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Enrichment and distribution of trace elements in Padhrar, Thar and Kotli coals from Pakistan: Comparison to coals from China with an emphasis on the elements distribution

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ABSTRACT

This paper reports the mineralogical and geochemical compositions of the Padhrar (salt-range), Thar (Block Nos. 3 and 5) and Kotli coals. The coal investigated in this study is lignite to sub-bituminous coal, with a broad range of ash yields, volatile matter content and sulfur contents. The mineralogical characteristic, major and trace elements were determined by X-ray diffraction, inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry, respectively. The mineral assemblages, sulfur contents, ash yields, and ($CaO + MgO + Fe_2O_3$)/($SiO_2 + Al_2O_3$) ratio varied significantly in the coal, which is attributed mainly to variation in the depositional environment. Pyritic sulfur is the main form of sulfur in the coals from Padhrar, Kotli and Thar coalfield. The minerals in the studied coals are dominated by quartz, pyrite, kaolinite, illite, along with calcite, feldspar, siderite, montmorillonite and gypsum. Sixteen trace elements, including Li, Be, B, Ti, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, and Ba and five major elements P, Ca, Al, Fe, and Si, were investigated in this study. The trace element concentrations show variety within the coal seams in the Thar coals and the affinities vary among locations. The concentration of Sr, Ti, Zn, Li, Ni, Cu, Sc, As, Be, and B in the present study are within the range of average Chinese coal values, with the exception of V, Cr, Fe, P, and Rb. On the other hand, compared with world coals, the studied coals have higher contents of B, Cr, Li, Fe, V, Rb, P, and Sc. Based on statistical analyses, most of the trace elements, show an affinity to ash yield and possible association with pyrite, kaolinite, and calcite.

1. Introduction

In the era of globalization, a rapidly increasing demand for energy and dependency of countries on energy indicate that energy will be one of the biggest problems in the world in the near future. This requires for alternative and renewable sources of energy. Today energy is indispensable factor and plays an important role in the production process (Choudry et al., 2010; Fassett and Durrani, 1994). Pakistan has been facing severe energy crisis. Pakistan needs around 15,000 to 17,000 MW electricity per day, and the demand is likely raised to approximately to 21,000 MW per day by 2016. Presently, it can produce about 15,500 MW per day and there is a shortfall of about 4000 to 4500 MW per day. At present Pakistan meets 7.5% of its energy needs by coal (Zaigham, 2003; Zaigham and Nayyar, 2005). Coal is a resource primarily used for electric power generation, and covers 41% global electricity needs (Choudry et al., 2010; Sheikh, 2010). Pakistan is a coal-rich country, but, unfortunately, coal has not been developed for power generation for more than three decades due to lack of infrastructure, insufficient financing and absence of modern coal mining technical expertise. The development of coal has an important multiplier effect by creating a number of supporting industries which can provide additional employment. Production of domestic coal will reduce the demand for imported fuels which put high pressure at Pakistan foreign exchange resources. Coal from different areas of Pakistan generally ranges from lignite to high volatile bituminous (Choudry et al., 2010; Fassett and Durrani, 1994). According to rough estimates, the

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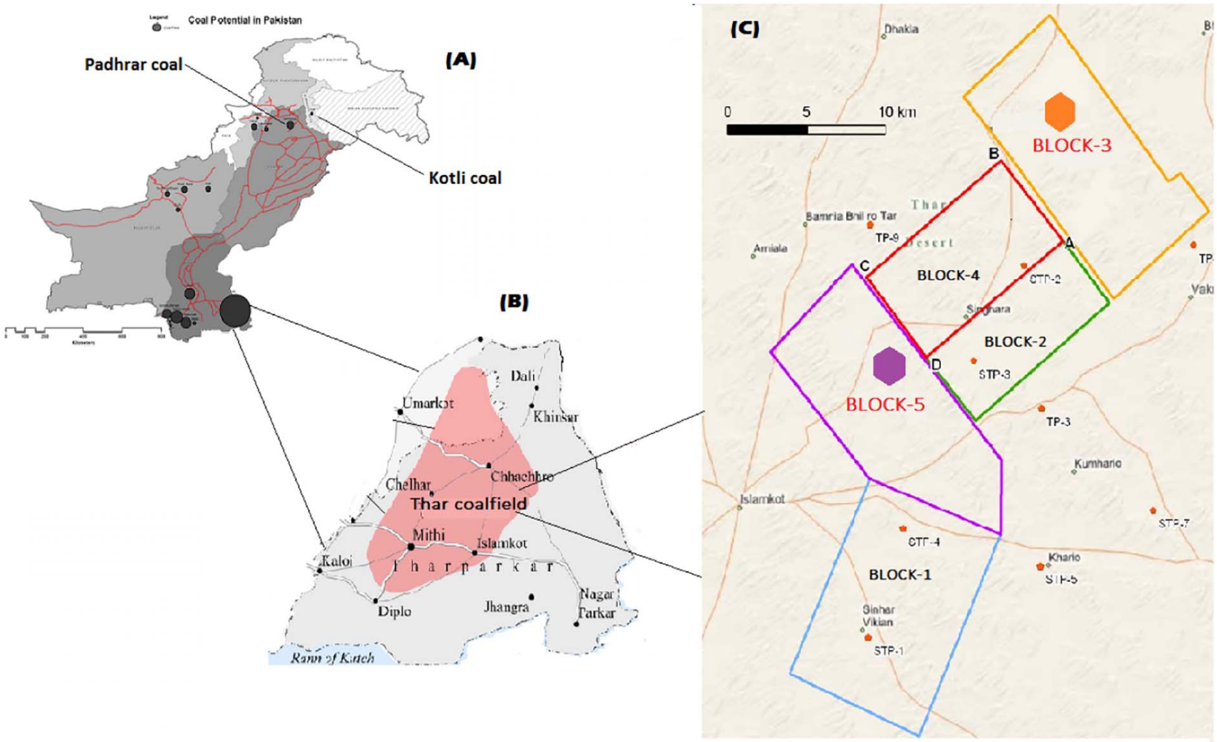

Fig. 1. (A) Map of Pakistan showing study area and distribution of coal resources in Pakistan; (B) Location of the Thar Coalfield; (C) Study map of Blocks 3 and 5, Thar coalfield, Pakistan.

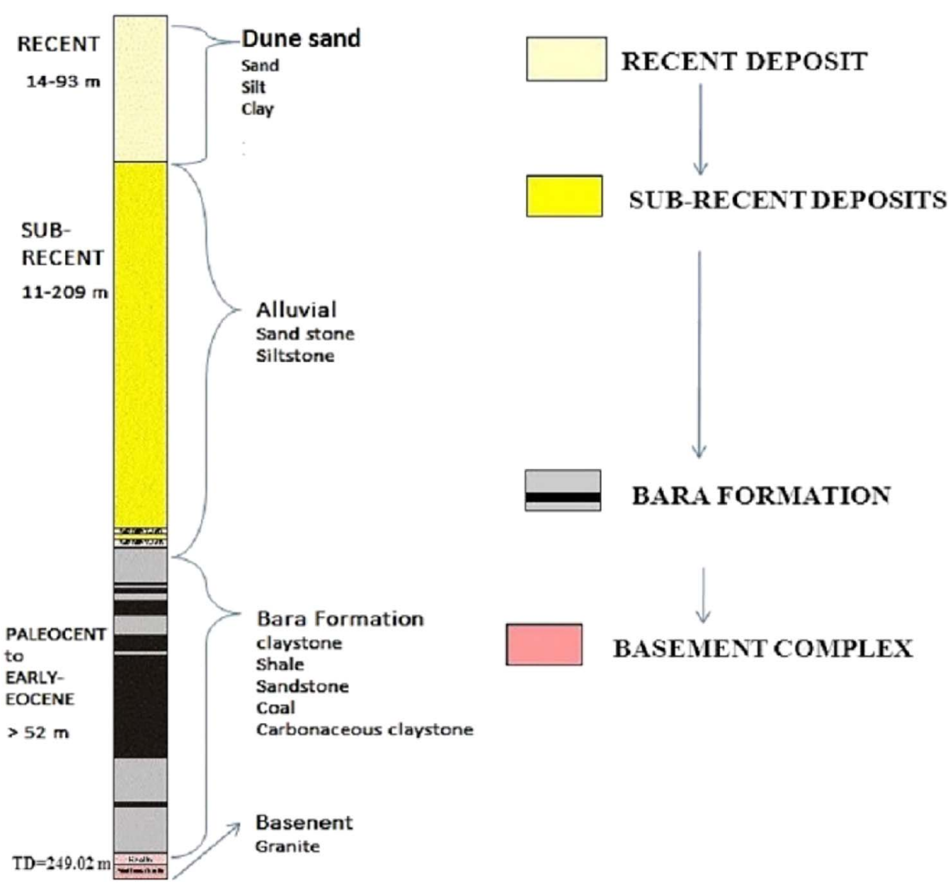

Fig. 2. Generalized stratigraphic column of the Thar coalfield.

Table 1
Sampling depth (m), proximate and ultimate analyses (%), forms of sulfur (%), and vitrinite random reflectance (%) of coals from the Padhrar, Block 3, Block 5 of the Thar coalfield and Kotli coals.

