***Preliminary Shale Gas Resources Evaluation of Permian and Triassic Shales of Pranhita-Godavari Basin Based on Organic Geochemical Studies***

M.S.Kalpana*, Devleena Mani, D.J.Patil, Nitish Singh, Sanyasi Rao
CSIR-National Geophysical Research Institute, Uppal Road, Hyderabad 500007, Telangana
Email: kalpana@ngri.res.in

**Keywords**

Organic rich shales, thermal maturity, biomarkers, Pranhita-Godavari Basin

**Summary**

Organic geochemical characteristics of shales from Barakar and Kamthi formations of Pranhita-Godavari Basin were studied to evaluate organic matter content, type, maturity, and shale gas generation potential as well as depositional environmental conditions. The total organic carbon (TOC) contents of the shales vary between 0.6 to 35 % indicating excellent source rock potential of shales. Hydrogen index, Tmax and Vitinite Reflectance values of the shales vary between 11 and 378mgHC/g TOC, 372°C to 470°C and 0.4 to 1.4%, respectively. HI vs. Tmax plots of the studied samples indicate that the organic matter in Barakar and Kamthi shales are dominated by Type II-III oil-gas prone kerogen and Type III gas prone kerogen. This is also confirmed from the Pristane/$n\mathrm{C}_{17}$ versus Phytane/$n\mathrm{C}_{18}$ plot which also infers that the shales were deposited under oxic to sub-oxic environment and received high contributions of terrigenous organic matter. Biomarker maturity indicators such as 22S/(22S + 22R) homohopane ratio indicate that Barakar shales are thermally mature, at the early-mature to peak oil window stage. Bulk organic geochemical and biomarker studies show that the Barakar Shale Formation holds a significant oil/shale gas potential in areas with appropriate maturity.

**Introduction**

Pranhita-Godavari (P-G) basin is identified as Category III sedimentary basin. The geochemical studies conducted in this basin for hydrocarbon exploration have indicated presence of anomalous concentrations of light gaseous hydrocarbons of petrogenic origin in near surface soils (Anuradha et al., 2011). The main hydrocarbon source rocks are of Barakar formation which is expected to be thermally mature in the deeper parts of the basin. The carbonaceous shales and grey shales of Barakar and Kamthi collected over a depth range of 612-674 m and 240-439 m, respectively belonging to three exploratory boreholes located in the Kothagudem and Lingala–Koyagudem coalbelts of Godavari Valley Coal field were investigated for rock eval pyrolysis, saturate biomarkers and carbon isotopes, to evaluate their organic richness, hydrocarbon generative potential, quality of organic matter, and thermal maturity.

**Analytical Procedures**

Rock Eval pyrolysis analyses of shale samples were carried out on Turbo Rock Eval 6 Pyrolyzer to determine organic matter richness, kerogen type and thermal maturity. Bulk carbon isotopic measurements were made on Flash Elemental Analyzer coupled to Finnigan-Delta PlusXP Isotope Ratio Mass Spectrometer via a ConFlo III interface. For biomarker analysis, the powdered core samples were subjected to solvent extraction with azeotropic mixture of Dichloromethane/Methanol (9:1) in a speed extractor. Extracts were subsequently concentrated using multivapor and fractionated into saturated and aromatic fractions using column chromatography.

The saturated fractions of the extracted bitumen were analyzed for biomarkers using a Varian 3800 Gas Chromatograph interfaced to Varian 320 Triple quadrupole mass spectrometer. A DB-1 capillary column (with 60 m length and 0.25 mm i.d., and 0.25 μm film thickness) was used, with helium as the carrier gas. One microliter of sample was injected in splitless mode. The oven temperature was increased from 70 to 200 °C at 5 °C/min and then to 320 °C at 8 °C/min, after which it remained isothermal for 20 min. Peaks were identified based on JR-1 standard and published literature. Triterpane and sterane distributions were quantified by measuring peak areas in the m/z 191 and m/z 217 chromatograms, respectively.

