Source rock potential assessment of the Paleocene coal and coaly shale in the Attock-Cherat Range of Pakistan

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Abstract

In this study the hydrocarbon generation potential of the coal and coaly shale samples collected from coal mines in Attock-Cherat Range of Pakistan is optically and analytically evaluated. These samples, representing the Paleocene Hangu Formation, are analyzed across a range of thermal maturity stages to understand their hydrocarbon generation potential. The visual examination of maceral type and values of vitrinite reflectance have been considered while interpreting the geochemical results for the coal and associated sediments from the Paleocene Hangu Formation. The maceral group is dominated by vitrinite, mainly collodetrinite, followed by inertinite and liptinite, and suggests Type III kerogen for the samples. The geochemical parameters suggest that the samples are post mature, however, the vitrinite reflectance measurements show late mature conditions for a gas-prone generation. The overall petrographical and geochemical data suggest that the coal and coaly shale appear to occupy the gas window and fall in the dry gas zone. Based on the maceral types and Rock–Eval data, an anoxic to terrestrial environment is inferred for the deposition of the coal and associated sediments. The vitrinite reflectance, Rock–Eval pyrolysis, and the type and frequency of macerals show that the coal is of good quality, i.e., medium to high volatile bituminous and hard brown coal, mature, and is lying in the gas window. Oxygen index is continuously low throughout the analyzed interval, which further supports that the coal is of good quality.

Keywords Paleocene coal · Hangu Formation · Vitrinite · Depositional environment · Thermal maturity · Hydrocarbon generation · Attock-Cherat Range · Pakistan

Introduction

The source rock maturity analysis is a set of organic geochemical analysis which is used in integration with geology to ascertain hydrocarbon source potential of any formation. Petroleum geochemistry deals with the applications of organic geochemistry to study the origin,

formation, migration, accumulation and alteration of hydrocarbons (Maslen 2010). Organic geochemistry describes the details of processes that happen to organisms from their burial to oil or gas generation; the information is used in the exploration and production of hydrocarbons (Tissot and Welte 1984). Such a study is carried to identify the sources of organic matter (OM), depositional environments, burial history of the sediment and alteration of OM under thermal maturation which can lead to the formation of hydrocarbons (Maslen 2010). Maturation is a diagenetic process, which brings about two types of change in organic matter, (1) releasing fluids and (2) aromatization of solid left over products resulting in their condensation (Taylor et al. 1998). The term maturation is widely adopted to describe the degree of diagenetic evolution of the organic matter leading to the generation of hydrocarbon and is characterized through measurements of vitrinite reflectance (Vandenbroucke and Largeau 2007). Maturation deals with the changes that are induced thermally

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in organic matter during catagenesis and alter its nature (Radke et al. 1997). Tissot and Welte (1984) suggested three stages for the organic matter maturity, i.e., immature, mature and post mature, keeping in mind the situation of oil window. They argued that the diagenetic changes such as biological, physical and chemical alteration produce immature organic matter, where no prominent effect of temperature exists.

Coal organic petrography is mostly concerned with description and classification of organic matter under microscope and is desired for determining environment of deposition and maturation level of coal and its gas generation potential. Earlier researchers have provided a detailed account of various optical and geochemical parameters in evaluating the richness, maturity and quality of source rocks, including vitrinite reflectance and maceral analysis, total organic content measurement, and Rock–Eval pyrolysis, as well as the relationships between maturity and hydrocarbon generation (Dow 1977; Tissot and Welte 1978, 1984; Thompson–Rizer 1993; Law 1999; Vandenbroucke and Largeau 2007; Isabel 2012; Uzoegbu 2013; Hakimi and Abdullah 2014; Singh et al. 2016a,b, 2017a,b). Quantitative and qualitative analyses of different kerogen types through visual determination together with geochemical investigation of organic matter provide a better understanding about the

generating potential (GP) of source rocks (Thompson and Dimbicki 1986; Isabel 2012).

