636 R. K. Saxena, A. Raina, H. C. Pandey, A. K. Bhatnagar, T. Gaba, H. Singh

Application of Compound Specific Isotopic Analysis to Fine tune Oil-Oil, Oil-Source Correlations in KG Basin, India

The compound specific stable carbon isotopic analysis (CSIA) is a state-of-the-art geochemical technique for finer oil-oil and oil-source correlations. There is a great variability in the isotope composition of the sedimentary lipids and it has been suggested that compound specific isotopic data could improve source characterization of oils. Krishna-Godavari Basin is a unique and lucrative petroliferous basin of India with enormous hydrocarbon generating potential, both on-land and offshore with occurrence of oils in different reservoir ages varying from Cretaceous to Pliocene. These reservoirs have been charged at different maturity levels of corresponding sources within different stratigraphic sequences. The location map of Krishna-Godavari Basin showing the studied wells is given in Fig.1.

Geological setting

The Krishna-Godavari Basin (KG basin) along the east coast of India covers the deltaic and interdeltaic areas of Krishna and Godavari rivers and extends into the offshore. The basin has significant hydrocarbon potential both in the Tertiary delta as well as in the channel-levee-overbank play types in the deepwater. The structural trend of the basin is NE-SW and has sedimentary fill from Paleozoic to Cenozoic. Major part of the basin is covered with alluvium and is dominated by two major rivers, Krishna and Godavari and their deltas. Igneous and metamorphic rocks, of Archaen age exposed to the west of basin form the basement. The generalized Stratigraphy of Krishna Godavari Basin is shown in Fig.2.

Based on gravity and magnetic studies, the basin is broadly divided five tectonic elements namely, (1) Krishna Graben, (2) Bapatla horst, (3) West Godavari sub-basin (including the median Kaza-Kaikulur horst separating the Gudivada and Bantumilli graben), (4) Tanuku Horst and (5) East Godavari sub- basin (extends into the offshore part).

Hydrocarbons have been discovered in the West Godavari, East Godavari and Godavari offshore sub-basins. In the Krishna-Godavari Basin, three following Petroleum systems have been proposed:

1. Permian-Late Jurassic to Early Cretaceous (TPS)
2. Late Jurassic to Early Cretaceous- Jurassic to Early Cretaceous (TPS)
3. Cret. & L. Paleo-E. Eocene & Mid to Late Eocene – Pliocene (CTPS)

Samples and Methodology

In present study, 38 oils/condensates and 23 source rocks samples were selected from Permian to recent ages covering East and West block of Godavari, coastal and shallow margins, Mandapeta graben, Bhimadolu graben, Bantumilli graben and Kaza-Kaikalur-Lingala High in KG basin. The bulk and biomarker parameters of studied oils are given in Table 1.

The powdered sediment samples were soxhleted with dichloromethane and methanol (93:7) for 8 hrs. in Soxhtherm extraction unit to obtain bitumen (EOM). The EOM and deasphaltened oil samples were fractionated into saturate, aromatic and NSO fractions using activated silica gel and alumina dual column by successive elutions with petroleum ether, benzene and methanol respectively. The bulk analysis was carried out as per the standard ASTM procedures. The saturate and aromatic fractions were analyzed on Perkin Elmer Clarus 500 GCMS. Stable carbon isotopic study is carried out on Thermo Scientific Continuous Flow-Isotope Ratio Mass Spectrometer interfaced with Trace GC Ultra, equipped with DB-5 GC column, 30mx0.32mm. Liquid sample (2-10μl) dissolved in HPLC grade n-hexane in the ratio of ~1:4 was introduced into the GC using an auto sampler. Helium was used as a carrier gas. A CO_2 gas was employed as reference to calibrate the isotope ratios of samples measured. The mass spectrometer was standardized using standard alkane mixture.

Results and Discussion

Gross and bulk parameters of oils: Bulk properties of the studied oils show that these are normal oils having moderate to high API gravities (31.9-52^o). The asphaltene contents are in the range of 0.1 to 6.77%.The Saturate/Aromatic ratio (>1) indicate paraffinic nature of oils.

