Characterization of organic carbon in black shales of the Kachchh basin, Gujarat, India

HEMA SRIVASTAVA¹, AJOY K BHAUMIK^{1,*}, DEVLEENA TIWARI²,
SARADA P MOHANTY¹ and DATTATRAY J PATIL²

¹Department of Applied Geology, Indian Institute of Technology (Indian School of Mines),
Dhanbad 826 004, India.

²Petroleum Geochemistry and Microbiology Group, National Geophysical Research Institute,
Hyderabad 500 007, India.

*Corresponding author. e-mail: ajoyism@gmail.com

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Thirty-three black shale samples from four locations on the onland Kachchh basin, western India were analyzed to characterize organic carbon (OC), thermal maturity and to determine the hydrocarbon potential of the basin. Upper Jurassic black shales from the Jhuran Formation (Dhonsa and Kodki areas) are characterized by the presence of chlorite, halloysite, high $T_{\max}$, low OC, low hydrogen index and high oxygen index. These parameters indicate the OC as type IV kerogen, formed in a marine environment. The rocks attained thermal maturity possibly during Deccan volcanism. Early Eocene samples of the Naredi Formation (Naliya-Narayan Sarovar Road (NNSR) and the Matanomadh areas) are rich in TOC, smectite, chlorite and framboidal pyrite, but have low $T_{\max}$. These indicate deposition of sediments in a reducing condition, probably in a lagoonal/marsh/swamp environment. Organic carbon of the Naredi Formation of NNSR may be considered as immature type III to IV kerogen, prone to generate coal. Core samples from the Naredi Formation of the Matanomadh area show two fold distribution in terms of kerogen. Organic carbon of the upper section is immature type III to IV kerogen, but the lower section has type II to III kerogen having potential to generate oil and gas after attaining appropriate thermal maturity.

Keywords. Black shale; organic carbon; Rock-Eval pyrolysis; thermal maturity; Kachchh basin.

1. Introduction

Black shales in stratigraphic records are considered as organic carbon rich sedimentary units, which are deposited in unique paleoenvironmental condition and are considered to be potential for hydrocarbon generation. These shales are described as dark coloured mud rocks containing a mixture of clay minerals, quartz silts and organic matter. The organic carbon in these rocks

generally ranges between 1 and 30% (Tourtelot 1979; Weissert 1981). The concentration of the organic matter within shale or mud gets enhanced during the period of aquatic anoxia. Preservations of organic carbons are mainly controlled by the clay mineralogy and availability of mineral surface area along with other depositional parameters (e.g., low oxygen content of the water column and pore water having <0.2 ml/l water, restriction in water circulation, lack of bioturbation, deposition

Figure 1. Location map of the studied sites in the Kachchh district, Gujarat, India (redrawn and modified after Mishra *et al.* 2014). Solid black stars represent sample collection sites.

of very fine-grained sediment particles of $<2\mu$, and an optimum sedimentation rate) (Kennedy *et al.* 2002). Black shale bears great economic interest as the main source rock of hydrocarbon generation. Estimate suggests that more than 90% of global recoverable oil and gas reserves were generated from black shale (Klemme and Ulmishek 1991). The quality and quantity of organic matter play important role in the generation of hydrocarbon. Source rock characterization using organic geochemical technique (Rock-Eval pyrolyser) is widely used to evaluate the quality, quantity, hydrocarbon generation potential and thermal maturity of organic carbon (Espitalié *et al.* 1986; Peters and Cassa 1994; Banerjee *et al.* 2006; Mani *et al.* 2014, 2015; Bourah and Ganapathi 2015). The total organic carbon (TOC) and biomarker studies are also helpful to characterize the type and maturity of organic matter in black shales and other organic carbon rich rocks (Banerjee *et al.* 2006; Sivan *et al.* 2008; Arora *et al.* 2015, 2017; Bourah and Ganapathi 2015; Mani *et al.* 2017).