Humic coals from New Zealand, Australia and Asia that are capable of generating and expelling non-volatile oil belong mostly to Cretaceous and Tertiary ages (Isaksen et al. 1998; Singh 2012; Singh et al. 2013). Coal is being mined by locals in Dag Ismail Khel, Bakhtai, Jabba Khattak, Shahkot and Shekhai areas for tens of years (Fig. 1). With sufficient coal reserve, the Hangu Formation is the main producing formation in Cherat area (Hussain et al. 1990; Shah 2001). Most of the studies conducted in Attock–Cherat Range have been carried out for better understanding the stratigraphy, structure and economic potential of the area. Minimum work has been carried out to find out the potential source rocks in the area, which may have a role in hydrocarbon generation. This study is an attempt to identify the type and quantity of organic matter, interpret the depositional environment based on the maceral types and determine organic geochemical characteristics of the Paleocene coal and associated coaly shales in the Attock–Cherat Range. In the current study, type of kerogen retained in the coal and coaly shale from the Paleocene Hangu Formation has been determined keeping in mind the nature of rock, the contained maceral type(s) and the amount of sulfur present in the samples. Environment of deposition is inferred from the type of kerogen and

Fig. 1 Geological map of the study area, showing the locations of coal mines (modified after Hussain 1995)

dominant maceral composition. Rank of the coal and the type and nature of hydrocarbons have also been determined in the current study with the help of optical and geochemical analyses of the samples.

Geological setting

The study area lies in the northern and southern blocks of the Attock-Cherat Range in the Nowshera District (Hussain et al. 1989; Fig. 1). The tectonic zonation of Himalaya suggests that Attock-Cherat Range is part of the hill ranges and comprises northern portion of the axial belt. The overall stratigraphic framework in the study area outcrops from

Precambrian Manki Formation to the Quaternary alluvial fan/lacustrine/loess/stream channel deposits, with fourteen recognizable formations and a unit of undifferentiated Cretaceous succession. The Paleocene succession is comprised of Hangu Formation, Lockhart Limestone and Patala Formation according to the stratigraphic order (Figs. 1 and 2). On the basis of different diagnostic features, Shah (2001) mentioned five distinct lithofacies within the Hangu Formation, namely laterite/bauxite lithofacies, cross-bedded sandstone lithofacies, bioclastic limestone lithofacies, coal, carbonaceous shale lithofacies and bioturbated sandstone lithofacies. While working with the samples it was established that Shah's classification was not fully applicable on the samples taken in this study,

Fig. 2 Lithological log showing stratigraphy of the study area (modified after Hussain et al. 1989; Hussain 1995; Shah 2001)

therefore, in the current study, following major lithological units have been recognized in the Hangu Formation: upper laterite unit, coal and coaly shale unit, bioclastic limestone and interbedded shale unit, middle laterite and bauxite unit, greenish sandstone unit and lower laterite unit (Fig. 2).

Coal is present in the form of lenses, stringers and lenticular beds having powdery dust like black coal with dark coaly shale and clayey material at the top and base of the coal seam having layers of sulfur with pyrite nodules and calcitic veins. This unit is equivalent to the coal, carbonaceous shale lithofacies of Shah (2001). The thickness of the coal seam in the Cherat area was measured between 1 and 1.5 m; however, at places it bulged out to 3 m, thinning to even a few centimeters at other sites. The area has undergone severe tectonic deformation, and the thickness of the coal seam varies through the area, having no uniform structure and not confined to one place. At some locations in the study area, the coal bulges out into a thick deposit, yet at others it pinches out into thin stringers. The powder form, more or less, is present inside or around the seam throughout the area. Coal seam is associated with coaly shale, dark carbonaceous shale with clay material, sulfur veins and pyrite nodules.

Methods and results

The channel sampling technique was used to collect the specimens. Out of the total 25 pits mined in the Hangu Formation, only ten were in working condition, and the rest were abandoned or collapsed (Fig. 1). A sum of ten samples was acquired for geochemical analysis from the mine face in two forms, either as intact rock specimens or in powdered form from five mining areas including Bakhtai (BK), Dag Ismail Khel (DG), Jabba Khattak (JB), Shahkot Bala (ST) and Shekhai (SK). Each sample was packed in polythene bags and marked with appropriate sample number and locality name.

Geochemical analysis

Ten samples were short listed for the geochemical analysis on the basis of visual inspection. The samples were crushed and ground by vibrating cup mill Pulveritte 9 FRITSCH, Germany, at the Gemology Laboratory of the NCE in Geology, University of Peshawar, to make powder of 200 mesh size for analysis.

