ratio are generated from organic matter deposited in more anoxic settings. Oils from Enang and Usan fields are have the most anoxic settings while oils from Abura and Umutu fields have the oxic settings.

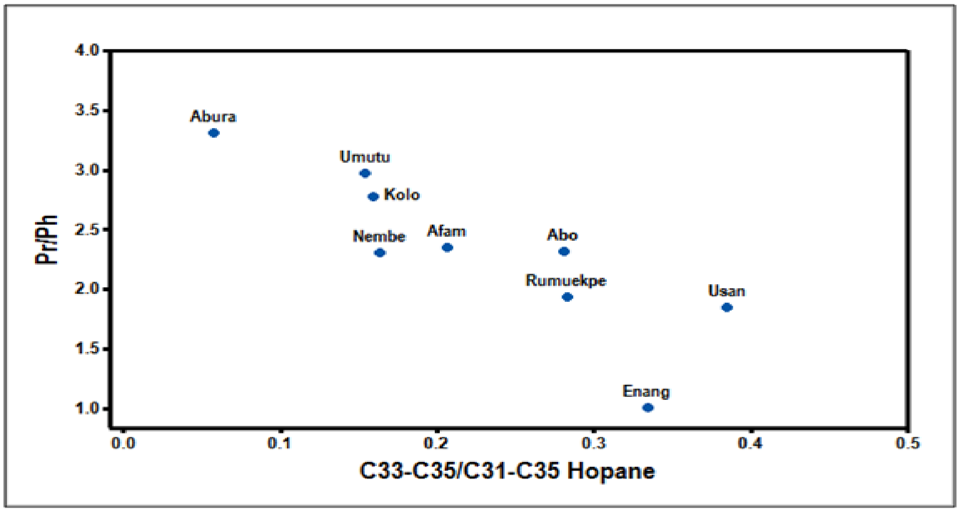

Figure 4. Plot of Pr/Ph ratio versus C_{33}–C_{35} hopane/C_{31}–C_{35} hopane ratio

Maturity.

The maturity of oils is always derived from the isomerization ratios. In this study, the homohopane isomerization ratios were used for derivation of maturity of the suite of oils used. Figure 5, is a plot of Oleanane/C_{30} hopaneand $\alpha\beta C_{32}$ homohopane.

The plot (Figure 5) shows that the oils bears nearconsistent maturity values, though the Nembe oil is more matured. However, the Oleanane/C_{30} hopaneshowed some variation across the plot depicting the variability of the content of vascular plant materials that could have been incorporated into the organic matter generating the oils.

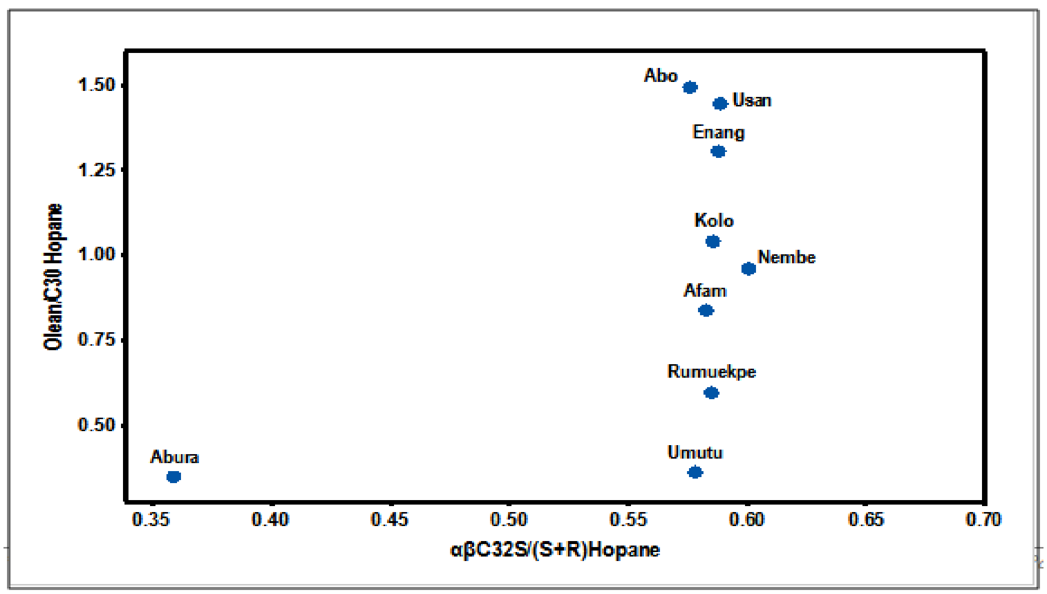

Figure 5. Plot of Oleanane/C_{30}Hopane versus $\alpha\beta C_{32}$ S/S+R Homohopanes.

