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Reconstruction of Neoproterozoic-Early Cambrian Clock: A Synthesis from Oils and Soluble and Insoluble Organic Matter Extracted from Sediments, Western India

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Abstract

The chemical signatures in oils and sediments recovered from Neoproterozoic-Early Cambrian succession (Marwar Supergroup), Bikaner-Nagaur Basin, western India have been investigated with gas chromatography-mass spectrometry. The Marwar Supergroup yielded two types of oils- marginally biodegraded from deeper sequences and severely biodegraded from a younger sequence. The slightly degraded and severely degraded oils have been geochemically characterized and two different gamuts of compounds are observed. The mildly degraded oil is characterized by normal alkanes, pristane, phytane, tricyclic terpanes, pentacyclic terpanes, gammacerane, steranes in the saturate fraction. The aromatic fraction bears naphthalenes, phenanthrenes, aromatic steroids, benzohopanes. The heavily degraded oil is characterized by extremely low abundance of normal alkanes and isoprenoids and significant abundances of degraded compounds like norhopanes and secohopanes in the saturate fraction. Biomarkers from sediments have also been analyzed and the chemistry reveals the presence of normal alkanes, pristane, phytane, triterpenoids and extremely low abundance of steranes from the saturate fraction. The kerogen fraction mostly consists of amorphous organic matter and a few palynomorphs. The analyses suggest that the organic matter was contributed by microbes like marine bacteria, algae and protists and the environment of deposition had been anoxic and highly saline.

Introduction

The Neoproterozoic-Early Cambrian time is a superlative chapter in the history of Earth since it witnessed several crucial climatic, tectonic and geobiological phenomena that led to a complete makeover of the planet. Unraveling the Neoproterozoic-Early Cambrian time frame is a mammoth task. This distant past, however, has been visualized to an appreciable extent through biomarkers, molecular fossils in which the original skeletal structure of the precursor organisms is preserved (Brocks and Pearson, 2005). The Bikaner-Nagaur Basin of India contains a proven infracambrian petroleum system. The comprehension and reconstruction of the Neoproterozoic-Early Cambrian biota and palaeoenvironment using biomarkers, isotope and palynomorphs as tool have been attempted. The present study also endeavors to present an elaborate account of the organic compounds that are generated during biodegradation in saturate fraction of crude oils.

Experimental details

Samples: 10 slightly degraded crude oils; 3 heavily degraded crude oils; 5 sediment samples.

The rock samples were pulverized to a mesh size range of 60-100 mesh in a brass mortar for Rock Eval pyrolysis analyses for assessing the bulk organic geochemistry. Oil and bitumen extracted from

sediments are subjected to column chromatography for fractionating into saturate and aromatic components. It began with the estimation of dead volume. The saturate was eluted using hexane (3/8 of dead volume) and the aromatic required a solution of hexane and dichloromethane (4DV proportioned into 4:1 respectively). The kerogen matter was extracted using maceration technique for micro-FTIR spectroscopic analysis.