Location	Sample no.	No. of replications	Sampling depth (m)	M_{ad}	A_d	V_{daf}	C_{Fix}	C_{daf}	H_{daf}	N_{daf}	O_{daf}	$S_{t,d}$	$S_{s,d}$	$S_{p,d}$	$S_{o,d}$	GCV (kcal/kg)	R_o
Padhrar	P-1	3	132	10.52	21.47	24.45	47.56	61.03	3.80	1.21	37.96	3.98	0.18	2.11	1.68	4292.96	0.46
	P-2	3	139	10.46	24.77	29.43	31.68	65.44	3.91	1.14	25.85	6.37	0.28	3.51	2.57	3893.49	0.39
	P-3	3	164	5.96	17.65	21.87	54.51	51.95	2.99	0.87	44.19	5.11	0.28	2.77	2.06	3097.97	0.33
	P-4	3	174	5.62	21.15	26.03	47.20	61.09	3.48	1.02	34.41	5.08	0.22	2.74	2.11	3494.17	0.40
	Average			8.14	21.26	25.45	45.24	59.88	3.54	1.06	35.60	5.13	0.24	2.79	2.11	3694.65	0.40
	Min			4.14	15.62	18.96	21.59	45.84	2.45	0.72	21.36	3.35	0.12	1.78	1.42		
	Max			12.70	25.54	31.09	64.41	72.95	4.40	1.40	58.23	7.64	0.47	4.09	3.07		
Block 3	B3-S-1	3	130–145	16.52	15.58	28.68	28.22	52.73	2.24	1.17	32.86	1.61	0.11	1.12	0.40	3541.57	0.36
	B3-S-2	3	160–165	16.48	18.19	24.53	33.13	55.59	2.05	0.84	33.86	2.17	0.10	1.78	0.30	3624.55	0.40
	B3-S-3	3	185–205	17.38	22.17	31.27	35.85	64.83	2.93	1.18	40.06	2.36	0.45	1.38	0.54	4877.72	0.38
	Average			16.79	18.65	28.16	32.40	57.72	2.41	1.06	35.59	2.05	0.22	1.43	0.41	4014.61	0.38
	Min			8.53	8.86	16.31	14.06	29.99	1.27	0.59	17.60	0.91	0.06	0.64	0.21		
	Max			21.94	28.57	40.28	59.09	88.78	3.78	1.53	51.12	3.04	0.57	1.75	0.69		
Block 5	B5-S-1	3	125–135	17.27	12.82	25.11	44.79	62.04	2.08	0.73	35.15	1.98	0.10	1.22	0.68	6216.66	0.37
	B5-S-3	3	170–175	17.47	15.17	24.05	45.31	58.28	2.18	0.55	40.99	2.01	0.03	1.44	0.47	6337.58	0.40
	B5-S-4	3	245–255	18.96	16.73	26.31	38.01	53.97	2.43	0.82	42.78	2.10	0.09	1.72	0.29	5625.90	0.45
	Average			17.90	14.91	25.16	42.70	58.10	2.23	0.70	39.64	2.03	0.07	1.46	0.48	6060.05	0.40
	Min			12.12	9.95	19.37	29.07	36.59	1.62	0.44	22.55	1.53	0.10	1.20	0.23		
	Max			21.56	19.98	31.42	72.57	74.09	2.91	0.98	67.20	2.51	0.12	2.05	0.81		
Kotli	K-1	3	122.5	1.55	26.24	22.84	49.37	71.70	2.62	0.75	24.93	4.47	0.06	4.16	0.24	5601.98	0.69
	K-2	3	123.56	1.24	25.25	21.24	52.28	63.05	2.54	0.55	33.86	4.90	0.04	4.28	0.57	5756.13	0.74
	K-3	3	128	0.97	17.97	15.39	65.67	41.56	1.80	0.46	56.19	3.27	0.03	2.95	0.28	3964.82	0.50
	Average			1.25	23.15	19.82	55.77	58.77	2.32	0.59	38.32	4.21	0.04	3.80	0.37	5107.64	0.64
	Min			0.75	14.09	13.91	40.25	30.89	1.71	0.26	19.23	3.16	0.02	2.89	0.15		
	Max			1.78	32.23	25.75	69.37	77.02	2.96	0.91	67.14	5.29	0.07	4.65	0.74		

M, moisture; A, ash yield; V, volatile matter; C, carbon; H, hydrogen; N, nitrogen; S_t, total sulfur; S_s, sulfate sulfur; S_p, pyritic sulfur; S_o, organic sulfur; R_o; vitrinite reflectance; GCV, gross calorific value; ad, air-dry basis; d, dry basis; daf, dry and ash-free basis.

Table 2
Concentrations (%) of major element oxides from the Padhrar, Block 3, Block 5 of Thar coalfield and Kotli coals.

Sample no.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SiO_2/Al_2O_3	Al_2O_3/TiO_2	K-value	Al_2O_3/Na_2O
P-1	11.45	0.38	15.89	3.58	0.03	0.30	0.44	0.09	0.39	0.02	0.72	43.30	0.16	191.66
P-2	9.10	0.28	16.13	8.61	0.03	0.23	0.36	0.07	0.24	0.02	0.56	55.16	0.35	223.90
P-3	6.04	0.20	10.30	5.72	0.03	0.17	0.29	0.05	0.15	0.01	0.59	51.72	0.38	226.94
P-4	8.36	0.27	13.86	10.01	0.02	0.16	0.37	0.04	0.18	0.01	0.60	51.31	0.47	386.67
Average	8.74	0.28	14.04	6.98	0.03	0.21	0.37	0.06	0.24	0.02	0.62	50.37	0.34	257.29
B3-S-1	22.23	0.26	4.84	3.57	0.01	1.11	0.96	0.57	0.01	0.04	4.09	16.53	0.19	7.60
B3-S-2	28.54	0.23	9.72	4.13	0.01	0.97	0.92	0.57	0.01	0.03	2.71	38.39	0.15	15.80
B3-S-3	25.77	0.37	11.04	6.80	0.01	1.18	0.41	0.33	0.00	0.02	2.54	32.22	0.25	36.38
Average	25.51	0.29	8.53	4.83	0.01	1.09	0.76	0.49	0.01	0.03	3.11	29.05	0.19	19.93
B5-S-1	17.98	0.09	9.63	3.37	0.02	0.44	1.39	0.16	0.01	0.02	1.87	105.51	0.19	60.34
B5-S-3	24.32	0.11	8.38	4.85	0.01	0.46	0.22	0.16	0.01	0.02	2.96	75.96	0.17	52.95
B5-S-4	26.28	0.14	12.20	5.19	0.02	0.62	0.86	0.14	0.01	0.03	2.15	87.91	0.17	87.19
Average	22.86	0.11	10.07	4.47	0.02	0.51	0.83	0.15	0.01	0.02	2.33	89.80	0.18	66.83
K-1	43.03	0.39	16.73	6.23	0.02	1.47	0.97	0.45	0.07	0.30	2.60	42.16	0.15	37.02
K-2	32.78	0.20	12.44	7.43	0.01	2.33	1.22	0.23	0.01	0.03	2.62	78.01	0.25	63.56
K-3	26.46	0.21	10.18	4.77	0.01	1.33	0.76	0.24	0.03	0.11	2.61	60.09	0.20	50.29
Average	34.09	0.27	13.12	6.14	0.01	1.71	0.99	0.31	0.04	0.15	2.61	60.09	0.20	50.29

total coal resources of Pakistan are > 185 billion tonnes (Fassett and Durrani, 1994). Coal resources available to Pakistan exist in all four provinces and in Azad Jammu and Kashmir (AJK). Pakistan is now the 6th richest nation of the world in respect of coal resources (Jaleel et al., 2002; Rafique et al., 2008). Pakistan did not appear even on the list of coal-rich countries before the discovery of Thar Coal.

