
Geochemical Characteristics of Carbonaceous Shales from the Surkha Lignite Mine, Saurashtra Basin, India: Implications for Gas Potential

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Abstract: *The carbonaceous shales collected from the Surkha lignite deposits of Saurashtra basin, Gujarat have been studied to decipher the source and quality of kerogen present in it. The pyrolysis and bulk carbon isotope ratio signatures have been determined using Rock Eval6 and EA-IRMS, respectively. Total Organic Carbon (TOC) content of thirty-five shale and lignite samples collected from the open cast lignite mine ranges between 0.4 and 52.4 %. The S1 and S2 values vary from 0.1 to 14.9 mg HC/g rock and 0.1 to 363.8 mg HC/g rock, respectively. Rock Eval thermal maturity indicator, Tmax values, varies between 404°C and 433°C respectively. The hydrogen index (HI) ranges between 5 and 695 mg HC/g TOC, whereas the oxygen Index (OI) values ranges between 15 and 307 mg CO₂/g TOC. Organic matter (OM) is typified predominately by Type III kerogen, with partial contribution from Type IV kerogen. The Tmax and calculated Rock Eval VRo% (< 0.6) suggests immature stage for hydrocarbon generation. Rock Eval parameters, S1, S2, and TOC correlate well with each other and suggest the well preserved and unaltered nature of organic components. Bulk carbon isotope ratios ($\delta^{13}C$) range between -22.7 to -26.5‰ and indicate the contribution of OM from terrestrial land plants. Major element composition determined using XRF technique indicates it to be Fe-shale, with mineral matrix rich in smectite and illites. With shale gas and shale oil emerging as alternate source of energy in recent times, this study provides useful insights on the kerogen properties of the Surkha shales.*

Keywords: *Kerogen, Shales, Lignite, Pyrolysis, Carbon Isotopes, Major elements.*

1. INTRODUCTION

Carbonaceous shales form important petroleum source rock globally. These are black to grey laminated shales, rich in organic content and pyrite. Generally, the shales are formed under reducing and anoxic conditions. OM present in the rocks under influence of pressure and temperature transforms to oil and gas in the subsurface. Oil shales, however, are not exposed sufficiently to necessary temperature and pressure for the transformation of OM and require external maturation conditions. Kerogen is the major source (80 to 90%) for generation of hydrocarbons in these rocks. Formation of kerogen involves the conversion of lipids, proteins and carbohydrates of once living organisms into the OM of sedimentary rocks through various low temperature condensation and polymerization reactions (Hunt, 1996). When buried deeper at high temperatures, kerogen cracks to bitumen, which degrades to form oil and gas. Properties of kerogen such as its concentration, quality or type and its thermal maturity are important for the generation of oil and gas (Mishra et al., 2015).

Depending upon the OM quantity, a total organic carbon content (TOC in weight %) of < 0.50 is considered poor; 0.50 to 1.0 as fair; 1.0 to 2.0 as good and that > 2.0 as excellent for generation of oil and gas in the source rocks (Hunt, 1996, Peter and Cassa, 1994). Based on the ratios of the elements carbon, hydrogen and oxygen the kerogen has been classified as into different Types namely I, II, III and IV (van Krevelen, 1961; Tissot and Welte, 1978). Type I and II generate oil and contain mainly aliphatic and few aromatic nuclei. The H/C ratio is high. The OM is derived from lipids of algae or from organisms that are enriched in lipids by microbial activity (Tissot and Welte, 1978). Type-II kerogen contains more aromatic and naphthenic rings. The H/C ratio and the hydrocarbon are lower. Type-II kerogen is generally found in marine organic matter deposited in reducing environments. Type-III kerogen generates largely gas, condensates and some waxes. It contains mostly condensed poly-aromatics and oxygenated functional groups, with minor aliphatic chains. The H/C ratio is low. The potential to generate oil is moderate for Type III kerogen. It may generate gas at greater depths.

The O/C ratio is comparatively higher. The OM is mostly derived from terrestrial higher plants (Tissot and Welte, 1984). Type IV kerogen generates little amount of methane and CO₂. The van Krevelen diagram (van Krevelen, 1961) is used to evaluate the quality of kerogen based on the HI/OI values. The Hydrogen Index vs Tmax (Temperature at peak kerogen cracking) relationship obtained from the pyrolysis is used to infer the maturation state along with the kerogen type in the sedimentary OM (Tissot and Welte, 1978; Hunt, 1996).

The interbedded carbonaceous shales of the Surkha lignite mine, South-East of Bhavnagar, Gujarat, have been studied here for their OM quantity and quality. A suite of thirty- three shales and two lignite samples have been investigated using the open system pyrolysis (Rock Eval6 pyrolyzer) and bulk carbon isotope analyses (Elemental Analyzer-Isotope Ratio Mass Spectrometer) for understanding the source, kerogen type and thermal maturity of OM. As the mineral matrix influences the gas generation mechanism, the major element composition is also studied using XRF to understand the role of different clay minerals in assessing the thermal maturity of kerogen and its cracking into the gaseous hydrocarbons.

2. GEOLOGICAL SETTING AND STRATIGRAPHY

Saurashtra basin is located on the western margin of Indian sub-continent and is bounded by bounded by Kutch rift basin in the north, Cambay rift basin in the east and the Surat depression in the south (Biswas, 1982; Merh, 1995). The basin forms a horst block and is characterized by Lower Cretaceous sedimentation, followed by Deccan basalts and the Neogene and Quaternary aged rocks. The outcropping area is surrounded on three sides by the Arabian Sea and Gulf of Kutch and Cambay, whereas, the Gujarat alluvial plains mark its northeastern limit (Fig. 1). The alluvium overlies the Cambay rift basin sediments (Biswas, 1982; 1987). Marine to fluvio-marine tertiary sediments are deposited along the Western Continental Shelf. The Paleogene strata lie on the off shore area while the Neogene strata comprise the surface on shore exposures. These occur all along the south western and southern coast. The on-shore Neogene beds are range in age from the early Miocene to Mio-Pliocene (Fedden 1884).