Geochemical characterization of oils: West Godavari oils are characterized by low pristane/phytane (Pr/Ph) ratio (1.9-2.9), moderate to high Pr/nC_{17} ratio (0.7-2.79), low Ph/nC_{18} ratio (0.3-0.4) and dominance of high molecular weight n-alkanes. The high Pr/Ph ratio for all the studied oils indicates the terrestrial/mixed organic matter input in source deposited under suboxic to oxic environment. While East Godavari oils except Mandapeta are characterized by moderate to high Pr/Ph ratio (2.9-6.4), moderate to high Pr/nC_{17} ratio (0.33-5.17), low to moderate Ph/nC_{18} ratio (0.09-0.75) and dominance of high molecular weight n-alkanes. Mandapetta Formation oils are characterized by moderate Pr/Ph ratio (2.4-3.4), moderate to high Pr/nC_{17} ratio (0.66-1.56), moderate Ph/nC_{18} ratio (0.3-0.4) suggesting the terrestrial/mixed organic matter input in source deposited under suboxic to oxic environment. The cross plot of Pr/nC_{17} vs Ph/nC_{18} (Fig.3) shows the terrigenous/mixed organic source input of these oils deposited in suboxic to oxic environment.

West Godavari oils show a predominance of C_{30} hopane over C_{29} hopanes indicating shaley/clay rich source input. These oils show low concentration of oleanane (< 5%). These oils show good abundance of all the C_{31} to C_{35} homohopanes in descending order. Sterane fingerprints show slight dominance of C_{29}steranes over their C_{27} and C_{28} homologues with good abundance of all the C_{27} to C_{29} steranes. East Godavari oils show predominance of C_{30} hopane over C_{29} hopanes indicating shaley/clayrich source input, these oils show low to moderate concentration of oleanane (13-37%). Tatipaka oil from Pasarlapudi Formation and most of Mandapeta oils have different values of the ratios $C_{29}H/C_{30}H$ (0.74 to 1.0) and absence of oleanane. Sterane fingerprints of all studied oils in East Godavari sub basin show slight dominance of C_{29} steranes over their C_{27} and C_{28} homologues and have very good abundance of all the C_{27} to C_{29} steranes. These parameters suggest mixed source input deposited in suboxic marine conditions. The ternary diagram (Fig. 4) showing the relative abundance of C_{27}, C_{28} and C_{29} regular steranes for these oils indicates terrestrial/mixed source organic input (Peters and Moldowan 2004).

Thermal maturities of oils: The maturity of studied oils assessed through biological marker isomerisation reactions of hopanes indicates that most of the oils have attained the equilibrium value of 0.60 ± 0.02. The moderate values of the C_{29} steranes isomerization ratios, i.e., 20S/ (20S+20R) and ββ/ (αα+ββ) (equilibrium values 0.55 at 0.8% VRo and 0.54 and 0.9% VRo respectively) indicate that most of the oils are generated from sources, which have crossed the diagenetic-catagenetic boundary but which have not yet reached the peak oil generation stage (<0.9% VRo).

n-Alkane isotope composition-CSIA studies: The stable carbon isotopic bulk analysis shows wide variation of $\delta^{13}C$ values for saturates and aromatic fractions of oils suggesting multiplicity of source organics. In general the analyzed oils show canonical values both, more than and less than 0.47 that is indicative of both terrestrial and marine dominated source inputs for various oils. The n-alkane isotopic profiles of studied oils show a variability trend of high and low isotopic values in different formations. Increased thermal cracking/kinetic isotope effect and/or evaporative fractionation are considered to be major factors, responsible for this kind of n-alkane isotope profiles (Chung et al., 1994). n-Alkane isotopic profile of oils/condensates shows that Cretaceous oils/condensates have heavier carbon isotopic values as compared to Tertiary age oils (Fig. 5).

