

# RASHMI ANAND, M. S. BISHT, KUSUM LATA PANGTEY, S. K. SAXENA, VIBHA PRABHAKAR and P. DWIVEDI Geochemistry Group, KDMIPE, ONGC, Dehradun 248 195 Email: <u>rashmianand01@yahoo.co.in</u>

#### Control ID: 667

# Evidences for Fresh Water Lacustrine Origin of Tertiary and Cretaceous Oils of Krishna-Godavari Basin, India

Hydrocarbon occurrences in the stratigraphic intervals ranging from Permo-Triassic to Pliocene, mark the Krishna-Godavari Basin as a premier area for exploration in the Indian subcontinent. Hydrocarbon occurrences over a long stratigraphic record in the basin demand a systematic approach to understand the hydrocarbon habitat. Presently the 'Petroleum Systems' approach is the most applied methodology. Identification of the various 'oil families' based on geochemical characterization constitutes one of the important inputs for defining the petroleum systems in the basin. Krishna-Godavari Basin is the thrust area for exploration in the east coast of India, because of several deep water commercial hydrocarbon finds in the recent past. Geochemical characterization of new finds may lead to better understanding of petroleum system in this tectonically active basin.

### Samples and Methodology

Eight liquid hydrocarbon samples from five exploratory wells were evaluated. Well A is an onshore well from East Godavari subbasin. Other four wells (B, C, D and E) are from offshore area (Fig.1 and Table 1). The samples were analyzed for bulk characteristics and molecular level parameters as per standard methods.

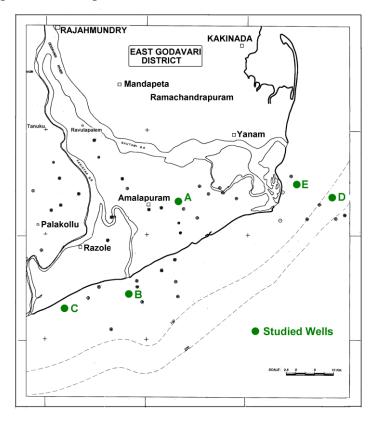


Figure 1 Well location map



### **Results and Discussion**

Geochemical data on hydrocarbon samples are presented in Table 1. The bulk parameters show that two samples are condensates (55.47 and 49.24 °API), rest are light oils with 34.13 to 44.67 °API. Golapalli Formation oils have low pour points (< 0 and 6°C) and Vadaparru Formation oils have high pour points (33 and 36°C). For oils/condensates of Matsyapuri Formation it varies from < 0 to 30°C. The condensate from Pasarlapudi Formation has pour point below 0°C.

All the oils are low sulphur oils. Early Cretaceous oil from Well E shows high sulphur content of 2340 ppm. All others have sulphur content in the range 40 to 400 ppm. The composition of condensate from Pasarlapudi Formation is unusual with very high saturates/aromatic ratio, 14.04. This is followed by Golapalli oils (4.48 and 6.37), rest of the oils fall in the range 2.42 to 3.83. Also, asphaltenes are absent in condensate from Pasarlapudi Formation, other oils have very low content of asphaltenes.

Normal alkane and isoalkane data show that all the samples have very high pristane to phytane ratios (5 to 6.63). Pristane is dominant peak in all the samples except Golapalli oils. Depth vs Pr/Ph cross plot shows that Pr/Ph ratio decreases with increasing depth for offshore samples (Fig. 2 & 2a). The onshore sample (Well A) shows the highest value for this ratio. Likewise offshore oils from Well D and E show very low values for Pr/nC<sub>17</sub> (0.22 to 0.26), while all other oils have values >1. These data for oils suggest terrestrial input with dominance of coals (Waples, 1985; Hunt, 1996). Also in Pr/nC<sub>17</sub> and Ph/nC<sub>18</sub> cross plot all the oils fall in the range of 'Terrestrial Coaly type III' organic matter (Fig. 3). However, totality of the oil characteristics do not conform to the coal related oils.

