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Research Article

GEOCHEMICAL CHARACTERISTICS OF PALAEOGENE OIL SHALES AND OIL SEEPS IN PARTS OF NAGA HILLS, NORTHEAST INDIA

Vekhoto Shijoh, Chiezou K and Pandey N

Department of Earth Sciences, Assam University, Silchar

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A B S T R A C T

The Tertiary rocks of NE India host number of oil and gas reserves which is an indication for the presence of good source rocks capable of generating such a prolific accumulation of oil and gas in the region. Twenty five oil shale samples collected from Palaeogene outcrops (Disang Group) of the study area were analyzed using Rock-Eval-VI. In addition, two oil-seep samples (Barail Group) have also been analyzed for their geochemical characteristics. The study reveals that the hydrocarbons in both the oil shales and the oil-seeps are in an immature stage and genetically relate to terrestrial sources.

INTRODUCTION

Oil shale is a kind of rock possessing high content of Kerogen (< 50%) which when heated exudes hydrocarbon oils. Under natural subsurface conditions over a long period of time (millions of years) it generates crude oil that accumulates in the oil fields. In North East India, presence of oil shale at the subsurface can logically be inferred as they are the source for prolific oil accumulations which are under production for more than a century. Nevertheless, investigations by Oil India Ltd., and others, have shown that similar rocks with most of their oil generating potentials are present at the surface as well as subsurface covering large area in Upper Assam, Arunachal Pradesh and Nagaland and could in all probability prove to be a huge source of crude oil in near future (Ratnam, 2006). In Nagaland, oil shale forms an integral part of the Cretaceous-Eocene Disang Group of rocks-the oldest among the Tertiary sedimentary deposits documented so far in the state. On the other hand presence of several oil seeps within the thrust-fold belt of Nagaland state is remarkable.

Despite the fact that the Nagaland and the adjoining areas hold good potentialities for hydrocarbon deposits, the region could not receive due attention possibly due to its remoteness and socio- political conditions. No detailed published works on the subject matter is available in the area except for the lithostratigraphy, structure and regional correlations.

Corresponding author: **Vekhoto Shijoh**
Department of Earth Sciences, Assam University, Silchar

Mention may be made of Mallet (1876), Evans (1932, 1964), Mathur & Evans (1964), Acharyya (1986, 1990, 1991), Banerji, (1979), Bhandari *et.al.* (1973), Biswas etal. (1993), Chakrabarti and Banerjee (1988), Naik *et al*., (1991) and Nandy (1983, 2000).

Study area

The area under investigation lies between north parallel of 25°36’00’’- 25°38’30’’ and east meridian of 94°10’00’’-94°15’00’’ in the topographic sheet no. 83 K/2 Survey of India. It covers nearly 100 Sq. Km and includes areas lying between Chakhabama (Kohima district) and Kikruma (Phek district) villages, Nagaland. The area displays poly-phase folding (Fig.1) involving monotonous splintery shale-oil shale-silt and occasional very fine to fine sand belonging to Disang Group (Upper Cretaceous to Eocene) that passes gradationally into arenaceous sequences named Barail Group (Oligocene).

The study area basically forms a part of the Naga Hills-the northern extension of the Indo Burma Range (IBR) that runs almost north-south along the Indo - Myanmar international border linking Himalaya to the north and Andaman Nicobar islands to the south. Based on morphotectonic elements, the Naga Hills has been longitudinally divided from west to east into four distinct units, namely the Schuppen Belt, Inner Fold Belt, Ophiolite Belt and the Naga metamorphic complex (Ghose *et al*., 2010). The Inner Fold Belt (IFB) a part of which forms the present area of investigation is thought to have been occupied by two synclinoria, the Kohima synclinorium to the south and Patkai synclinorium to the north (Mathur and Evans, 1964, Chakrabarty and Banerjee, 1988) the point of culmination being the Mokokchung anticline. The study area occupies a place outside the Kohima synclinorium where it shows mature topography compared to Kohima synclinorium.