## Results & Discussion

The Rock Eval pyrolysis results show that the Barakar and Kamthi shales have TOC content in the range of 0.6 to 35 % with an average of 7.4% indicating excellent source rock potential of shales. The S1 (thermally liberated free hydrocarbons) and S2 (hydrocarbons from cracking of kerogen) values range between 0.01-2.85 mgHC/gRock (milligram hydrocarbon per gram of rock sample) and 0.07-127.36 mgHC/gRock, respectively. Tmax ranges between 372-470°C corresponding to calculated Vitrinite Reflectance values from 0.4 to 1.4%. The crossplot of Hydrogen Index (HI) vs. Tmax indicates that the Barakar and Kamthi shales are dominated by Type II-III oil-gas prone kerogen and Type III gas prone kerogen and Barakar shales are comparatively more mature than Kamthi shales (Fig 1a & 1b).

The GCMS chromatograms of saturated hydrocarbon fractions from shale extracts of P-G Basin show a full suite of saturated hydrocarbons between $C_{12}$–$C_{33}$ *n*-alkanes including the main acyclic isoprenoid hydrocarbons. The chromatograms of n-alkanes display a unimodal distribution with odd over even carbon n-alkanes and a predominance of $nC_{25}$ and $C_{27}$ (Fig 2). The carbon preference index(CPI) is the ratio obtained by dividing the sum of the odd carbon-numbered alkanes to the sum of the even carbon-numbered alkanes. CPI values for Barakar shales vary from 1.07 to 1.6 while for Kamthi shales it varies from 1.22 to 2.7. The CPI values > 1 suggest dominance of higher plant organic matter. The bulk carbon isotopic analysis of shales also infers terrestrial source of organic matter (-23.85 to -21.2 ‰ (V-PDB)). The acyclic isoprenoids occur in significant amounts in P-G shales, with pristane/phytane ratios > 2 indicating coastal swamp/peat swamp depositional environment under oxic to sub-oxic conditions. The crossplot of Pr/*n*-$C_{17}$ and Ph/*n*-$C_{18}$ ((Fig. 3). also indicate the shales contain terrestrial organic matter deposited under oxic to sub-oxic environment. Fig. 3 also suggests source of organic matter in Barakar and Kamthi shales are dominated by Type II-III oil-gas prone kerogen and Type III gas prone kerogen.

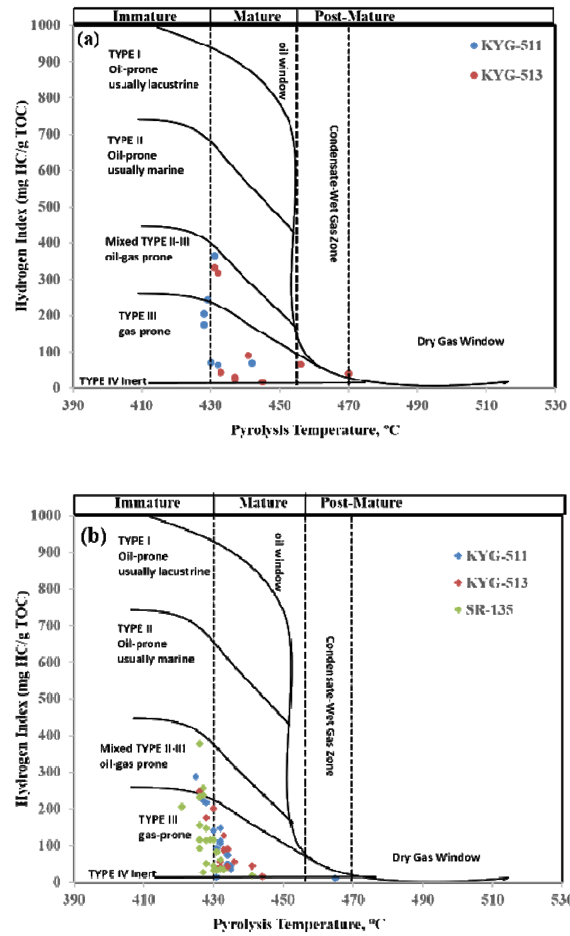


Figure 1: Hydrogen Index (HI) vs. Tmax (after Espitalie et al., 1987) for shale samples of (a) Barakar Formation from KYG-511 and KYG-513 boreholes and (b) Kamthi Formation from KYG-511, KYG-513 and SR-135 boreholes.