Black shales have been reported from several sedimentary basins of India, which include the Paleoproterozoic Cuddapah basin (Manikyamba *et al.* 2008), Mesoproterozoic to Neoproterozoic Vindhyan basin (Banerjee *et al.* 2006; Paikaray *et al.* 2008; Bhaskar 2013), Permian Gondwana basin of the Krishna–Godavari valley (Rao 2001;

Bhaskar 2013), Permian to Mesozoic Gondwana basins of the Damodar Valley (Bhaskar 2013; Bourah and Ganapathi 2015; Mani *et al.* 2015; Tewari *et al.* 2016), Permian–Triassic basins in the Himalayan Region (Mani *et al.* 2014), Paleogene Cambay basin (Banerjee and Rao 1993; Bhaskar 2013), Paleogene of the Cauvery basin (Chandra *et al.* 1991; Bhaskar 2013) and the Mesozoic–Paleogene rocks of the Kachchh basin (Dutta *et al.* 2011; Sahay 2011; Mishra *et al.* 2014; Arora *et al.* 2015, 2017). Thick and well-developed organic-rich black shales constitute distinct stratigraphic units of the onland Kachchh basin of western India (figure 1). The Kachchh basin has been classified as a category II basin (identified prospectivity) owing to its favourable depositional and thermal history for hydrocarbon generation (DGH 2017). The Cambay basin along the eastern and southeastern side of the Kachchh basin is a proven petroliferous basin, having the Cambay shale of Eocene age as the source rock. The Kachchh basin is flanked by the hydrocarbon-producing Mumbai offshore basin in the south, and the South Indus basin of Pakistan in the north. Oil and gas shows have been observed in several wells drilled on offshore and onshore Kachchh basin (Patil *et al.* 2013). Characterization of black shales from the northern and southern onland part of this basin were previously done from the Jhuran Formation in and around

Khari River channel, Rudramata bridge, and Zara, Dharang and Jhumara, Palara and Ler villages (Arora *et al.* 2015, 2017). Similar studies have been carried on the black shales of the Naredi Formation from the Panandhro, Umarsar and Matanomadh lignite mines in this basin (Dutta *et al.* 2011; Sahay 2011; Mishra *et al.* 2014). In addition, it is important to note that sediments from upper Jurassic as well as Late Cretaceous to Eocene times contributed 25 and 2.8% of global hydrocarbons (oil and gas), respectively (Klemme and Ulmishek 1991).

Black shale samples of Jhuran and Naredi Formations have been collected from four new localities (Bhuj–Kodki Road, near Dhonsa village, Naliya–Narayan Sarovar Road and Matanomadh), which are situated within the central part of the basin, for the present study. Thus, organic carbon within these black shales needs to be characterized in terms of quantity, quality, thermal maturity and hydrocarbon generation potentiality. The present research work deals with the geochemical (Rock-Eval pyrolysis) and SEM study on 33 samples collected from these locations.

2. Locations and geological settings

The Kachchh basin was developed at the boundary of the African and Indian blocks during the breakup of the Gondwana land at ~170 Ma (Besse and Courtillot 1988). This breakup gave rise to the development of different horsts and grabens forming the sites for deposition of the Jurassic sediments (Biswas 2016). The basin had an eruption of the Deccan volcanics during Late Cretaceous–Early Paleocene. The basin had further subsidence and deposition of Cenozoic sediments. The stratigraphic units mapped in the basin by different early workers are presented in table 1.

The samples were collected from four different zones in the western part of the Kachchh district, Gujarat, India. These areas are close to the Dhonsa village, on Bhuj–Kodki Road, and between Javda and Harudi/Baranda villages on Naliya–Narayan Sarovar road (figure 1). Further, core samples were collected from an area close to the Matanomadh lignite mine (figure 1). The first location is along a recently exposed road cutting section (23°19′35.44″N; 69°37′25.96″E) 1 km before the Dhonsa village (hereafter termed as Dhonsa). This section consists of alternate bands of finely laminated black shales and fine-grained