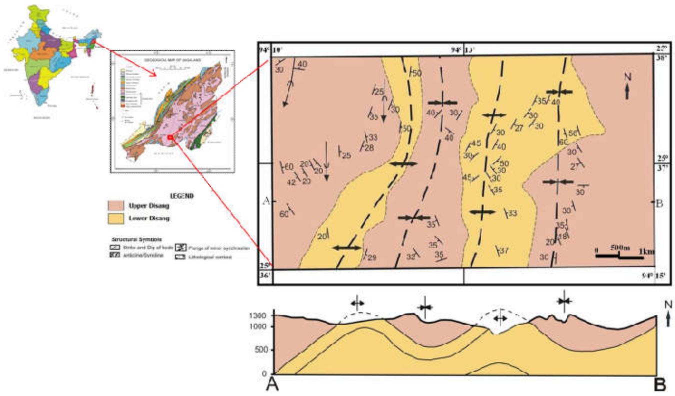

Fig 1 Geological map of the study area with profile section (modified after GSI). Inset geo-tectonic map of Nagaland.

MATERIAL AND METHODS

All together 25 oil shale samples were collected along the road section and river cuttings. Two oil seep samples, one each from Upper Tiru, Mon district and Changki, Mokokchung district, Nagaland were also collected for the purpose of comparison. The analytical methods used in analyzing the oil shale and oil-seep samples are described below:

Rock Eval analysis of Oil Shale samples

The oil shale samples were pyrolized using Rock-Eval-VI at KDMIPE Laboratory Dehradun. The samples were dried, pulverized and small amount of samples (70-100mg) were put into the small drum which is labeled with the sample number and programmed into the computer. The pyrolysis machine automatically picked up the drum and analyzed samples under different sets of temperature and also under oxidation condition. The following parameters were obtained:

TOC Percentage (w/w) of total organic carbon of the rock sample

S1: Free hydrocarbons present in the rock (mg HC/g of rock)
S2: Remaining generation potential (mg HC/g of rock)
S3: Oxidizable carbon, mg CO_2/g rock
T_{max} : Temperature maximum at peak of S2, a Rock-Eval thermal maturity parameter
HI: Hydrogen Index, (S2/TOC) X 100 mg HC/g TOC
OI: Oxygen Index, (S3/TOC) x 100 mg CO_2/g TOC
PI: Production index denoting rate of free hydrocarbons to total hydrocarbons S1/(S1+S2)
MINC%: Mineral Carbon Percent

Analysis of Oil seep Samples

The oil samples were analyzed by latroscan TLC-FID analyzer for group type composition of hydrocarbons. After asphaltene removal, samples were fractionated into saturate and aromatic compounds by column chromatography using Alumina: silica by successive elution with petroleum-ether and benzene. The saturate fractions were further separated into normal alkanes and branched / cycloalkanes by urea adduction.

Gas Chromatographic (GC) analysis

Saturate fraction were analyzed for normal and isoprenoid alkanes distribution on Varian CP3800 Gas Chromatograph using WCOT fused silica column 60m x 0.32mm x 0.25, programmed from 80 - 300˚ C @ 3˚ C/ min hold time 30 min. and nitrogen as carrier gas.

Gas chromatography-Mass spectrometric (GCMS) analysis

Branched / cycloalkanes were analyzed on GCMS Perkin Elmer Clarus 500 using fused silica capillary column DB-1MS (30m x 0.25mm x 0.25) and Helium as carrier gas. Initial oven temperature was kept at 80˚C increased @ 3˚ C/min up to 300˚C and final hold time of 20 min.

The aromatic fractions were analyzed for the distribution of phenanthrene and methylated isomers of phenanthrenes on GCMS Perkin Elmer Clarus 500 using fused silica capillary column MS-5, 30m x 0.25mm and Helium as carrier gas. Initial oven temperature was kept at 80˚C for 1 min increased @ 2.5˚ C/min up to 260˚ C and @ 3.5˚ C up to 300˚C. The Final hold time is 20 min.