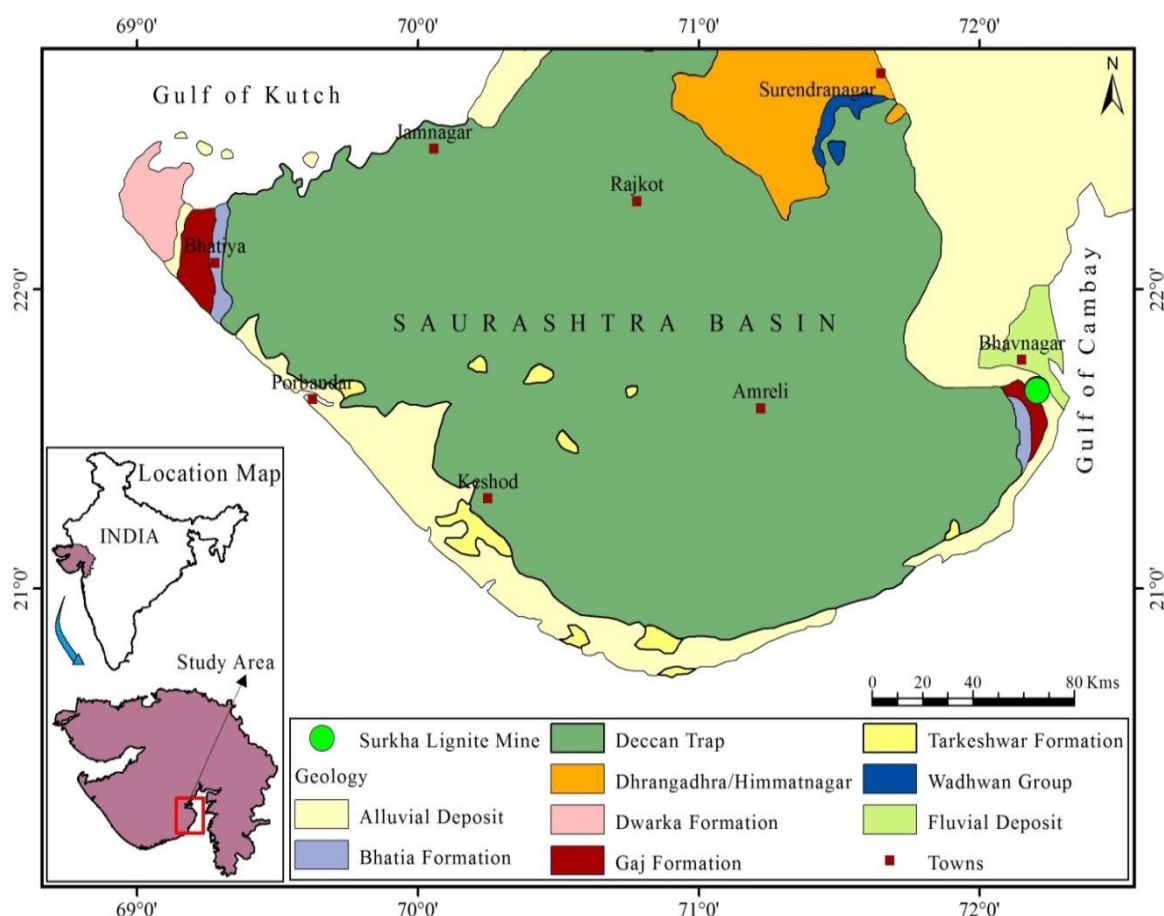


Fig1. Geological map of the Saurashtra basin showing the location of Surkha lignite mine (after Merh, 1995)

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The collected samples form part of the Gaj Formation belonging to Middle Miocene age. Gaj formation beds are divided into two members - the lower Ashapura Clay Member and upper Ranjitpur Limestone Member (Bhatt, 2000; Pandey et al., 2007; Kundal et al., 2014) (Table 1). The Ashapura Clay Member contains variegated clay with gypsiferous bands and the Ranjitpur Limestone Member contains yellow and brown coloured fossiliferous limestone. In Gaj formation, the differential weathering of the constituent rocks has given rise to a gently undulating topography. The formation is highly fossiliferous, occupies a wide area of about 300 km². The formation underlies the Dwarka Formation, which ranges from Middle Miocene to Lower Pleistocene, and divisible into three members. The Positra limestone member contains bioclastic and coralline limestone with few dolomitic bands. The Shankhodar sand-clay Member contains sandy clay and sandstones and the Kalyapur Limestone Member contains recrystallized fossiliferous limestone and sandy limestone. Gaj formation is followed by the underlying Deccan Trap formation (Kundal et al., 2014). Detailed lithostratigraphy of the Surkha mine is given in Table 1.

Table 1. Lithostratigraphy of Cenozoic- Quaternary deposits of Saurashtra basin (After Kundal et al., 2014)

Stratigraphic Unit		Lithology	Age
Formation	Member		
Holocene deposits		Beach and dune sands, tidal clays, alluvium	Holocene
Unconformity			
Chaya Formation	Armada Reef Member (4 m)	Coral algal reef, coral bafflestone and algal rudstone with micro and mega fossils	Middle to Late Pleistocene
	Okha Shell Limestone Member (10 m)	Cross bedded pack to rudstone, bioturbated shell limestone with mega fossils.	
Unconformity			
Miliolite Formation	Adatiana Member (5-50 m)	Pelletoid limestones (Calcarenites)	Middle to Late Pleistocene
	DhobaliyaTalav Member (8-10 m)	Alternating sequence of pelletoid limestone and fine-grained limestone (micrites)	Early Middle Pleistocene
Unconformity			
Dwarka Formation	Kalyapur Limestone Member (30 m)	Recrystallized fossiliferous limestone and sandy limestone	Lower Pliocene
	Shankhodar Sand-clay Member (60 m)	Sandy clays and sandstones	Upper Miocene
	Positra limestone member (25 m)	Bioclastic and coralline limestone with few dolomitic bands	Middle Miocene
Unconformity			
Gaj Formation	Ranjitpur Limestone Member (5 m)	Yellow and brown fossiliferous limestone	Lower to Middle Miocene
	Ashapura Clay Member (90 m)	Variegated clays with gypsiferous bands, Carbonaceous shales, lignites	
Nonconformity			
Deccan Trap		Basalt and other derivatives covered at places by laterite and bauxite	Upper Cretaceous to Eocene

3. MATERIALS AND METHODS

3.1. Field Sampling

Thirty-five carbonaceous shale and lignite samples were collected from the open cast mine of Surkha of Saurashtra Basin, Gujarat, India (Fig. 1). A 500g of carbonaceous shale samples were collected from an elevation of 7 – 8 m by manual hammering of the shale horizons. The locations were marked using Global Positioning System (GPS). A field photograph of lignite and shale horizons in Surkha lignite mine is shown in Fig. 2.