light pink coloured sandstones (figure 2). The rocks of this section belong to the Jhuran Formation (Katrol Series) having upper Jurassic age (Biswas 1977). The second location is on another fresh road cutting (23°14′38.05″N; 69°34′57.47″E) along the Bhuj–Kodki Road, which is observed around 2.5 km from the Kodki village (hereafter mentioned as Kodki). This section also comprises alternate bands of fine grained pink coloured sandstone and black shales (figure 3) of the Jhuran Formation of upper Jurassic age (Biswas 1977). The third sampling location is situated along the left side of the Naliya–Narayan Sarovar road (hereafter termed as NNSR), between Javda and Harudi/Baranda villages (23°31′28.29″N; 68°41′8.35″E, figure 1). This area consists of several humps of gypsiferous shale of the Naredi Formation of Early Eocene age (Biswas 1992). The shale unit contains abundant larger foraminifera (Assilina). Samples were collected from a small section at the basal part of one hump of black shale with glittering lustre similar to coal (figure 4).

Core samples were collected from a single drill hole (Borehole number KAM-164 of Gujarat Mineral Development Corporation Ltd.; hereafter designated as core) near the Matanomadh lignite mine area (figure 1). The core penetrated to a depth of 94 m, extending up to the Deccan basalt of upper Cretaceous age. The Paleocene sedimentary sequence is not developed in this zone. Samples were collected from Early Eocene sediments (at 44–74 m depth), which belong to the Naredi Formation (Biswas 1992; Merh 1995) and consist of thick alternate bands of black shale and lignite beds.

3. Materials and methods

A total of 33 samples (8 from Dhonsa, 4 from Kodki, 3 from NNSR and 18 from core, respectively) were studied for their bulk organic properties using Rock-Eval 6 Pyrolyser. The samples were pyrolyzed in Rock-Eval 6 (Turbo Version) unit in CSIR – National Geophysical Research Institute, Hyderabad. The instrument was calibrated using IFP standard 16,000 ($T_{\max} = 416^{\circ}\text{C}$ and $S_2 = 12.43$ mg/g rock) after getting the stable signals from the detectors. Approximately 60–70 mg of finely homogenized powdered samples were weighed in pre-oxidized crucibles and were pyrolyzed in an inert atmosphere using nitrogen gas under analysis mode using bulk rock method and basic cycle of Rock-Eval 6 (Mani *et al.* 2014).

Table 1. Mesozoic and Cenozoic stratigraphy of the Kachchh basin (after Biswas 2016). Solid black stars indicate stratigraphic positions of samples. (a) Stratigraphy of the Dhonsa–Kodki areas, and (b) stratigraphy of the NNSR and Matanomadh areas.

(a)

AGE		FORMATION	LITHOLOGY
LATE CRETACEOUS TO PALEOCENE		DECCAN TRAP 500 m	Basalt flow
ALBIAN TO NEOCOMIAN	POST-RIFT	Unconformity	Mainly sandstones with ferruginous bands and shale interbeds with plant fossils
		BHUJ 850 m	
TITHONIAN TO MID-OXFORDIAN	LATE-SYNRIFT	JHURAN 760 m ★	Sandstones with calcareous bands and shale (delta front), middle part mainly shale (prodelta)
		Unconformity	
EARLY OXFORDIAN	CLIMAX	JUMARA 275 m	Mainly shale with thin limestone beds, oolite bands on top
CALLOVIAN			
BATHONIAN TO BAJOCIAN	SYNRIFT	JHURIO 290 m+	Interbedded shale and limestone with golden oolites. Upper part: bedded limestone
PRECAMBRIAN		Unconformity	
		Basement	Not exposed

(b)

