Journal of
Applied Sciences

science
alert

ANSI_net_
an open access publisher
http://ansinet.com

Assessment of Compositional Heterogeneities of Core Samples from Harding (9/23b-10) and Gryphon (9/18b-17) Oil Columns

Salihu Aliyu

Department of Biochemistry, Ahmadu Bello University, Zaria, Nigeria

Abstract: This study focuses on geochemical assessment of thirteen core samples from two wells (9/23b-10-Harding and 9/18b-17-Gryphon) that lie on the same block; so as to determine their compositional heterogeneities and to compare other biomarker parameters in these columns. Iatroscan TLC-FID showed that saturated, aromatic hydrocarbons, resins and asphaltene fractions were in agreement with where thermogenic hydrocarbons had existed. All the core samples were found to be associated with each other based on diagnostic biomarker parameters including Pris/Pris+Phy vs. $C_{27}\beta\alpha$ Dias/ C_{27} sterane, Ts/Ts+Tm, 22S/22S+22R homohopane and the presence of 28,30 bisnorhopane from GC-MS analyses, which were related to their organic matter source and thermal maturity. This study reveals that vertical compositional heterogeneities remain in the two columns.

Key words: Compositional heterogeneities, biomarker, biodegradation, thermal maturity, core samples

INTRODUCTION

Geochemical analyses increase exploration efficiency by accounting for several parameters controlling the volumes of petroleum available for entrapment; this includes source rock quality and richness, thermal maturity and the timing of generation, migration and accumulation relative to trap formation; these require incorporation of other disciplines, such as seismic sequence stratigraphy and reservoir characterization (Peters and Fowler, 2002; Purvis *et al.*, 2002; Simoneit, 2004). Accurate and subsurface description is necessary to provide reservoir engineers with model for dynamic simulation (Purvis *et al.*, 2002; Wei *et al.*, 2008).

Large scale heterogeneities in petroleum composition within reservoirs have been known for many years but the topic received less attention until 1980s when sufficient analytical technologies became available to probe the phenomenon. The work of England *et al.* (1987) and England and Mackenzie (1989) has brought the explanation of petroleum reservoir geochemistry especially the concept of heterogeneity to the forefront of petroleum geochemistry (Stoddart *et al.*, 1995). These compositional differences are sometimes preserved on a lateral kilometre scale across communicating reservoirs over geological time but rarely within the vertical scale of a petroleum column (Stoddart *et al.*, 1995). The order of magnitude time scales for reservoir fluid mixing by diffusion as a function of reservoir properties was established by England and Mackenzie (1989). Homogenization times for inherited petroleum column heterogeneities on a kilometre scale by lateral diffusion are on the order of 100 Ma while for vertical diffusion on a reservoir thickness scale of 100 m is about 1 Ma (England *et al.*, 1987; England and Cubit, 1995). For reservoirs filled during Late Tertiary times, some level of vertical homogenization would be expected in a petroleum column composition with persistence of a significant lateral heterogeneity (Larter and Aplin, 1995). Thus, these variations can be used to determine fill direction assuming that the most mature petroleum entering the reservoir last displaces the less mature petroleum (England *et al.*, 1987).

The variations in geochemical composition of petroleum fluids exist for one or more of the following reasons:

- The oils may be obtained from different source rocks, or may have differing contributions of oil from multiple source rocks as well as filling history (Killops and Killops, 1993; Tissot and Welte, 1984)
- Microbial alteration of petroleum during migration and emplacement (Baylis, 1998) and other processes including interaction of polar petroleum compounds with reservoir surfaces may affect homogenization even on small scales (Larter, 1992)
- Maturity differences may be preserved as compositional variations in a petroleum column due to incomplete mixing of petroleum in a reservoir (Horstad *et al.*, 1990)

Many development and production problems can be understood using rapid and common petroleum

geochemical methods (such as Rock eval pyrolysis, TLC-FID, GC, GC-MS, etc.). Traditional exploration focuses on subsurface traps and the play concept in sedimentary basins described according to tectonic style (Peters and Fowler, 2002; Wei *et al.*, 2008). Sophisticated analyses such as GC-IR-MS or Nitrogen compound and phenol analysis are found useful in the study of oils and core samples (Larter and Aplin, 1995).

