Organic Geochemical Characterization of Paleogene Crude Oils and Rocks in Assam Basin, India

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Abstract

The Paleogene time marks the evolution of terrestrial ecosystems with concurrent changes in climatic and tectonic histories. The Assam Basin, India records such megafloral diversities, which is reflected by biomarker relations within the source rocks and crude oils. The early Paleogene biota comprises abundant angiosperm and gymnosperm families. The late Paleogene biota is dominated by angiospermous vegetation with rare or no occurrence of gymnosperms. The high abundances of higher plant biomarkers reflect the vegetational diversities during Paleogene time.

Introduction

The major source rocks have been classified into two petroleum systems in the Assam Basin within the Late Paleocene to Middle Eocene (Langpar and Lakadong-Therria member of the Sylhet Formations) and the Late Eocene to Oligocene (Kopili and Barail formations) rocks (3). A shallow marine depositional environment in a passive continental margin setting prevailed till Early-Middle Eocene. The Eocene-Oligocene sediments were deposited in a restricted marine to deltaic-estuarine condition (3).Organic geochemistry of crude oils and rocks (coal-shale units) was carried out from both these systems and was investigated by GC-MS technique.

Samples

Early Paleogene coal samples were collected from different localities from Garo, Khasi, and Jaintia hills, Meghalaya. These rocks, which occur within the Lakadong sandstone member of the Sylhet Formation, Jaintia Group, are exposed along the hilly tracts of the Shillong Plateau. Late Oligocene coal-carbonaceous shale units were collected from Tirap coal mine in Makum coal fields belonging to Late Oligocene Tikak Parbat Formation, Barail Group, Assam. These occur along a linear belt of overthrusts, known as the "belt of Schuppen". Crude oils from Eocene Langpar and Lakadong Formations and Oligocene Barail Formation and Miocene Tipam and Girujan Formation were analyzed for biomarker characterization and correlation.

Experimental Details

The bulk geochemical compositions were validated by "Standard" Rock-Eval 6 Pyrolyzer. Prior to analysis of biomarkers, the soluble organic matter (OM) or bitumen was extracted from the sediments by ultrasonication with 9:1 ratio of DCM:Methanol. Asphaltenes were separated from the bitumen fraction by precipitating with *n*-pentane. The separation of aliphatic and aromatic compounds from was carried out by column chromatography. The biomarkers of individual compounds were analyzed using Gas Chromatography-Mass Spectrometry.

Results and Discussion

The bulk geochemical characterization of organic rich rocks by Rock-Eval pyrolysis reveals an early catagenetic stage. The dominance of liptinite-rich terrestrial OM reflects the generation of mixed oil and gaseous hydrocarbons upon maturation. The exceptionally high TOC (~>60%) and hydrogen indices (>300) highlights the same. The GC-MS results of rocks and crude oils also validate the terrestrial dominance of the OM. The dominance of high MW odd-chained n-alkanes and C29 rearranged steranes, relative to C₂₈ and C₂₇ steranes is recorded. High Pristane/Phytane ratios (>2) are suggestive of oxic-suboxic depositional environments. Several C14 and C15 sesquiterpenoids, ionene, and 4β(H)-Eudesmane are related to higher plant terpenes (Fig. 1). A series of drimanes are believed to have generated from multiple sources i.e., higher plant terpanes and bacterial precursors. Signatures of bacterial contribution/degradation are evident by the presence of ubiquitous hopanes (m/z 191). These are believed to have been derived from bacterial membrane lipids. Diterpane signatures are typically found in early Paleogene samples. These reflect the contribution of gymnosperms to the OM. Prominent diterpanes include, tricyclic diterpanes such as rimuane, pimarane, rosane, and isopimarane (MW 276) and tetracyclic diterpanes such as ent-beyerane, 16β (H)-phyllocladane, ent-16β (H)-kaurane, 16α (H)-phyllocladane, ent-16α (H)-9 kaurane (MW 274). (2) identified these compounds to be related to diterpanes abundant to leaf resins of conifers belonging to Podocarpaceae and Araucariaceae families. The presence of C₁₇ and several C₁₈ diterpanes are also noted. The occurrence of rosane is the first to be documented in crude oils from Eocene reservoirs of Assam Basin, India. The contribution of angiosperms is reflected by the presence of Oleanane and Bicadinane skeletons in Paleogene rocks and crude oils. Bicadinanes are produced by the catagenetic depolymerisation of cadalene, which is an important constituent found in dammar resins derived from Dipterocarpaceae family. The occurrence of dammar or Class II resins from Early Eocene coals has been studied earlier (1). The plot (Fig. 2) of bicadinane (Bicad T/(Bicad T + C₃₀Hopane)) and oleanane indices (Ol/C₃₀Hopane) shows their dominance in Eocene oils than the Oligocene oils. Oils from Tipam and Girujan reservoirs show trends corresponding to the Oligocene oils. Similar observation was accounted for the Eocene rocks. This study reports the presence of a wide diversity of plant groups in early Paleogene time. Biomarker signatures reveal the presence of both angiosperms and gymnosperms during early Paleogene period. This study also reports the absence of conifer derived biomarkers from Oligocene coal-shale units.