Modes of occurrence of trace elements in coal can provide useful information on technological performance, environmental and health impacts, and coal genesis (Dai et al., 2012a,b, 2002, 2016; Li et al., 2017; Zheng et al., 2017). Study of trace elements in coal has been given more concern these days owing to their environmental implications. They not only provide information regarding paleo-depositional environment and coal bearing horizons but also reveal the regional tectonic history (Chou, 2012; Li et al., 2017; Permana et al., 2013; Ren, 1996; Zheng et al., 2017). Concentration of trace elements is related to peat accumulation, diagenesis, coalification process, and interaction of organic matter with the basinal fluids (Dai et al., 2008; Permana et al., 2013; Tian et al., 2014). The major minerals in coal such as silicates, sulphides, and carbonates, are the main carrier of the elements (Dai et al., 2012a, 2012b; Finkelman, 1995; Wang et al., 2016; Tian et al., 2014). While other elements like Ge, Br, Be, B, and Cl which are normally associated with the organic matter (Xu and He, 2003; Zhao et al., 2014). The determination of trace elements in coal also reveal useful information required to address the environmental implications resulting from coal utilization (Wang et al., 2016; Zhao et al., 2014). A number of the trace elements in coal are potentially toxic, and among these Hg, As, Se, Cd, Pb, Cr, and F are the most important (Dai et al., 2012b; Kortenski and Sotirov, 2002). Although these elements are commonly at the low parts-per-million (ppm) range in the coal ashes, continuous emission from coal combustion can increase their concentration in the environment (Dai et al., 2012b). Several studies in this field have been conducted (Dai et al., 2012a; Liu et al., 2005; Permana et al., 2013; Prachiti et al., 2011). Some coal and coal burnt ashes are potential source of hazardous elements like As, Ni, Mo, Mn, F, Ge, Ga,

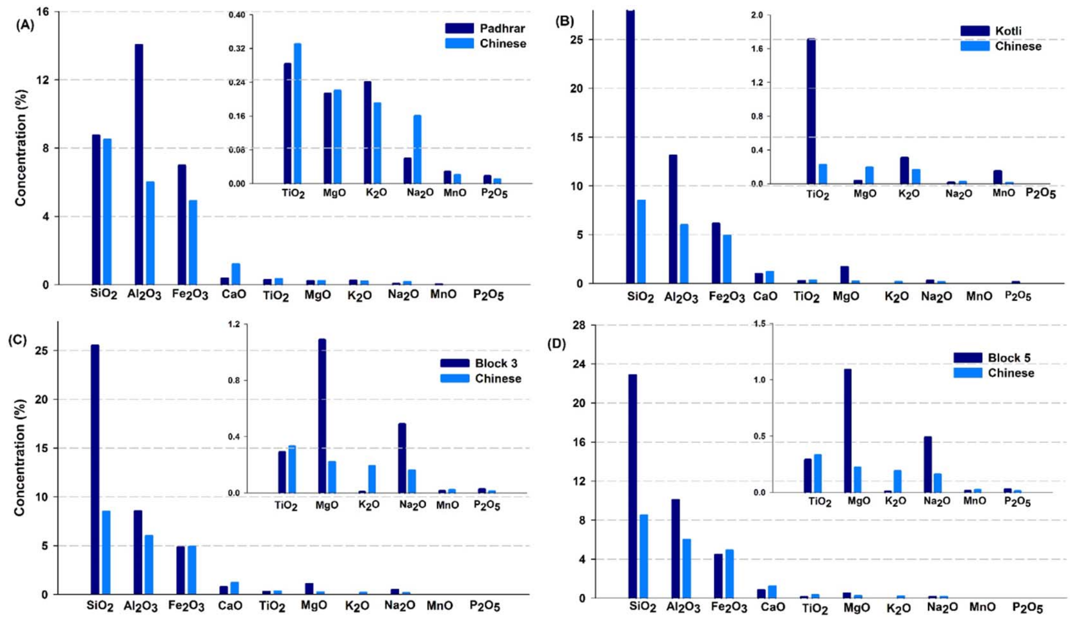

Fig. 3. Comparison of major elements oxides of (A) Padhrar coals, (B) Kotli coals, (C) Block 3, (D) Block 5 of the Thar coalfield to those of the average Chinese values.

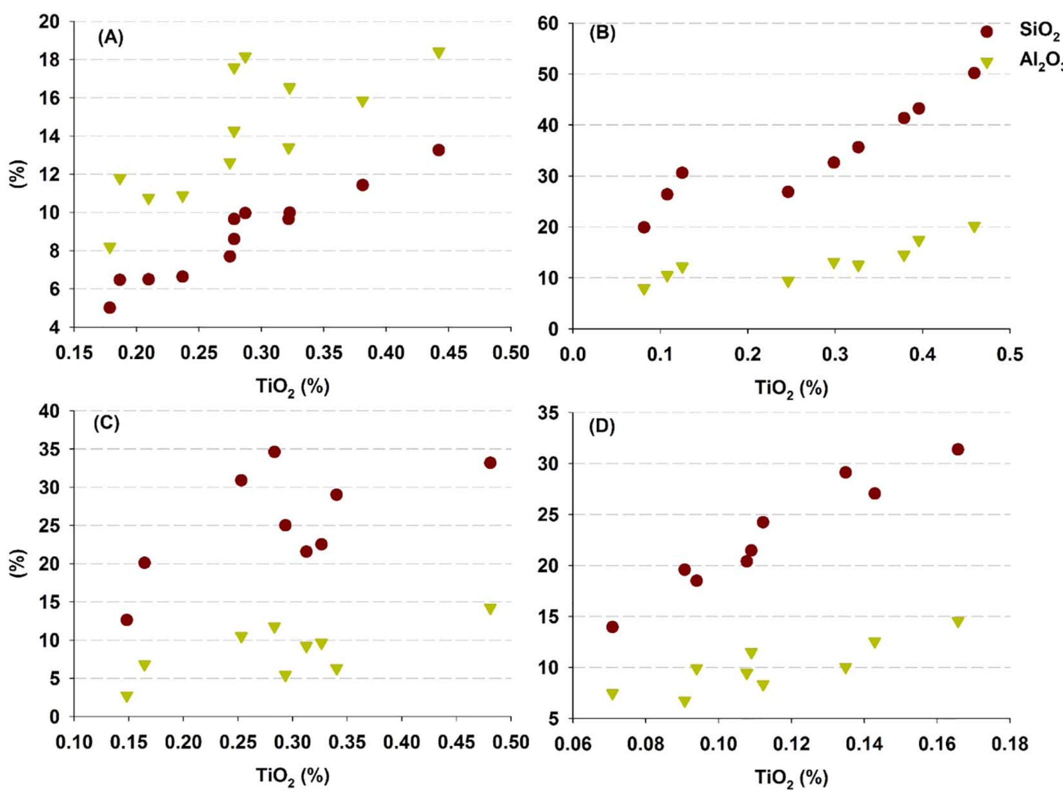

Fig. 4. Al_2O_3 vs. TiO_2 and SiO_2 vs. TiO_2 for coal samples from the (A) Padhrar, (B) Kotli, and (C) Block 3, (D) Block 5 of the Thar coalfield.

Nb, Zr, U and REEs (Silva et al., 2011; Singh and Siddique, 2015). The understanding of distribution and concentration of trace elements in coal is useful in designing suitable strategies to minimize the environmental pollution (Dai et al., 2012a, 2012b, 2016; Wang et al., 2009; M. Sun et al., 2012; Y. Sun et al., 2012).

Pakistan coals have not been studied in detail with respect to the mineralogical, concentration and distribution of trace elements and whatever data are available are only from the sporadic samples from different coal mines. Malkani (2012) have studied the coal resources and share of coal in energy sector of Pakistan. Sarwar et al. (2012, 2014) have studied the coal chemistry and morphology of Thar coalfield and concluded that the surface of coal has been characterized by macro, meso and micro-pores with the irregular aggregates of minerals of sodium, potassium, calcium, and aluminum. Previous study results showed that the Thar coals were ranked as lignite and subbituminous and, minerals identified were quartz, kaolinite, and dickite (Sarwar et al., 2014). Ali et al. (2016) applied various sequential extraction methods to assess the mercury (Hg) contents bounded with different chemical fractions of coal collected from four different seams of the blocks III and V in Thar coalfield, Pakistan. In another study proposed