TOC was measured using Eltra CW-800 Multiphase CO₂/H₂O Determinator at Petroleum Geochemistry Laboratory at NCE in Geology, University of Peshawar. TOC measurements for the analyzed samples (20 mg each) are shown in Table 1. Among the studied samples, SK-4 is the richest sample with highest value of 76.83 wt% TOC, while DG-1

Table 1 Rock-Eval data for the pyrolyzed samples

S. no	S. ID	Lithology	TOC wt%	S1 mg/g	S2 mg/g	S3 mg/g	T _{max} °C	GP S1+S2	PI S1/S1+S2	HI	OI	Total carbon wt%	PC wt%	RC (TOC-PC) wt%
1	BK-1	Coal	72.22	0.81	24.19	0.03	486	25.00	0.03	33	0	72.52	2.09	70.13
2	BK-4	CS	44.33	0.62	13.24	0	484	13.86	0.04	30	0	44.63	1.16	43.17
3	DG-1	CS	7.02	0.42	5.88	0	491	6.30	0.07	84	0	7.38	0.53	6.49
4	DG-2	CS	22.37	1.67	28.24	0	484	29.91	0.06	126	0	23.05	2.50	19.87
5	JB-1	Coal	51.21	1.21	31.78	0.07	497	32.99	0.04	62	0	51.56	2.79	48.42
6	JB-3	Coal	59.66	1.51	51.40	0.21	496	52.91	0.03	86	0	60.12	4.44	55.22
7	SK-3	Coal	55.87	1.40	37.71	0.10	499	39.11	0.04	67	0	56.36	3.29	52.58
8	SK-4	Coal	76.83	1.99	57.69	0.05	500	59.68	0.03	75	0	79.03	5.00	71.83
9	ST-1	Coal	54.51	0.25	12.78	9.55	493	13.03	0.02	23	18	54.58	1.81	52.70
10	ST-6	CS	48.33	1.28	22.17	5.14	486	23.45	0.05	46	11	48.51	2.42	45.91

TOC Total organic carbon, S1 existing hydrocarbon (HC) content, mg HC/g rock, S2 remaining HC generative potential, mg HC/g rock, S3 organic carbon dioxide yield, mg CO₂/g rock, T_{max} temperature of maximum pyrolytic yield at S2, GP generation potential = S1 + S2, PI production index = S1/(S1 + S2), HI hydrogen index = S2 × 100/TOC, mg HC/g TOC, OI oxygen index = S3 × 100/TOC, mg CO₂/g TOC, PC pyrolysable organic carbon, RC residual carbon, T/C total inorganic carbon, CS coaly shale

has the lowest value of 7.02 wt% TOC, with average values of 61.71 wt% for coal and 30.51 wt% for coaly shale samples from the Paleocene Hangu Formation in Attock-Cherat Range. Locations Shekhai and Bakhtai appear to be the richest areas with 66.53 wt% and 58.27 wt% TOC values, respectively, followed by Jabba Khattak (55.43 wt%), Shahkot (51.42 wt%) and Dag Ismail Khel (14.7 wt%). However, measuring TOC alone does not reveal the current potential yield of a source rock; for this purpose, pyrolysis is carried out, which is a measure of maturity and richness in terms of hydrocarbon and is determined through S2 peak (Tissot and Welte 1984). In this study, Rock–Eval pyrolysis for 10 surface samples (30–50 mg each) has been carried out using Rock–Eval 6 at the Geological and Reservoir Laboratories of the Oil and Gas Development Company Limited (OGDCL). The values of the different pyrolysis parameters for the selected samples are shown in Table 1.

Contents of total sulfur were determined using Euro EA-3000 Elemental Analyzer in the Geochemistry Laboratory of the NCE in Geology, University of Peshawar, Pakistan. The analyzer functions in relation to the mechanism of flash combustion of the sample places inside the furnace. The percent composition of sulfur in the samples is shown in Table 2.

Petrography of organic matter type

Coal petrography is done to describe and classify organic matter under microscope and is desired for determining environment of deposition and maturation level of sediments to corroborate other methods. The analyses are carried out under the microscope using reflected white light. Relative abundance of inert and reactive constituents of the samples is determined during this study. Polished blocks of the coal samples are prepared and placed under the microscope to identify maceral groups in an immersion medium with the help of their reflectance, morphology and color. For this purpose, a point counter is attached to the stage and quantitative composition of macerals is determined (ICCP 1971; Stach et al. 1982; Shahzad 2006).