Oil-oil correlation: Ravva Formation oils of Miocene age show consistently light values of $\delta^{13}C$ for n-alkanes from C_{14} to C_{18} indicating predominance of terrestrial source deposited under anoxic to suboxic environment. The gentle inclination in slope of CSIA curve towards carbon isotopic values enriched in $\delta^{13}C$ for n-alkanes from C_{19} to C_{31} is indicative of subtle change in depositional environment from terrestrial to marine. The variations in isotopic values from C_{19} to C_{31} in the Miocene oils of Ravva formation show mixed source input. These oils are correlatable and form one oil family (Fig. 6). Oligocene (Masyapuri Formation) oils have three distinct families; Group A and B oils with light carbon isotopic values are derived from predominantly terrestrial organic input. Group C oils show enrichment of ^{13}C, heavier isotopic values are indicative of marine input (Fig. 7). The oils from Eocene (Vadaparru Formation) also have three distinct oil families. The Permian to Paleocene aged oils broadly show two distinct groups, Group A oils are derived from predominantly terrestrial with mixed source input and are less enriched in ^{13}C. Group B oils are of predominantly marine source input. The CSIA curves of these oils show variations in their isotopic values. It indicates subtle variations of organic matter and variations in their depositional environment.

Oil-Source correlations: On comparing the stable carbon isotopic ratios of *n*-alkanes from source rock extracts and related oils of the KG Basin, stable carbon isotopic values of *n*-alkanes of EOM show that $\delta^{13}C$ values of *n*-alkanes vary largely. According to oil-source correlations, the oils of Godavari, Matsyapuri and Vadaparru formations have better correlation with GD-1 and VD-1 sources of Pasaralapudi Formation (Fig.8). The oils of Cretaceous age from Tirupati, Raghavapuram and Kanukollu formations are sourced from HG-HR shale (Fig. 9). The Mandapeta oils of Cretaceous age show good correlation with Permian source. The Gajulapadu Shale sequence does not indicate any correlation with the studied oils as per CSIA profiles.

Conclusions

The studied oils of KG Basin are normal oils and have low to moderate maturity. CSIA study of oil/condensates has brought out three type of oil families: i) low mature, isotopically lighter oils, ii) moderate mature, isotopically heavier oils, and iii) intermediate isotopic values with moderate maturity. The oils of Vadaparru Formation are genetically correlated with Vadaparru-Pasaralapudi Shales. Marine oils of Pasarlapudi Formation are sourced from Palakollu Shale. Raghavapuram oils are derived from Kanukollu source rock layers. The oils of Mandapeta Formation show good correlation with Permian source while oils from Tirupati, Raghavapuram and Kanukollu formations are sourced from HG-HR shale. Oil-oil and oil-source correlation studies suggest that area south of east Godavari sub basin may be prospective for further exploration and exploitation for hydrocarbons. The Gajulapadu Shale having good source potential might have generated and expelled hydrocarbon to other reservoir in West Godavari sub basin which may be the prospective area for further exploration.

Acknowledgements

Authors are highly thankful to ONGC for granting permission to publish the paper. The authors are highly indebted to Shri P.K.Bhowmick ED-HOI- KDMIPE for constant inspiration and keen interest in this work.

References

Chung, H.M., Claypool, G.E., Rooney, M.A. and Squires, R.M. (1994) Source characteristics of marine oils as indicated by carbon isotopic ratios of volatile hydrocarbons. Bull. Am. Assoc. Pet. Geol. 78, 396-408.

Peters K.E. and Moldwan J.M. (2004) The biomarker guide interpreting molecular fossils in petroleum and ancient sediments, Prentice Hall, Englewood cliffs, NJ.

