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Source of organic matter and depositional environments of the middle Paleocene Lakhra coals, Sindh Province, Pakistan

H. M. Zakir Hossain*, Yoshikazu Sampei**,[a], H. M. Ratul-Al-Istiak*, Tanvir Rahman Mahid*, Amila Sandaruwan Ratnayake***, Sadaf Naseem**** and Asghar A. A. D. Hakro*****

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Abstract

The middle Paleocene sub-bituminous coals and lignites in the Lakhra coalfield, Sindh Province, Pakistan were investigated to clarify source of organic matter and depositional environments in the Indus Delta. Here we present multiproxy approach such as C/N and C/S ratios, *n*-alkane indicators such as average chain length (ACL), carbon preference index (CPI), and aquatic index (P_{aq}), as well as pristane/phytane (Pr/Ph) ratio, oleanane/hopane (Ole/Hop) ratio, and Ts/(Ts + Tm) ratio to evaluate the peat accumulation conditions at the Lakhra coalfield. The TOC, TN and TS contents range from 8.15 to 55.1%, 0.08 to 0.93% and 2.14 to 11.4%, respectively. The C/N ratios (51.2-96.5) indicate a dominant control of organic matter by terrestrial higher plants to the peat bog. The values of C_{32} hopanes 22S/(22S + 22R) and C_{29} sterane 20S/(20S + 20R) are 0.14-0.36 and 0.26-0.29, respectively, showing that the maturity level is immature. The depositional environment was evaluated to be lagoonal brackish water pond or marsh where depositional condition was anoxic to dysoxic based on the datasets of high sulfur contents (2.1-11.4%), low to high C/S ratios (0.7-26) and low Pr/Ph ratios (0.14-1.00) without UCM. The Lakhra coals and lignites are characterized by high C/N ratios (51-97), high oleanane/C_{30}-hopanes ratios (<1.30), medium to high CPI (~2.0-9.8), medium ACL (27.6-28.7) and low to medium P_{aq} values (0.13-0.34). According to these results, main origin of the coals was probably angiosperm reed/grass. The coals are also minorly accompanied by aquatic/submerged plants and specific mosses without *Sphagnum*. The Lakhra coals are not abundant in regular steranes and characterized by high contents of diasteranes probably due to fine clay rich depositional environment.

1. Introduction

Sub-bituminous coal and lignite are abundant in Pakistan, and the Sindh is one of the most coal-bearing provinces in Pakistan with probable the Eocene and Paleocene coals reserve of 184 billion tonnes. Several coalfields were discovered in the Sindh Province, namely Thar, Lakhra, Badin, Sonda and Meting Jhimpir. The Lakhra coalfield is placed at a distance of about 193 km to northeast of Karachi and about 75 km to northwest of Hyderabad (Fig. 1). The Lakhra coal is characterized by sub-bituminous coal and lignite in rank, medium to high ash (4.3-49.0%) and high sulfur (1.2-14.8%) contents (Rehman et al., 2016; Siddiqui et al., 2017), and lies in the lower part of the Paleocene Bara Formation (Hakro and Baig, 2014; Fig. 2). These low grade coals/lignites in the Lakhra coalfield are also contained high concentrations of total moisture (9.7-38.1%), volatile matter (18.3-38.6%) and fixed carbon (9.8-38.2%) (Rehman et al., 2016).

Investigations on the elemental and biomarker characteristics of organic matter in coals and coaly shales provide key controls on the functioning of primary allochthonous/autochthonous source material input and reconstruction of the paleo-depositional environment to the mires (e.g., Bordovskiy, 1965; Eglinton and Hamilton, 1967; Meyers and Ishiwatari, 1993; Meyers, 1994; Schwark et al., 2002; Peters et al., 2005; Bechtel et al., 2007; Zech et al., 2013; Hossain et al., 2009, 2019; Bliedtner et al., 2018). However, organic geochemical studies especially on sub-bituminous coal

* Department of Petroleum and Mining Engineering, Jashore University of Science and Technology, Jashore 7408, Bangladesh
** Department of Geoscience, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan
*** Faculty of Science and Technology, Uva Wellassa University, Passara Road, Badulla 90000, Sri Lanka
**** Department of Geology, University of Karachi, Karachi 75270, Pakistan
***** Centre for Pure & Applied Geology, University of Sindh, Jamshoro 76080, Pakistan
[a] Corresponding author. e-mail address: sampei@riko.shimane-u.ac.jp, Tel:+81-852-32-6453; Fax:+81-852-32-6469

Fig. 1. Generalized map of the Pakistan and its surrounding areas, showing location of the studied Lakhra coalfield (modified after Ahmad et al., 2015).

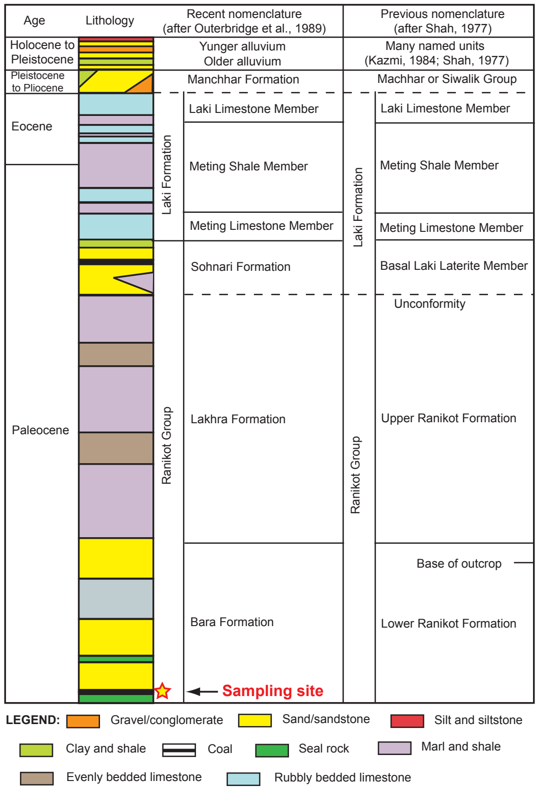

Fig. 2. Stratigraphic succession of the Lakhra anticline, Sindh Province, Pakistan (Outerbridge et al., 2007).

and lignite in Pakistan have been rarely performed to date in the Indus River delta area. Studies based on the application of elemental and biomarker parameters for evaluation of source and conditions of the sub-bituminous coal and lignite-bearing areas in the Sindh Province are quite limited, and were performed only on the Thar coalfield in Sindh (Khan et al., 1996; Ahmad et al., 2015).