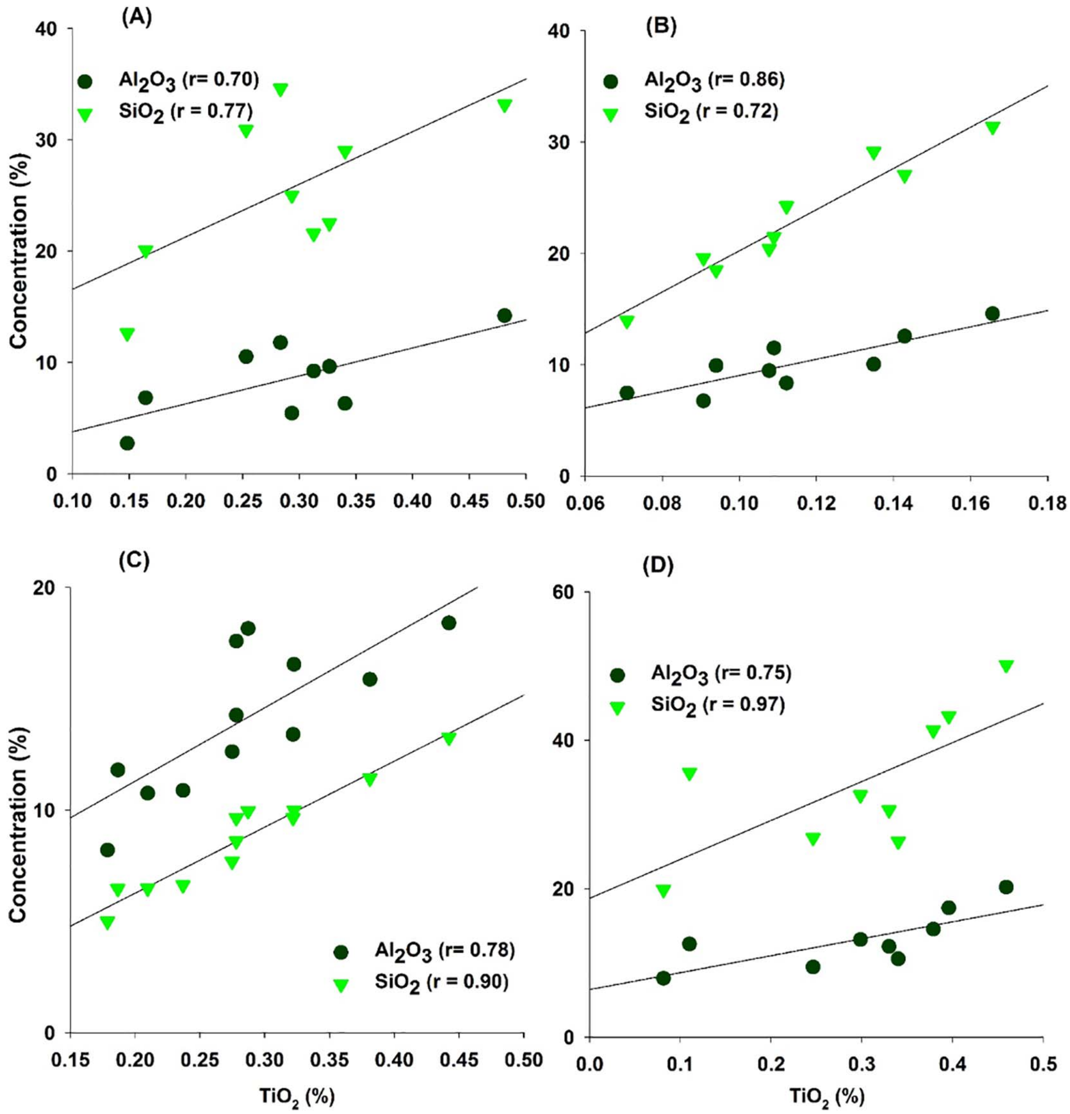

Fig. 5. Correlation between Al_2O_3 vs. TiO_2 and SiO_2 vs. TiO_2 for samples from the (A) Padhrar coals, (B) Kotli coals, and (C) Block 3, (D) Block 5 of the Thar coalfield.

by Ali et al. (2015), concluded the ultimate, proximate and exposure of arsenic (As) from coal samples collected from Thar coalfield before and after burning were evaluated. The As contents of in coal samples of site-3 of Thar coalfield was found to be higher as compared to site-5, it may be due to difference in geochemical and mineral composition. Few researchers have worked on the coal quality from Salt Range, Punjab province, such as (Ali and Khan, 2015; Malkani, 2012) studied the characterization of Khushab coal. The Kotli coal mine located near to the AJK about 80 km south-east of Islamabad (Fig. 1A). One or two coal beds occur in the steeply dipping Patala Formation. The coal beds have an average thickness of 0.6 m. The total coal resources of AJK are estimated at 0.06 million tonnes. The coal is classified as Sub-bituminous and the volatile matter (%) and sulfur contents ranges from (5.10–32.00) % and (0.30–6.80) %.

This study deals with the contents of trace elements in coal samples from the Padhrar, Kotli, and Thar coalfield (Blocks 3 and 5), including proximate parameters, forms of sulfur, trace elements and major element oxide concentrations, maceral and mineral compositions. An attempt has been made to understand the affinities of the trace elements by statistical analysis (correlation and linear multiple regression) of data on the major elements and the ash yield and sulfur contents.

2. Geological setting

The Province of Sindh is located in the south of Pakistan (Fig. 1A, B). The area is semi-arid with low rainfall. The Coalfield rests on Pre-Cambrian shield rocks and is covered by sand dunes. The coal thickness varies from 0.20–22.81 m, whereas the cumulative coal thickness in one of the drill holes is 36 m. The total coal resources of Sindh have been estimated to 184.6 billion tonnes whereas the coal deposits of Thar alone are estimated at 175.5 billion tonnes, which can ideally be utilized for power generation, covers an area of 9000 km^2. Coal resources of the four blocks are estimated at 9629 M·t (Fig. 1C). The number of coal seams varies from hole to hole, and a maximum of 20 seams have been logged in some of the drill holes. The Thar coalfield area is covered by dune sand (Fig. 2) that extends to an average depth of over 80 m and rests upon a structural platform in the eastern part of the desert. The thickness of overburden varies from 112 to 203 m. At the depth of < 275 m the basement rock is generally granite (Fig. 2). The granitic rocks of the Thar coalfield may belong to the Proterozoic malani magmatism of western Rajasthan, India (Ahmad and Chaudhry, 2007). The basement rocks comprised of epidote amphibolite facies of metamorphic rocks ranging from mafic to granite composition, the coal is grayish black, black and brownish black in color. The kaolin deposits are generally covered by thick sand dunes and alluvium extending

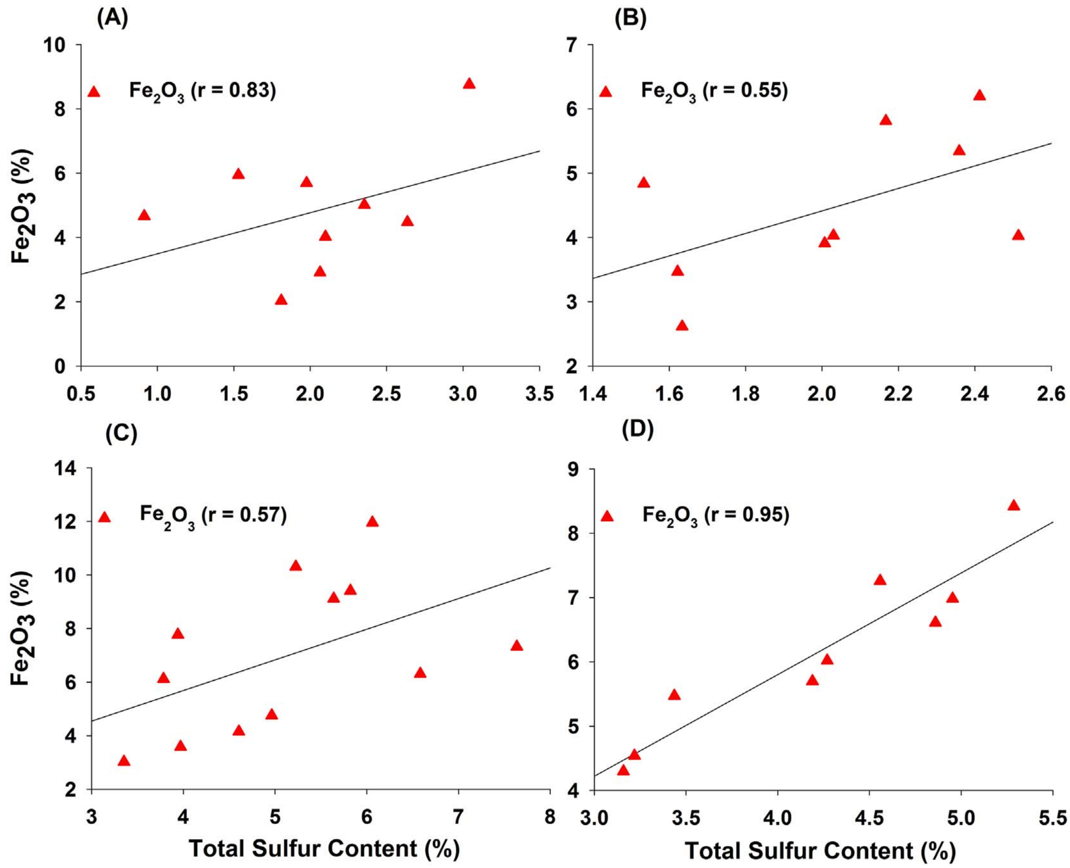

Fig. 6. Correlation between F_2O_3 vs. total sulfur contents for samples from the (A) Padhrar coals, (B) Kotli coals, and (C) Block 3, (D) Block 5 of the Thar coalfield.

down to an average depth of 30 m. The depth of the kaolin pockets is estimated to be 2–8 m below the surface (Naseem et al., 2010). The Paleocene-Eocene coal bearing horizons of claystone, carbonaceous claystone, sandstone and siltstone occur with interlaminated coal beds shown in Fig. 2.

Fig. 2 shows that the coal bearing horizon of the Paleocene-Eocene sediments above the basement complex is designated as bara-formation and has highly altered kaolinite (Ahmad and Chaudhry, 2007; Malkani, 2012). It was reported in the literature that geo-electrical drilling and geo-physical log data indicate four major divisions of lithological sequences in the whole Thar coalfield shown in (Figs. 1C, 2). These zones are sand dune, sub-recent deposits, coal bearing formations of Paleocene, igneous and basement complex of Precambrian age (Rafique et al., 2008; Zaigham, 2003). The overburden consists of three kinds of material; sedimentary sequence, alluvium, and dune sand (Fig. 2). The roof and the floor rocks are claystone and loose sandstone beds. The reserves of Block-1 show 3566 Mt with detail as 620 Mt measured, 1918 Mt indicated and 1028 Mt inferred. Block-2 shows 1584 Mt with 640 Mt measured and 944 Mt indicated, whereas Block-3 shows 2006 Mt with 411 Mt measured, 1337 Mt indicated and 258 Mt inferred reserves. Block-4 shows 2559 Mt with 637 m Mt measured, 1640 Mt indicated and 282 Mt inferred reserves with rest of Thar Coalfield (Ahmad and Chaudhry, 2007). While the main coalfields of Punjab are in the Salt-Range and at Makarwal (Fig. 1A). The Salt-Range coalfield covers an area of about 260 km^2, between Khushab, Dandot and Khewra in the Sargodha and Jhelum Districts of Punjab. The total reserves of the Salt-Range coal are approximately 213 million tonnes, Padhrar Coal project (PCP) in Khushab lies in the Salt-Range. There are more than two coal seams present in the Salt-Range, only one is mineable which varies in thickness from 0.3 m to 1.5 m with an average thickness of 0.75 m (Ali and Khan, 2015).