AGE	STAGE	FORMATION	LITHOLOGY
? Late Miocene to Pliocene	Kankawatian Super-stage	SANDHAN 249 m+	Sandstone, minor limestone and shale Upper part calc. concretionary
Burdigalian	VINJHANIAN	CHHASRA 16 m	Upper:silty shale Lower:shale/ limestone highly fossiliferous
Aquitanian	AIDAIAN	KHARI NADI 65 m	Variegated siltstone and sandstones
Chatian	WAIORIAN	MANYARA FORT 35 m	Upper:Foram. limestone/oolite sandstone, Middle: limestone with coral biotherm, Lower: lumpy claystone, glauc. gypseous shale
Rupelian	RAMANIAN		
Priabonian	HIATUS	---Paraconformity---	
Bartonian	RAKHADIAN	FULRA LIMESTONE 60 m	Dense foraminiferal limestone
Lutetian	BABIAN	HARUDI 14m	Claystone/ limestone, coquina highly fossiliferous
	Hiatus	---Paraconformity---	
Ypresian	KAKDIAN	NAREDI 40 m ★	Upper: ferruginous claystone. Middle: Assilina limestone. Lower: glauconitic gypseous shale
Thanetian	MADHIAN	MATANOMADH 49 m	Laterites & volcanoclastics: tuffaceous shales & sandstones bentonite clay
Maastrichtian to Danian		DECCAN TRAP	Basalt

The pyrolysis oven was programmed with an initial temperature at 300°C, with stepwise increase to 650°C at an increment rate of 25°C/min. Released hydrocarbons were measured by Flame Ionization

Detector (FID). The samples were then oxidized in an oxidation oven. Temperature of the oxidation oven was increased stepwise from 300 to 850°C with an increment rate of 20°C/min.

Figure 2. Photograph of the road section near Dhonsa village. Arrows indicate the positions of samples collected for this study. Length of the scale is 30.5 cm.

Figure 3. Photograph of the Kodki road section. Arrows indicate sampling positions.

The SEM observations were undertaken at Central Research Facilities, Indian Institute of Technology (Indian School of Mines), Dhanbad using Zeiss Supra 55 FESEM instrument.

Figure 4. Photograph of the black shale-sampling site in NNSR. Arrows indicate sampling positions. Length of the pen is 14.5 cm.

4. Results

SEM analyses of 12 selected samples show dominance of chlorite. However, smectite in samples of the Naredi Formation (NNSR) and halloysite in the Jhuran Formation (Kodki) are recorded along with chlorite (figure 5). Additionally, samples from NNSR and core contain numerous well-developed pyrite crystals (figure 5).

Rock-Eval pyrolysis was carried out to understand quantity, quality and thermal maturity of organic matter as well as hydrocarbon generation potential of the black shales. Different parameters obtained through the pyrolysis are presented in table 2. Surface samples from Dhonsa show very low to moderate TOC content ranging from 0.43 to 0.96%. The S_1 (thermo-vaporized free hydrocarbons) and S_2 (hydrocarbons from cracking of organic matters) values are low (up to 0.02 and 0.15 mg HC/g rock) in these samples. The hydrogen index (HI) and oxygen index (OI) were calculated for each samples using the formula $HI = (100 \times S_2) / TOC$ and $OI = (100 \times S_3) / TOC$, respectively (Lafargue *et al.* 1988; McCarthy *et al.* 2011; Mishra *et al.* 2014). The HI and OI lie between 8–28 mg HC/g TOC and 105–286 mg CO_2 /g TOC, respectively. The T_{max} (temperature having highest yield of hydrocarbons generated by cracking of kerogen) values for these samples range between 440 and 607°C. Mineral carbon contents of these samples are low and are within the range of 0.05–0.19% (table 2). Surface samples of Kodki do not have any detectable values of S_1 , S_2 and T_{max} . The TOC and mineral carbon content of these samples are also in lower end and range between

Figure 5. FESEM images of minerals present in black shales collected from different locations in this study: (a) chlorite in shale collected from Dhonsa, (b) chlorite and halloysite from Kodki, (c) smectite in NNSR, (d) pyrite crystals in NNSR, (e) chlorite in core samples, and (f) pyrite crystals in core samples.

0.44–0.87% and 0.12–0.2%, respectively (table 2). Surface samples from NNSR show S_1 and S_2 values ranging between 0.08–0.22 and 0.04–24.89 mg HC/g rock, respectively. TOC values for these samples lie within 0.08–20.46%. The HI and OI values are confined with the ranges 50–122 HC/g TOC and 81–525 $\text{CO}_2/\text{g TOC}$, respectively. Mineral carbon content lies within 0.03–0.94% (table 2). Core samples from the Matanomadh area are rich in TOC, which ranges between 3.01 and 27.2%. The S_1 and S_2 values are ranging between 0.01–2.98 and 2.36–107.88 mg HC/g rock, respectively. The T_{max} values for these samples lie within 394–431°C. Mineral matters within these samples vary from 0.13 to 1.03% (table 2).