Fig2. Field photograph of the shale and lignite horizons exposed in the Surkha lignite mine

3.2. Geochemical Analysis

The carbonaceous shale and lignite samples were crushed into fine powder of about less than 63μ for the geochemical investigations. These samples were analyzed for TOC content and Rock Eval pyrolysis, bulk carbon isotope analysis ($\delta^{13}C_{org}$) using EA-IRMS and major oxides compositions using X-ray Fluorescence spectrometry.

3.2.1. Rock Eval Pyrolysis

In Rock Eval pyrolysis, the OM is cracked thermally according to a programmed temperature pattern to know the quantity and quality of kerogen. A weighed sample of crushed source rock (~ 70 - 80 mg) is placed into a crucible, which is inserted into one of the holders of the automatic sampler fitted to the Rock Eval instrument. The analysis takes place in two steps. In the first step during the pyrolysis, the thermo-vaporized free hydrocarbons contained in the rock are released and detected by flame ionization detector (FID). With increasing temperature, the heavy hydrocarbons are liberated due to the cracking of OM (kerogen) in the rock, giving rise to the S2 peak and the simultaneously evolved CO and CO₂ are detected by Infrared cell (S3 peak). S3 is an indication of the amount of oxygen contained in the kerogen and is used to calculate the oxygen index. Tmax is the temperature at the maximum of S2 peak during the pyrolysis process and is an indication of the maturation state of the OM. In the second step during oxidation process, the CO and CO₂ resulting from the combustion of rock, is measured by means of Infrared cell (S4CO, S4CO₂). The TOC content of the rock is determined by adding up of the pyrolyzable organic carbon and that of oxidation under air (residual organic carbon). The mineral carbon content is also measured as the sum of pyrolyzable and oxidative inorganic carbon content (Mani et al., 2014; 2015).

3.2.2. EA-IRMS

Bulk carbon isotope analysis ($\delta^{13}C_{org}$) of the shales was performed on a Thermo Finnigan Flash-Elemental Analyzer (TC/EA) attached to Delta plus XP isotope ratio mass spectrometer (IRMS). Sample weight of about 300-500 μ g. filled in the tin capsules was placed into the auto sampler. These samples were purged with a continuous flow of helium and then dropped into a vertical quartz tube maintained at 900°C (combustion reactor packed with Copper Oxide). Flash combustion of sample took place in the helium stream enriched with oxygen. The isotopic composition of CO₂ was measured using IRMS. The Flash EA-IRMS was calibrated using international standards, NBS-22 and graphite, and the precision was found to be within $\pm 0.3\%$ of the reported value (Mani et al., 2015).

3.2.3. X-ray fluorescence spectrometer analysis (XRF)

The major elemental concentrations were determined in Philips Magi-X PRO Model PW 2440 X-ray fluorescence spectrometer attached to automatic sample changer PW 2540 and software SUPER Q 3.0 (Philips, Eindhoven, The Netherlands). The samples were ignited at 660°C for 40 minutes in silica crucibles for loss on ignition. The powdered samples were used to prepare pressed pellets of 40 mm diameter using collapsible aluminum cups the analysis. The cups were filled with boric acid and 1 to 2 grams of the finely powdered carbonaceous shale samples were evenly sprayed and hydraulically pressed to form a pellet. Matrix matching certified reference materials GSR-4 for sandstone and GSR-5 for shale were used to calibrate the instrument (Mani et al., 2016).

4. RESULT AND DISCUSSION

The Rock-Eval pyrolysis results and the bulk carbon isotope compositions are given in the Table 2. The lignite samples (S-01, S-31) show a high value for thermo-vaporized free hydrocarbons (S1=8.94 and 14.89 mgHC/g rock) those from the cracking of OM (S2=197.23 and 363 mgHC/g rock). The thermal maturity indicator or the Tmax values are lower, 417°C and 413°C respectively for the two lignite samples. CO₂ from organic source (S3) are 8.52 and 7.98 (mgCO₂/g Rock). TOC values are 48.15 and 52.38 (wt. %) (Table 2). HI values, which is the ratio of S3 and TOC are 410 and 695 mg HC/g TOC). OI values, which is the ratio of S3 and TOC are 18 and 15 (S3/TOC, mgCO₂/g TOC) respectively.

The carbonaceous shales have lower S1 values, ranging between 0 and 0.89 mgHC/g rock, (Table 2). The S2 values range between 0.1 and 41.06 mgHC/g Rock (Table 2). Tmax values range between 404 and 433°C, indicating a thermally immature OM for the oil and gas generation (Table 2). TOC values lie between 0.4 and 24.34 % (Table 2). S3 values range between 0.46 and 10.01 mgCO₂/g rock. HI values range between 29 and 212 (S2/TOC, mgHC/g TOC), and indicates the kerogen to be Type III and Type II/III (Peters and Cassa, 1994; Table 2). OI values range between 17 and 307 mgCO₂/g TOC. A representative pyrogram containing the pyrolysis and oxidation curves for the studied sample is shown in Fig. 3. The bulk carbon isotopic values ($\delta^{13}\text{C}_{\text{org}}$) range between -22.7 and -26.6 ‰ for the selected samples.

Table2. Rock Eval pyrolysis parameters data of Surkha carbonaceous shales from Saurashtra Basin