Out of the total ten samples that were geochemically analyzed, five samples were considered for petrographic analysis and vitrinite reflectance (VR) based on their

Table 3 Percent composition of organic matter (on mineral matter free basis)

S. no	*Abundance of organic matter	Organic matter composition %			% Ro (mean reflectance values)
		Vitrinite	Inertinite	Liptinite	
BK-1	5	90	5	5	1.27
DG-2	3	90	9	1	1.25
JB-3	3	95	5	–	1.24
SK-4	4	95	5	–	1.26
ST-6	5	95	4	1	1.25
% Ro Grand Average					1.25

* Abundance shows the population of organic matter inside the sample as very abundant 5, abundant 4, common 3, little 2, very little to barren 0–1

genetic potential (one from each sampling area). The microscope Carl Zeiss Axio Imager Z1M with point counter and photometer attached at Hydrocarbon Development Institute of Pakistan (HDIP) laboratories was used for the analysis. The vitrinite reflectance measurements are provided in Tables 3 and 4. Maximum and minimum values of VR in individual samples are recorded as 1.27% and 1.24% from Bakhtai and Jabba Khattak, respectively, with an average value of 1.25% in the area. Statistical details of VR measurements in the selected samples are given in Table 4 and Fig. 3.

In this study, the macerals have been identified as per the classification by ICCP System 1994 (ICCP 1998, 2001), Taylor et al. (1998) and Šýkorová et al. (2005) (Table 5, Figs. 4 and 5). Collodetrinite could only be recognized in general abundance (~90), followed by macerals from inertinite and liptinite groups. It is characterized by a spotted vitrinitic ground mass binding amorphous vitrinite particles and other coal components, and lacking a textural continuity. The vitrinite components in subbituminous to bituminous coals are not recognizable; instead, they appear as dark spots (Šýkorová et al. 2005).

The detailed petrography of the samples is given in Table 6.

Table 2 Percent composition of sulfur

Sample no	Rock type	Sulfur %
BK-1	Coal	1.26
DG-2	Coaly shale	1.02
JB-3	Coal	0.98
SK-4	Coal	0.97
ST-6	Coal	0.96

Table 4 Statistical details of vitrinite reflectance measurements

Sample	Min	Max	Standard deviation	Mean
BK-1	1.05	1.49	0.12	1.27
DG-2	1.02	1.46	0.13	1.25
JB-3	1.03	1.44	0.11	1.24
SK-4	1.03	1.47	0.12	1.26
ST-6	1.12	1.38	0.07	1.25
Grand average				1.25

Fig. 3 Vitrinite reflectance histograms of the selected samples from Bakhtai (BK-1), Dag Ismail Khel (DG-2), Jabba Khattak (JB-3), Shekhai (SK-4) and Shahkot Bala (ST-6) areas

Table 5 Description of maceral types

Organic matter type	% composition	Description of macerals against samples				
		BK-1	DG-2	JB-3	SK-4	ST-6
Vitrinite	~90	Collodetrinite				
Inertinite	~5	Inertodetrinite				
		Fusinite				
		—	Macrinite	—	—	—
		—	Micrinite	—	—	—
		—	Semifusinite	—	—	Semifusinite
Liptinite	~5	Alginite				
		—	—	—	—	Resinite
		Cutinite				

Discussion and interpretation

Type of kerogen

The hydrogen index (HI) and oxygen index (OI) values were plotted on the van Krevlen's diagram (van Krevlen

1961) to identify the type of kerogen (Fig. 6a). However, because of very low HI and OI values, it is difficult to differentiate the kerogen types. Petrographically, collodetrinite is the most abundant vitrinite maceral (~90%, Table 5), belonging to the subgroup detrovitrinite, and it is the major part of Type III kerogen (Sýkorová et al. 2005).

Fig. 4 Photomicrographs showing **a** collodetrinite having inertodetrinite (circled) in sample BK-1, **b** unstructured organic matter (bituminite?) of probable algal origin fluorescing yellow in sample BK-1, **c** collodetrinite in sample BK-1, **d** collodetrinite having cutinite (A) and inertodetrinite (B) in sample BK-1, **e** collodetrinite having fusinite (white) in sample BK-1, **f** collodetrinite having iner-

todetrinite (circled) in sample DG-2, **g** collodetrinite having inertodetrinite (A-C) and fusinite (D) in sample DG-2, **h** collodetrinite having cutinite (circled) in sample DG-2, and **i** collodetrinite having macrinite (A), cutinite (B) and inertodetrinite (C) in sample DG-2 [images taken using reflected white light (except 'b' under fluorescence blue light), immersion oil objective, X600]

The low amounts of sulfur encountered in the present study (Table 2) also dismiss the possibility of presence of Type IIS kerogen.