3. Experimental

3.1. Sampling details

To examine the mineralogical and geochemical composition of the Thar Pakistan coals, samples were collected from 3 coal seams (S-1, S-2, and S-3) of Block No. 3 and (S-1, S-2, and S-4) of Block No. 5 at different depths (125–265 m beneath surface), a total of 6 coal samples were collected from the each seam of the Blocks 3 and 5 of Thar coalfield. While 4 coal samples were collected from 4 different locations in the Padhrar coal mine from Salt-Range and 3 samples were collected from Kotli coal mine Azad Jammu & Kashmir, according to the standard procedures of ASTM for the collection of coal samples and then transported to China. Detailed information about the samples is presented in Table 1.

3.2. Analytical methods

Channel samples were air-dried, sealed in polyethylene bags to prevent contamination and oxidation, ground to pass 200 mesh sieves, and stored in bottles for chemical analyses. The proximate and ultimate analysis (i.e., A_{ad}, M_{ad}, V_{daf}, $St_{,d}$, C_{fix}, C_{ad}, H_{ad}, and N_{ad}) of the coal samples were determined in accordance with ASTM standards (ASTM Standard D3174-11, 2011; ASTM Standard D3173-11, 2011; ASTM Standard D3175-11, 2011; ASTM Standard D5373-08, 2008; and ASTM Standard D3177-02, 2007, respectively). Mean random reflectance of vitrinite (percent $R_{o, ran}$) was determined using a Leica DM-4500P microscope (at a magnification of 500 ×) equipped with a Craic QDI 302™ spectrophotometer. The maceral compositions of coal samples were determined by counting points of polished coals under a reflecting microscope according to the Chinese National Standard GB/8899-1998 (comparable to ASTM D2798-11a-2011). Mineralogical analyses of coal

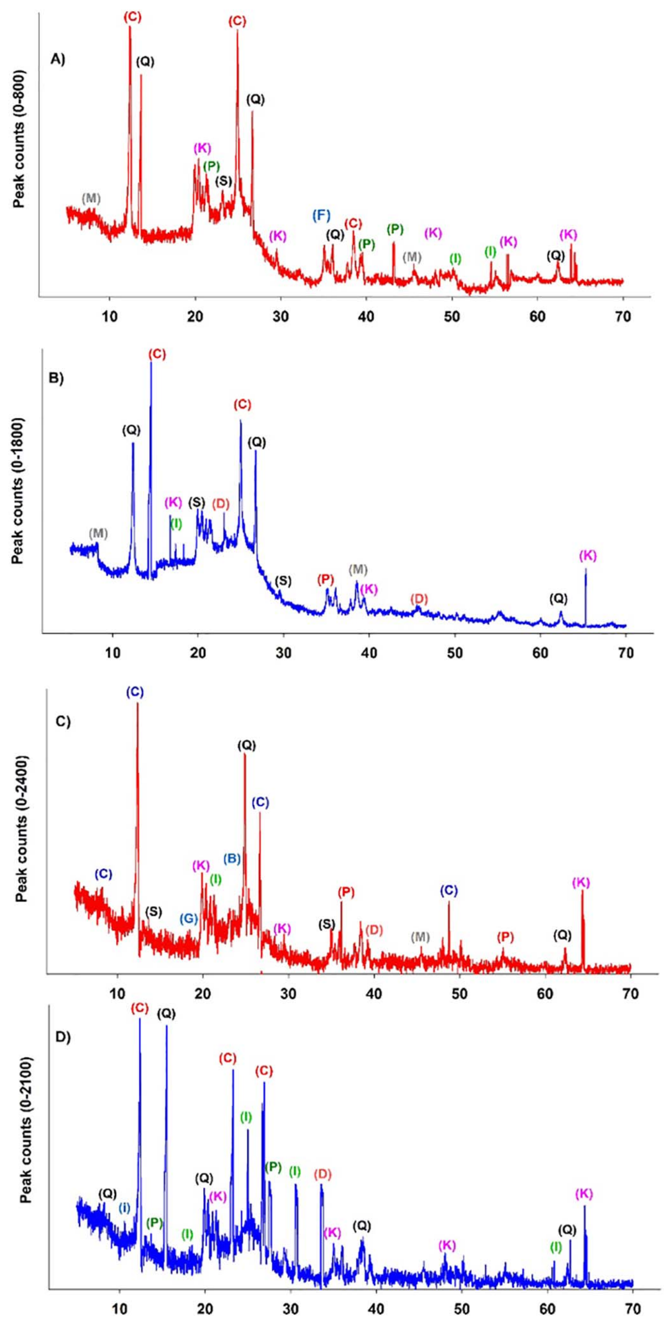

Fig. 7. The XRD diagrams of some selected samples. (A) B3-S-1 /1 sample, (B) B5-S-3 /1 sample, (C) P-2 /1 sample, (D) K-2/1 sample.

samples were performed by X-ray diffraction (XRD, Philips X'Pert PRO), using a target voltage of 40 kV, and an emission current of 30 mA with a scanning angle of 5–70° 2θ at rate of 0.1° per second. Each coal sample was also high-temperature ashed at 815 °C, and loss on ignition was calculated. X-ray fluorescence spectrometry (XRF, XRF-1800) was used to determine the oxides of major elements, including SiO_2, Al_2O_3, CaO, K_2O, Na_2O, Fe_2O_3, MnO, MgO, TiO_2, and P_2O_5, in each coal ashed sample. The major elements including Ti, Ca, Al, Fe, and P and trace elements B, Mn, Co, Rb, Sr, and Ba, in the coal samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 7300DV). While other trace elements including Be, Sc, V, Cu, Zn, Ni, As, and Cr were measured by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series 2).

3.3. Data analysis and quality assurance

The accuracy of the elements was evaluated by the standard reference material NIST-1632b (coal), while standard reference material (NIST-674b) was used to evaluate the accuracy of X-ray diffraction (XRD) method. The recovery rates (95.9–105.2%) for all the selected trace and major elements in the standard reference material of coal were within the range of the certified limitations. The recovery was ranged between 93.8 to 102.6% when digested solutions with known concentrations of elements were used. The relative standard deviation was within 5% for most of the elements in replicated samples. Each sample was analyzed thrice and accuracy of ICP-MS and ICP-AES was verified by testing two standards, after every ten (10) samples. The calibration curves for all major and trace elements were linear and within the range ($R2 > 0.99$) showing that the analytical method for major and trace elements determination was accurate and consistent. In addition, a quality control program was developed and implemented for XRF that, at a minimum includes detailed written procedures for all of the following activities: a) Procedures for performing drift checks on a daily basis, including but not limited to, zero drift, upscale drift, and sample volume measurement drift; b) Procedures and methods of adjusting your multi-metal continuous emission monitoring systems (CEMS) in response to the results of the drift checks; c) Preventative maintenance of your XRF multi-metals CEMS; d) Data recording, calculations, and reporting; e) Procedures for required audits, including transport efficiency audits (if necessary), linearity audits, and relative bias audits; f) Procedures for adjusting your CEMS based on audit results; g) A program of corrective action and stack operation procedures in case of a CEMS malfunction and an out of control period.

4. Results

4.1. Coal characteristics

The results of the ultimate and proximate analyses of samples from the Pakistani coals are tabulated in the Table 1.

For Padhrar coals, moisture and ash yield vary between 4.14–12.71% and 15.62–25.54%, respectively. While the moisture contents of the Thar coals vary from (8.83–21.94) % and ash yield ranges between (8.86–28.57) % and for Kotli coals moisture contents (0.75–1.78) % and ash yield ranges (14.09–32.23) % (Table 1). According to Chinese National Standard (GB/T, 15224.1-2004, 2004, 10.01% to 16.00% for low ash coal, 16.01% to 29.00% for medium ash coal, and > 29.00% for high ash coal) suggesting that the Padhrar, Block 3 and Kotli coals are medium ash coals, while Block 5 coals are low ash coals. The volatile matter (dry ash free basis; daf), vitrinite reflectance values (%) and gross calorific value (moisture ash free basis; maf) of coals were evaluated for coal rank classification using the ASTM (1991) classification (Stach et al., 1982). The average volatile matter, vitrinite reflectance values and gross calorific value of Padhrar (25.45%, 3694.65 kcal/kg, 0.40%, respectively), Block No. 3 (28.16%, 4014.61 kcal/kg, 0.38, respectively), Block No. 5 (14.91%, 6060.05 kcal/kg, 0.40%, respectively) of Thar coalfield, and Kotli coals (19.82%, 5107.64 kcal/kg, 0.64%, respectively) (Table 1), suggesting that the Padhrar coals are medium volatile sub-bituminous, Block 3 coals are medium-high volatile lignite to sub-bituminous, Block 5 coals are medium volatile sub-bituminous and Kotli coals are low volatile sub-bituminous rank.