Table.1 Bulk and biomarker parameters of studied oils of KG Basin

S.N.	**Formation**	**API^o**	**Asph. wt %**	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**VRc %**	**$C_{29}H/C_{30}H$**	**OI Index**	**$C_{32}H$ S/S+R**
1	Ravva	35-44.8	0.1-1.3	2.9-5.4	0.3-1.3	0.2-0.7	0.72-0.81	0.64-0.7	13-22	0.55-0.60
2	Matsyapuri	31.9-49.2	0.4-6.7	2.3-6.4	1.11-1.81	0.2-0.6	0.57-0.73	0.54-0.84	13-37	055-0.60
3	Vadaparru	34.1-35.9	0.5-0.8	3.5-5.8	1.11-2.0	0.2-0.5	0.63-0.76	0.58-0.90	21-36	0.56-0.60
4	Pasarlapudi	39.8-52	0.7-0.9	2.3-4.8	2.4-2.5	0.4-0.7	0.66-0.73	0.54-1.0	16-21	0.56-0.60
5	Raghavpuram	41.5	0.2	2.9	0.7	0.3	0.56	0.38	2	0.58
6	Kanukollu	39.1	0.7	1.9-2.3	0.8-2.8	0.3-0.4	0.81	0.93	4	0.55
7	Gollapalli	49.2	0.2	2.5-3.0	0.7-0.8	0.2-0.3	0.60-0.70	0.39-0.89	nil	0.47-.52
8	Mandapeta	48.1	0.6	2.4-3.4	0.6-1.6	0.3-0.4	0.71-0.81	0.74-0.95	nil	0.56-0.58