This study is aimed at determining whether variations occur within and between the two oil columns located in Harding and Gryphon fields based on geochemical analyses associated with their maturity, biodegradation, source, etc. by analyzing oil saturated cores obtained from the exploration wells in the two fields.

MATERIALS AND METHODS

The samples used in this study were a gift from Dr. Martin of Newcastle University, upon Tyne, UK; comprising thirteen core samples: Eight samples from Harding oil column (9/23b-10) and five from Gryphon oil column (9/18b-17). The Gryphon oil field is located in block 9/18b, North-East of Aberdeen which was deposited during Late Palaeocene-Early Eocene; while the Harding field (Late Palaeocene-Early Eocene) lies principally across Block 9/23b North-East of Aberdeen. All reagents used in this study were of analytical grade except otherwise stated.

Iatroscan (Thin layer chromatography-flame ionization detector): Core extracts were analysed by Iatroscan TLC-FID. A TH-10 Mk IV instrument equipped with a flame ionization detector was used for rod scanning and quantification as described by Karlsen and Larter (1991). Silica rods type chromarods-S III (pore diameter 60', particle size 5 µm) were used for TLC. Normal hexane and toluene were used as mobile phases for the separation. The amounts of saturated and aromatic hydrocarbons and polar compounds (resins and asphaltenes) were identified by a digital recorder (LabSystem Atlas v3.0 software).

Thin Layer Chromatography (TLC): The TLC plates were prepared using aqueous slurry of 0.5 mm thick Keiselgel 60 G; the plates were activated for an hour at 100-120°C. The samples were spotted on separate TLC plates at about 2-3 cm from the bottom using a capillary tube. The plates were then separated in petroleum ether. Rhodamine 6 G was sprayed on the plates to identify different bands under UV light, aliphatic and aromatic hydrocarbon bands were identified and scraped off into different prepared elution tubes which were washed with about 40-50 mL

dichloromethane. The extract for each was reduced in volume using a rotary evaporator and then placed in auto-sample vial. Aliphatic hydrocarbon fractions were taken for further analysis.

Gas Chromatography-Mass Spectrophotometry (GC-MS): GC-MS analyses of the aliphatic hydrocarbon fractions were performed on a Hewlett Packard 5890 gas chromatograph interfaced to a VG AutoSpecQ Ultima (electron energy 70 eV; electron multiplier 250 V; filament current 200 µA; source temperature 280°C) tuned to 1000 resolution. Chromatography was carried out on a fused silica column (30 m×0.25 mm i.d.) coated with DB5MS (modified 5% phenyl, 95% methyl silicone, 25 µm film thickness), using a splitless injection technique. The oven was programmed for an initial temperature of 40°C for 2 min, followed by heating at 4°C min^{-1} to 310°C and held at a final temperature for 20 min. The samples were run using full scan and Single Ion Monitoring (SIM) and data obtained was recorded and processed using a HP ChemStation data system.

RESULTS AND DISCUSSION

Well 9/23b-10 (Fig. 1) showed approximately 15-90% saturated hydrocarbons, 10-49% aromatic compounds, 0.6-26% resins and 0-29% asphaltenes; also, well 9/18b-17 (Fig. 2) was relatively uniform with a slight increase in saturated hydrocarbons (e.g., from 45-68% at 5748-5782 m, respectively). The highest percentage of saturates in this well was observed at a depth of 5782 m, which has a very low concentration of resins and asphaltenes.