The plot showed that the offshore oils (Abo, Enang, Usan) had higher Oleanane/C_{30} hopane ratios. The Nembe oil is fairly more matured relative to other oils. the Abura oil is least matured. Earlier studies show that maturity of oils as portrayed by the gas to oil ratios across the Niger Delta averagely increases from the Northern Depo Belt to the Offshore Depo Belt. The consistency may infer oils from similar formation but different facies. Tuttle et al (1999), Demaison & Murris (1984)

V. CONCLUSION.

The study unveils that the offshore oils (Abo, Enang, Usan) have higher Oleanane/C_{30}hopane ratio and higher C_{33}–C_{35} hopane/C_{31}–C_{35} hopane ratio and a plot of these ratios can be applied to discriminate offshore oils from onshore oils.The study also show that some offshore fieldsare located close to clay channels or canyons.

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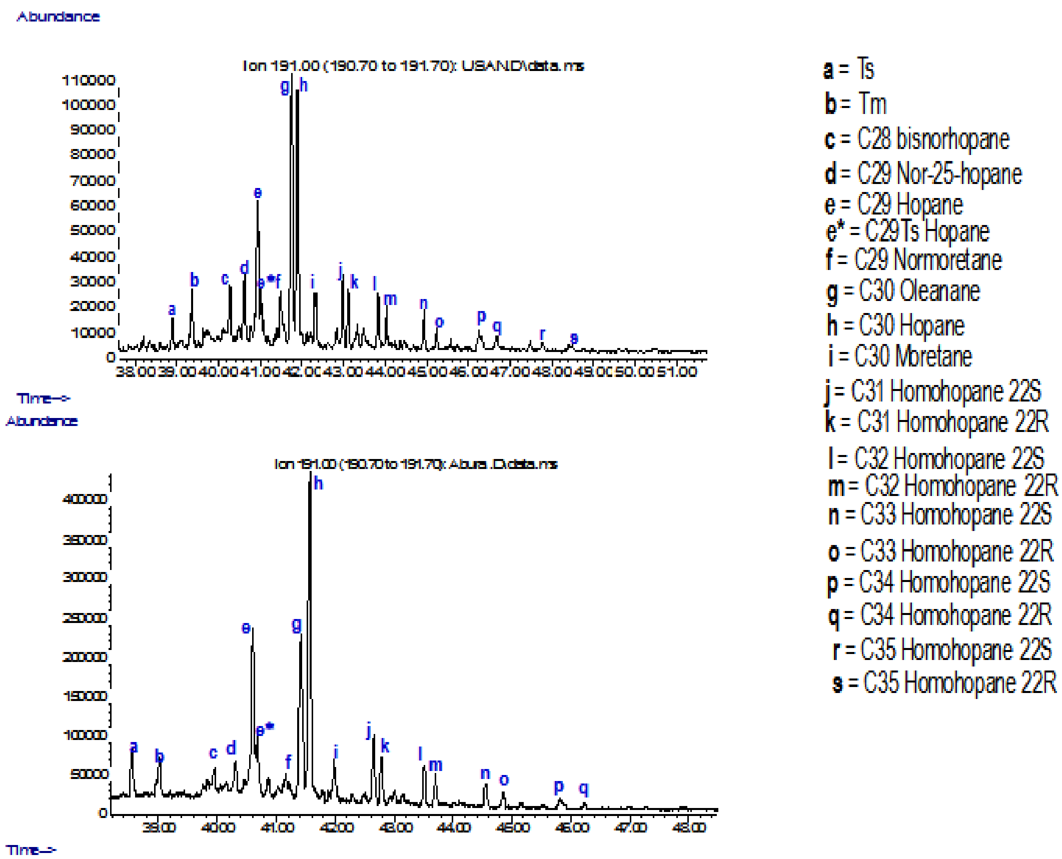

Mass chromatograms of Ion 191 for Usan and Abura oils. Notice the high Oleanane and C35 homohopanes for Usan oil relative to the Abura oil.

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