Sample	S1	S2	Tmax	S3	TOC%	HI	OI	MINC %	RE VR ₀ %
S-01 (lignite)	8.94	197.23	417	8.52	48.15	410	18	1.12	0.35
S-02	0.22	31.26	426	3.83	18.28	171	21	0.4	0.51
S-03	0.25	8.33	428	1.26	3.92	212	32	0.14	0.54
S-04	0.89	40.32	423	10.01	24.34	166	41	0.65	0.45
S-05	0.48	41.06	427	7.06	19.85	207	36	0.49	0.53
S-06	0	0.33	420	0.46	0.94	35	49	0.13	0.4
S-07	0.02	1.08	429	1.67	1.99	54	84	0.22	0.56
S-08	0.01	0.45	420	0.74	0.89	51	83	0.11	0.4
S-09	0	0.42	419	0.77	1.01	42	76	0.15	0.38
S-10	0.01	0.36	422	0.81	0.78	46	104	0.12	0.44
S-11	0	0.23	415	0.48	0.55	42	87	0.07	0.31
S-12	0	0.02	433	0.33	0.4	5	82	0.68	0.63
S-13	0	0.13	430	1.31	0.91	14	144	6.58	0.58
S-14	0	0.1	432	1.72	0.56	18	307	0.58	0.62
S-15	0	0.3	423	1.17	1.85	16	63	0.19	0.45
S-16	0	0.52	417	4.44	3.11	17	143	0.46	0.35
S-17	0	0.17	422	2.41	1.14	15	211	0.18	0.44
S-18	0.01	0.52	421	1.26	1.95	27	65	0.16	0.42
S-19	0.08	3.67	430	2.28	5.02	73	45	0.43	0.58
S-20	0	0.82	425	1.53	2.16	38	71	0.24	0.49
S-21	0.2	2.52	421	2.37	4.22	60	56	0.33	0.42
S-22	0.27	10.91	416	4.13	9.34	117	44	0.35	0.33
S-23	0.73	16.05	426	2.21	10.1	159	22	0.28	0.51
S-24	0.38	11.59	416	2.85	10.4	111	27	0.32	0.33
S-25	0.23	9.14	428	1.27	5.83	157	22	0.22	0.54
S-26	0.25	10.12	426	1.43	6.06	167	24	0.16	0.51

S-27	0.22	8.38	424	1.54	6.14	136	25	0.16	0.47
S-28	0.03	1.26	423	1.42	2.84	44	50	0.21	0.45
S-29	0.29	11.29	430	2.12	5.55	203	38	0.21	0.58
S-30	0.24	9.7	428	0.88	5.13	189	17	0.16	0.54
S-31 (lignite)	14.89	363.79	413	7.98	52.38	695	15	0.74	0.27
S-32	0.11	4.17	427	1.24	2.91	143	43	0.11	0.53
S-33	0	0.4	422	0.54	0.67	60	81	0.24	0.44
S-34	0.04	0.36	404	0.82	1.26	29	65	0.12	0.11
S-35	0.28	13.52	428	1.79	5.55	244	32	0.17	0.55

[TOC (wt. %); S1, S2 (mgHC/g Rock); S3 (mgCO₂/g Rock); Tmax (°C);

HI (S2/TOC, mgHC/gTOC); OI (S3/TOC, mgCO₂/g TOC); &

Rock Eval Vitrinite Reflectance (RE VR₀) %=0.018 × Tmax-7.16]

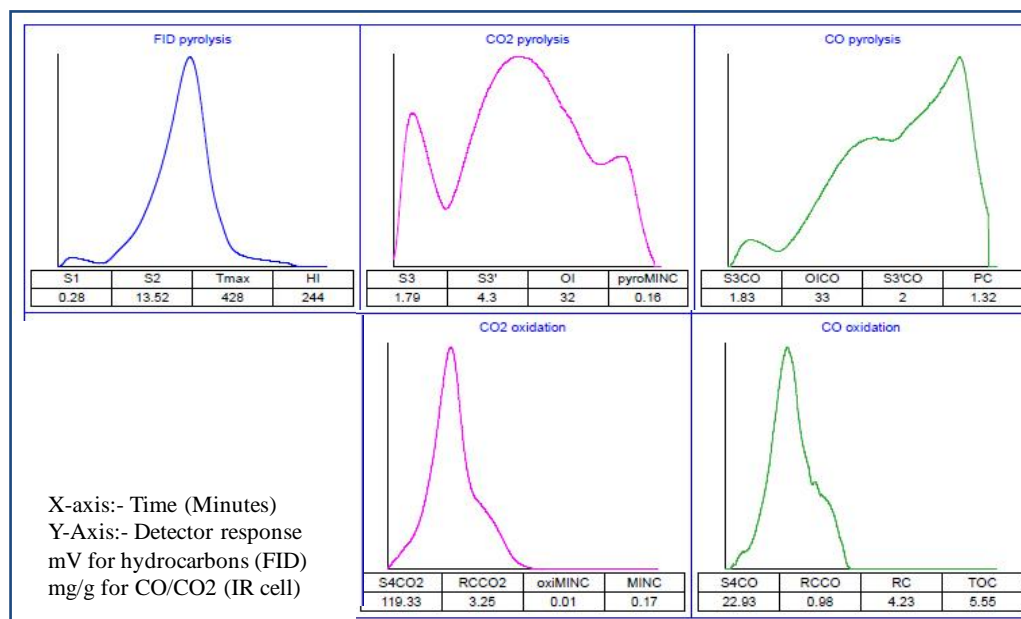


Fig3. Representative Rock Eval pyrolysis and oxidation curves of the carbonaceous shale sample (S-35) from Surkha lignite mine.

The OM in Surkha shales is characterized by a high TOC, which suggests it to have potential for the oil and gas generation (Peters and Cassa, 1994). There exists a very good to excellent correlation between S1 and S2 values ($r^2=0.9$). These parameters also vary linearly with the TOC ($r^2=0.8$) content of the OM, indicating the well preserved and unaltered nature of OM in the shales (Tissot and Welte, 1978). A modified van Krevelen diagram (van Krevelen, 1961; Tissot and Welte, 1984) has been used to determine the type and maturation state of kerogen based on HI/OI values. The HI versus OI plot of the shales associated with lignite mine from Surkha indicates that the OM is characterized by Type III and Type IV kerogen (Fig. 4). A large majority of samples have HI>50 and nearly 50% of such samples have HI between 150-200, which suggests that OM is capable of generating oil and gas. When OM and coals have high hydrogen content relative to carbon, they can form oil (Hunt, 1996). The HI value below 50 mg HC/g TOC suggests a Type IV kerogen which produces no oil and gas. Type III kerogen, ranging between 50 and 200 mg HC/g TOC, produces gas. Type II/III kerogen, ranging between 200 and 300 mg HC/g TOC, produces mixed oil and gas. Type II ranging between 300 and 600 mg HC/g TOC produces oil. Type I ranging above 600 mg HC/g TOC produces oil. The Tmax values below 435 °C show an immature stage for hydrocarbon generation; the values 435 to 465°C suggest a mature stage for oil generation; whereas above 465°C show a post mature stage suitable for gas generation (Mishra et al., 2014). The HI versus Tmax correlations of the shales associated with lignite mine from Surkha shows thermally immature OM, characterized by Type III and Type IV kerogen (Fig. 5). Rock Eval vitrinite reflectance, calculated using the Tmax data of Surkha samples ($0.018 \times Tmax - 7.16$; Jarvie and Lundell, 1991), ranges from 0.3 to 0.6 Ro % (Table 2). It suggests that samples are not exposed to sufficient heat for the oil or gas generation. These shales, where buried at deeper horizons in the basin, may achieve an appropriate thermal maturity for the generation of liquid and gaseous hydrocarbons.