The plot of Pris/Pris+Phy versus $C_{27}\beta\alpha$ S+R Dias / C_{27} steranes (Fig. 3) indicated a genetic relationship between the samples. Biomarker parameters such as 22S/22S+22R
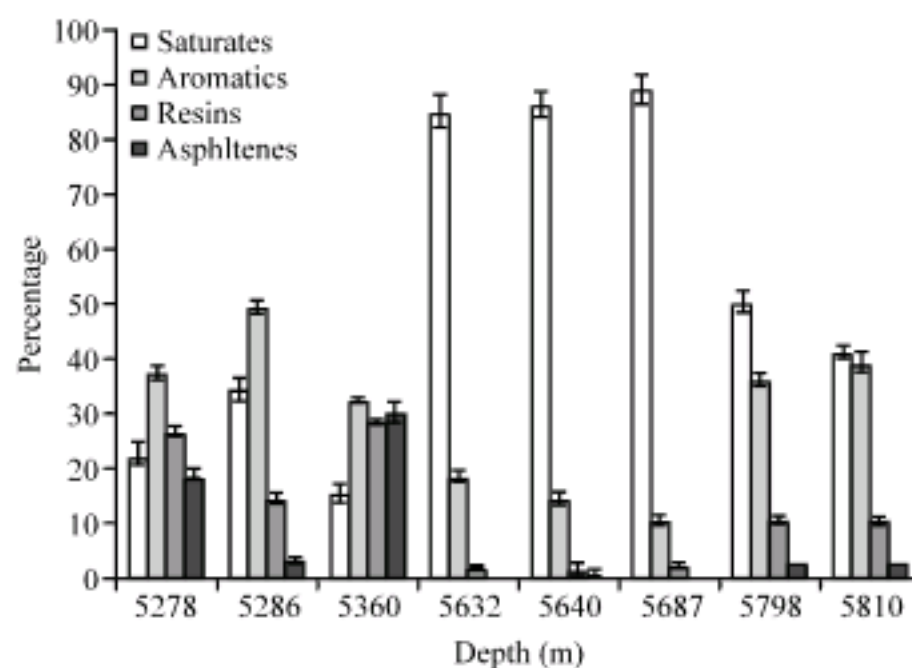

Fig. 1: Distribution of components of the core extracts in Harding oil column (9/23b-10) obtained from TLC-FID analyses
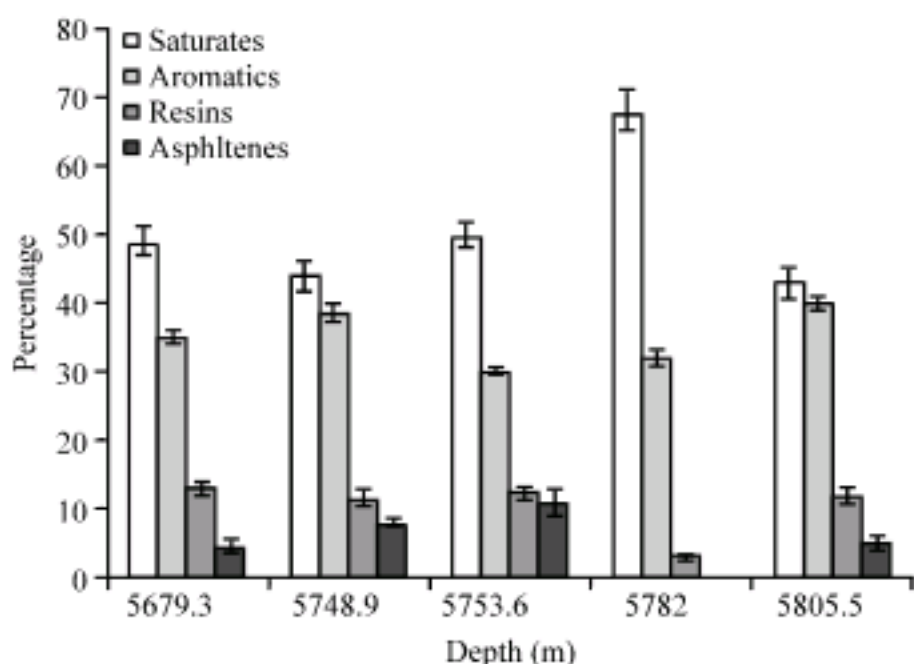
Fig. 2: Distribution of components of the core extracts in Gryphon oil column (9/18b-17) obtained from TLC-FID analyses
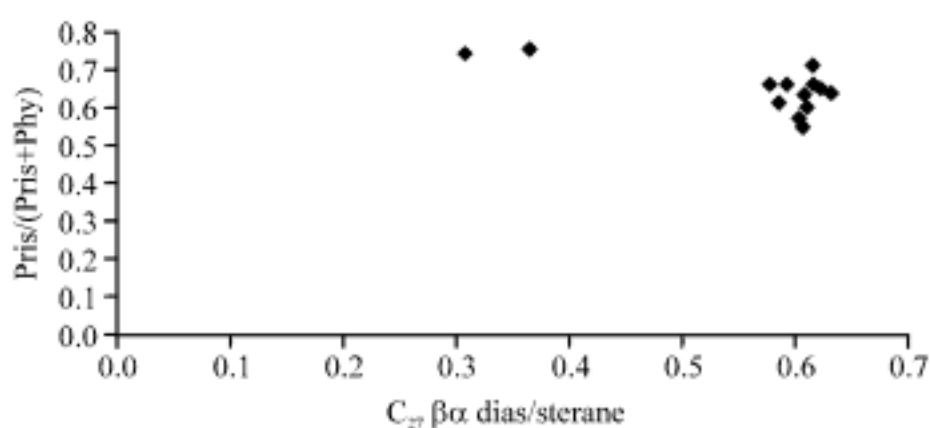