Results and Discussion

The normal alkanes range from C_{12} to C_{29} in the slightly degraded crude oils. These oils are characterized by high concentration of both tricyclic terpanes and pentacyclic hopanes. Tricyclic terpanes are mostly derived from algae although bacteria have also been considered as precursor. Pentacyclic terpanes are bacterial derivatives. Steranes are detected and the predominance of C_{29} regular steranes over C_{27} and C_{28} indicates significant green algal contribution (Volkman et al., 1994). The unusually low pristane/phytane and occurrence of substantial quantity of gammacerane, monomethyl-2-methyl-2-(2,4,8-trimethyltridecyl) chroman and 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene are indicative of anoxic, stratified, highly saline condition of the environment of deposition. The occurrence of evaporite in the stratigraphic sequence also supports the fact that there had been a phase of enhanced salinity when the sediments got deposited. Putative C_{19} norsterane, probably indicative of sponge input is recorded in the studied samples. Apart from being a salinity marker, methylated chromans have further importance since these are reported for the first time from samples older than Permian. Methylated chromans are structurally similar to tocopherols (vitamin E) and both may have similar biosynthetic pathway. The presence of shale layers within a carbonate sequence and several relevant biomarker parameters suggest a mixed source rock. Also, biomarker parameters are indicating low thermal maturity of the source rock. Normal alkanes (*n*-C_{17} and *n*-C_{18}) and isoprenoids (pristane and phytane) are highly depleted in $\delta^{13}C$. The $\delta^{13}C$ value for *n*-C_{17} ranges from -33.65 to -34.38 ‰ and that of *n*-C_{18} from -30.21 to -35.50 ‰. The $\delta^{13}C$ value for pristane ranges from -36.01 to -37.45 ‰ and for phytane from -36.38 to -37.88 ‰. The overall biomarker distribution and carbon isotope data of oils from Bikaner-Nagaur Basin show similarities with that of other infracambrian oils like Huqf oils from Oman (Grosjean et al., 2009) and Baykit High oils from eastern Siberia. As mentioned previously, the Marwar Supergroup hosts two types of oils with different geochemistry. Oils from younger succession are depicting a magnified unresolved complex mixture (UCM), quintessential of an extremely biodegraded oil. However, normal alkanes and isoprenoids are detected, albeit in low abundance, and this is due to mixing of the biodegraded crude oil with slightly degraded oil. Regular tricyclic terpanes being stable molecules survived biodegradation and are observed in the range from C_{20} to C_{26}. Apart from the regular tricyclics, novel tricyclic terpanes have also been observed although in low abundance and ranging from C_{18} to C_{20}. The novel tricyclic terpanes similar to the regular tricyclics are recalcitrant. The vulnerable high molecular weight extended hopanes are degraded but the low molecular weight hopanes are displaying an amalgamated distribution of remnant nondegraded hopanes as well as newly formed degraded hopanes. C_{26}, C_{28} and C_{29} norhopanes are observed in *m/z* 177 which are probable degradation products of hopanes (Moldowan and McCaffrey, 1995). Regular steranes are below detection limit. However, putative C_{19} norsteranes and tentatively identified short chain steranes- pregnane and homopregnane are recorded in the highly degraded oil samples. A homologous series of secohopanes, ranging from C_{27} to C_{34} are present in these oils which strengthens the fact that these have suffered extensive biodegradation. Bulk organic analyses of sediments suggest that the kerogen is type II/type III and belong to low thermal maturity zone. However, the kerogen type has influence of mineral matrix effect. The micro-FTIR spectrum is characterized by both aliphatic and aromatic components. However, the aromatic functional groups are a little more predominant and this might be due to the intrinsic nature of the kerogen (Marshall et al., 2005). The kerogen matter mostly constitutes amorphous remains which are probably derived from degradation of sapropelic organic matter. Also, a few acritarchs could be distinguished in the kerogen matter. The palynomoprh suite consists of the eukaryotic protists, acritarchs- *Micrhystridium* sp., *Lophosphaeridium* sp. and *Leiosphaeridia* sp.

Conclusions

The integrated investigations of molecular fossils from oils and sediments and kerogen fractions extracted from sediments belonging to Neoproterozoic-Early Cambrian succession shed light on the nature of biota that persisted during the deep time. The Marwar Supergroup yielded two types of oils- marginally biodegraded from deeper sequences and severely biodegraded from a younger sequence. The severely degraded oils are characterized by degraded compounds like norhopanes and secohopanes. The biomarker distribution from mildly degraded oils and sediments suggests a diverse microbial community predominated by simpler life forms. The entire gamut of normal alkanes in oils and bitumen from sediments indicates algal and bacterial input. The presence of C_{29} steranes particularly implies green algal input which had been a dominant biota at the Neoproterozoic. Protists also contributed into the organic matter as evident from the detection of gammacerane and probable sponge input is suggested by the presence of putative C_{19} norsteranes. Acritarchs had been significant source of organic matter in ancient time and a few forms like *Micrhystridium* sp., *Lophosphaeridium* sp. and *Leiosphaeridia* sp. are recognized in the organic residues, although the palynomorph abundance is sparse. The kerogen matter is dominated by amorphous organic matter generated by slight alteration of biotic material. Both aliphatic and aromatic functional groups have been detected in the kerogen matter as reflected by micro-FTIR spectroscopic analyses. The aromatic moiety show very high abundance and might reflect the inherent character of the kerogen residues. The organic matter was deposited in marginal marine to inner neritic environment and mostly in calm water condition. The environment of deposition was characterized by stratified water column induced by salinity greater than the usual level which can be inferred from the presence of gammacerane, 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene and monomethyl-2-methyl-2-(2,4,8-trimethyltridecyl) chroman. Normal alkanes (*n*-C_{17} and *n*-C_{18}) and isoprenoids (pristane and phytane) are highly depleted in $\delta^{13}C$. The overall biomarker distribution and carbon isotope data of oils from Bikaner-Nagaur Basin show similarities with that of other infracambrian oils like Huqf oils from Oman and Baykit High oils from eastern Siberia.

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Table 1: Ratios of saturate cyclic compounds calculated from samples belonging to Neoproterozoic-Early Cambrian Formation (Marwar Supergroup, Bikaner-Nagaur Basin, western India).