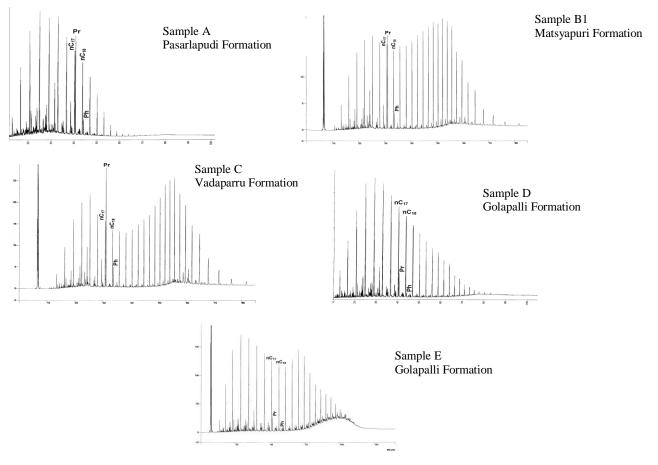




Figure 2 Gas chromatograms of oils

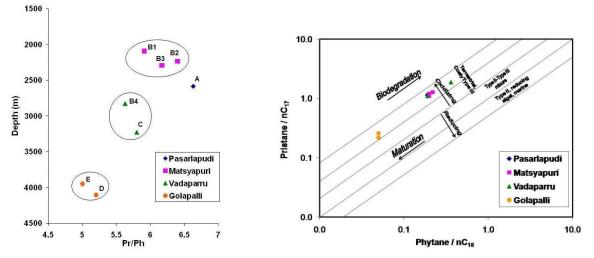


Figure 2a Depth vs Pristane/Phytane ratios

Figure 3 Cross-plot of Pr/nC<sub>17</sub> and Ph/nC<sub>18</sub>

In last fifteen years a lot of data have been published on characteristics of freshwater and hypersaline lacustrine oils and their comparison with terrestrial and marine oils. It is interesting to note that above imprints of coal type organic matter are also shown by fresh water lacustrine oils (Tieguan et al., 1997; McCaffrey, 2004 and Visser, 2008). Also the fresh water lacustrine oils show a typical decreasing pattern of homohopanes  $C_{32}$  to  $C_{35}$  in the triterpane fragmentogram. This pattern is seen in all the oils under present study suggesting fresh water algal matter as possible source input for these oils. Also the Pasarlapudi oil shows very high saturate to aromatic ratio (14.04,Table 1), a characteristic of immature lacustrine oils (Tieguan et al., 1997). Even so being the case source input for the Lower Cretaceous oil from Well E, seems to be different as in this oil, the fragmentogram of triterpanes shows dominance of  $C_{29}$  hopane over  $C_{30}$  hopane, whereas, in all other oils  $C_{30}$  hopane dominates over  $C_{29}$ . Also oleanane is absent in this oil while it is present in all other oils (Table 1 and Fig. 4).



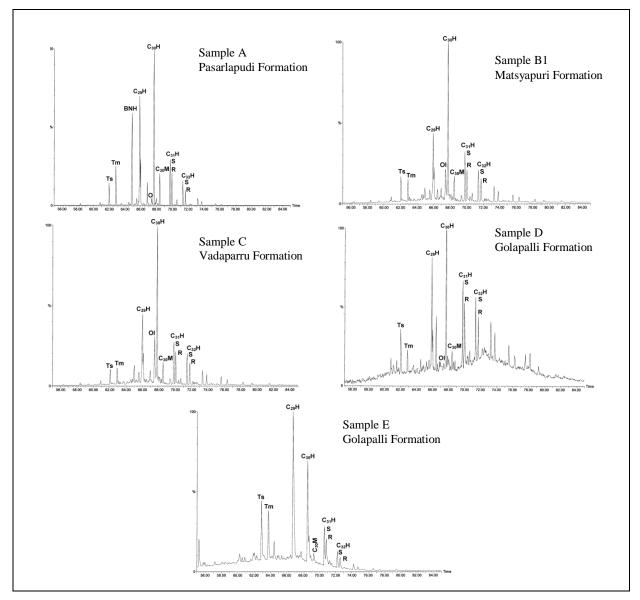


Figure 4 Triterpane mass fragmentograms (m/z 191) of oils

The GC-MS tracing of onland East Godavari oil (Well A) of Pasarlapudi Formation shows presence of bisnorhopane (Fig. 4) Recent literature suggests it to be typical of horizons indicating high algal productivity and oxygenated depositional environments (Yamamoto and Watanabe, 1994). Oils of Vadaparru to Matsyapuri formations show high Oleanane Index (18.25 to 28.35), suggesting increasing higher land plant input to algal source organics. The Oleanane Index decreases with decreasing depth of occurrence of oils (Table 1 and Fig. 5).