Carbon Isotopic Analysis

Stable carbon isotopic study was carried out on VG IsoPrime Continuous Flow-Isotope Ratio Mass Spectrometer interfaced with Euro EA elemental analyzer, equipped with a chromium oxide-silvered cobaltous-cobaltic oxide oxidation reactor at 1020˚C and a copper reduction tube maintained at 650˚C. The liquid samples were introduced into the EA combustion reactor encapsulated in tin foils in a batch run. The combusted sample enters the reduction furnace and resultant gas mixture is passed through a moisture trap into the GC column which is a 3m Porapak Q column where it gets separated into Nitrogen and CO_2 the resultant CO_2 and N_2 is then introduced into the source of mass spectrometer. A CO_2 gas is employed as reference to calibrate the isotope ratios of samples measured. The mass spectrometer is standardized using an international standard NBS-22. Standard samples are also included in each run. The isotopic ratio was expressed in the usual delta notation as follows.

$$\delta^{13}C\ (‰) = \left(\frac{^{13}C/^{12}C_{sample}}{^{13}C^{12}C_{standard}} - 1 \right) \times 1000$$

RESULTS

Oil shale analysis

The Rock Eval Pyrolysis data of oil shale samples are presented in Table-1. And the HI / Tmax and HI/ OI plots of the samples showing type of organic matter are given in Figs. 2, 3, 4, 5 & 6

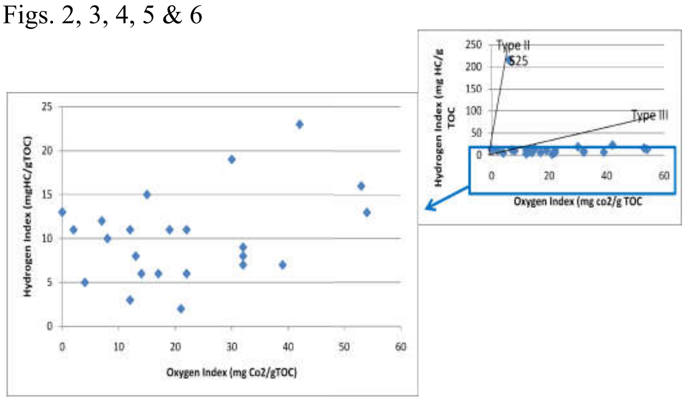

Fig 2 Crossplots of HI vs OI for oil shale of the study area

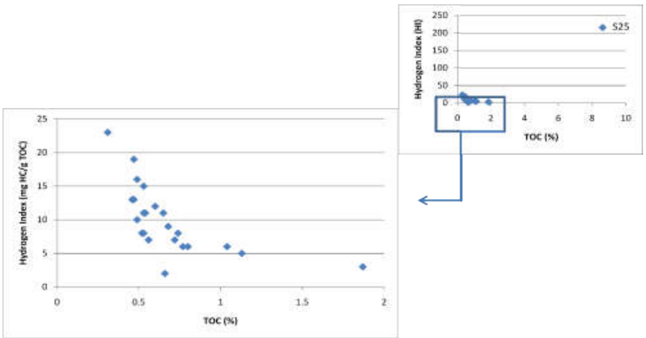

Fig 3 Hydrogen Index vs TOC graph for oil shale of the study area

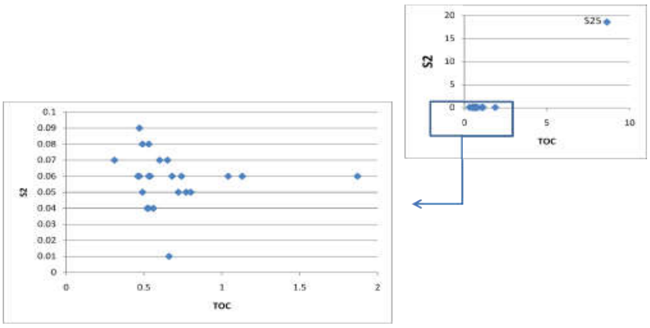

Fig 4 S_2 vs TOC diagram for oil shale of study area

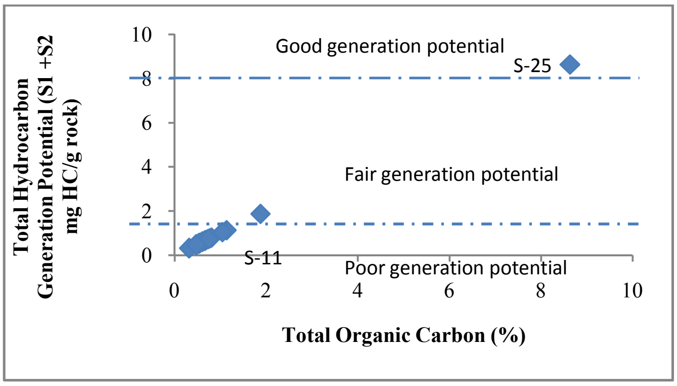

Fig 5 S_1+S_2 versus TOC plot indicating hydrocarbon generation potential of oil shale samples of the study area.