The distribution of triterpanes (hopanoids) and steranes were studied using the mass fragmentograms at m/z 191 and m/z 217 (Fig. 4 and 5). Hopanoids are dominated by a series of $C_{27}$-$C_{30}$ hopanes, followed by $C_{31}$ to $C_{33}$ homohopane doublets comprising of R and S isomers. $C_{31}$ or $C_{32}$-homohopane ratios are used as thermal maturity indicator. The 22S/(22S+22R) ratio rises from 0 to 0.6 during

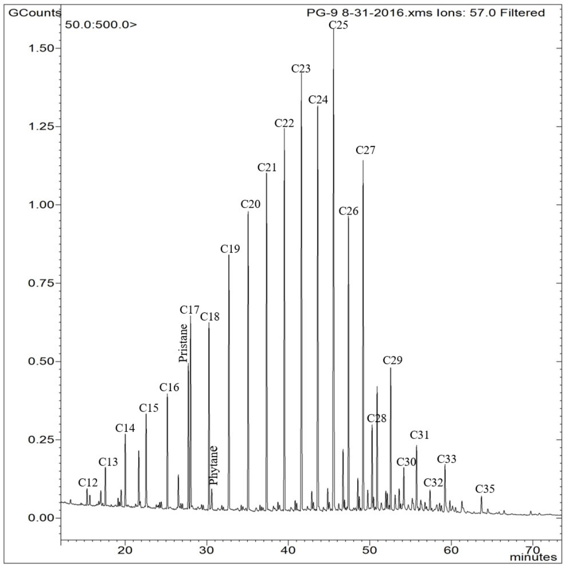


Figure 2: m/z 57 mass chromatogram of *n*-alkanes extracted from Barakar shales, Pranhita-Godavari Basin.

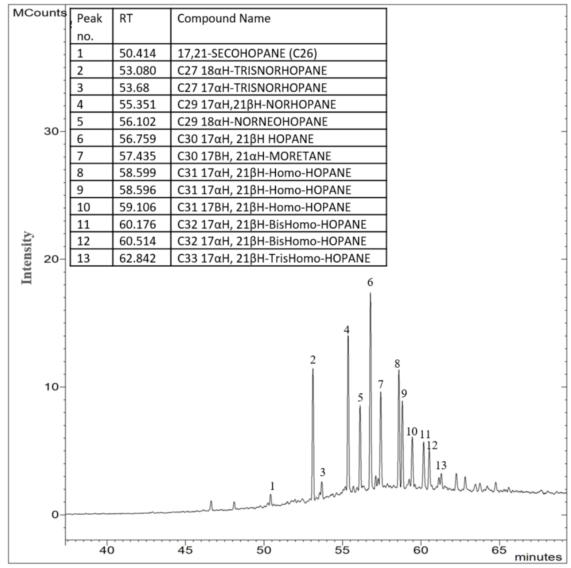


Figure: 4 m/z 191 mass chromatogram of hopanes showing pentacyclic triterpanes.

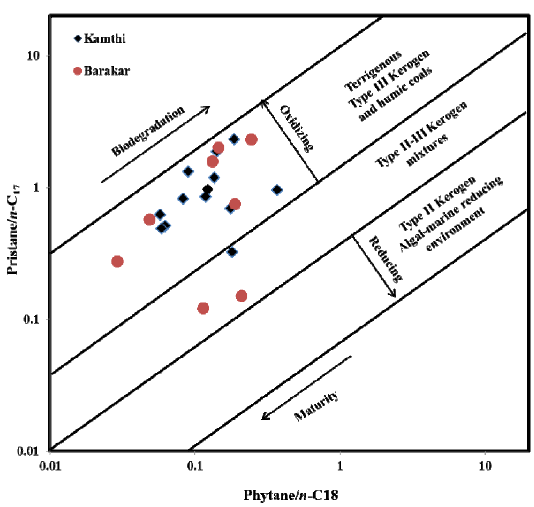


Figure: 3 Pr/ $C_{17}$ and Ph /$C_{18}$ ratios indicating the kerogen type and thermal maturity in shales from Pranhita-Godavari Basin (after, Connan and Cassou, 1980)