In the present study, CNS elemental compositions and biomarker parameters (*n*-alkanes, acyclic isoprenoids, steranes, and hopanes) of sub-bituminous coal, lignite and coaly shale samples from Lakhra coalfield, Sindh, Pakistan were examined in order to make clear possible source of organic matter and environmental conditions during deposition of organic matter in the peat-forming wetland.

2. Geological setting

The Lakhra coalfield is in the southern part of the Sindh Province, Pakistan. This coalfield is placed at about latitudes 25°32’45” N and longitudes 68°00’15” E (Fig. 1). The Lakhra coalfield is covering an area of approximately 100 km^2, and the estimated coal reserves in the field is nearly 240 million tonnes (Siddiqui et al., 2017). The thickness of each coal seam varies from 1.5 to 3.5 m (Siddiqui et al., 2017). The Lakhra anticline, which is close to the investigated coalfield, is approximately 30 km wide and 100 km long, and its elevation is about 0.2 km above the mean sea level (Outerbridge et al., 2007). This anticline has been developed between the collision of the Arabian, Eurasian and Indian plates in the Pleistocene and still uplifting (Outerbridge and Khan, 1989). It is gently folded between the Laki Range and the Indus River. Stratigraphic succession of the Lakhra anticline is sub-divided into the Bara Formation, Lakhra Formation, Laki Formation (Sohnari and Chat Members), Siwalik Group (locally called as Manchhar) and alluvium, in ascending order (Shah, 1977; Kazmi, 1984; Hakro et al., 2013; Hakro and Baig, 2014; Hakro et al., 2016a, b) (Fig. 2).

The lower Bara Formation (middle Paleocene) consists predominantly of sandstone, shale, coal seam and carbonaceous claystone (Hakro et al., 2013, 2016a, b; Hakro and Baig, 2014; Ahmad et al., 2015). Sediments in the Bara Formation were deposited under humid climatic conditions (Hakro et al., 2013). The upper contact of the Bara Formation is erosional. The Lakhra Formation (late Paleocene) is conformably underlying the Bara Formation which consists mainly of limestone and shales. The Laki Formation (early Eocene) is subdivided into Sohnari Member and Chat Member (Shah, 1977; Hakro et al., 2013, 2016a, b; Hakro and Baig, 2014). The Sohnari member of Laki Formation (early Eocene) composed predominantly of sandstone, shale, coal and clay (Outerbridge et al., 2007; Hakro et al., 2016a, b, 2018). The Siwalik Group (Manchhar: Pliocene to Pleistocene) unconformably overlies the Laki Formation, which consists chiefly of gravel, sand and clay (Shah, 1977; Hakro et al., 2013, 2016a, b; Hakro and Baig, 2014). The upper most part of the Lakhra anticline is recent alluvium and composed mainly of limestone, gravel, sand, silt and clay.

3. Samples and methods

The coal and coaly shale samples (n = 12) were collected from the Lakhra coalfield, Sindh Province, Pakistan (Fig. 1). These samples were from the lower part of the Bara Formation (Fig. 2). The coals are mainly dull, brownish to black in color, brittle, laminated with uneven to conchoidal fractures (Table 1). The clean coal/coaly shale samples were ground to a fine powder using an agate mortar and pestle.

For CNS elemental analysis, all the fine powdered coal/coaly shale samples (∼ 4 mg) were taken in Ag foil cups and added 1M HCl to remove carbonates, and successively dried at 110°C for *ca*. 1 hour. The acid treated samples were again placed in Sn cups and sealed. TOC, TN and TS contents were examined by an elemental analyzer (FISSONS, EA 1108). The elemental data were calibrated against a BBOT standard [2, 5-bis-(5-tert-butyl-benzoxazol-2-yl)-thiophene]. The analytical precision (coefficient of variation) inherent in this technique is about ± 3%.

Biomarker analysis was conducted on selected coal samples (n = 6: Table 2). The six samples for GC-MS analysis were selected from the sub-bituminous coals. About 5 g powdered sample was extracted using a soxhlet apparatus by adding dichloromethane (DCM) and MeOH mixture (9:1) for 72 h. Elemental sulfur was eliminated using granular copper. The extracted solvent was condensed using rotary vacuum evaporator at 35° C. The hydrocarbon fractions were separated using thin layer chromatography on activated silica gel pre-coated plates (Kiselgel 60 PF254, Merck). These fractions were then analyzed by GC/MS instrument (Shimadzu QP2010). The GC was equipped with a fused-silica capillary column (30 m × 0.25 mm i.d.) coated with (5% phenyl) methylpolysiloxane μm film (DB-5MS: Agilent Technologies). The oven temperature was programmed from 50°C to 300°C at 8°C/min. The GC instrument was performed with pure helium as carrier gas (G1 grade). The extract sample was injected splitless mode in the GC system. All the n-alkanes, biomarkers and aromatics were identified from the GC retention time and mass spectra and were quantified using peak areas or heights. PAHs were identified by comparison of GC retention times, mass spectra with published data and standard PAH Solution Mix (Accu Standard Inc., Z-013-17).

4. Results

4.1. Elemental composition of Lakhra coal

The analytical results on the samples from the Lakhra coalfield, Sindh Province, Pakistan are listed in Tables 1 and 2. TOC contents of the coal and coaly shale samples are more than 40%, two samples contain ∼20% and a single sample has TOC lower than 10% (Table 1). The TOC contents are ranging from 8.1 to 55.1% with an average of 39.7%. A single sample

Table 1. CNS elemental compositions of coals/coaly shales in the Lakhra coalfield, Sindh Province, Pakistan.