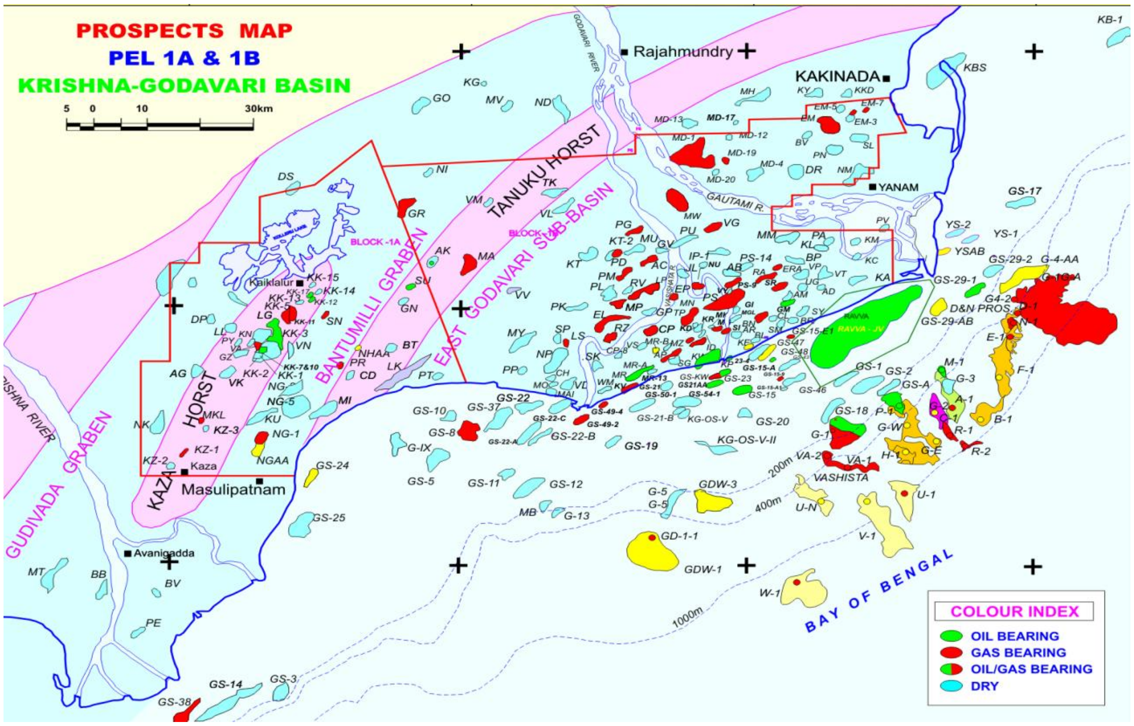

Fig. 1 Location Map of Krishna Godavari Basin

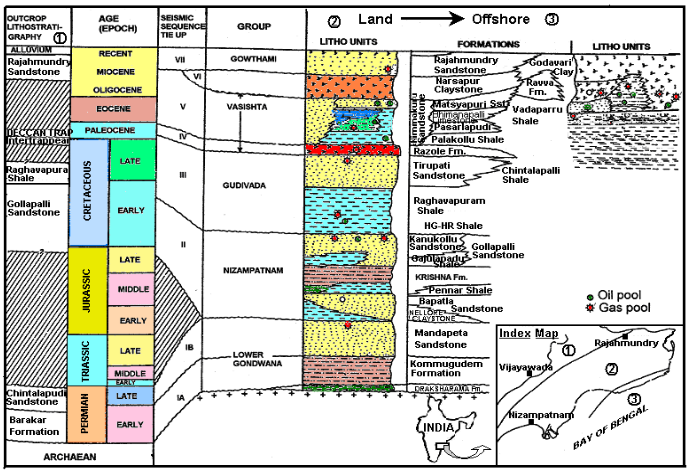

Fig 2: Generalized Stratigraphy of Krishna Godavari Basin

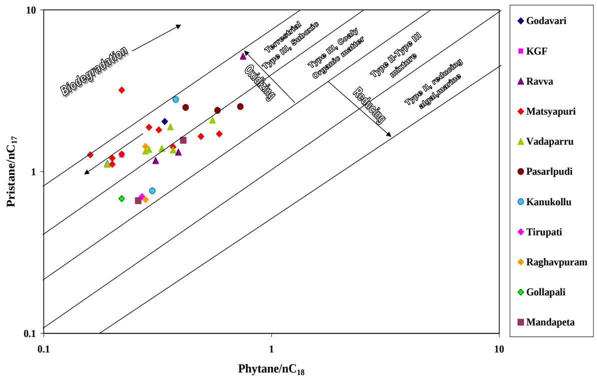

Fig. 3 Cross plot of Pr/nC17 vs Ph/nC18 of oils of KG Basin showing predominance of terrestrial source input

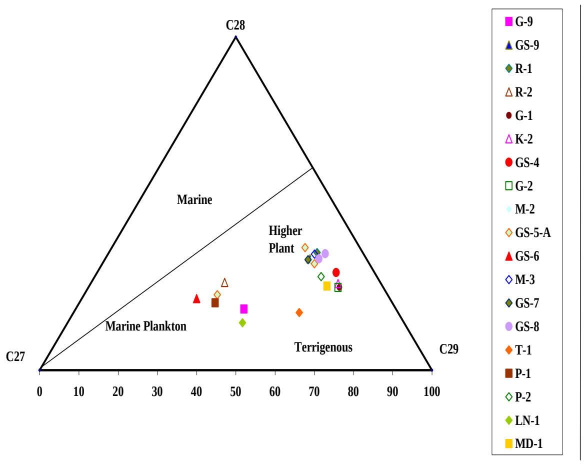

Fig. 4 C_{27}, C_{28} and C_{29} regular steranes ternary diagrams of studied oils showing mixed terrestrially dominated organic input

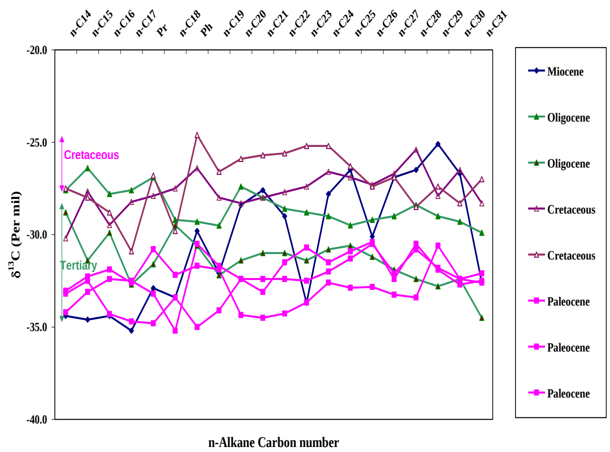

Fig. 5 n-Alkane C-isotopic profile of oils showing that cretaceous oils have heavier isotopic values as compared to Tertiary age oils