5. Discussion

5.1 Organic carbon richness

Organic carbon richness is an important factor for classifying the hydrocarbon generation potential of

sediments. Sediments may be broadly subdivided into five groups based on organic carbon content. The hydrocarbon generation potential is considered poor where the TOC values lie within 0–0.5%, fair where they are within 0.5–1%, good for values within 1–2%, very good for values within 2–4% and excellent where the values are >4% (North 1985; McCarthy *et al.* 2011). Upper Jurassic black shale samples from the Jhuran Formation of Dhonsa and Kodki region have very low TOC concentration (<1%, table 2). Thus, these black shales do not show characteristics of good source rock. The sediments in these areas are rich in chlorite along with some occurrence of halloysite (figure 5b). Platy mineral chlorite has large surface area, which might had greater capacity to retain organic carbon during the deposition of sediments (Kennedy *et al.* 2002). It has been observed that in TOC lean sediments, the mineral matrix with quartz, calcite, etc., may retain some of the S_2 content and also catalyse the thermal decomposition of kerogen, altering the S_2

Table 2. Rock-Eval pyrolysis data obtained from Jhuran black shales of Dhonsa, and Kodki areas as well as Naredi black shales of NNSR and core.

Sample id	S ₁ (mg/g rock)	S ₂ (mg/g rock)	T _{max} (°C)	TOC (%)	HI	OI	MINC (%)
Jhuran Foundation, Age: Upper Jurassic (Kimmeridgian to Tithonian)							
Dhonsa-1	0.02	0.15	607	0.54	28	107	0.05
Dhonsa-2	0.01	0	0	0.8	0	166	0.09
Dhonsa-3	0.01	0.11	607	0.65	17	105	0.09
Dhonsa-4	0	0.08	440	0.96	8	119	0.19
Dhonsa-5	0	0	0	0.76	0	172	0.19
Dhonsa-6	0	0	0	0.43	0	286	0.17
Dhonsa-7	0	0	0	0.56	0	171	0.16
Dhonsa-8	0	0	0	0.45	0	209	0.12
Kodki-1	0	0	0	0.44	0	164	0.12
Kodki-2	0	0	0	0.64	0	186	0.2
Kodki-3	0	0	0	0.8	0	136	0.18
Kodki-4	0	0	0	0.87	0	53	0.2
Naredi Formation, Age: Early Eocene (Ypresian)							
NNSR-1	0.08	0.04	421	0.08	50	525	0.03
NNSR-2	1.41	24.89	415	20.46	122	81	0.94
NNSR-3	0.22	4.08	418	3.37	121	110	0.34
core 44.10	0.01	2.36	430	3.01	78	21	1.03
core 44.90	2.98	107.88	423	27.2	397	18	0.56
core 45.90	0.05	2.31	417	3.32	70	51	0.24
core 46.30	0.03	3.29	428	3.28	100	60	0.21
core 47.10	0.02	3.02	431	3.06	99	30	0.15
core 49.70	0.03	5.26	431	4.09	129	37	0.61
core 51.70	0.46	9.61	404	12.74	75	36	0.39
core 52.70	0.06	4.23	426	2.88	147	3	0.13
core 55.30	1.23	29.7	412	16.57	179	27	0.39
core 57.10	0.38	6.95	394	12.31	56	30	0.26
core 59.10	0.11	5.35	424	3.61	148	48	0.16
core 60.70	0.72	28.68	423	11.67	246	39	0.31
core 60.90	0.11	10.05	427	8.66	116	44	0.83
core 66.70	0.75	30.31	422	11.62	261	44	0.37
core 70.90	0.8	43.51	423	15.19	286	31	0.4
core 72.30	0.4	25.44	425	8.86	287	33	0.32
core 72.90	0.97	42.14	420	14.63	288	39	0.43
core 74.10	0.56	32.17	426	10.19	316	51	0.37