Fig. 3: Source related biomarker indicating the level of relationship between core samples in the two columns; this is obtained from GC-MS fingerprints

Fig. 4: Mass chromatogram (m/z 191) showing the presence of bisnorhopane

Table 1: Some of the diagnostic biomarker parameters in the two columns

Well depth (m)	Sample code	Ts/Ts+Tm	Sterane/hopane	Homohopane
5278.00	9/23b-10	0.49	0.93	0.54
5286.20		0.50	0.60	0.54
5360.00		0.58	0.82	0.56
5632.11		0.65	0.84	0.58
5640.00		0.62	0.86	0.57
5686.70		0.49	0.79	0.57
5797.80		0.65	0.54	0.57
5810.00		0.61	0.77	0.58
5679.30	9/18b-17	0.69	0.49	0.59
5748.90		0.71	0.81	0.58
5753.60		0.69	0.50	0.59
5782.00		0.72	0.61	0.60
5805.60		0.69	0.50	0.59

Where Ts/Ts+Tm (C_{29} 17α-hopane/C_{29} 17α-hopane + C_{27} 17α-hopane); Sterane/hopane [(C_{27},C_{28}, C_{29} ααα (20S+20R) + C_{27},C_{28}, C_{29} ααβ (20S+20R))/(17α-hopane C_{29}-C_{33} Pseudohomologs 22S+22R for C_{31}-C_{33})] and homohopane [(C_{35}/C_{31}-C_{35}) 17α (22S+22R) hopane]. All of these were obtained from m/z 191 and m/z 217 chromatograms

homohopane, Ts/Ts+Tm and sterane/hopane were measured for the two wells (Table 1) to determine the extent of these ratios in the two columns. Representative mass chromatogram (m/z 191) for hopane shows the presence of bisnorhopane (Fig. 4) in all the samples which is a source related parameter. Slight to moderate biodegradation of the samples occurred in both wells (9/23b-10 and 9/18b-17) as represented in Fig. 5a-d.

Utilizing the GC and GC/MS techniques made it possible to arrive at a clear characterization according to organic source materials, environmental conditions during deposition, the thermal maturity experienced by a rock or oil and the degree of biodegradation. This has been achieved using fingerprints from acyclic isoprenoids, steranes and terpanes biomarkers (El-Gayar *et al*., 2002a; Bost *et al*., 2001).