The coal series earlier were classified separately as a specific type of kerogen (Type IV) with a little lower position in the Van Krevelen's diagram (Tissot 1984); however, Durand et al. (1977) showed that Type III organic matter and coals can be classified together within the same type after isolating kerogen segments with the usual acid treatment. Combaz and de Matharel (1978) carried out extensive studies on the maturity of the Eocene-Miocene Mahakam Delta sediments in Indonesia and concluded that Type III shales and pure coals incorporated together have been derived from the same sources. Huc et al. (1986) through detailed geochemical investigation of the Gironville series (Paris Basin) revealed similar maturity trends for coaly shales and pure coals.

In reference to the sulfur content, the elemental analysis data support that the terrestrial organic matter generally

holds lower sulfur as compared to the marine ones (Chou 1990; White et al. 1990; Vandenbroucke and Largeau 2007). During the riverine transport, continuous oxygenic conditions prevail and only terrestrial organic debris arrives at the sea, combining together with the detritic minerals in deltaic systems, a practice induced by the salinity change. The terrestrial organic particulates when arrive at its settling place, they already have passed through severe degradation and a general high burial rate in the deltaic systems prevents strong bacterial action at this stage (Hedges and Oades 1997), and thus the terrestrial kerogens are devoid of organic sulfur most often. The occurrence of sulfur-rich kerogens in marine environment is wider than in the lacustrine setups (Damste et al. 1993). According to Orr (1986) Type IIS organic matter is characterized by high initial atomic H/C and low initial atomic O/C ratios and is formed from detrital organic debris deposited under strictly non-oxidizing conditions in marine environments. Type III kerogen, however, is

Fig. 5 Photomicrographs showing **a** fusinite (white) enclosed in the matrix of micrinite in sample DG-2, **b** micrinite having inertodetrinite (A & B) and semifusinite (C) in sample DG-2, **c** micrinite in sample JB-3, **d** collodetrinite having macrinite (A & B) and inertodetrinite (C) in sample JB-3, **e** collodetrinite having macrinite (white) in sample JB-3, **f** collodetrinite having inertodetrinite (circled) in sample

SK-4, **g** collodetrinite having inertodetrinite (circled) in sample SK-4, **h** collodetrinite having inertodetrinite (A & B) and semifusinite (C) in sample ST-6, and **i** collodetrinite having inertodetrinite (A) and resinite (B) in sample ST-6 [images taken using reflected white light, immersion oil objective, X600]

Table 6 Detailed petrography of the coal and coaly shale samples

S. no	Description of organic matter type
BK-1	Abundant and of coarser grain size. Vitrinite is the main maceral (~90%), having abundant collodetrinite. Inertinite, comprising of inertodetrinite and fusinite, and liptinite, comprising of alginite and cutinite, are enclosed in the ground mass of collodetrinite (Fig. 4a–e)
DG-2	Common and of medium grain size. Vitrinite is the main maceral (~90%), which is composed predominantly of collodetrinite. Inertinite is the next frequent maceral, comprising of micrinite, macrinite, fusinite, semifusinite and inertodetrinite. Liptinite is present in the form of cutinite (Figs. 4f–i and 5a–c)
JB-3	Common and of medium grain size. Vitrinite is the main maceral (~95%), consisting of collodetrinite with embedded masses of macrinite and inertodetrinite (Fig. 5d, e)
SK-4	Abundant and of coarser grain size. Vitrinite is the main maceral (~95%) and consists of collodetrinite in major abundance. Inertinite, comprising of inertodetrinite, is present rarely (Fig. 5f, g)
ST-6	Predominant and of coarser grain size. Vitrinite is the main maceral (~95%), comprising of collodetrinite. Inertinite is the next frequent maceral, which consists of inertodetrinite and semifusinite. Liptinite is present in the form of resinite (Fig. 5h, i)

derived from higher land plants and has a close resemblance to terrestrial organic matter. It is rich in lignin and cellulose generally and yields gas only. However, if enriched in

cutinite, sporinite or resinite, the products may be different. Again, if Type III kerogen is enriched with plant cuticles (i.e., waxy materials from higher plants), it produces waxy

Fig. 6 Modified van Krevelen's diagram to determine **a** kerogen type (after van Krevelen 1961; Tissot and Welte 1984), and **b** depositional environments (after Last and Ginn 2005)

oil from terrestrial organic matter (Barker 1974; Nuñez-Betelu and Baceta 1994).