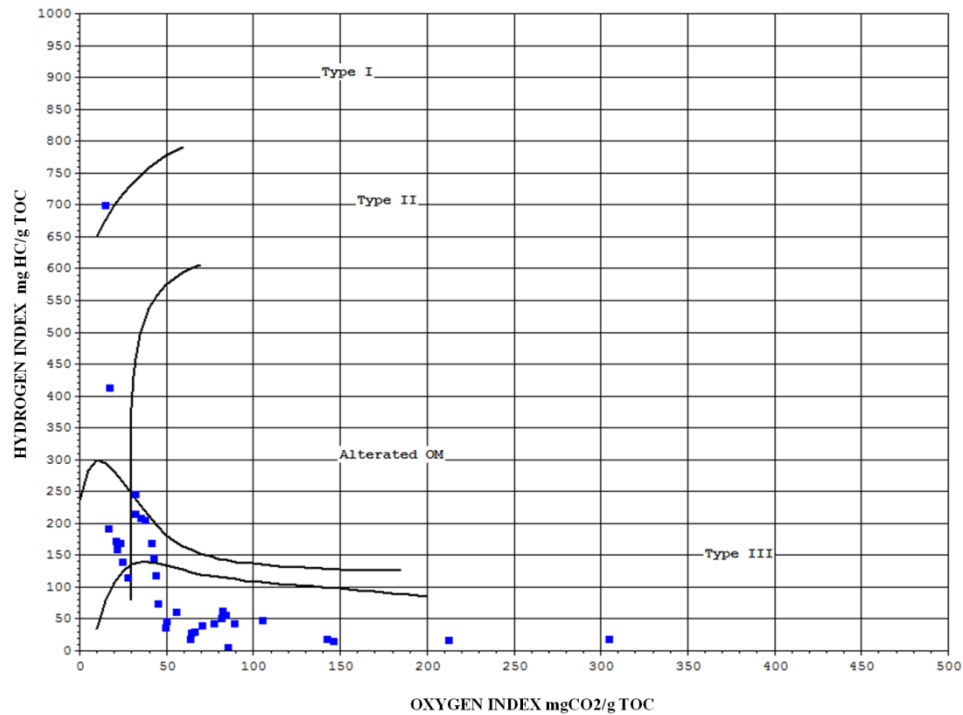


Fig4. HI versus Tmax correlation of the OM in the Surkha carbonaceous shales, Saurashtra Basin