The gross compositions of core extracts screened by Iatroscan TLC-FID were determined; thus all samples in the two wells seem to represent regions where migrated petroleum has existed (Fig. 1, 2). This is due to the fact that the values obtained are higher than what were suggested by B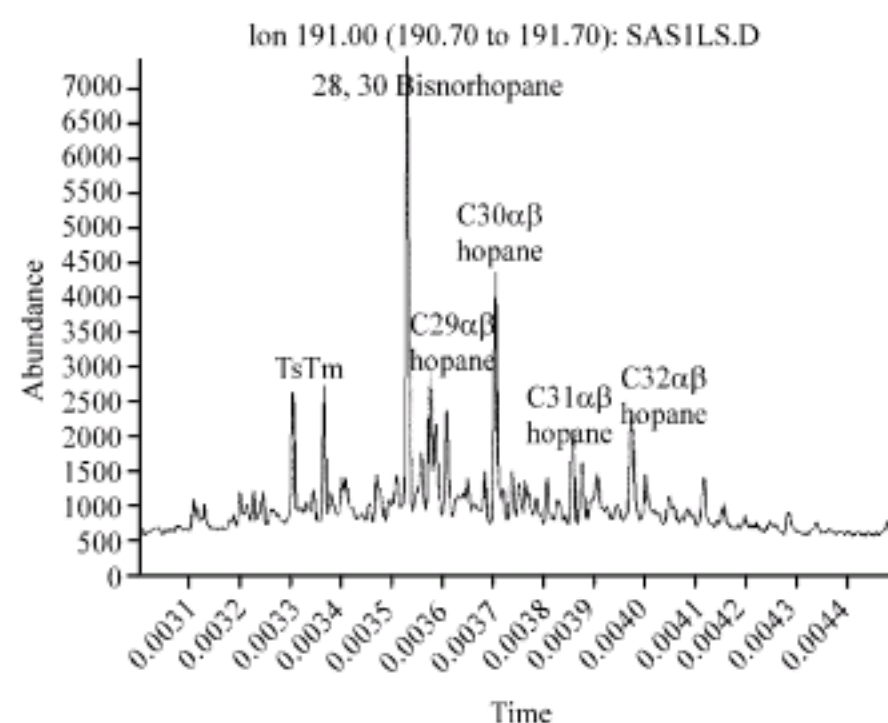hullar *et al*. (1998) who showed that any core extract that contained less than 10% saturates, less than 20% aromatics and greater than 70% polar compounds had no thermogenic hydrocarbons and rather the extract was generated in-situ and does not represent a migrated petroleum. Some of the core samples especially those from 9/23b-10 showed the abundance of saturated hydrocarbons which are in agreement with suggested values (>60) of good saturated oils (Younes, 2003).

A genetic relationship between the core extracts is examined in Fig. 3; showing a convergence of points which indicates a common source with only two outliers; these outliers are the shallower samples of well 9/23b-10 which their fingerprints suggest that they were affected by biodegradation. This might likely be the reason that made them appeared different from the rest of the data because such difference is likely due to secondary processes rather than source.
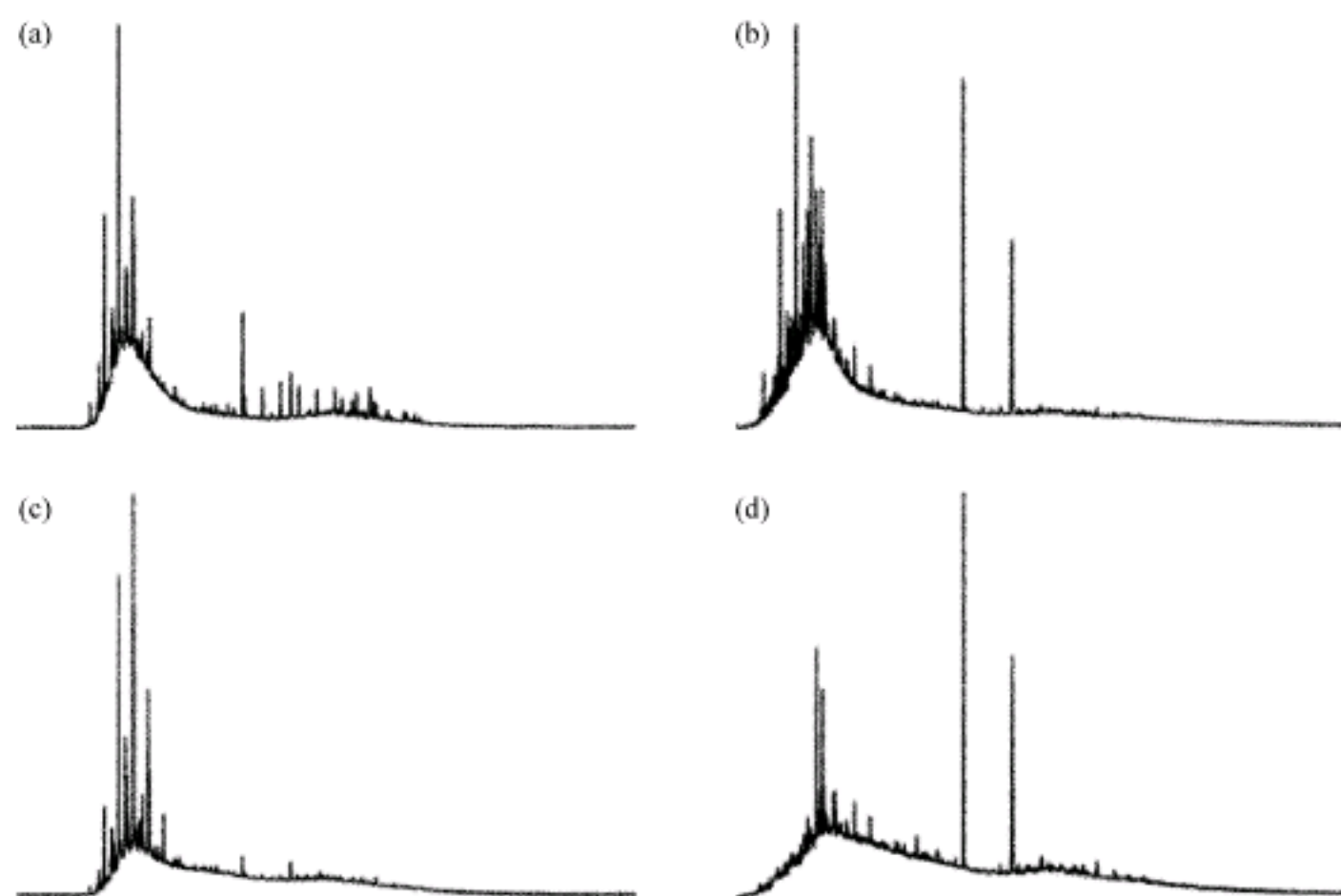
Fig. 5: Total hydrocarbon gas chromatograms indicating the presence of biodegraded oil and oil based mud signature from well-9/23b-10 (two at the top) and well-9/18b-17 (two at the bottom) from GC-MS analyses. (a) TIS: SAS2LSD (b) TIC: SAS15LSD (c) TIC: SAS12LSD and (d) TIC: SAS14LSD