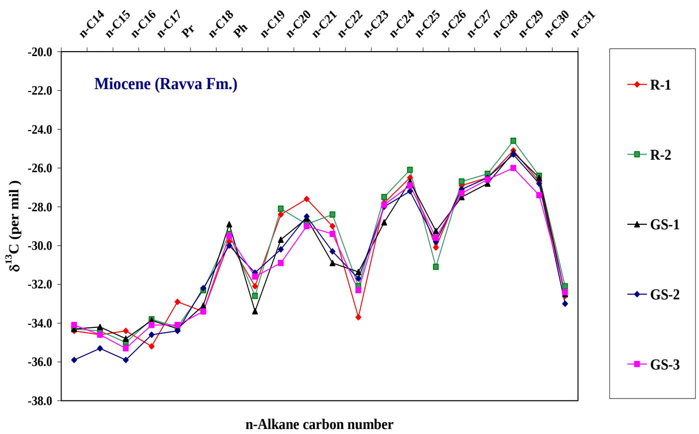

Fig. 6 n-Alkane C-isotopic profile of oils of Miocene age in KG Basin showing Fair correlation

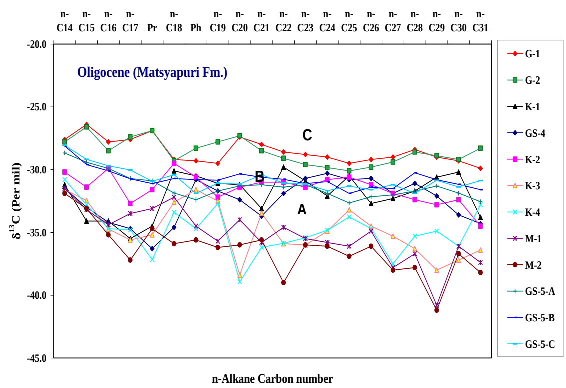

Fig. 7 n-Alkane C-isotopic profile of oils in Oligocene age shows three types of oils. Group A and B oils are derived from predominantly terrestrial source input while Group C are marine sourced oils.

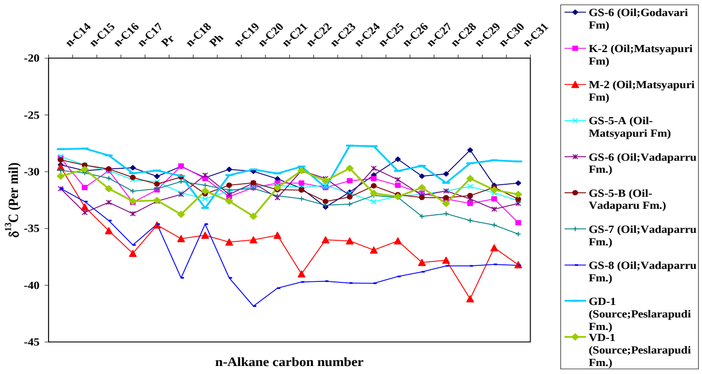

Fig. 8 n-Alkane C-isotopic profiles of oils and EOM's shows that the oils from Godavari, Matsyapuri and Vadaparru Formations have better correlation with GD-1 and VD-1 sources.

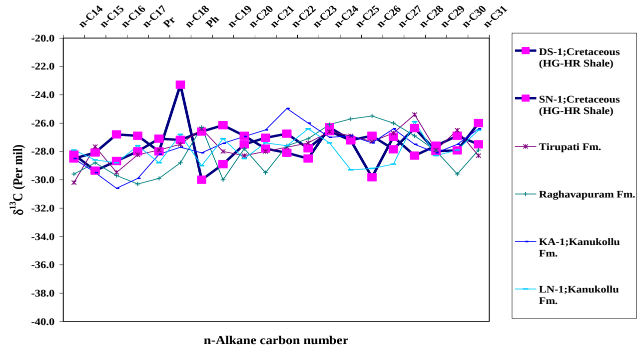

Fig. 9 n-Alkane C-isotopic profiles of oils and EOM's shows that the cretaceous oils are sourced from HG-HR shale of cretaceous age.