Sample No.	Mine No.	Coal description	Core depth (m)	C, N, S elemental data				
				TOC (wt %)	TN (wt %)	TS (wt %)	C/N (wt ratio)	C/S (wt ratio)
LCF-01	MINE-30	Dull, brownish-black : sub-bituminous coal	0.91	44.2	0.81	4.7	54.4	9.4
LCF-02	MINE-26A	Dull, bright, black : sub-bituminous coal	2.35	55.1	0.93	2.1	58.9	25.7
LCF-03	MINE-26B	Dull, grey to brown, white spot : lignite	2.38	8.1	0.08	11.4	96.5	0.7
LCF-04	MINE-34	Dull, brownish-black : sub-bituminous coal	4.41	44.3	0.75	5.4	59.3	8.2
LCF-05	MINE-08	Dull, brownish-black : sub-bituminous coal	4.65	43.4	0.70	5.3	62.0	8.1
LCF-06	MINE-13CA	Dull, brownish-black : sub-bituminous coal	4.87	24.3	0.37	7.9	64.9	3.1
LCF-07	MINE-18E	Dull, brownish-black : sub-bituminous coal	4.93	41.2	0.81	8.0	51.2	5.2
LCF-08	MINE-13CB	Dull, grey to brown, white spot : lignite	4.93	21.6	0.34	10.6	62.5	2.0
LCF-09	MINE-27	Bright, dull, black : sub-bituminous coal	5.03	53.5	0.93	3.5	57.5	15.5
LCF-10	MINE-18	Dull, brownish-black : sub-bituminous coal	5.07	44.2	0.70	4.1	63.2	10.8
LCF-11	MINE-17C	Bright, black : sub-bituminous coal	5.28	46.6	0.72	3.3	64.7	14.0
LCF-12	MINE-18B	Dull, black : sub-bituminous coal	5.37	49.9	0.81	4.8	61.2	10.5

(LCF-03: MINE-26B) contain exceptionally low TOC content (8.1%; Table 1). Similarly, abundances of TN and TS are ranging from 0.08 to 0.93% (average 0.66%) and 2.1 to 11.4% (average 5.93%). The TOC positively correlates with TN (r = 0.98) and negatively correlates with TS (r = -0.93) (Figs. 3a and b), but correlations are poor between TOC and C/S ratios in the investigated samples (Fig. 3c). The C/N ratio varied from 51.2 to 96.5 (average 63.0) and C/S ratio ranged from 0.72 to 25.7 (average 9.43), with the lowest C/S ratios (0.72) observed in LCF-03: MINE-26B sample (Table 1).

4.2. Molecular compositions of hydrocarbons

Total ion chromatograms (TICs), hopanes (*m/z* 191) and steranes (*m/z* 217) distributions are shown in Fig. 4. The *n*-alkane patterns of the Lakhra coal samples are ranging from *n*-C_{17} to *n*-C_{36} (Fig. 4a). The relatively high *n*-C_{27} alkane peak is observed in samples LCF-05 (MINE-08), LCF-12 (MINE-18B), and LCF-09 (MINE-27), whereas *n*-C_{29} peak is abundant in LCF-11 (MINE-17C), LCF-02 (MINE-26A), and LCF-01 (MINE-30). The peak *n*-C_{31} alkane is relatively lower than both *n*-C_{27} and *n*-C_{29} peaks. *n*-Alkanes are dominated by long chain *n*-alkanes (>*n*-C_{27}) with strong odd over even carbon predominance. The unknown peak right side by *n*-C_{25} alkane is phthalic acid ester compounds. Average chain length (ACL) of *n*-alkanes (Eglinton and Hamilton, 1967; Zech et al., 2013; Bliedtner et al., 2018) are between 27.6 and 28.7 (Table 2; average 28.2). Carbon Preference Index (CPI; Bray and Evans, 1961) values varied between 1.98 and 9.82 (Table 2; average 5.38). Aquatic proxy of *n*-alkane (P_{aq} = (*n*-C_{23} + *n*-C_{25}) / (*n*-C_{23} + *n*-C_{25} + *n*-C_{29} + *n*-C_{31}); Ficken et al., 2000) is from 0.13 to 0.34 (Table 2, average 0.23). The low abundance of acyclic isoprenoids pristane (Pr) and phytane (Ph) are observed. The Pr/Ph ratios range from 0.14 to 1.00 (average 0.50), and Pr/*n*-C_{17} and Ph/*n*-C_{18} values range from 0.48 to 4.67 (average 2.09) and 0.13 to 1.91 (average 0.97), respectively (Table 2). The hopanoid patterns in the Lakhra coals are characterized by the occurrence of 17α(H)-22,29,30-trisnorhopane (Tm) and 18α(H)-22,29,30-trisnorhopane (Ts), and Ts/(Ts + Tm) values varied between 0.17 and 0.39 (Table 2, average 0.28). Triterpane ratios of C_{32} 22S/(22S + 22R) are from 0.14 to 0.36. The sterane distributions for the Lakhra coal samples are characterized by a dominance of diasteranes (Fig. 4c). Peaks of regular steranes of cholestane (C_{27} 20R), ergostane (C_{28} 20R) and stigmastane (C_{29} 20R) showed very small comparing to the diasteranes (Fig. 4c).