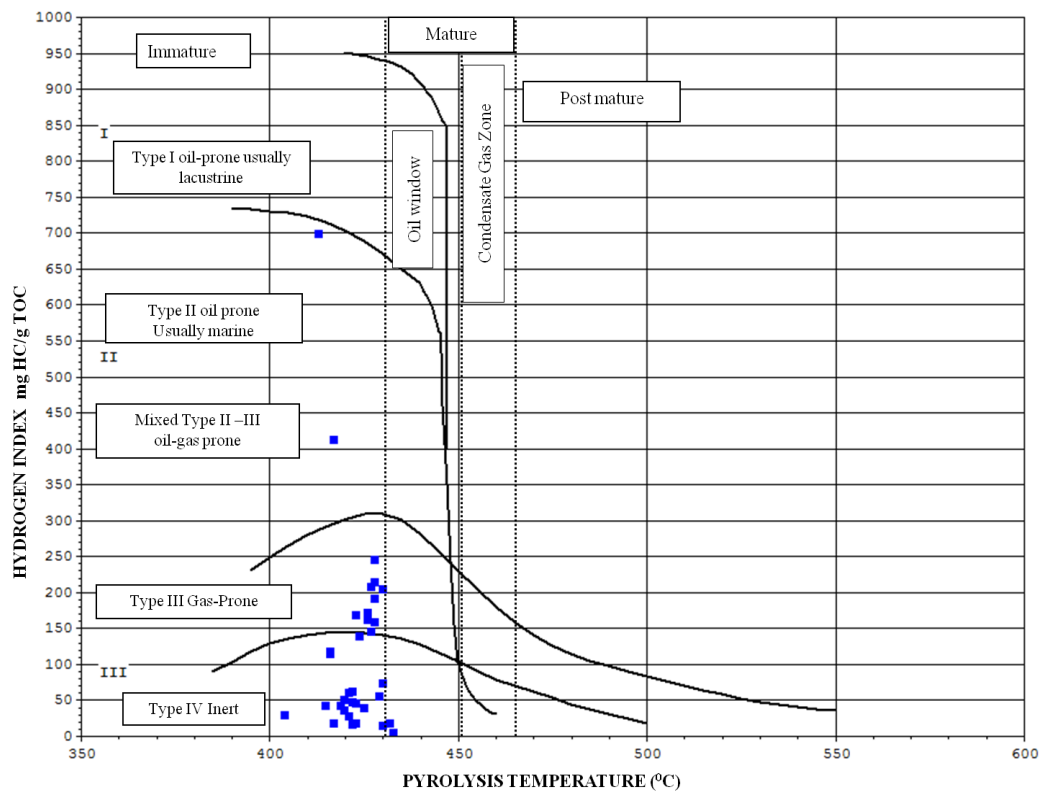


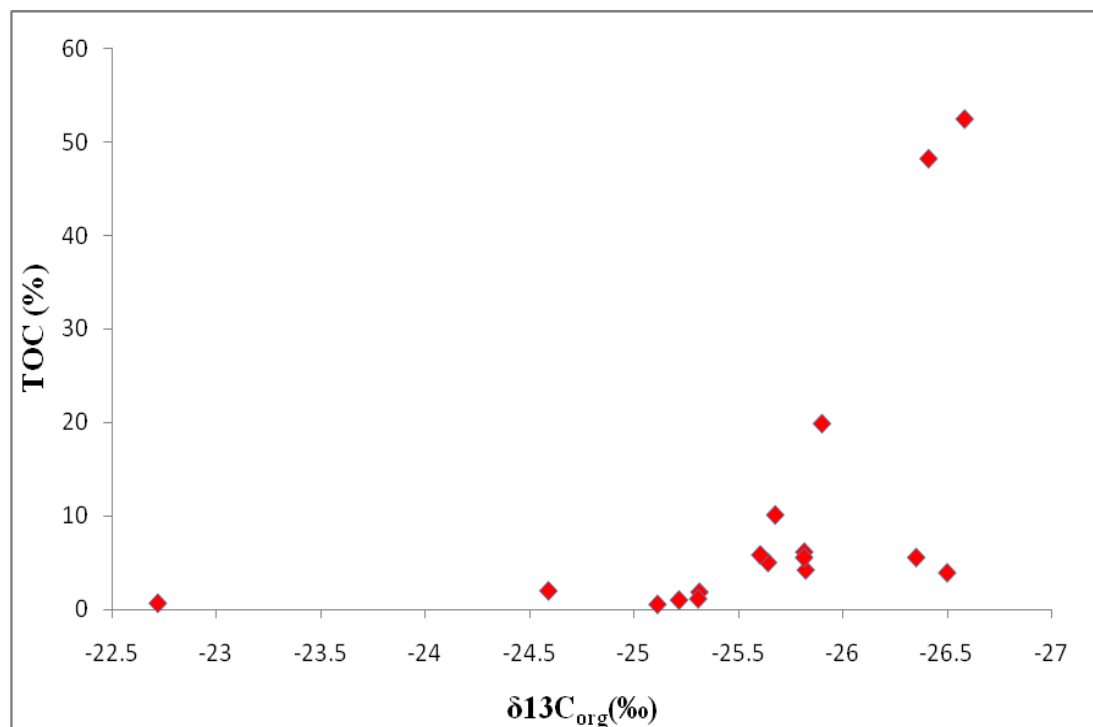
Fig5. Correlation between the HI and OI values in OM from the Surkha carbonaceous shales, Saurashtra Basin

The bulk stable carbon isotope composition indicates the contribution from terrestrial higher plants (Table 3). Differences in the carbon sources of the marine and continental (terrestrial and freshwater) plants are depicted in their $\delta^{13}\text{C}$ isotopic compositions (Mani et al., 2015). In general, $\delta^{13}\text{C}$ for marine plants ranges from -8‰ to -17‰, whereas for land plants it ranges from -22‰ to -29‰ (Hoefs, 2009). The bulk OM in Surkha shales is derived from the polyaromatic woody tissues of higher land plants and is capable of generating gas. The variation of carbon isotope ratios with TOC is given in Fig. 6 (Wang et al., 2015). The samples with high TOC have depleted $\delta^{13}\text{C}$ values, which also suggest the input of terrigenous material during the deposition of these sediments.

Table3. Bulk organic carbon isotope ratios for the carbonaceous shales from the Surkha lignite mine, Saurashtra Basin

Sample	S-01 [Ⓢ]	S-03	S-05	S-07	S-09	S-11	S-15	S-17	S-19
$\delta^{13}\text{C}_{\text{org}}(\text{‰})$	-26.412	-26.501	-25.901	-24.591	-25.218	-25.113	-25.314	-25.308	-25.642
Sample	S-21	S-23	S-25	S-27	S-29	S-31 [Ⓢ]	S-33	S-35	
$\delta^{13}\text{C}_{\text{org}}(\text{‰})$	-25.823	-25.676	-25.606	-25.816	-26.352	-26.584	-22.720	-25.815	

[Ⓢ]S-01 & S-31 samples are lignites

**Fig6.** Variation of bulk carbon isotope values with TOC content in the carbonaceous shales from the Surkha lignite mine (after Wang et al., 2015)

The major elemental oxides data of selected carbonaceous shales from Surkha lignite mine were determined using XRF (Table 4). The SiO_2 content of the shales varies from 34.2 to 40.5 %. The Al_2O_3 content ranges from 10.1 to 21.5%. Fe_2O_3 content varies between 4.15 to 12.02% and MnO varies from 0.02 to 0.08 %. The major element content of carbonaceous shales is nearly similar to the published values of average shale (PAAS and NASC) (Clarke, 1924). However SiO_2 values are comparatively lower (Figs. 7; 8). Elevated concentrations of MgO , CaO and Na_2O are observed in the studied samples (Table 4 ; Fig. 7).

Table 4: Major oxides data of Surkha carbonaceous shales compared to PAAS and NASC.

Sample No	S-01	S-04	S-19	S-23	S-29	PAAS	NASC
SiO_2 (%)	34.22	39.61	38.99	39.65	40.52	62.8	64.8
Al_2O_3 (%)	10.14	21.54	18.55	16.57	19.09	18.9	16.9
Fe_2O_3 (%)	4.15	5.55	11.55	12.02	10.87	7.61	6.33
MnO (%)	0.03	0.02	0.08	0.04	0.05	0.11	0.06
MgO (%)	26.37	22.87	22.54	23.14	23.14	2.2	2.85
CaO (%)	16.6	4.49	2.02	2.03	1.21	1.3	3.56
Na_2O (%)	5.74	1.85	0.69	0.86	0.74	1.2	1.15
K_2O (%)	0.05	0.05	0.68	0.27	0.32	3.7	3.99
TiO_2 (%)	3.11	3.04	3.17	4.07	3.89	1.0	0.78
P_2O_5 (%)	0.07	0.04	0.53	0.1	0.1	0.16	0.11