Conclusions

The study reports the wide floral diversity of early Paleogene vegetation. The late Paleogene vegetation is dominated by angiosperm related taxa with notable absence of gymnosperms. These signatures are evident from the biomarker compositions in rocks and related crude oils. The higher bicadinane and oleanane indices of the Eocene oils reflect the generation of both the oils from different organofacies.

References

- 1. A. Rudra, S. Dutta and S.V. Raju, "Molecular composition and paleobotanical origin of Eocene resin from northeast India", Journal of Earth System Science, 123, 935–941, 2014.
- 2. R.A. Noble, R. Alexander, R.I. Kagi and J. Knox, "Identification of some diterpenoid hydrocarbons in petroleum", Organic Geochemistry, 10, 825-829, 1986.
- 3. S.V. Raju and N. Mathur, "Petroleum geochemistry of a part of Upper Assam Basin, India: A brief overview", Organic Geochemistry, 23, 55-70, 1995.

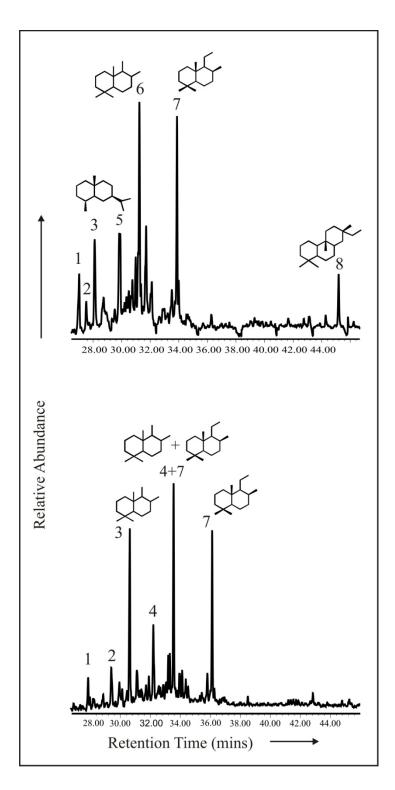


Fig. 1 Selected Ion Chromatogram (m/z 123) showing the distribution of Sesquiterpenoids of crude oils from Eocene (top) and Oligocene (bottom) reservoirs. The assignments of the compounds are listed in Table 1.

Table 1. Peak assignments in Fig. 1

Peak	Compound	Base Peak	Parent Ion
1	C ₁₄ -Bicyclic Sesquiterpenoid	179	194
2	C ₁₄ -Bicyclic Sesquiterpenoid	179	194
3	C ₁₅ -Bicyclic Sesquiterpenoids	193	208
4	C ₁₅ -Bicyclic Sesquiterpenoids	193	208
5	4β(H)-Eudesmane	109	208
6	8β(H)-Drimane	123	208
7	8β(H) homodrimane	123	222
8	Rosane	247	276

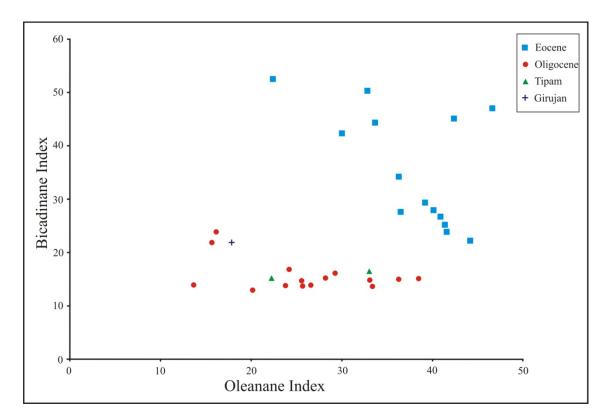


Fig. 2 Crude Oils from respective reservoirs showing the distribution of Bicadinane and Oleanane Indices.