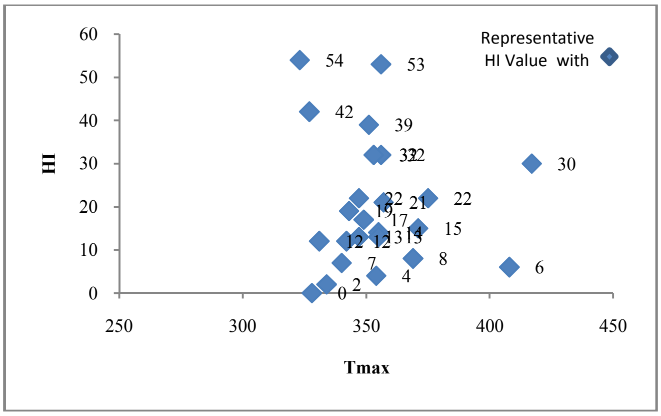

Fig 6 HI versus Tmax plot of outcrop oil shale sample of the study area

Oil seep analysis

The results of analysis are placed in Table-2. API gravity of the oils is in the range of 34.70-35.78 indicating normal nature of oils.

GC fingerprinting

The n-alkane distribution can be affected by maturity and source organic matter inputs. The difference in n-alkane distribution in MO-1 & MO-2 oils is due to variation in source organic input and both Oils have been originated at different maturity. Presence of n-alkanes (C10-C37) indicates terrestrial organic matter input.

High predominance of Pr over nC17 (1.04-2.78) also point towards variation in maturity and source organic matter. Pr/ nC17 generally less than 0.5 indicate mature source rocks.

The high value of Pr/ Ph ratio (6.11 & 5.17) and a cross plot of Pr/ nC17 vs. Ph/ nC18 shows that oils are generated from predominantly terrestrial source organics**,** deposited under oxic environment. Isotopic studies also suggest that oils have been generated from terrestrial organic matter and variation in isotopic values is due to difference in source organic matter.

Table 1 Rock Eval Pyrolysis Data of Oil Shale Samples

Sl.No	Sample No.	Lithology	TOC (%)	Tmax (˚C)	S1 mg. HC/g rock	S2 mg. HC/g rock	S3 mg. CO2/g rock	HI mg. HC/g TOC	OI mg. CO2/g TOC	PI	MINC %
1	S-1	Shale	0.66	357	0.01	0.01	0.14	2	21	0.5	0,89
2	S-2	Shale	0.47	328	0.04	0.06	0	13	0	0.4	0.53
3	S-3	Shale	0.31	327	0.03	0.07	0.13	23	42	0.3	0.69
4	S-4	Shale	0.54	343	0.02	0.06	0.1	11	19	0.25	1.02
5	S-5	Shale	0.77	347	0.02	0.05	0.17	6	22	0.286	0.81
6	S-6	Shale	0.65	342	0.02	0.07	0.08	11	12	0.222	0.78
7	S-7	Shale	0.65	375	0.02	0.07	0.14	11	22	0.222	0.87
8	S-8	Shale	0.49	356	0.04	0.08	0.26	16	53	0.333	0.91
9	S-9	Shale	0.53	334	0.02	0.06	0.01	11	2	0.25	0.50
10	S-10	Shale	1.13	354	0.03	0.06	0.05	5	4	0.333	1.10
11	S-11	Shale	1.87	331	0.08	0.06	0.22	3	12	0.571	0.76
12	S-12	Shale	0.53	371	0.02	0.08	0.08	15	15	0.2	0.92
13	S-13	Shale	0.56	356	0.01	0.04	0.18	7	32	0.2	0.84
14	S-14	Shale	0.68	353	0.02	0.06	0.22	9	32	0.25	0.87
15	S-15	Shale	0.49	369	0.01	0.05	0.04	10	8	0.167	1.06
16	S-16	Shale	0.72	351	0.02	0.05	0.28	7	39	0.286	0.85
17	S-17	Shale	0.80	355	0.02	0.05	0.11	6	14	0.286	0.92
18	S-18	Shale	0.60	340	0.03	0.07	0.04	12	7	0.3	0.93
19	S-19	Shale	0.46	323	0.04	0.06	0.25	13	54	0.4	2.06
20	S-20	Shale	0.52	355	0.02	0.04	0.07	8	13	0.333	0.70
21	S-21	Shale	0.53	347	0.02	0.04	0.07	8	13	0.333	0.64
22	S-22	Shale	0.74	353	0.04	0.06	0.24	8	32	0.4	0.81
23	S-23	Shale	0.47	417	0.01	0.09	0.14	19	30	0.1	0.73
24	S-24	Shale	1.04	349	0.02	0.06	0.18	6	17	0.25	0.91
25	S-25	Shale	8.63	408	1.09	18.54	0.51	215	6	0.056	0.5