Environment of deposition

The depositional settings of massive coals and organic-rich shales are associated with Type III kerogen and characterized by no transportation of detrital sediment under oxidizing conditions and in situ deposition of nearly pure organic debris. However, some alteration of the organic matter may occur due to the sterilizing effect of certain decomposition products, e.g., phenols (Vandenbroucke and Largeau 2007). Law (1999) suggested the Type III kerogen to be gas prone in its predominant hydrocarbon potential, having small amount of hydrogen and of terrestrial origin.

The petrography of the coal and associated sediments indicates collodetrinite as the major vitrinite maceral (~90% of the total organic matter) (Table 5, Figs. 4 and 5). According to Sýkorová et al. (2005), collodetrinite is derived from parenchymatous (ground tissues of non-woody structures) and woody tissues of roots, stems and leaves that are composed of cellulose and lignin. In the peat stage of coal formation, the original plant tissues are decomposed and the tiny components are bound by humic colloids. These components after passing through gelification are subsequently homogenized; the process is called vitrinitization. van Krevelen's (van Krevelen 1961) diagram was adopted by Espitalié et al. (1977) for use of the HI versus OI atomic ratio; the latter has been modified to evaluate the depositional environment of the coal, suggesting a transitional environment between anoxic and terrestrial (Fig. 6b).

Thermal maturity

The term maturation is widely adopted to describe the degree of diagenetic evolution of the organic matter leading to the generation of hydrocarbon and is characterized through measurements of vitrinite reflectance (Vandenbroucke and Largeau 2007). In the course of maturation, the $T_{\max}$ is also closely related to the chemical nature of a kerogen as for different kerogen types, and the response of $T_{\max}$ would be different (Law 1999). According to Bacon et al. (2000), the organic matter type (kerogen I, II, III) refers to different maturity levels for the oil window across a range of vitrinite reflectance and $T_{\max}$ values.

Coal in Cherat, like that in Hangu area (Khyber Pakhtunkhwa province) and Baluchistan province, has high fixed carbon content and heating value as compared to other coal-fields of Pakistan, and the maturity of these coals is believed to have enhanced as a result of extensive tectonism Shah (2001).

The range of VR values in the current study (1.24–1.27) depicts a late mature stage for a gas-prone generation as suggested by previous studies (Dow 1977; Senftle and Landis 1991). A late mature level has been proposed also by Ibrahimbas and Reidger (2004) for the current range of VR values. According to Dow (1977), Tissot and Welte (1978), Tissot and Welte (1984), Teichmüller (1987), Taylor et al. (1998) and Vandenbroucke and Largeau (2007), sediments having VR values in this range are mature and susceptible to hydrocarbon generation provided the other parameters also are promising.

The overall geochemical parameters suggest that the samples are post mature; however, the range of vitrinite reflectance values for a gas-prone generation shows a peak mature stage. For knowing the maturity level of the coaly sediments, two cross-plots of HI versus $T_{\max}$ have been drawn (Fig. 7).

Fig. 7 **a** Type and maturity level of organic matter (after Hunt 1996), and **b** maturity level of organic matter (after English et al. 2004)

The plots show a post mature zone for the overall samples, which has also been confirmed by the maturity levels defined by Bacon et al. (2000) and Ibrahimbas and Reidger (2004) based on $T_{\max}$ and vitrinite reflectance values. The genetic potential section also shows higher degree of kerogen conversion (a range beyond immature zone).

In the current study, the samples showed vitrinite particles in abundance (~90%), which were used to measure the vitrinite reflectance (Fig. 3, Tables 3 and 4). The means of VR values for the samples varies between 1.24 and 1.27% (average 1.25%), thus indicating late mature conditions for the studied samples. The type of kerogen associated with the coal (Sýkorová et al. 2005) and organic-rich shale (Durand et al. 1977; Combaz and de Matharel 1978) is Type III. Figure 8 shows that the VR value for Type III kerogen indicates an inclination toward condensate to wet gas zone, thus signifying for the coal and coaly shale the potential to generate

hydrocarbons after destructive distillation. All the analyzed samples have a much higher $T_{\max}$ values (484–500 °C) as mentioned in Table 3; this could be probably related to the richness of these samples with respect to vitrinite (~90%), which is highly reactive in nature.