The total sulfur contents of Padhrar range (on average 5.13%; 3.35–7.64%), Block 3 (on average 2.05%; 0.91–3.04%), Block 5 (on the average 2.03%; 1.53–2.51%), and Kotli vary (on the average 4.21%; 3.16–5.29%) (Table 1), indicating that the Thar coals are low-medium sulfur, while Padhrar and Kotli coals are high sulfur coals, according to Chinese National Standard (GB/T, 15224.2-2004, 2004, < 1% for low sulfur coal, 1.00% to 3.00% for medium sulfur coal, and > 3.00% for high sulfur coal). The forms of sulfur analyses of the coal samples

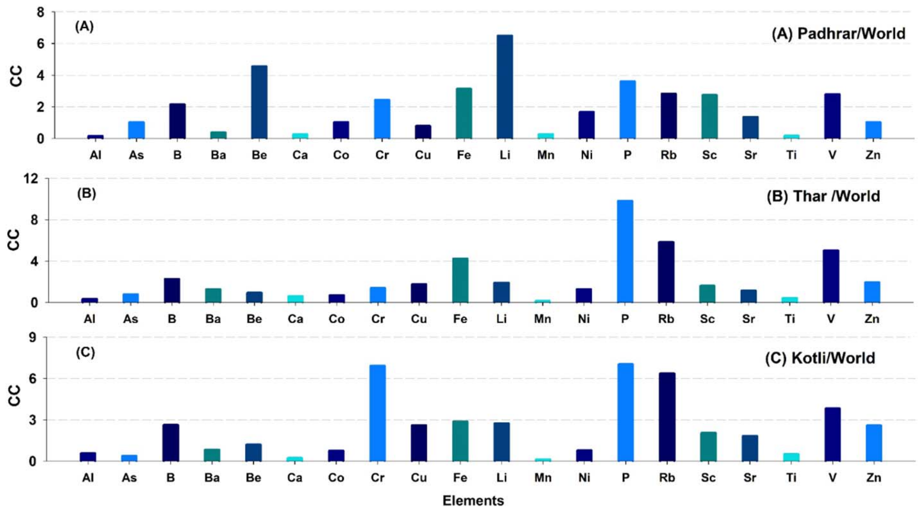

Fig. 8. Concentration coefficients of trace elements in the (A) Padhrar coals vs. world hard coals, (B) Thar coals vs. world hard coals, (C) Kotli coals vs. world hard coals. Data for trace elements in world hard coals are from Ketris and Yudovich (2009).

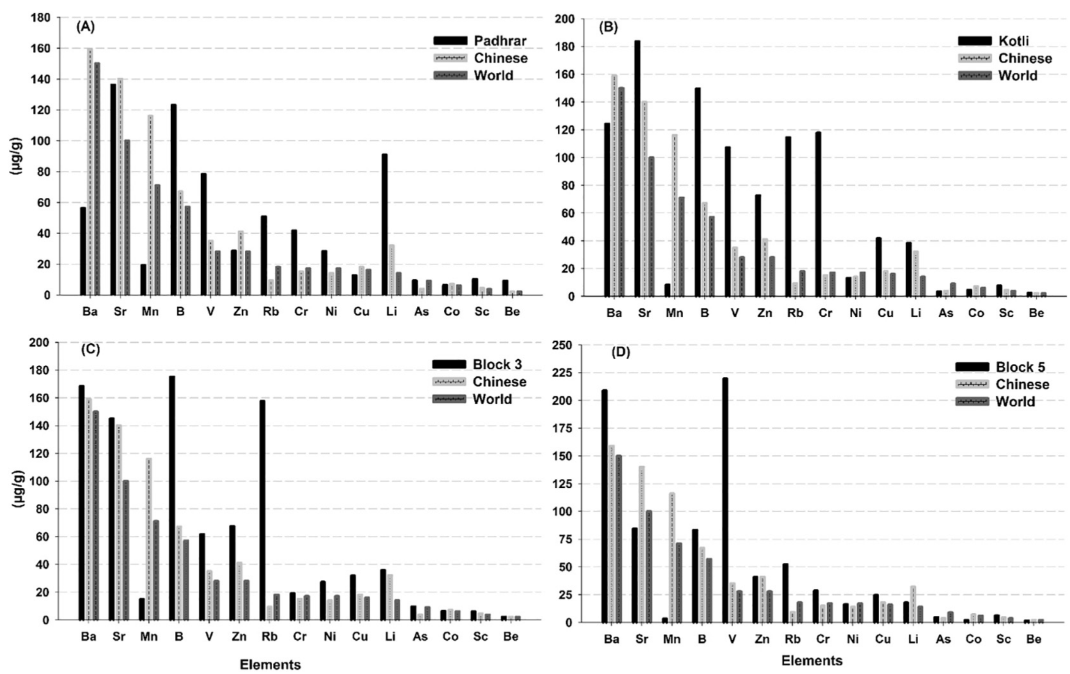

Fig. 9. Comparison of present study trace elements with average Chinese coal values. (A) Padhrar coals, (B) Kotli coals, and (C) Block 3, (D) Block 5 of the Thar coalfield.

showed that the sulfur is mainly pyritic and organic (Table 1), however; pyritic sulfur is the dominant in the Padhrar coals, Block 3, Block 5, and Kotli coals. The presence of high sulfur content was attributed to the regional volcanic activity, peat environment and as well as to alkaline depositional environments with intensive sulphide mineralization (Gürdal, 2008; Gürdal and Bozcu, 2011). The pyritic content variation in the Nos. 3 and 5 coals are correlated closely with the variation in total sulfur (Table 1). Average contents of ash yield, volatile matter contents, sulfur contents, gross calorific value, and vitrinite random reflectance of each coal seam are given in Table 1.

4.2. Major element oxides

The contents of major element oxides in the coal determined by XRF are given in Table 2 and Fig. 3. Compared with Chinese coals (Dai et al., 2012b), TiO_2, and CaO contents are depleted in the studied coals (Fig. 3). While K_2O and MnO contents are enriched in the Padhrar coals and depleted in the Thar and Kotli coals. Al_2O_3, SiO_2, MgO and P_2O_5 contents are enriched in the Padhrar, Thar and Kotli coals (Fig. 3A–D).

The SiO_2/Al_2O_3 ratio in the Padhrar coals (0.62) is lower than that in kaolinite (1.2) (Table 2; Fig. 4A), which is attributed mainly to the substitution of Si for Al in the tetrahedral sheets, while SiO_2/Al_2O_3 ratios in the Block No. 3 (on average 3.11), Block 5 (2.33), and Kotli (2.61) coals are significantly higher than the theoretical ratio for kaolinite (1.2; Dai et al., 2012b), indicating the more occurrence of free SiO_2 in the studied coals, which is in accordance with the relatively high amounts of quartz in the Kotli and Thar coals (Table 2; Fig. 4B, C, D). The $(CaO + MgO + Fe_2O_3)/(SiO_2 + Al_2O_3)$ ratio of coal (k value) is effective indicator of the depositional environment in the stage of peat accumulation (Chou, 2012; Dai et al., 2012b; Ward et al., 2001; Zhao et al., 2007). Coal with a K value ≥ 0.23 is influenced mainly by seawater during peat accumulation, and a K ≤ 0.22 value represents the influence of fresh water. The K value of Padhrar coals varies from (on the average 0.34; 0.16–0.47) is influenced by seawater during peat accumulation (Table 2), While the Thar coals (0.19; 0.15–0.25) and Kotli coals (on average 0.20) indicates that the coal is influenced by fresh water (Table 2). (See Fig. 5.)