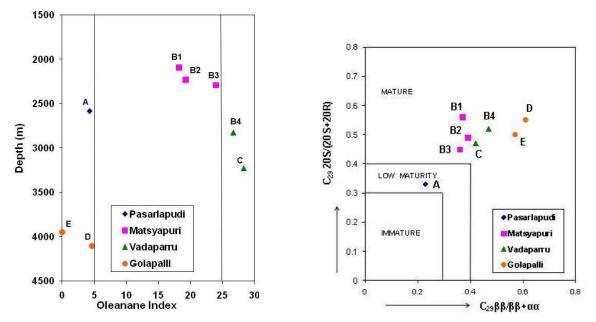
All the oils except the Golapalli oils show  $Pr/nC_{17}$  ratios more than one (Table 1), which suggests highly oxic environment of deposition for the source organic matter. The low values (0.26 and 0.22) of  $Pr/nC_{17}$  for the offshore Golapalli oils suggest that their source organic matter was deposited in restricted, less oxic environments (Waples, 1985; Hunt, 1996).

The C<sub>29</sub> Sterane  $\beta\beta/(\alpha\alpha+\beta\beta)$  ratios of the oils are shown in Table 1. It may be seen that the Pasarlapudi oil shows least maturity level with lowest value for this ratio, 0.23 and the



offshore Golapalli oils are the most mature oils of the lot with values 0.57 and 0.61. Other offshore oils of Vadaparru and Matsyapuri fall in between with values in the range 0.36 to 0.47 suggesting them to be of intermediate maturity.

In a cross plot of C<sub>29</sub> Sterane 20S/(20S+20R) and C<sub>29</sub> Sterane  $\beta\beta/(\alpha\alpha + \beta\beta)$  the Pasarlapudi oil falls in the range of low maturity, the Golapalli oils are seen to be the most mature (Fig. 6). It may be observed that the equilibrium ratio of 0.7 is not reached even by the so called most mature oils of the study, the Golapalli oils, suggesting their maturity level, too, being below "peak of oil window" maturity (Peters and Moldowan, 1993).



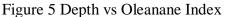


Figure 6 C<sub>29</sub>Sterane maturity cross-plot

There are many other noteworthy observations in relation to maturity level of these oils. All the oils except the Golapalli oils show dominance of pristane in the gas chromatogram. Also the normal alkane distribution is dominated by the ones that come directly from the bio-organics suggesting low maturity of the oils.

The Pasarlapudi oil also shows considerable content of bisnorhopane, which is known to be contributed directly from the bio-organics (Dahl, 2004; Visser, 2008). As said earlier Pasarlapudi oil has exceptionally high saturate to aromatic ratio (14.04, Table 1), which is observed with immature oils of lacustrine origin (Tieguan et al., 1997). One more unusual observation with Pasarlapudi oil is that it shows same stable carbon isotopic composition (-28.1 per mil) for saturate as well as aromatic fraction (Table 1). This suggests that there is no maturity effect on the oil and the stable carbon isotopic composition reflects the average isotopic composition of the source organics.

These observations are well in support of the recently proposed Chinese Model of low maturity oils which suggests a minor oil window in maturity range VRo 0.35 to 0.6 % (late diagenetic to early catagenetic stage of maturation) in addition to conventional "Tissot-Welte oil window" (catagenetic stage of maturation). It is noteworthy that all such immature oils are of lacustrine origin (Huang, 1997; Tieguan et al., 1997).

# Conclusions

Geochemical evaluation in light of recent geochemical literature suggests that the oils/condensates occurring in Tertiary and Cretaceous sequences may be of 'Fresh-



Water-Lacustrine Origin' deposited under varying environments of deposition, least oxic for offshore oils from Golapalli Formation and more oxic for Pasarlapudi, Vadaparru and Matsyapuri formations.

Evaluation of maturity levels shows that the Pasarlapudi formation condensate is generated at very low thermal stress (late diagenetic to early catagenetic). Golapalli Formation oils are the most mature oils in the present study but at levels lower than "peak oil generation". Other offshore oils from Vadaparru and Matsyapuri formations are of intermediate maturity.

Acknowledgements

Authors are indebted to Shri P. K. Bhowmick, ED-HOI, KDMIPE for constant inspiration and keen interest in the studies. Authors are grateful to Dr. R. R. Singh, GM (Chem)-Head, Geochemistry Group for guidance and fruitful suggestions during the course of this study. Thanks are also due to Shri Harish Pande, Suptdg. Chemist and Ms. Hina Kausar, Chemist for generating stable carbon isotopic and GC-MS data.