Following the derivation from geochemical parameters of Peters (1986) and Al-Obaidi et al. (2013), a “very good” quantity of hydrocarbons can be suggested for the analyzed samples. The geochemical attributes show that the coal and coaly shale are post mature, but as believed by Hunt (1996), the sediments post mature for oil are mature for gas. As the S_2 is greater than 0.2, the $T_{\max}$ can be used as an indicator of thermal maturation (English et al. 2004). The possible reason for the higher maturity of Paleocene coal could possibly be related to tectonic activity which might have enhanced the coalification process, while the

Fig. 8 **a** Approximate boundaries for kerogen type I, II and III, and **b** scheme of kerogen (organic matter) evolution on the van Krevelen's diagram (both from Tissot and Welte 1984)

lower HI values support the idea that sufficient generation of hydrocarbons has occurred (Fowler et al. 1991).

Source rock potential (SP)

SP is the sum of S_1 and S_2 values obtained from Rock–Eval pyrolysis. Rocks with SP value below 2 kg/t indicate insignificant oil but low gas potential, while the rocks having SP values between 2 and 6 kg/t fall in the category of moderately rich source rocks with fair oil potential (Tissot and Welte 1984; Dymann et al. 1996). $\text{TOC} > 2\%$ is often the indicator of excellent source potential with highly reducing environment (Bacon et al. 2000). Barker (1996) further defines the 1.0% TOC as the bottom line for source rock, as rocks with lesser TOC are unable to generate enough oil capable of initiating primary migration. Figure 9a, illustrating the relation between S_2 and TOC values, gives promising result in regard to hydrocarbon resource. The values for vitrinite, liptinite and inertinite listed in Table 4 have been plotted on the (LVI) ternary plot (Fig. 9b) of Tyson (1995), indicating the potential hydrocarbon (oil, wet gas and/or dry gas), which might have generated. The samples appear to be gas prone and fall in the dry gas zone.

The VR values depict a late mature stage, while for a gas-prone generation, it shows a peak mature stage susceptible to hydrocarbon generation with a tendency toward condensate to wet gas zone (Table 3, Fig. 8).

Genetic potential (GP)

The genetic potential ($S_1 + S_2$) of a stratum is defined by the ability of kerogen to generate if subjected to suitable time and temperature (Tissot and Welte 1984). The nature and

richness of kerogen controls this potential, which is in close association with the original organic contribution at the time of sedimentation. The process proceeds together with the settings of microbial reworking along with the reorganization of the organic matter within the sediments. Tissot and Welte (1978) used genetic potential to define the quality of the source rock and regarded $\text{GP} > 6$ to be “good” in terms of source rock potential. The potentiality in respect of hydrocarbon generation of the studied samples was determined by plotting GP values against the TOC values (Fig. 10). The results indicate excellent potentiality for the coal and coaly shale in terms of generating hydrocarbons.

Tissot (1984) suggested the onset Ro value for significant hydrocarbon generation against the Type III kerogen to be 0.8. This value is the initiation of hydrocarbon generation for Type III kerogen, providing further strength in suggesting the same kerogen type for the analyzed sediments.

Production index (PI)/transformation ratio (TR)

PI is the ratio of the amount of already generated hydrocarbon to potential hydrocarbon content calculated during pyrolysis analysis and is measured as $S_1/S_1 + S_2$ (Peters and Cassa, 1994). Type III kerogen in the catagenesis generally has PI between 0.1 and 0.2 (Tissot and Welte 1978; Durand and Paratte 1983). According to Ghori (2002), PI can be used to show how far catagenesis process has been recognized in the sediments considering a maturity stage of PI exceeding 0.2 (Ghori 2002). Low ratios of PI indicate immature or extremely over-mature organic matters (Peters and Cassa 1994; Pandey et al. 2018). The value of $\text{PI} > 0.30$ was suggested for gas generation/oil cracking in a stepwise

Fig. 9 a Source rock potential for the coal and coaly shale sediments (after Hakimi and Abdullah, 2014), and b ternary plot indicating the potential hydrocarbons generated by the sediments (oil, wet gas and/or dry gas) (after Tyson, 1995)

Fig. 10 Source rock quality information for the coal and coaly shale samples (after Burwood et al. 1995; Uzoegbu 2013)

Fig. 11 Kerogen conversion and maturity for the coal and coaly shale (after Akinlua et al. 2005)

increase in PI through the oil window by Law (1999); however, a gas zone was proposed for $T_{max} > 465^\circ$. Figure 11 shows kerogen conversion and maturity, suggesting a higher level of the contained kerogen conversion and a gas zone for the analyzed samples.