The samples in both wells seem to be mature with higher values (Table 1), which conform to those described by Peters *et al*. (2005) where 22S/22S+22R homohopane ratios of 0.5-0.54 indicated a range of samples that have entered oil generation and those with 0.57-0.62 have reached the main phase of oil generation; they further added that once this stage has been reached, no further maturity information would be available because the ratio remains constant. This is in agreement with C_{31} homohopanes measured for oil samples studied by El-Gayar *et al*. (2002b) and Harb *et al*. (2003); where all the values were closer or even higher than the steady-state value of 0.60 and as such the oils were suggested to have been derived from source rocks at advanced stage of thermal maturity.

Also, Waseda and Nishita (1998) described Ts/Ts+Tm ratio as one of the most reliable maturity indicator and the ratio increases from 0 to 1 with increasing maturity. Thus, the values obtained suggested some level of maturation in both wells. The Ts/Ts+Tm ratios obtained from this study were lower than those obtained from Western Desert samples that have higher values of ≥1 (Shi *et al*., 2005; Harb *et al*., 2003); and much higher than those from Paleozoic reservoir rocks in the Tataria and Perm basins, of Russia as found by Aizenshtat *et al*. (1998). Also, facies dependence could be exhibited by this ratio (Ts/Ts+Tm) where less than unity indicates marine depositional environment (Younes, 2003; Peters *et al*., 2005).

Source related biomarker (sterane/hopane) has been described by Moldowan *et al*. (1985) where marine sources with major inputs from planktons and or benthic algae have sterane/hopane ratio ≥1, while non marine sources with high terrestrial inputs tend to have very low values (near zero); therefore, all the values measured from this ratio are closer to 1, suggesting mixed inputs which may be linked to Kimmeridge source as the major source of oils in the North Sea (Dahl, 2004).