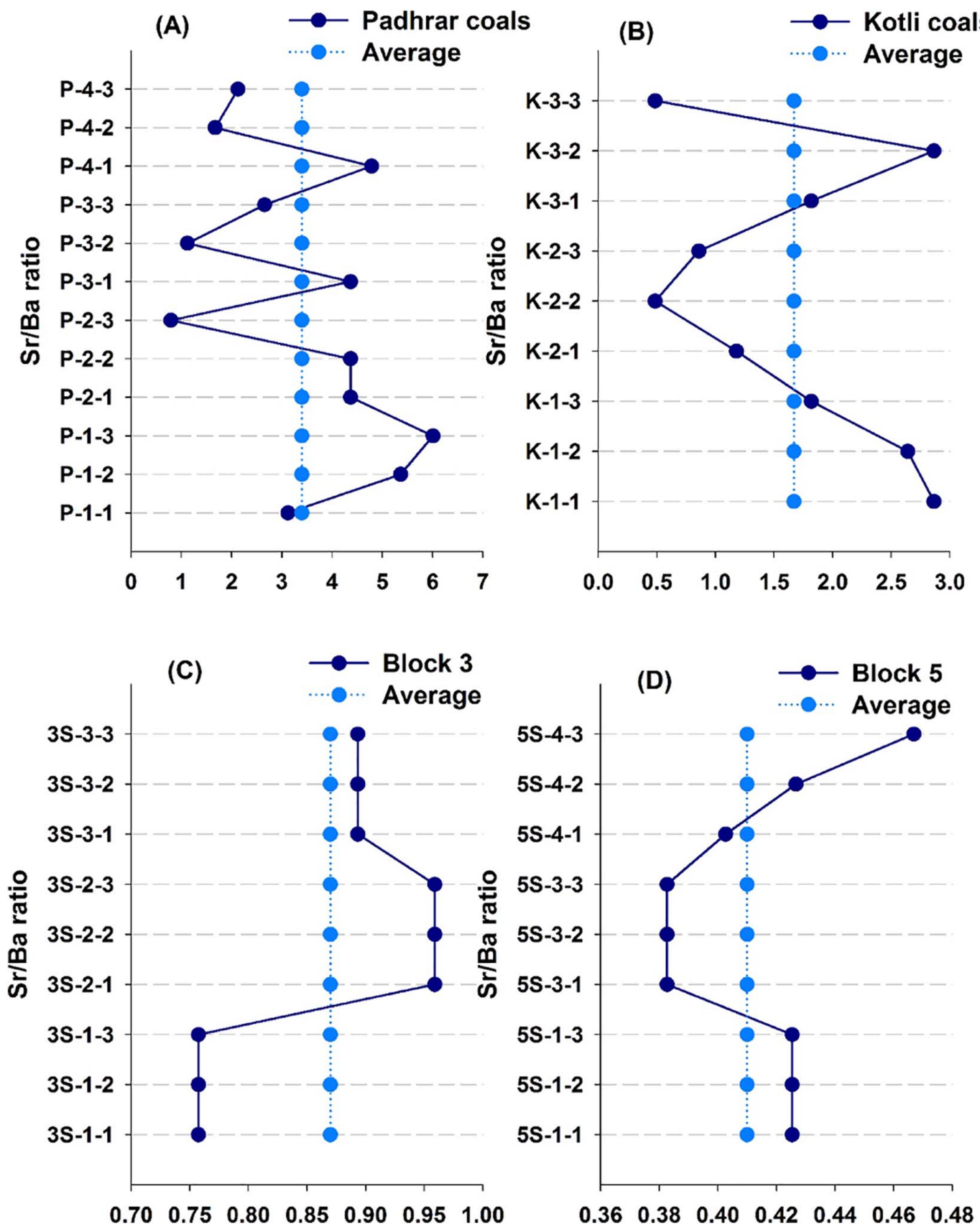

Fig. 10. Sr/Ba ratio of present study. (A) Padhrar coals, (B) Kotli coals, and (C) Block 3, (D) Block 5 of the Thar coalfield.

4.3. Maceral composition

The data concerning maceral composition (vitrinite, inertinites, fusinite, and liptinites) of selected coal mines have been presented in Table 3. Vitrinite contents are dominated in Kotli coals (71.24% on the average), while Block 3 coals contain vitrinite contents (37.37% on the average), Block 5 (52.57% on average) and Padhrar coal (57.95% on the average) (Table 3). While liptinite, fusinite, and inertinite are present in the following order (Table 3) Padhrar (fusinite < liptinite < inertinite), Kotli, and Block 3 coals (liptinite < fusinite < inertinite) and Block 5 coals (liptinite < inertinite < fusinite).

4.4. Minerals in coal

The XRD analysis results and some selected X-ray diffractograms in the Padhrar, Kotli, and Blocks 3 and 5 of the Thar coalfield are given in Table 4 and Fig. 7. The phases identified in the coals include quartz, pyrite, kaolinite, illite, along with calcite, siderite and, in some samples, montmorillonite, gypsum, and dolomite minerals were also detected (Table 4; Fig. 7). The X-ray diffractograms of the four samples selected from the Padhrar, Block Nos. 3 and 5 of the Thar coalfield and Kotli coals are shown in Fig. 7(A–D). Common major minerals identified in the crystalline matter of the LTAs from the three coals are quartz, pyrite, and kaolinite. However, mineralogy characteristic from the four coals shows a minor variation. In the Thar coals (Blocks 3 and 5) Fig. 7A, B, calcite, kaolinite and quartz are the most abundant mineral, while pyrite, montmorillonite and illite minerals are present in the lower amounts. In the Fig. 7B Block 5 coal sample quartz and kaolinite are the major mineral and the calcite, clay minerals, pyrite and dolomite contents are lower (Fig. 7B). In the Padhrar coal sample (Fig. 7C), kaolinite and calcite are the major minerals and the pyrite, quartz, dolomite, gypsum and clay mineral contents are lower. Similarly,

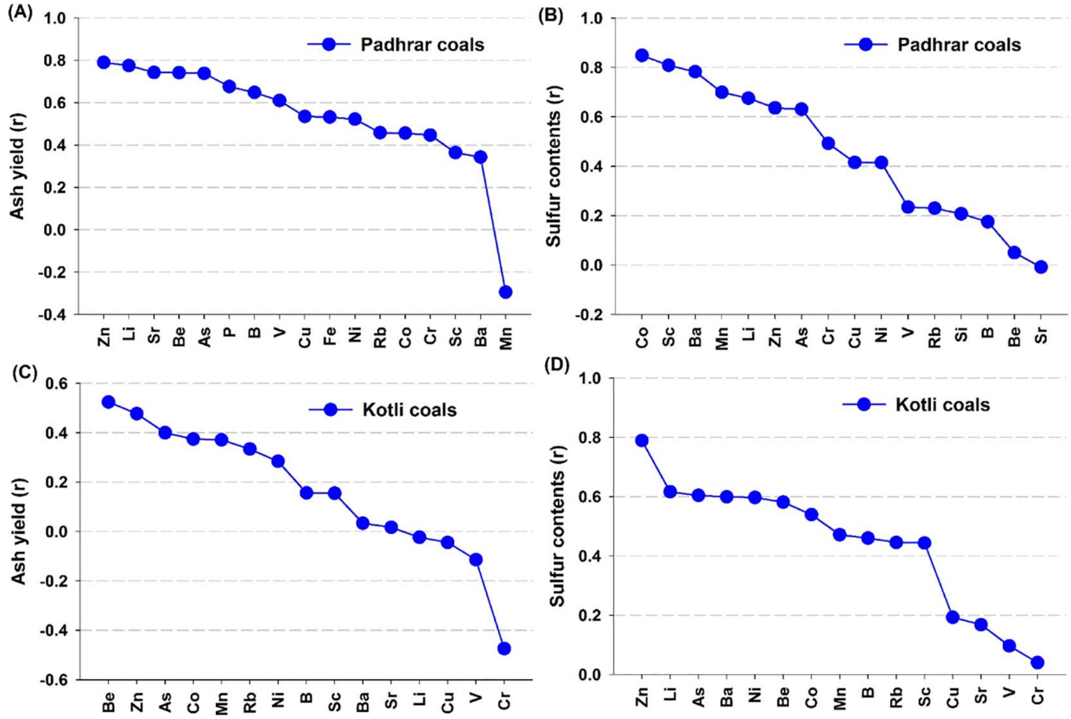

Fig. 11. Relations between ash yields, sulphur contents and trace elements. (A) Ash yields and trace elements in Padhrar coals, (B) sulfur contents and trace elements in Padhrar coals, (C) Ash yields and trace elements in Kotli coals, (D) sulfur contents and trace elements in Kotli coals.