Residual carbon and TOC (%)

The residual carbon (RC) is the sum of the organic carbon (wt%) obtained from the CO and CO₂ during the pyrolysis analysis (Johannes et al. 2006). It is the measure of TOC, which gives organic carbon along with the non-pyrolisable organic carbon. Figure 12 shows close relation between residual carbon and TOC values for the selected samples, representing that most of the hydrocarbons have been produced and there is a little generative potential left in the overall samples. This further reinforces that the studied sample are post mature.

Fig. 12 Residual carbon estimation for the Paleocene coal and coaly shale (after English et al. 2004)

Fig. 13 Indigenous nature of hydrocarbons for the coal and coaly shale (after Hunt 1996)

Nature of hydrocarbons

Hunt (1996) proposed that when plotted against the increasing TOC % values, the rise in S_1 distinguishes the indigenous hydrocarbons from the migrated ones. It is obvious from Fig. 13 that the overall samples from all the five locations show indigenous hydrocarbons.

Coal rank

Collodetrinite is the abundant maceral in the coal and coaly shale under investigation. According to Sýkorová et al. (2005), collodetrinite carries the highest content of volatile matter, degasses first during the process of carbonization and reacts readily during combustion, thus suggesting a higher rank for the samples. These macerals were analyzed optically for reflectance measurements (Tables 3 and 4). VR values range from 1.24 to 1.27% for the Paleocene coal in the Attock-Cherat Range with an average reflectance value 1.25%. According to the classifications of Tissot and Welte (1978) and Teichmüller (1987), the rank of the coal is in medium to high volatile bituminous and hard brown coal stage (Fig. 14). Most of the pre- and post-Paleocene coals in Pakistan are not of good grade since they contain more water content, but in this case the water content is negligible.

Conclusions

Collodetrinite maceral from vitrinite group is in abundance (~90), followed by macerals from inertinite and liptinite groups, which suggests Type III kerogen for the sediments. The environment of deposition, associated with Type III

kerogen and vitrinite group macerals, is concluded to be terrestrial and characterized by no transportation of organic debris under oxidizing conditions. Rock–Eval data further specify the environment as anoxic to terrestrial. Based upon the VR values and the maceral type and frequency, the rank of the coal is in medium to high volatile bituminous and hard brown coal stage.

The TOC and other geochemical parameters suggest a good to very good potentiality for the Paleocene coaly sediments to serve as a source rock, and mature for gas generation mostly, but may also be capable to produce wet gas or condensate. The major maceral groups and the VR values also suggest that the coal and the coaly shale are gas prone. OI is continuously low throughout the analyzed interval, which further supports that the coal is of good quality and is gas prone. It can be further inferred from the VR values that there was sufficient hydrocarbon potential in the basin originally, which after the release of most of the hydrocarbon has low HI values currently. Moreover, the coal occurs as stringers and thin seams, which favor primary migration.

Recommendations

In the light of the conclusions, following recommendations are made:

1. The Hangu coal may serve as a sink for the carbon (carbon sequestration) particularly produced by the cement plants in Khyber Pakhtunkhwa such as Cherat Cement

Fig. 14 a Rank stages determined from microscopic rank/maturity parameters in relation to oil and gas production (from Dow 1977), and b maturity scales for sedimentary organic matter and coal evolution (from Tissot and Welte 1978)

Plant in Cherat, Askari Cement Plant in Nizampur and Lakki Cement Plant in Lakki Marwat.

2. Due to its gas-prone potential, the coal in Attock-Cherat Range may also serve as a source of coal bed methane in the vicinity.
3. The coal, although, possesses slight higher sulfur content and can still be used for industrial and domestic utilities and electric power generation.
4. The work can be extended to the coals present in Upper Indus Basin and Hazara area for a basinal-level study.

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Declarations

Conflict of interest On behalf of all the co-authors, the corresponding author states that there is no conflict of interest.

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