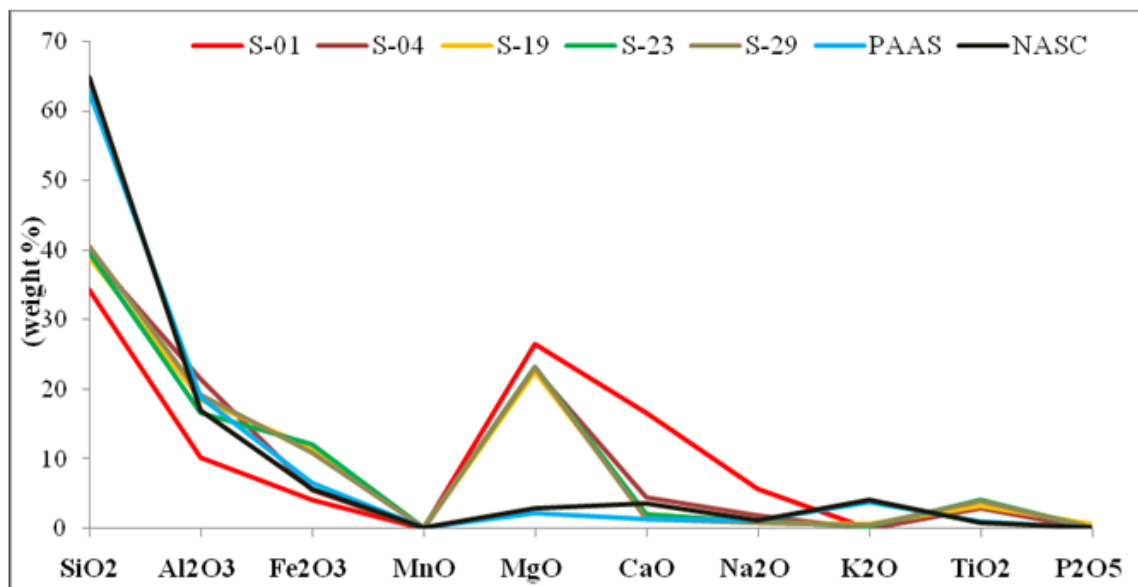


Fig7. The Major elemental chemistry of Surkha carbonaceous shales versus PAAS and NASC (after Mani et al., 2016).

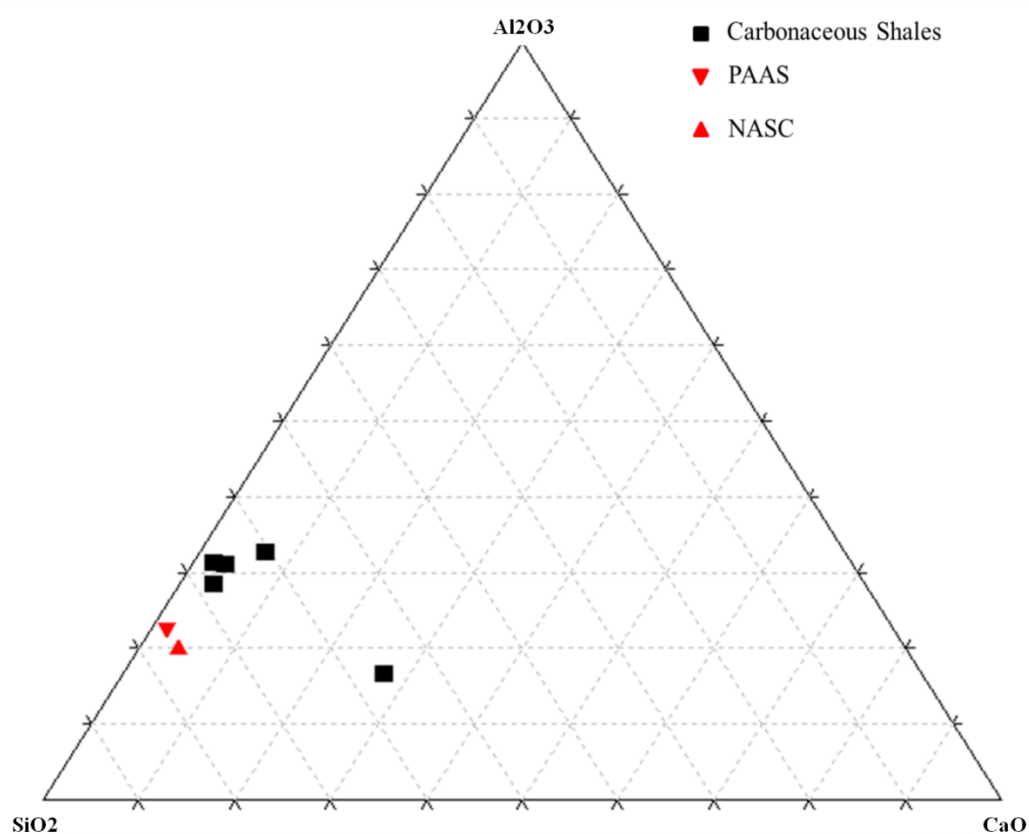


Fig8. Q-F-C Ternary diagram of carbonaceous shales from Surkha lignite mine, Saurashtra Basin.

These sediments owe their provenance from Deccan Basalts which cover a large part of Saurashtra basin (Fig. 1). The studied shales have been characterized using classification of Heron, 1988 [$\log(\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ vs $\log(\text{SiO}_2/\text{Al}_2\text{O}_3)$]. The major oxides show a distribution in the Fe-shale lithofacies (Fig. 9). In the A-CN-K diagram, intensely weathered samples are plotted with high CIA (80-100), where incipiently weathered samples plot near the feldspar zone CIA (50-70) (Mani et al., 2016). The XRF data of the studied samples show the CIA value vary between 75-90, which indicates a moderate to high degree of weathering and alteration. In A-CN-K diagram (Fig. 10), sample trend suggests the Smectite - Illite source composition. The relationship of Na_2O with Al_2O_3 ($r^2 = 0.671$, Fig. 11) suggests that these elements are associated with a constant detrital source.

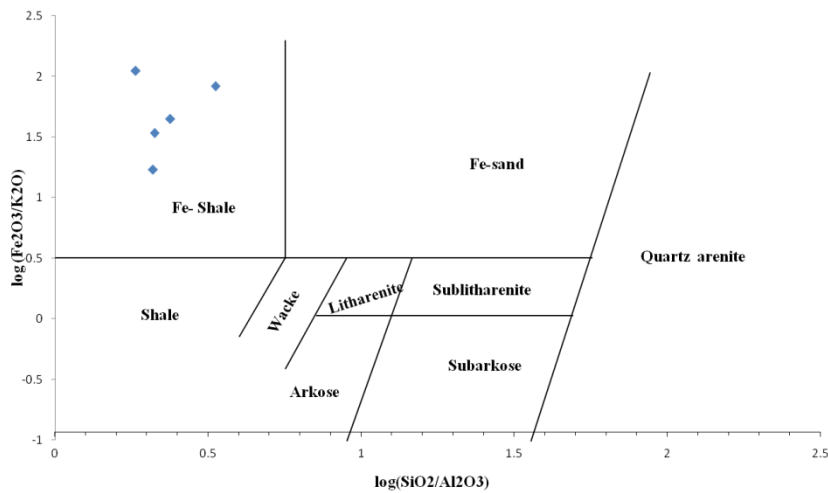


Fig9. Classification of terrigenous sandstones and shales using major oxide data [$\log(Fe_2O_3/K_2O)$ versus $\log(SiO_2/Al_2O_3)$] of Surkha lignite mine, Saurashtra Basin(after Herron, 1988)