For aromatic diterpanes (Otto et al., 1997), only ferruginol (*m/z* 271) was recognized, and dehydroabietane (*m/z* 255), simonellite (*m/z* 237), diaromatic totarane (*m/z* 237), retene (*m/z* 219) were unknown. According to Otto et al. (1997), such sesquiterpanes as isonorpimarane (*m/z* 233), norpimarane (*m/z* 233), norabietane (*m/z* 109), pimarane (*m/z* 247) and phyllocladane (*m/z* 259) have peaks between *n*-C_{18} and *n*-C_{21} alkanes in TIC chart. In the present study, these peaks and the peaks of diterpanes were not clearly detected. For aromatic oleanoids, only one significant clear peak of dimethylpicene (*m/z* 306) or A ring methylated tetraaromatic pentacyclic triterpenoids (*m/z* 324, oleanane type: Nakamura et al., 2010) were supposed. Selected PAHs were also monitored at *m/z* 178 (P: phenanthrene, An: anthracene), *m/z* 192 (MP: methylphenanthrene), *m/z* 202 (Fla: fluoranthene, Py: pyrene), *m/z* 228 (BaAn: benz[a]anthracene, Chry + Tpn: chrysene/triphenylene), *m/z* 252 (Bflas: benzofluoranthenes, BePy: benzo[e]pyrene, BaPy: benzo[a]pyrene, Pery: perylene), *m/z* 276 (InPy: indeno[1,2,3-cd]pyrene, BghiP: benzo[ghi]perylene), and *m/z* 300 (Cor: coronene) according to Jiang et al. (1998) and Hossain

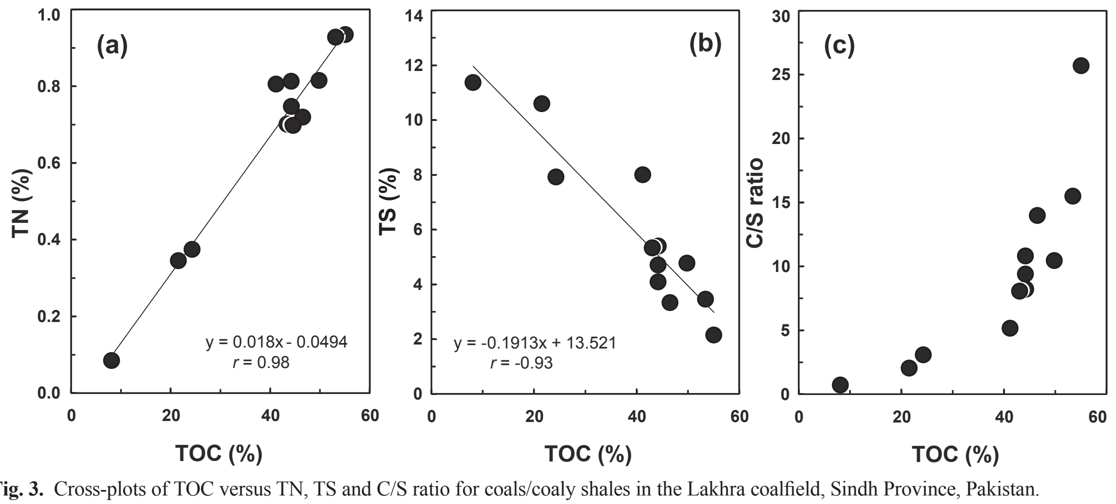

Fig. 3. Cross-plots of TOC versus TN, TS and C/S ratio for coals/coaly shales in the Lakhra coalfield, Sindh Province, Pakistan.