Samples	$C_{24}/C_{23}T$	$C_{22}/C_{21}T$	$T_s/(Ts+T_m)$	$C_{29}/C_{30}H$	T_s/H	Moretane/ C_{30} H	$C_{31}/C_{30}H$	$C_{31}H$ 22S/(22S+22R)	Gammacerane index
Rac-1/B/D.Lst/1	0.78	0.12	0.27	0.63	0.26	0.25	0.89	0.59	1.09
Rac-1/B/D.Lst/2	0.35	0.21	0.18	0.68	0.09	0.20	0.73	0.60	0.62
Rac-1/B/D.Lst/3	0.44	0.04	0.22	0.69	0.18	0.33	0.86	0.50	1.21
Rac-1/B/D.Lst/4	0.38	0.17	0.23	0.63	0.11	0.23	0.64	0.59	0.67
Rac-1/B/D.Lst/5	0.40	0.15	0.23	0.62	0.17	0.29	0.80	0.59	1.11

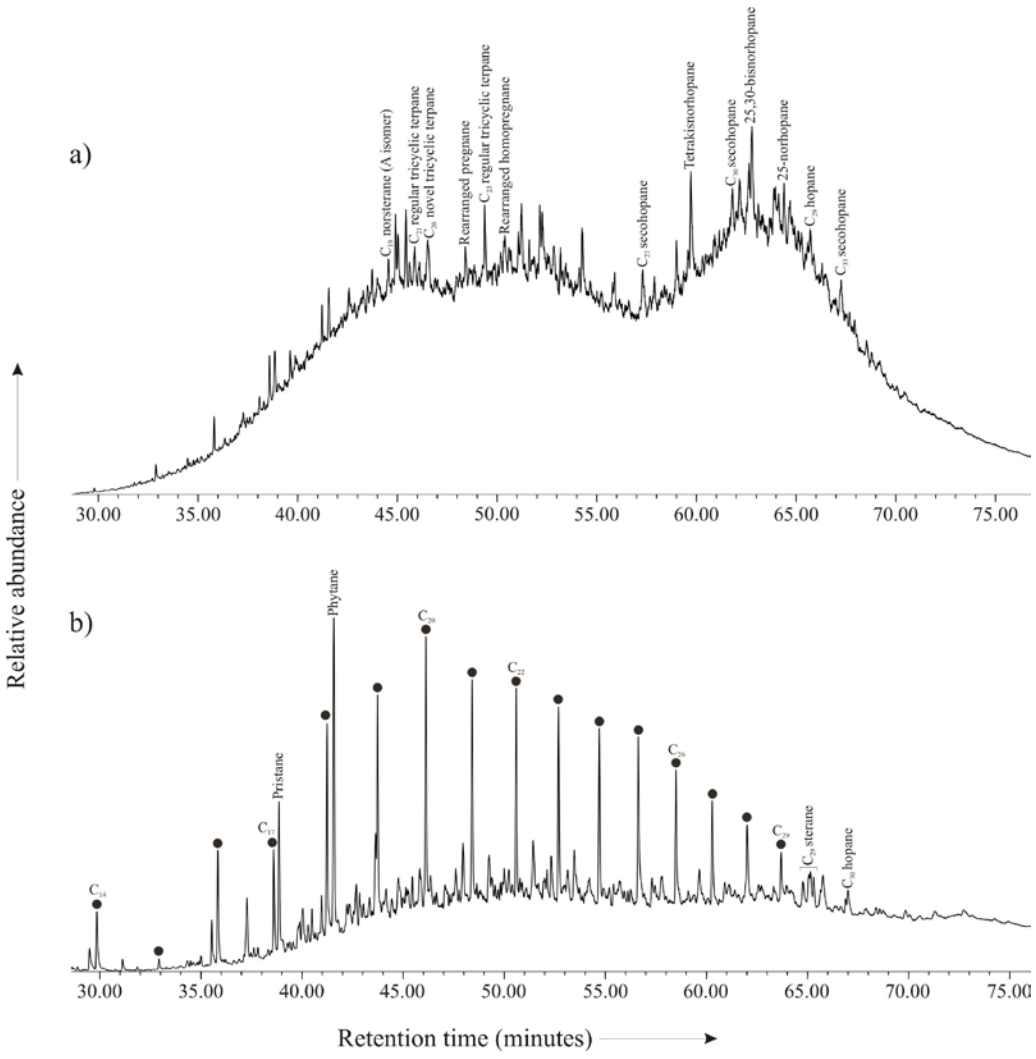

Figure 1: Total ion chromatograms along with names of compounds in a) heavily biodegraded crude oil b) very mildly degraded crude oil recovered from Neoproterozoic-Early Cambrian succession, Bikaner-Nagaur Basin, western India.