The occurrence of relatively high amounts of 28, 30-bisnorhopane in the m/z 191 mass chromatograms from most of the core samples in the two fields has been observed (Fig. 4). This feature seems to provide a good evidence for the source of these samples and tends to follow the findings from several studies which proposed the presence of bisnorhopane in the Viking Group, Kimmeridge Clay bitumen and oils from Oseberg Back Basin, Viking Graben, Heather Formation and Upper Jurassic Draupne Formation (Dahl, 2004). Thus 28, 30-Bisnorhopane found in the core extracts in this study indicates that the extracts were sourced from Kimmeridge Clay Formation. Thus, bisnorhopane isomers are found to be a helpful tool to group Viking Graben derived oils into families as represented in several petroleum systems and reservoir geochemistry analysis (Johannesen *et al*., 2002).

Slight to moderate biodegradation occurred as most of the n-alkanes have been removed. These results agree with the study of Baylis (1998) and Peters and Fowler (2002) which showed that alteration of core materials and

contamination of samples with Oil-Based Mud (OBM) commonly give a saturated gas chromatogram with a hump of unresolved compounds; they further showed examples of hump in the C_{13}-C_{16} n-alkane range where the sample was contaminated by Biovert (emulsion of water and highly paraffinic low aromatic mineral oil). This may be similar to what has been observed in Fig. 5. Also, the loss of straight-chain and isoprenoids as seen in the Fig. 5 corresponds to what was observed in Cuban oils studied by Grimalt *et al*. (2002); suggesting that mixing of severely biodegraded oil with undegraded oils during accumulation in the reservoir contributes to different patterns of biodegradation as well as oxidative activities of microbes within the reservoir (Campos *et al*., 1996).

Based on these parameters; it could be concluded that all the core samples examined in this study, though obtained from the same block but are heterogeneous, with common source and compositional variations existed in the two columns indicating that vertical reservoir equilibration has not yet being established.

ACKNOWLEDGMENT

REFERENCES

Aizenshtat, Z., S. Feinstein, I. Miloslavski, Z. Yakubson and C.I. Yakubson, 1998. Oil-oil correlation and potential source rocks for oils in Paleozoic reservoir rocks in the Tataria and Perm basins Russia. Organic Geochem., 29: 701-712.

Baylis, S.A., 1998. Geochemical comparison of core extracts and oil samples in reservoir. Organic Geochem., 29: 463-484.

Bhullar, A.G., D. Karlsen, A. Holm, K.B. Owe, K. Le and K. Tran, 1998. Petroleum geochemistry of the FrØy field and Rind discovery, Norwegian continental shelf. Implication for reservoir characterization, compartmentalization and basin scale hydrocarbon migration patterns in the region. Organic Geochem., 29: 735-768.

Bost, F.D., R.F. Suau, T.J. McDonald, K.E. Peters and P.J. Morris, 2001. Aerobic biodegradation of hopanes and norhopanes in Venezuelan crude oils. Organic Geochem., 32: 105-114.

Campos, P.G., J.O. Grimalt, L. Berdie, J.O.L. Quintero and L.E.N. Reyes, 1996. Organic geochemistry of cuban oils I the Northern geological Province. Organic Geochem., 25: 475-488.

Dahl, B., 2004. The use of bisnorhopane as a stratigraphic marker in the oseberg back basin North Viking Graben Norwegian North Sea. Organic Geochem., 35: 1551-1571.

El-Gayar, M. Sh., A.E. Abdelfattah and A.O. Barakat, 2002a. Maturity-dependent Geochemical markers of Crude petroleums from Egypt. Petroleum Sci. Technol., 20: 1057-1070.

El-Gayar, M.Sh., A.R. Mostafa, A.E. Abdelfattah and A.O. Barakat, 2002b. Application of geochemical parameters for classification of crude oils from Egypt into source-related types. Fuel Process. Technol., 79: 13-28.

England, W.A., A.S. Meckenzie, D.M. Mann and T.M. Quigley, 1987. The movement and entrapment of petroleum fluids in the subsurface. J. Geol. Soc. Lond., 144: 327-347.

England, W.A. and A.S. Meckenzie, 1989. Some aspects of organic geochemistry of Petroleum fluids. Geologische Rundschau, 78: 291-303.

England, W.A. and J.M. Cubit, 1995. Geochemistry of Reservoirs, an introduction. The Geochemistry of Reservoirs. Geol. Soc. Special Publ., 86: 1-3.