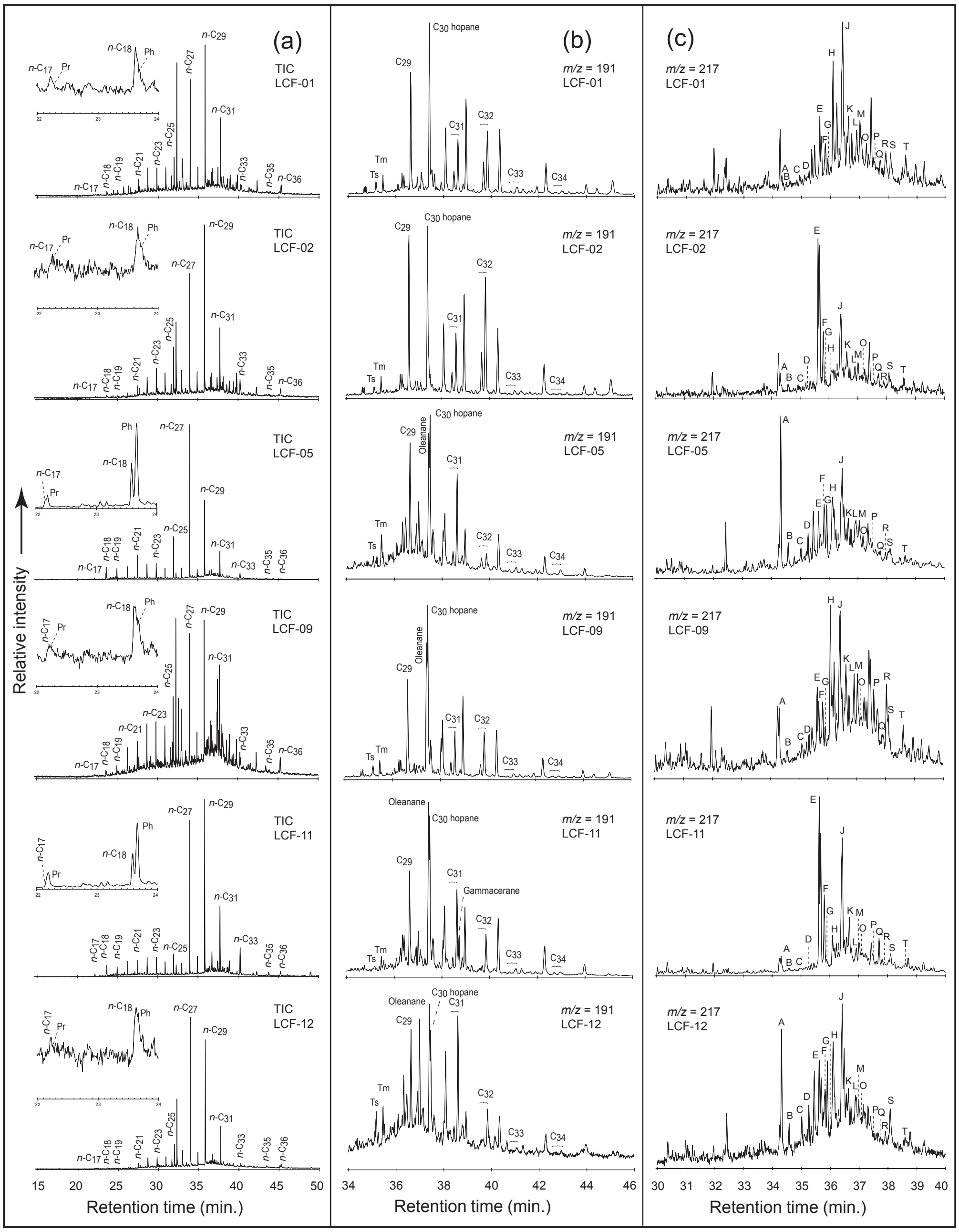

Fig. 4. Mass chromatograms of TICs, hopanes (*m/z* 191) and steranes (*m/z* 217) of coals in the Lakhra coalfield, Sindh Province, Pakistan. Peak identification in the *m/z* 217 mass fragmentograms (steranes) for peaks A to T was according to Mostafa and Younes (2001) as follows:

A: 13β (H), 17α (H)-diacholestane (20S), B: 13β (H), 17α (H)-diacholestane (20R), C: 13α (H), 17β (H)-diacholestane (20S), D: 13 α (H), 17β (H)-diacholestane (20R) + 24-Methyl-13β (H), 17α (H)-diacholestane (20S), E: 24-Methyl-13β (H), 17α (H)-diacholestane (20R), F: 5α (H), 14α (H), 17α (H)-cholestane (20S), G: 5α (H), 14β (H), 17β (H)-cholestane (20R) + 24-Ethyl-13β (H), 17α (H)-diacholestane (20S), H: 5α (H), 14β (H), 17β (H)-cholestane (20S) + 24-Methyl-13β (H), 17α (H)-diacholestane (20R), I: 5α (H), 14α (H), 17α (H)-cholestane (20R). J: 24-Ethyl-13β (H), 17α (H)-diacholestane (20R), K: 24-Ethyl-13α (H), 17β (H)-diacholestane (20S), L: 5α (H), 14α (H), 17β (H), 24-methycholestane (20S), M: 5α (H), 14α (H), 17β (H), 24-methycholestane (20R)+24-Ethyl-13α (H), 17β (H)-diacholestane (20R), N: 5α (H), 14β (H), 17β (H), 24-methylcholestane (20S), O: 24-Propyl-13α (H), 17β (H)-diacholestane (20S), P: 5α (H), 14α (H), 17α (H), 24-methylcholestane (20R), Q: 5α (H), 14α (H), 17α (H), 24-ethylcholestane (20S), R: 5α (H), 14β (H), 17β (H), 24-ethylcholestane (20R), S: 5α (H), 14β (H), 17β (H), 24-ethylcholestane (20S), T: 5α (H), 14α (H), 17α (H), 24-ethylcholestane (20R).

Table 2. n-Alkane and biomarker ratios of coals in the Lakhra coalfield, Sindh Province, Pakistan.

Sample No.	Mine No.	Isoprenoid ratios			Alkanes					Steranes						Triterpanes		
												C29	Ratios (%)					
		Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	n-C_{29}/n-C_{19}	n-$C_{<20}$/total n-alkanes	ACL[a]	CPI[b]	Paq[c]	$C_{27}/(C_{27}+C_{29})$	$C_{29}/(C_{27}+C_{29})$	20S/(20S+20R)	C_{27}	C_{28}	C_{29}	Ole/Hop	Ts/(Ts+Tm)	C_{32} (22S/22S+22R)
LCF-01	MINE-30	1.00	0.48	0.13	97.4	0.02	28.5	3.45	0.19	0.32	0.68	0.26	24	24	52	0.00	0.34	0.36
LCF-02	MINE-26A	0.84	0.89	0.37	345.2	0.01	28.2	3.69	0.25	0.52	0.48	0.29	45	14	41	0.00	0.25	0.28
LCF-05	MINE-08	0.14	1.45	1.81	7.7	0.07	27.6	9.82	0.34	-	-	-	-	-	-	0.86	0.17	0.32
LCF-09	MINE-27	0.32	0.72	0.73	9.7	0.05	28.0	1.98	0.31	0.35	0.65	-	28	23	50	0.78	0.39	0.20
LCF-11	MINE-17C	0.25	4.30	1.91	18.2	0.05	28.7	6.97	0.13	-	-	-	-	-	-	1.14	0.20	0.14
LCF-12	MINE-18B	0.45	4.67	0.85	341.8	0.01	28.1	6.38	0.15	-	-	-	-	-	-	1.30	0.34	0.19

[a]ACL = $[23(n\text{-}C_{23}) + 25(n\text{-}C_{25}) + 27(n\text{-}C_{27}) + 29(n\text{-}C_{29}) + 31(n\text{-}C_{31}) + 33(n\text{-}C_{33})] / (n\text{-}C_{23} + n\text{-}C_{25} + n\text{-}C_{27} + n\text{-}C_{29} + n\text{-}C_{31} + n\text{-}C_{33})$

[b]CPI = $((n\text{-}C_{25} + n\text{-}C_{27} + n\text{-}C_{29} + n\text{-}C_{31}) / (n\text{-}C_{24} + n\text{-}C_{26} + n\text{-}C_{28} + n\text{-}C_{30}) + (n\text{-}C_{25} + n\text{-}C_{27} + n\text{-}C_{29} + n\text{-}C_{31})/(n\text{-}C_{26} + n\text{-}C_{28} + n\text{-}C_{30} + n\text{-}C_{32})) / 2$ (Bray and Evans, 1961).