#### References

Dahl, Birger (2004) The use of bisnorhopane as stratigraphic marker in the Oseberg Back Basin, North Viking Graben, Norwegian North Sea, Org. Geochem., 35, p.1551-1571.

Huang Difan (1997) Advances in hydrocarbon generation theory (I) –Immature oils and generating hydrocarbons and evolutionary model, In Sun Z.C. et al. (Editors), Proc. 30th Intl. Geol Congr., 18, p. 3-15.

Hunt, J.M. (1996) Petroleum geochemistry and geology, W.H. Freeman and Company, New York, USA.

McCaffrey, Mark A. (2004) Modern geochemical techniques for the efficient exploration and exploitation, Advance Training Course in Petroleum Geochemistry, ONGC Academy, ONGC, Dehradun.

Peters, K.E. and J.M. Moldowan (1993) The biomarker guide, Prentice Hall, New Jersey, USA.

Tieguan, Wang, Zhong Ningning, Hou Dujie, Huomg Guanghui, Bao Jiangping and Li Xianqing (1997), Genetic mechanism and occurrence of immature hydrocarbon, Petroleum Industry Press, Beijing, China.

Visser, W. (2008) Modern organic chemistry for exploration of oil and gas, Advance Training Course in Petroleum Geochemistry, ONGC Academy, ONGC, Dehradun.

Waples, D.W. (1985) Geochemistry in petroleum exploration, IHRDC, Boston, USA.

Yamamoto, M. and Y. Watanabe (1994) Biomarker geochemistry and paleoceanography of Miocene Onnagawa diatomaceous sediments, In Proceedings of the 29th International Geologic Congress Part C (Eds) A. lijima, A. M. Abed and R. I. Garrison, VSP BV, A. H. Zeist, The Netherlands.



Table 1 Bulk parameters, n-alkane, isoalkane, triterpane, sterane biomarker and stable carbon isotopic data of oils/condensates

Well No.	А	В				С	D	Е
Sample No.	А	B1	B2	B3	B4	С	D	Е
Age	L. Eocene	Miocene	Miocene	Miocene	Eocene	Eocene	E. Cretaceous to	Early Cretaceous
							L. Cretaceous	
Formation	Pasarlapudi	Matsyapuri	Matsyapuri	Matsyapuri	Vadaparru	Vadaparru	Golapalli	Golapalli
Depth (m)	2583-2586	2091-2094	2232-2236	2292-2293.5	2823-2826	3229-3234	4103-4171	3947-3968
°API Gravity	55.47	38.02	49.24	40.37	37.31	34.13	44.67	41.19
Pour Point (°C)	<0	30	<0	27	33	36	6	<0
Sulphur Content (ppm)	40	245	90	220	248	400	153	2340
Saturates wt %	86.06	63.83	65.27	68.73	64.73	64.27	79.12	75.28
Aromatics wt %	6.13	22.55	17.04	19.26	25.51	26.58	12.43	16.82
Asphaltenes wt %	Nil	0.55	0.45	0.50	0.54	0.78	0.02	Traces
Sat /Aro	14.04	2.83	3.83	3.57	2.54	2.42	6.37	4.48
$\delta^{13}$ C Saturate $^{\circ}/_{oo}$	-28.1	-28.0	-28.8	-29.5	-29.4	-26.0	-26.8	-26.3
$\delta^{13}$ C Aromatic $^{\circ}/_{oo}$	-28.1	-24.6	-27.3	-27.6	-27.9	-24.5	-24.7	-24.6
Pr/Ph	6.63	5.91	6.40	6.17	5.63	5.80	5.20	5.00
Pr/nC <sub>17</sub>	1.15	1.11	1.28	1.21	1.11	1.89	0.26	0.22
Ph/nC <sub>18</sub>	0.19	0.20	0.22	0.20	0.19	0.36	0.05	0.05
Oleanane Index	4.29	18.25	19.28	24.00	26.72	28.35	4.64	Oleanane Absent
20S/(20S+20R) C <sub>29</sub> Sterane	0.33	0.56	0.49	0.45	0.52	0.47	0.55	0.50
$\beta \beta/\alpha \alpha + \beta \beta C_{29}$ Sterane	0.23	0.37	0.39	0.36	0.47	0.42	0.61	0.57
Bisnorhopane	Present	Absent	Absent	Absent	Absent	Absent	Absent	Absent