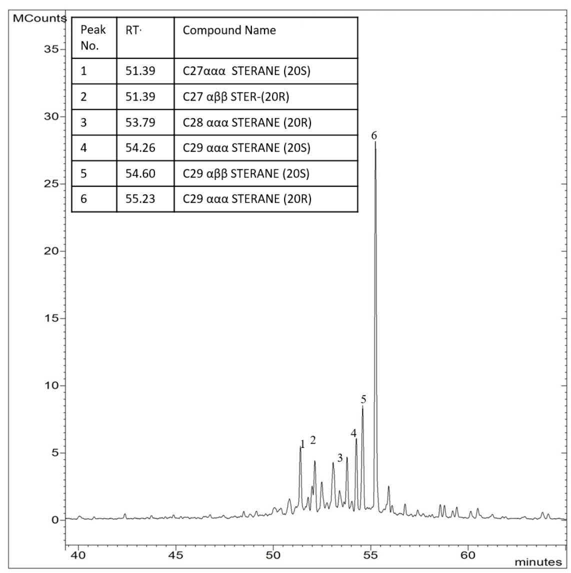


Figure: 5 m/z 217 mass chromatogram of steranes.

maturation (Seifert and Moldowan, 1980). The $C_{32}$ homohopane ratios of Barakar and Kamthi shales are in the range of 0.54 to 0.56 and 0.22 to 0.42. The ratios of Barakar samples are close to the equilibrium values (0.6) indicating that the samples have entered the phase of oil generation. The distribution of regular steranes is similar in all the samples with a dominant $C_{29}$ over $C_{28}$ and $C_{27}$ sterane suggesting a strong terrestrial contribution of organic matter (Peters et al., 2005).

## Conclusions

The bulk geochemical and biomarker analysis of Permian and Triassic shales of Pranhita-Godavari basin indicate that the shales are organic rich and contains a mixture of Type II-III oil-prone and Type III gas-prone kerogen. Biomarker ratios such as pristane/phytane, pristane/*n*-C17 versus phytane/*n*-$C_{18}$, CPI and predominance of $C_{29}$ steranes suggest that the shales were deposited in sub-oxic-oxic environment and the organic matter is derived from terrestrial higher-plant. The thermal maturity parameters suggest that the Barakar shales exhibit fairly good potential for generating oil and thermogenic gas upon thermal cracking.

References

Anuradha, B, Raasheed , M.A., Srinivas Rao, P.L., Kalpana, M.S. and Dayal, A.M., 2011, Light Hydrocarbons Geochemistry of Surface Sediments from Pranhita-Godavari Basin, Andhra Pradesh. Journal Geological Society of India, 78, 477-483

Connan, J., and Cassou, A.M., 1980, Properties of gases and petroleum lipids derived from terrestrial kerogen at various maturation levels. Geochim. Cosmochim. Acta 44, 1-23.

Espitalie, J., Marquis, F., Sage, L., 1987. Organic geochemistry of the Paris Basin. In: Brooks, J., Glennie, K. (Eds.), Petroleum Geology of North West Europe. Graham and Totman, London, 71-86.

Seifert, W.K. and Moldowan, J.M. 1980, The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *Physics and Chemistry of the Earth*, 12, 229–37.

Peters, K.E., Walters, C.C. and Moldowan, J.M., 2005, The Biomarker Guide volume 2: Biomarkers and Isotopes in Petroleum Exploration and Earth History, 2nd Ed., Cambridge University Press.

## Acknowledgments

The Director, NGRI is thanked for permitting presentation of this work. Officials of Singareni Collieries Company Limited are thanked for extending their support during field visit and providing the core samples. Oil Industry Development Board, New Delhi is acknowledged for funding towards establishing the laboratory facilities at NGRI.