[c]Paq = $(n\text{-}C_{23} + n\text{-}C_{25}) / (n\text{-}C_{23} + n\text{-}C_{25} + n\text{-}C_{29} + n\text{-}C_{31})$ (Ficken et al., 2000).

et al. (2013). BePy, BaPy, Pery, InPy and BghiP were detected only in the samples LCF-05 and LCF-11. However, Ret, P, MP, Fla, Py, BaAn, Chry, Tpn, Bflas and Cor were not detected in all coal samples.

5. Discussion

5.1. Maturity level of coal

The maturity parameter C_{32} hopanes 22S/(22S + 22R) (Seifert and Moldwan, 1980; Peters et al., 2005) of the Lakhra coals is low from 0.14 to 0.36 (Table 2), indicating immature level. Another maturity parameter C_{29} sterane 20S/(20S + 20R) (Seifert and Moldwan, 1981; Peters et al., 2005; Waseda and Nishita, 1998; Fabiańska et al., 2013) of 0.26-0.29 (Table 2) supposes immature or early stage of oil generation. In the present study, reliability of the data of C_{29} sterane 20S/(20S + 20R) for the Lakhra coals seems to be low, because peaks of the steranes are very small and accompanied by some coeluting peaks (Fig. 4c). Therefore, the maturity of the Lakhra coals should be interpreted as immature level, and therefore original distributions of *n*-alkane and biomarker in the Lakhra coals were probably not affected by highly heating arrangement. Accordingly, based on the *n*-alkanes and biomarkers of the Lakhra coals, paleoenvironment and the origin of organic matter can be properly discussed.

5.2. Depositional environment

Variations of TOC (8.1-55.1%; Table 1) of the Lakhra coals/coaly shales could mainly attribute to the availability of clastic sediments and water level fluctuation in the peat-forming mires. The Lakhra coals/coaly shales are characterized by high sulfur contents (2.1-11.4%; Table 1 and Fig. 3). Rehman et al. (2016) also reported that Lakhra coals have abundant sulfur concentrations, varied between 1.2% and 14.8%. The C/S ratio of sediments and sedimentary rocks can provide useful information about seawater/freshwater environmental conditions during accumulation of organic matter in a basin (Berner and Raiswell, 1984). The C/S ratios (>10) indicate terrestrial freshwater conditions, and low values (0.5 to 5) indicate marine environmental conditions (Berner, 1982, 1984; Berner and Raiswell, 1984). In the present study, the C/S ratios vary from 0.7 to 26 (Table 1), indicating environmental change from seawater to freshwater conditions. In addition, the TS shows a negative correlation with TOC (r = -0.93, Fig. 3b), supporting that bog mire in the Lakhra coal field could change from a seawater shallow-pond to a low saline-water/freshwater mire. The seawater/saline-water invasion to the mires could make the depositional environment to be anoxic and dysoxic/suboxic to fix the sulfate ion as sedimentary pyrite. This interpretation is consistent with the result by Hakro et al. (2013, 2016a, b) and Hakro and Baig (2014), which reported that the coal-bearing Bara Formation deposited in fluviatile/beach, lagoon and/or dead end marsh channels on the basis of grain size distribution and textural and mineralogical composition of sandstones. Sediments in the Bara Formation, Sindh Province also contained high sulfur contents due to the present of metabolizable organic matter, sulfate-reducing bacteria, and dissolved sulfide in the wetlands and peat bogs (Hakro et al., 2013).

For evaluation of aquatic oxic/anoxic environment, Pr/Ph ratio has been commonly used (Powell and McKirdy, 1973; Didyk et al., 1978; Bechtel et al., 2007). The Pr/Ph ratios <1 indicate anoxic environmental conditions, whereas ratios >3 are indicative of oxic conditions or input of organic matter from land plants (Didyk et al., 1978). The Pr/Ph ratios in the Lakhra coals range from 0.14 to 1.00 (Table 2), and suggest anoxic to suboxic conditions prevailed during deposition and peatification. Very low UCM (unresolved complex mixture) in TIC of the aliphatic fraction (Fig. 4a) is also consistent with the reconstructed anoxic depositional environment. Although Ts/(Ts + Tm) ratio depends on depositional environment, origin, and maturity of organic matter, relatively low Ts/(Ts + Tm) ratios from 0.17 to 0.39 (average 0.28) of the Lakhra coals are not conflict with the evaluated anoxic/suboxic bottom water environments (Moldowan et al., 1985, 1986). BePy, BaPy, Pery, InPy and BghiP in the samples LCF-05 and LCF-11 are possibly due to small wildfire around the peat area (Hossain et al., 2013). The C_{35}-homohopane could not be discussed in the present study, because of co-eluted unknown peaks around the C_{35}-homohopane.

5.3. Sources of organic matter

The C/N ratio is frequently applied as a proxy for identification of organic matter source either terrestrial or algal derived (Bordovskiy, 1965; Meyers, 1994; Sampei and Matsumoto, 2001; Ratnayake and Sampei, 2015). Bacteria and algae/plankton have C/N ratios of ~4 to 10 (Bordovskiy, 1965) due to their high protein content, whereas terrestrial plants have C/N ratios of >20 (Ertel and Hedges, 1985; Meyers, 1994). Schellekens et al. (2015) reported that *Sphagnum*-rich peatlands have higher C/N ratios (>50). In the present study, C/N ratios differ from 51 to 97 (Table 1), and therefore clearly indicate that the Lakhra coals are not algaenite. TOC contents show strong positive correlation with TN contents (r = 0.98: Fig. 3a), suggesting a consistent contribution of source material to the mire.