Grimalt, J.O., P.G. Campos, L. Berdie, J.O.L. Quintero and L.E.N. Reyes, 2002. Organic geochemistry of the oils from the southern geological Province of Cuba. Applied Geochem., 17: 1-10.

Harb, F.S.D., M.M. El-Nady and J.S. Basta, 2003. Oil oil correlation for some oil fields in the North Western Part of the Western Desert, Egypt. Petroleum Sci. Technol., 21: 1583-1600.

Horstad, I., S.R. Larter, H. Dypvik, P. Aagaard, A.M. BjØrnvik, P.E. Johansen and S. Eriksen, 1990. Degradation and maturity controls on oil field petroleum column heterogeneity in the Gullfaks field Norwegian North Sea. Organic Geochem., 16: 497-510.

Johannesen, J., S.J. Hay, J.K. Milne, C. Jebsen, A. Gunnesdal and A. Vayssaire, 2002. 3D-oil migration modeling of the Jurassic petroleum system of the Statfjord area, Norwegian North Sea. Petroleum Geosci., 8: 37-50.

Karlsen, D.A. and S.R. Larter, 1991. Analysis of Petroleum fractions by TLC-FID: Application to petroleum reservoir description. Organic Geochem., 17: 603-617.

Killops, S.D. and V.J. Killops, 1993. An Introduction to Organic Geochemistry. John Wiley, New York, ISBN: 0632065044, pp: 265.

Larter, S.R., 1992. Reservoir geochemistry the definition of migrational conduits and the subtle trap. Geol. Soc. Special Publ., 67: 27-28.

Larter, S.R. and A.C. Aplin, 1995. Reservoir Geochemistry methods application and oppurtunities. Geol. Soc. Lond. Special Publi., 86: 5-32.

Moldowan, J.M., W.K. Seifert and E.J. Gallegos, 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. Am. Assoc. Petroleum Geologists Bull., 69: 1255-1268.

Peters, K.E. and M.G. Fowler, 2002. Application of petroleum geochemistry to exploration and reservoir management. Organic Geochem., 33: 5-36.

Peters, K.E., C.C. Walters, J.M. Moldowan, 2005. Biomarker Guide Biomarker and Isotopes in Petroleum Exploration and Earth History. Cambridge University, Cambridge, ISBN: 0521837626, pp: 1155.

Purvis, K., J. Kao, K. Flanagan, J. Henderson and D. Duranti, 2002. Complex reservoir geometries in a deepwater clastic sequence gryphon field UKCS Injection structures, geological modelling and reservoir simulation. Marine Petroleum Geol., 19: 161-179.

Shi, D., M. Li, X. Pang, D. Chen, S. Zhang, Y. Wang and Q. Jin, 2005. Fault fracture mesh petroleum plays in the Zhanhua Depression Bohai Bay Basin Part 2. Oil-source correlation and secondary migration mechanisms. Organic Geochem., 36: 203-223.

Simoneit, B.R.T., 2004. Biomarkers (molecular fossils) as geochemical indicators of life. Adv. Space Res., 33: 1255-1261.

Stoddart, D.P., P.B. Hall, S.R. Larter, J. Brasher, M. Li and M. BjorØy, 1995. The reservoir geochemistry of the Eldfisk field, Norwegian North Sea. Geol. Soc. Lond. Special Publ., 86: 257-279.

Tissot, B.P. and D.H. Welte, 1984. Petroleum Formation and Occurrence. 2nd Edn., Springer-Verlag, Berlin, ISBN: 0387132813, pp: 699.

Waseda, A. and H. Nishita, 1998. Geochemical characteristics of terrigenous and marine-sourced oils in Hakkaido, Japan. Organic Geochem., 28: 27-41.

Wei, Z., Z. Jinliang and X. Jun, 2008. Research on reservoir bed heterogeneity interlayers and seal layers and controlling factors of 2+3 sands of upper second member Shahejie Formation in the west of the pucheng oil field. Petroleum Sci., 5: 135-144.

Younes, M.A., 2003. Organic and carbon isotope geochemistry of crude oils from ashrafi field southern gulf of suez province, Egypt implications for the processes of hydrocarbon generation and maturation. Petroleum Sci. Technol., 21: 971-995.