signatures (Espitalié *et al.* 1980, 1984; Dembicki 1990). Shales from Dhonsa and Kodki region have low TOC with dominance of quartz and clay minerals, which could possibly account for the reduced amount of pyrolyzed hydrocarbons during the Rock-Eval pyrolysis (Mani *et al.* 2016). Furthermore, it is known that colour of black shale develops mainly due to the high concentration of carbonaceous matter deposited in reducing environment (Tourtelot 1979). In general, the black shale contains more than 1% of organic carbon (2–10% is the common range) (Tourtelot 1979). The shale samples collected from Dhonsa and Kodki are dark in colour. Thus, these samples might have

contained more TOC during the time of deposition, but post depositional alterations could be responsible for the low TOC recorded.

Arora *et al.* (2015) have reported relatively higher TOC (average 1.34–3.4%) of black shales from the Jhuran Formation (extending from Rudramata bridge to Zara village). The depositional environment of the Jhuran black shale along the northern part of mainland is suggested as shallow marine, formed during oceanic anoxia with substantial input of continental organic material (Desai *et al.* 2008; Arora *et al.* 2015). Biswas (2016) suggested the black shales of the Jhuran Formation to be prodelta deposits below the deltaic

sandstone. However, their sampling sites are far in north from the sample locations in this study.

It is understood that the organic carbon content within the geologically old sediments does not reflect its original TOC values. Part of the initial preserved TOC may get lost within subsurface condition during diagenesis or by thermal maturation (Harwood 1982). Therefore, both of these long-standing sedimentary successions (upper Jurassic of Dhonsa and Kodki) were probably affected during the Deccan volcanism (Biswas 1987; Thakkar *et al.* 2006; Morino *et al.* 2008). We assume that sediments of these zones were uplifted and affected by severe tectonic activities. Owing to these events, sediments have lost their original TOC, either by thermal over maturation or due to oxidative weathering. This inference also helps us to explain the existence of halloysite within these areas (figure 5b). Earlier research works have shown that co-existence of halloysite with chlorite might be an indicator of formation of halloysite from chlorite either by weathering or due to thermal alteration (Cho 1992; Papoulis *et al.* 2009). Modeling of temperature and pressure conditions of chlorite formation using the thermodynamic approach in a closed system have shown a systematic increase in Fe^{3+} with decreasing temperature, which is compatible with the decrease in $a\text{O}_2$ buffered by magnetite- or hematite-chlorite equilibrium (Vidal *et al.* 2016). Similar temperatures are calculated for low-temperature chlorites ($T < 300^\circ\text{C}$) using equations of semi-empirical thermometers, assuming that all iron in chlorite are ferrous (Inoue *et al.* 2009). Formations of minerals like halloysite suggest low temperature hydrothermal origin. Thus, thermally induced alterations of organic matter pocketing these minerals are likely to occur, thereby, lowering the TOC content of these shales.

Both the NNSR and core samples belong to the Naredi Formation (Early Eocene age). The TOC values recorded in NNSR and core samples are ranging from 0.08 to 20.46% and 2.88 to 27.2% respectively (table 2). Thus, the samples from both NNSR and core are rich in organic carbon. Excellent positive correlation between S_1 and S_2 is also observed in both the sites ($R = 0.99$ for NNSR and $R = 0.93$ in core). Mishra *et al.* (2014) suggested good positive correlation between S_1 and S_2 could be an indicator of common source of organic matter as well as absence of contamination. Hence, we consider that higher organic carbon in both the areas might have been derived from