Short-chain n-alkanes less than C_{20}, which are commonly derived from algae and bacteria (Allen et al., 1971; Cranwell et al., 1987), are low abundances (Fig. 4a), suggesting low contribution of algal/bacterial organic matter to the mires. The Lakhra coals in the middle and lower layers are characterized by high oleanane/C_{30}-hopanes ratio (up to 1.30, Table 2 and Fig. 5d). In general, coals deposited in oxic freshwater mire often have a very low concentration of oleanane, even though the coals are originated from angiosperm plants. Oleanane-rich coals are found only in the layers which deposited in anoxic condition influenced by seawater (Murray et al., 1997). The Lakhra coals are marked by high sulfur contents and low Pr/Ph ratios as shown above, suggesting that the oxygen-poor aquatic environment could decrease oxic decomposition of oleanane. Accordingly, angiosperm plants could be one of the major origins for the Lakhra coals. Low oleanane abundance in the upper most two samples

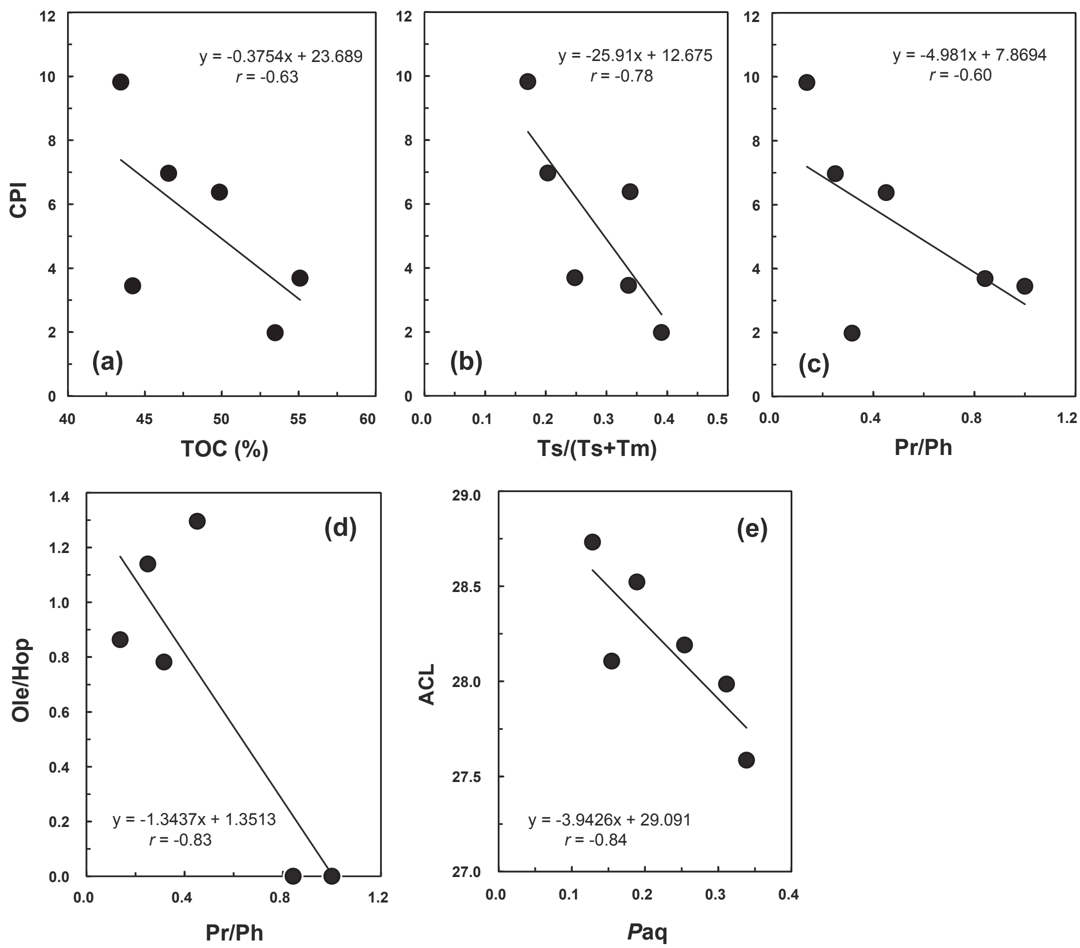

Fig. 5. Cross-plots of CPI versus TOC (%), Ts/(Ts + Tm) and Pr/Ph, Ole/Hop versus Pr/Ph and ACL versus P_{aq} for coals in the Lakhra coalfield, Sindh Province, Pakistan.

LCF-01 and LCF-02 could probably reflects both vegetation type and redox condition in the mire. The upper most layers have relatively high n-C_{29}/n-C_{19} alkane ratios and high Pr/Ph ratios, suggesting higher abundance of terrestrial plant OM.

The Lakhra coals are also characterized by medium to high CPI. High CPI values (>2) indicate waxy hydrocarbons input from land plants (Eglinton and Hamilton, 1967) and low CPI values (<～1) indicate aquatic or bacterial/algal origin of organic matter in immature samples (Cranwell et al., 1987; Rieley et al., 1991). The CPI values in the Lakhra coals are ranging from ～2.0 to 9.8 (Table 2), and signify a dominant control of organic matter input from terrestrial vascular plants. Duan and He (2011) reported that the representative CPI values are 6.4-17.3 for tree leaves, 4.6-15.0 for reed and 3.5-12.8 for grass in eastern Asia (between latitudes 22° and 39° in China). Consequently, the n-alkanes of the Lakhra coals could be mainly from grass and reed category. The CPI values have a negative correlation with TOC contents (r = -0.63), Ts/(Ts + Tm) ratios (r = -0.78), and Pr/Ph ratios (r = -0.60) (Figs. 5a, b and c), and therefore, high CPI wax could be deposited under oxygen-poor depositional environments.

n-Alkanes of the Lakhra coals show low abundances of algal/bacterial derived organic matter, and are dominated by odd long-chain epicuticular wax of n-C_{27}, n-C_{29} and n-C_{31} (Fig. 4a). Terrestrial vascular plants contain abundant long-chain n-alkanes with high maximum peaks of n-C_{27}, n-C_{29}, and n-C_{31} homologues (Eglinton and Hamilton, 1967). These n-alkane distributions of the Lakhra coals are not similar with that of *Sphagnum* moss, although one of the major possible origin of peat is generally *Sphagnum* moss. The n-alkane distributions in *Sphagnum* species are basically bimodal, with abundant C_{23} and C_{31} homologues (Nott et al., 2000). The abundances of n-C_{23} peak in the studied Lakhra coals are relatively low, therefore, contribution of *Sphagnum* in the peat-forming mire systems was probably quite insignificant in this area. Similarly, submerged plants are predominant at n-C_{23} alkane with no clear odd carbon predominance (Ficken et al., 2000), so that such plants also could not be major origin of the Lakhra coal.