GCMS Analysis: The GCMS m/z 191(triterpanes and hopanes) and m/z 217 (steranes) mass fragmentograms for the oil samples show significant quantity of oleanane and dominance of C29 sterane over their C27 and C28 homologues indicates the terrestrial nature of source organic matter. Through hopanes and sterane fingerprints of the MO-1 and MO-2 oils are similar, dominance of oleanane over C30 hopanes and presence of bicadinane even in m/z 217 mass chromatograms suggest that MO-2 oil has got more angiospermic contribution than MO-1 oil. Maturities based on aromatic compounds suggest that MO-2 oil has generated form relatively more mature source rock than MO-1 oil.

Carbon Isotopic Analysis: The results are presented in Table 2 with respect to PDB.

Table 2 Geochemical parameters of oil samples

Parameters/ Sample No.	MO-1 (Upper Tiru)	MO-2 (Changki)
Gross Parameters		
Density at 15˚C	0.8515	0.8455
API Gravity	34.70	35.78
TLC-FID data		
Saturate%	53.51	54.03
Aromatic%	44.78	44.85
NSOs%	1.42	0.77
Asphaltene%	0.28	0.35
GC based Parameters		
Pr/Ph	6.11	5.72
Pr/nc17	2.78	1.04
Ph/ nC18	0.45	0.21
Pr+nc17/ Ph+nC18	2.57	1.92
nC21+nC22/ nC28+nC29	1.15	2.80
GCMS Parameters		
Hopanes m/z 191		
C29H/C30H	0.75	0.46
C30H/ H+M	0.79	0.89
C31HS/ S +R	0.59	0.65
C32HS / S+R	0.61	0.61
Oleanane Index	55.35	108.92
Ts/ Tm	0.73	0.62
Ts/Tm +Ts	0.42	0.38
Steranes m/z 217		
C29αααS/S+R	0.36	0.40
C29ββ/αα+β	0.57	0.62
Aromatic Biomarkers		
MPI-1	0.46	1.10
VRc%	0.68	1.06
Isotopic Data		
δ13C Sat.	-28.5	-27.4
δ13C Arom.	-26.5	-25.8

Pr: Pristane, Ph: Phytane, C29H: Hopane, C30H: C 30 Hopane
MPI: Methyl Phenanthrene Index
αααS/S+R, ββ/αα+ββ: Isomeric ratio of C29 sterane.

CONCLUSION

The pyrolysis results of the Oil Shale samples from serial number 1 to 25 indicate that these samples are devoid of any hydrocarbon generation potential (S2: 0.04-0.08 mg HC/g rock) although samples have poor to fair organic richness (TOC: 0.31-1.87%). At very low values of TOC and S2; the other Rock-Eval parameters like Tmax., HI and PI are irrelevant. The sample S-25 is rich in organic carbon content (TOC: 8.63%) having very good generation potential (S2: 18.4 mgHC/g rock) but still in an immature stage (Tmax: 408^{o}C). As far as thermal maturity is concerned, all the oil shale samples are in the immature stage (Av.VRo% ranging from 0.27 to 0.4 and Tmax : 403-414^{o}C). The oils are of medium API gravity. These were generated from predominantly terrestrial source with significant contribution from both flowering and resinous plants deposited in oxic environmental conditions. However, the contribution from flowering and resinous material is more in the oil of MO-2. Oil MO-2 has generated from relatively more mature source rock than the MO-1 oil. Isotopic studies also suggest that oils have been generated from terrestrial organic matter and variation in isotopic values is due to difference in source organic matter.

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