a common source and the samples have witnessed negligible to minimal surficial contamination. Samples of NNSR show significant presence of smectite, whereas core sediments are dominated by chlorite (figure 5c–e). Kennedy *et al.* (2002) observed that larger reactive surface of smectitic are capable of sorbing significant amount of organic materials from water and may be rich in organic materials. The depositional setting of the black shale in the Naredi Formation is described as coastal marsh or back swamp environment (Biswas 1992). The black shales of the Matanomadh are considered to be deposited in humid tropical climate in a reducing environment (Dutta *et al.* 2011). Sahay (2011) suggested that the black shales in the Panandhro lignite mine, which is situated very close to the Matanomadh area, were deposited in a brackish mangrove to freshwater swampy environment during the sea level low stand. Our investigation shows that sediments of both the studied sites contain framboidal pyrite (figure 5d–f). Presence of pyrite within these samples thus indicate deposition of sediments in a highly reducing condition either in a lagoonal environment or restricted marine setting like marsh/swamp which corroborates the earlier observations (Biswas 1992; Dutta *et al.* 2011; Sahay 2011).

5.2 Quality and hydrocarbon generation potentiality of organic matter in black shales

Quality assessment of source rock in terms of kerogen type is important to infer the origin of organic matter as well as hydrocarbon generation potentiality. Sedimentary rocks having high hydrogen-carbon ratio (H:C) or high hydrogen index (HI) and low oxygen-carbon ratio (O:C) or low oxygen index (OI) values are considered as good source rock (kerogen type I and II). These types of source rocks are capable to yield oil and gas by thermal maturation. The relationship of gradually reducing HI values with an increase of OI values indicates the transformation of kerogens from type I to type IV, which has low potential to generate oil. The type III and type IV kerogens are more prone to generate coal and gas (Selley 1998; McCarthy *et al.* 2011). Type I kerogens are rich in lipid, usually marine or lacustrine in origin and are derived from algae, phytoplankton or strongly reworked organic matter by bacteria or microorganism. Type II kerogen is usually marine, liptinitic, formed in deep marine setting in reducing conditions from phyto and

zooplanktons. Organic carbon in type III kerogen is derived from terrigenous organic carbon deposited in marine or other fluvial environments. Whereas type IV kerogen is the reworked organic matter formed after sub-aerial oxidation and alteration owing to weathering (Tissot and Welte 1984; North 1985; Selley 1998; McCarthy *et al.* 2011). Study of McCarthy *et al.* (2011) showed that source rocks having HI index of 50–200 are capable to generate gas, 200–300 are capable to produce gas as well as oil and above 300 may produce oil.

Samples from both Dhonsa and Kodki of the Jhuran Formation contain very low amount of TOC. In addition, these samples do not produce thermo-vaporized free hydrocarbons (S_1) and those that are liberated after cracking of organic matter (S_2) during pyrolysis (table 2). A lower HI (≤ 28) and higher OI (53–286) values are shown by these samples (table 2). Thus, Rock-Eval parameters clearly suggest that they are characterized by type IV kerogen indicating no potential to generate hydrocarbon in terms of gas or oil (inert type; figures 6–7). Study of McCarthy *et al.* (2011) also showed that source rock having HI values < 50 are not even gas prone. It is important to note that type III kerogen are produced from higher woody terrestrial plants whereas type IV are the oxidized, altered and recycled organic matter during earlier thermal event (North 1985; Selley 1998). Thus, the kerogens of Dhonsa and Kodki clearly indicate their terrestrial origin with exposure to previous thermal maturity events, which corroborates our earlier propositions.

The organic content is high in the samples collected from the Naredi Formation (NNSR and Matanomadh area). The organic richness of the samples are higher in NNSR area, yet two out of three samples show almost equal HI and OI values and one shows higher OI than HI indicating presence of type III and IV organic carbon (table 2; figure 6). This indicates events of alteration/oxidation of terrestrial organic carbon without any potential to generate hydrocarbons. The range of HI values (50–200) of these sediments also indicates potential to yield gas (McCarthy *et al.* 2011), prone to generate coal after attaining appropriate maturation.

Samples of core from the Matanomadh area show two fold distribution pattern in terms of kerogen. Sediments from 44.1 to 59.1 m (10 samples) show the kerogen nature restricted within type III/IV (figures 6 and 7). One sample from the depth 46.30 m and 6 samples within the depth 60.70–74.1 m belong to type II/III kerogen. One

Figure 6. HI vs. OI plot indicating the kerogen type in black shales from the Kachchh basin, India.