ACL of n-alkanes is widely used to differentiate deciduous trees and shrubs from grass/herb vegetation (Eglinton and Hamilton, 1967; Zech et al., 2013; Bliedtner et al., 2018). High ACL values (>29) indicate grass or herb vegetation, whereas low values (～27) indicate mostly trees and shrubs (Kirkels et al., 2013; Bliedtner et al., 2018). Duan and He (2011) also reported that long-chain n-alkanes with high peaks at n-C_{27} or n-C_{29} are found in tree leaves, n-C_{27}, n-C_{29} or n-C_{31} peaks in reed, and n-C_{29} or n-C_{31} peaks in grass, with average ACL values of 27.9, 28.4 and 29.5, respectively. The high ACL values in these plant types at low latitude and elevation areas suggesting a lengthy growth period and more potential inward radiation that protect their leaves with longer chain n-alkanes from water deficiency (Duan and He, 2011). The ACL of the Lakhra coals are 27.6-28.7 (average 28.2), which are similar with those of reed plants (angiosperm). Consequently, the main origin of the Lakhra coals could be angiosperm reed plants. In the LCF-05 sample, aromatic oleanoids are supposed. In addition, such minor specific bog mosses as *Vaccinium oxycoccus* and *Hypnum cupressiforme* with maximum peak of n-alkane at C_{29} and *Aulacomnium palustre* with maximum peak at C_{27} (Nott et al., 2000), and these mosses may be another candidate source plants in the Lakhra coalfield.

The aquatic plant proxy, P_{aq} = [(n-C_{23} + n-C_{25})/(n-C_{23} + n-C_{25} + n-C_{29} + n-C_{31})], may also be used to estimate waxy materials input from aquatic macrophytes and/or submerged plants (Ficken et al., 2000; Hossain et al., 2019). The P_{aq} values of >0.4 shows submerged and floating macrophytes, between 0.1 and 0.4 specify emergent macrophytes, and values of <0.1 indicate terrestrial plants (Ficken et al., 2000). The P_{aq} values of the Lakhra coals are relatively low from 0.13 to 0.34 (Table 2, average 0.23), and have a negative correlation with ACL values (r = -0.84, Fig. 5e). These results suggest that the aquatic/submerged plants could contribute to this mire but could not be a main source.

The relative distributions of C_{27}, C_{28}, and C_{29} steranes can be used to understand the depositional environment and source of organic matter (Huang and Meinschein, 1979; Hossain et al., 2009, 2019). However, the Lakhra coals are not abundant in regular steranes (Fig. 4c). The Lakhra coal samples display a strong predominance of diasteranes (Fig. 4c), which represented by 13β (H), 17α (H)-diacholestanes (20S and 20R), 24-Methyl-13β(H), 17α (H)-diacholestane (20R), 5α (H), 14β (H), 17β (H)-cholestane (20S) + 24-Methyl-13β (H), 17α(H)-diacholestane (20R), and 24-Ethyl-13β (H), 17α(H)-diacholestane (20R). These high contents of diasteranes in the examined coals/lignites suggesting clay-rich depositional environment. Moldowan et al. (1986) noted that diasteranes are the diagenetic products of sterols in reducing conditions with clay. Relatively low sterane and high diasterane in low-ash coals of the Lakhra basin could probably indicate the larger resistance of diasteroids during biodegradation pathways (Killops and Killops, 2005). Although the early Eocene coals deposited in a dry and low temperature climate (Hakro et al., 2018), the Paleocene coals in the Bara Formation of the present study deposited under humid climatic conditions (Hakro et al., 2013). Therefore, the humid climate could form a lot of such fine clay minerals as kaolinite and montmorillonite which become the catalysts to form diasteranes, and the clays deposited as a significant ash in coals of the Bara Formation. The Lakhra coal is known as medium to high ash (4.3-49.0%) coals (Rehman et al., 2016; Siddiqui et al., 2017).

6. Conclusions

Our main conclusions are as follows:

(1) Maturity level of coal

The maturity parameter values of C_{32} hopanes 22S/(22S + 22R) and C_{29} sterane 20S/(20S + 20R) are 0.14-0.36 and 0.26-0.29, respectively. These values indicate that the maturity level is immature and distributions of *n*-alkanes/biomarkers of the Lakhra coals are original without highly heating arrangement of content peaks.

(2) Depositional environment

The Lakhra coals/coaly shales are characterized by high sulfur contents (2.1-11.4%) with low C/S ratios (0.72-26) and could be affected by seawater or low saline-water at lagoonal deposition. The influence of seawater/low saline-water could make this depositional environment to be anoxic/oxygen poor, and then organic matter with low Pr/Ph ratios (0.14-1.00) deposited without UCM.

(3) Sources of organic matter

The Lakhra coals are characterized by high C/N ratios (51-97), high oleanane/C_{30}-hopanes ratio (up to 1.30), medium to high CPI (~2.0-9.8), medium ACL (27.6-28.7) and low to medium P_{aq} values (0.13-0.34). The CPI has a negative correlation with Pr/Ph ratio and TOC content, and the P_{aq} values have a negative correlation with ACLs. These results indicate that the main origin of the Lakhra coals is reed/grass minorly accompanied by aquatic/submerged plants and specific mosses without *Sphagnum*. The Lakhra coals are not abundant in regular steranes and characterized by high contents of diasteranes probably attributed to clay rich depositional environment.

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