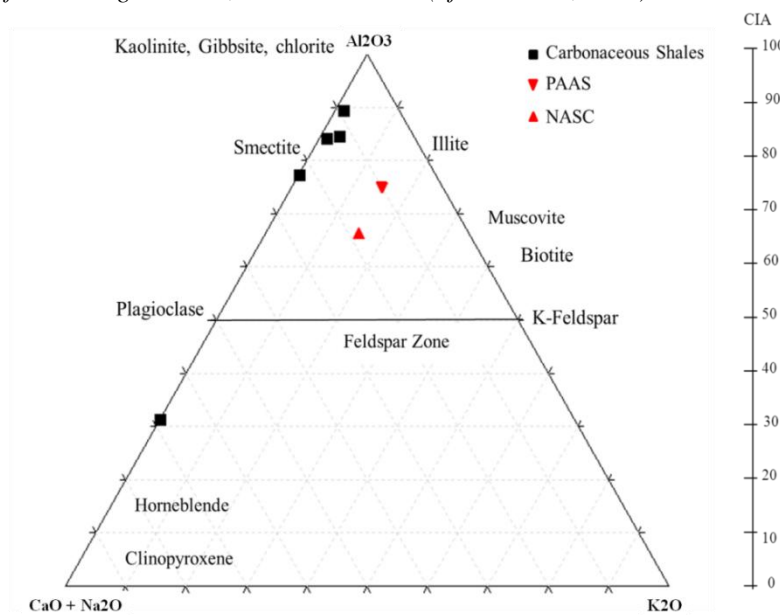


Fig10. Al_2O_3 - $CaO+Na_2O$ and K_2O (A-CN-K) Ternary diagram for the CIA values of carbonaceous shales from Surkha lignite mine, Saurashtra Basin

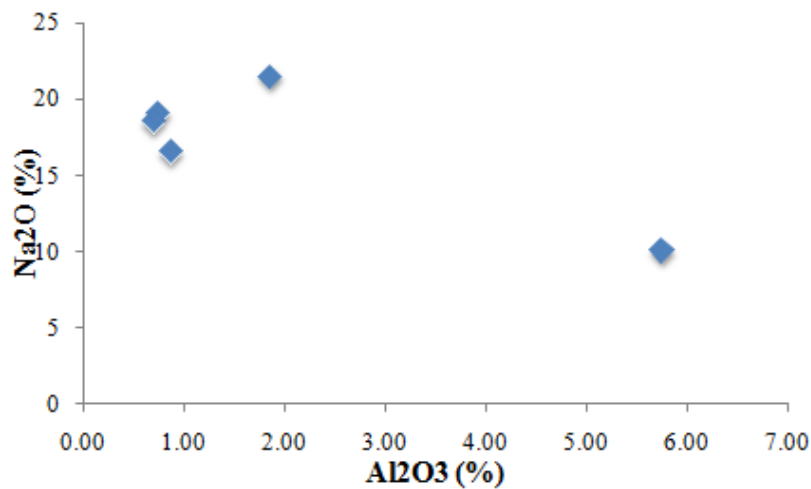


Fig11. Correlation of Al_2O_3 with Na_2O concentrations in carbonaceous shales from Surkha lignite mine, Saurashtra Basin

The clay mineralogy of the studied samples is dominated by the Smectite and Illite composition (Fig. 10). Due to the small particle size, high surface area and ability to complex with polar organic substances, smectites achieve intimate mixing with organic substances and produce highly dispersed

clay-organic system (Johns, 1979). It has been observed that subsurface diagenetic conditions, particularly the temperatures, for generation of hydrocarbons coincides with the clay mineral alterations such as changes from montmorillonite to mixed-layer montmorillonite/illite to illite and changes in ordering of illite/smectite (I/S) from random to ordered I/S. Percentage of I/S decrease sharply where the Tmax values are in oil generation zones. The Rock Eval Tmax data of the studied samples suggests it to be in immature to early oil window. This is also supported by the XRF data where the samples tend to show more of the smectite composition and hence a random or lowered I/S (Fig. 10).

Mineralogy plays important role in controlling the kerogen pyrolysis products. Particularly, the clay mineral smectite tends to get expanded and act as a catalyst during the thermal decomposition of OM in the subsurface (Johns, 1979). It has been observed that during Rock Eval pyrolysis of samples having lower TOC, the mineral matrix with quartz, calcite etc. may retain some of the S₂ or catalyze the thermal decomposition of the kerogen, thereby altering the S₂ signatures (Espitalie et al., 1980, 1984; Dembicki, 1983). The shales studied here have low TOC with abundance of quartz and clay minerals, which could possibly account for the reduced amount of pyrolysed hydrocarbons during the open system pyrolysis. The variability for both the Tmax and HI is wide, which also suggests some effect of surficial weathering and oxidation on the outcrop samples.

Thus, as indicated by the S₁, S₂ and TOC content, the shales are rich in OM but have low thermal maturity for the generation of hydrocarbons. This is also supported by the mineral data with a low I and S ratio. The shales buried at a greater depth in the basin may have appropriate thermal maturity and can be investigated for detailed studies. The high silica and alumina content of the shale samples offers the brittleness property, which makes it suitable for hydraulic fracturing considerations as well (Fig. 8).

5. CONCLUSION

The Rock Eval pyrolysis results of the interbedded carbonaceous shales from the Gaj formation of Surkha lignite mine of Saurashtra Basin, Gujarat indicate high TOC content, with dominantly gas prone Type III & IV kerogen in thermally immature stage. The kerogen is likely to be in mature stage in the deep seated shale horizons. Bulk carbon isotope ratios suggest that the gas prone kerogen is derived largely from the higher terrestrial land plants. However; with high hydrogen content, the kerogen of the Surkha shales is capable of generating oil and gas. With smectites as major clay mineral, its contribution on thermal maturity and cracking of kerogen also holds importance in pyrolytic yields. The study provides encouraging results for detailed characterization of shales at greater depth in the basin in terms of their lithology, porosity, permeability etc. towards its assessment for shale gas and shale oil prospects.

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