Figure 7. HI vs. T_{max} plot indicating the thermal maturity of black shales from the Kachchh basin, India.

shale sample (at 60.9 m depth) belongs to type III/IV kerogen (figures 6 and 7). Thus, it is clear that the top section (44.1–59.1 m) of black shales consists of an inert type of organic matter having tendency to generate coal and gas upon suitable maturation. The lower section of the sequence (60.7–74.1 m) confirms presence of type II/III kerogen, which bears capability to generate oil and gas (table 2; figure 6). The higher HI values (246–316) in the lower section (table 2) also support the production capability of gas and oil (McCarthy *et al.* 2011). Earlier study pursued on black shales collected from subsurface mining zones

of the Matanomadh area also show similar results with association of type II/III and samples of surface area having type III/IV kerogen (Mishra *et al.* 2014). The study of Dutta *et al.* (2011) shows shale samples in the Matanomadh mine to have type IV kerogen.

5.3 Thermal maturity of organic carbon

$T_{\max}$ is the temperature at which the organic carbon may yield heavy hydrocarbons after thermal cracking during pyrolysis (McCarthy *et al.* 2011). It is a maturity parameter and corresponds to the temperature at which maximum amount of hydrocarbons are released from the thermal degradation of kerogen, i.e., the temperature at which S_2 peak reaches its maximum. $T_{\max}$ does not designate actual burial temperature of the sediments. It represents a relative value of thermal maturity and can give idea to understand the temperature requirement for thermal maturation of organic carbon (Muñez-Betelu and Baceta 1994; McCarthy *et al.* 2011). The higher $T_{\max}$ values (440–607°C) for three black shales of the Jhuran Formation from Dhonsa and Kodki region indicate that these samples have been exposed to high temperature during the geological past (table 2; figure 7). Hence, these are in matured to post-matured stage for hydrocarbon generation. We presume that the Deccan volcanism had left some of the plutons occurring at shallow depth and contributed towards heat dissipation during later periods. This high heat flow was possibly responsible for the over maturation of kerogen. The maturation of the organic matter might be responsible for lowering its organic carbon content as inferred earlier in this work. Additionally, the $T_{\max}$ obtained may not be reliable in samples, where the value of S_2 is quite low (table 2).

Relatively low $T_{\max}$ values (394–431°C) are recorded for the samples of the Naredi Formation collected from NNSR and core (table 2; figure 7). The lower $T_{\max}$ values of black shales indicate that the sediments of these regions have undergone diagenesis and yet not evolved to the matured stage. It also suggests the sediments to be in early stage of maturation/oil generation. This inference corroborates the observation of Sahay (2011), which suggests that the Eocene Panandhro organic sediments have not yet suffered enough geothermal heat and remained in the immature stage. The samples may be prone to generation of oil and gas on attaining appropriate thermal maturity.

6. Conclusions

Organic carbon characterization of black shales from the upper Jurassic Jhuran Formation of Dhonsa and Kodki showed that organic carbons are low in concentration, marine (brackish or lagoonal), consisting of type IV organic carbon without any potential to generate hydrocarbon. Lower amount of organic matter (<1%) is either related to thermal over-maturation due to several tectono-thermal activities that prevailed in the past in the region such as Deccan volcanism and Katrol fault or due to oxidative weathering.

Early Eocene black shales of the Naredi Formation (Naliya-Narayan Sarovar Road and core samples) are relatively rich in organic carbon, chlorite, smectite and framboidal pyrite. All these features suggest that the shale was deposited in a highly reducing lagoonal/marshy or swampy environment. These shales are characterized by immature type III and IV organic carbon, having potential to generate coal and gas after attaining suitable maturation. The upper part of core (44–59 m) bears relatively high organic carbon, which is characterized by immature, type III/IV kerogen, prone to yield coal and gas upon suitable maturation. Whereas the lower portion of the core (60–74 m) contains highest amount of type II/III immature organic carbon, bearing high potential to generate oil on attaining appropriate maturation.

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