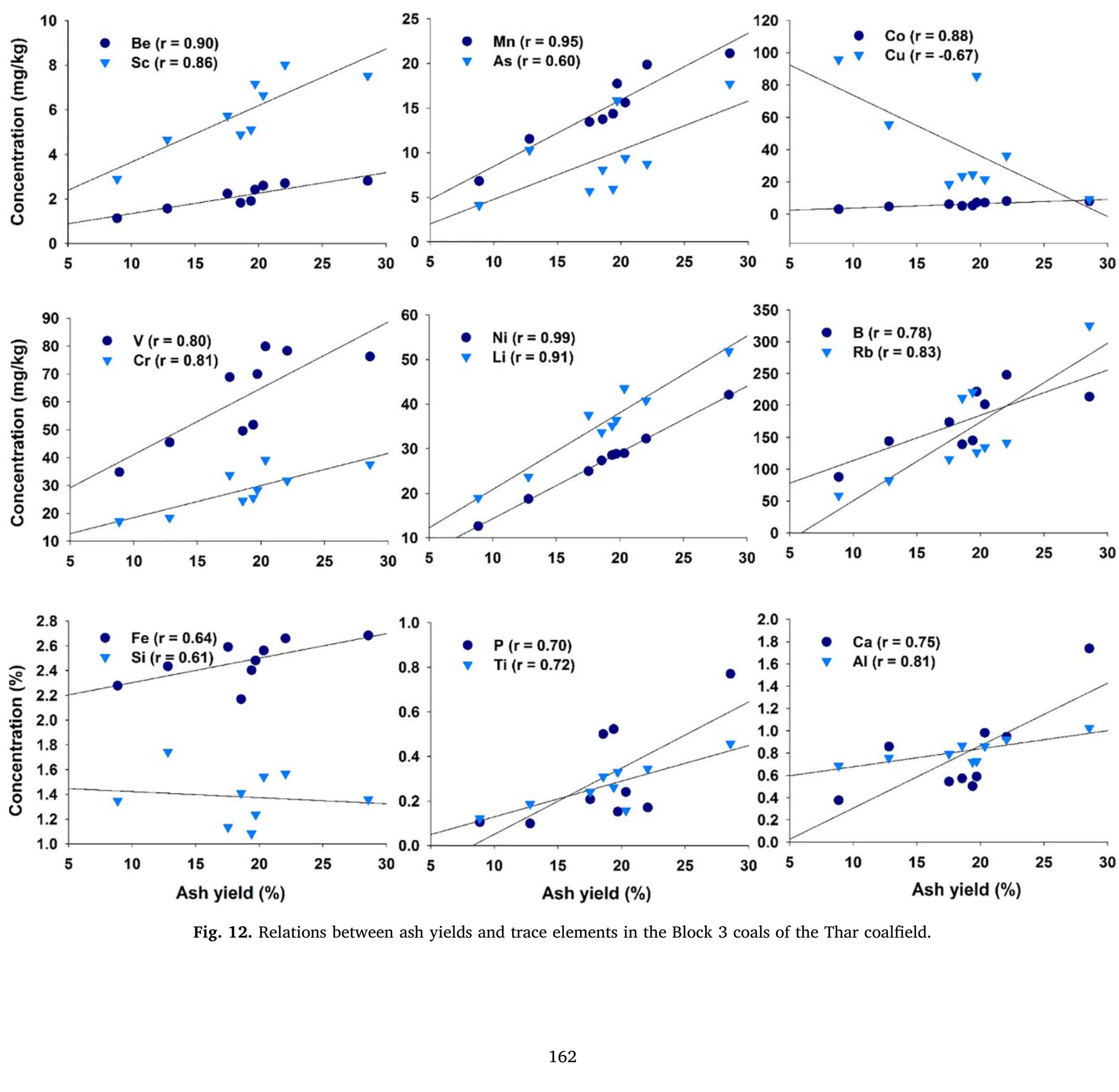

Fig. 12. Relations between ash yields and trace elements in the Block 3 coals of the Thar coalfield.

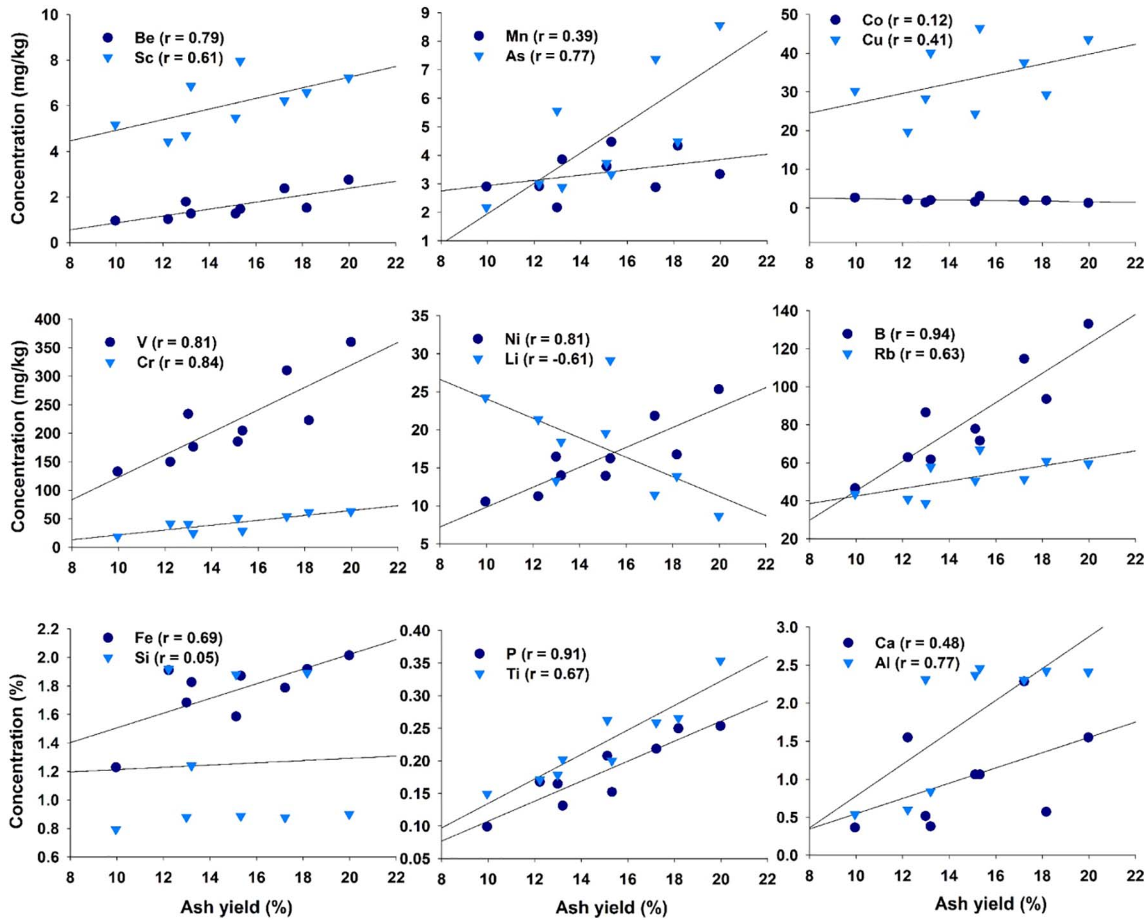

Fig. 13. Relations between ash yields and trace elements in the Block 5 coals of the Thar coalfield.

Table 3
Maceral composition of the coal samples from the Padhrar, Block 3, Block 5 of Thar coalfield and Kotli coals (vol%).

Sample no.	Vitrinite total	Liptinite total	Fusinite total	Inertinite total
P-1	70.56	11.56	7.88	29.60
P-2	58.66	18.49	15.31	27.84
P-3	49.23	12.30	13.89	17.65
P-4	53.38	8.74	5.96	22.40
Average	57.95	12.77	10.76	24.37
B3-S-1	26.55	7.90	28.76	34.66
B3-S-2	43.74	5.17	10.29	16.72
B3-S-3	41.82	4.06	12.73	15.76
Average	37.37	5.71	17.26	22.38
B5-S-1	48.40	7.54	20.94	18.80
B5-S-3	64.49	7.68	24.76	21.64
B5-S-4	44.82	8.50	15.00	17.67
Average	52.57	7.91	20.23	19.37
K-1	80.87	14.47	19.67	37.88
K-2	77.56	19.63	18.46	36.11
K-3	55.30	11.90	13.31	25.83
Average	71.24	15.33	17.15	33.27

Table 4
XRD analysis results of the samples.

Sample No.	Mineral descriptions
3S-1	Montmorillonite, quartz, kaolinite, illite, pyrite, siderite, feldspar, calcite
5S-3	Montmorillonite, quartz, kaolinite, illite, dolomite, pyrite, siderite
P-2	Calcite, quartz, pyrite, gypsum, dolomite
K-2	Calcite, quartz, pyrite, illite, feldspar

calcite, quartz, pyrite, illite, and feldspar were identified in the Kotli coal sample (Fig. 7D).

4.5. Trace elements

In contrast to the common Chinese coals (Dai et al., 2012b), the Padhrar coals are slightly enriched in Rb (50.75 μg/g), Be (9.09 μg/g), Fe (1.57 μg/g), Li (90.86 μg/g), Cr (41.55 μg/g), As (9.26 μg/g), Sc (10.16 μg/g), P (902.92 μg/g), V (78.24 μg/g), and Ni (28.30 μg/g) (with enrichment factors between 2 and 6; Fig. 9A; Tables 5, 6, 7); and the Thar coals are slightly enriched in Rb (104.82 μg/g), P (2452.51 μg/g), Fe (2.12 μg/g), V (61.64 μg/g), and B (129.11 μg/g) (with enrichment factors between 2 and 12; Fig. 9B, C, Tables 5, 6, 7). While the Kotli coals are enriched in Rb, Cr (117.76 μg/g), P (149.55 μg/g), Fe (1.43 μg/g), V (107.11 μg/g), Cu (41.60 μg/g), and B (149.55 μg/g) (with enrichment factors between 2 and 13; Fig. 9D; Tables 5, 6, 7). Other elements such as Sr and Br in the Padhrar coals, As, Cr, Cu, Ni, Sc, Zn, Ba, Ti, and Ca in the Thar coals and Zn, Sc, Sr, Ti, Li, and Be in the Kotli coals are close to the average Chinese coals (with enrichment factors between 1–2; Fig. 9A–D; Tables 5, 6, 7). All other trace elements are depleted in the studied coal, compared to average Chinese coal values (Table 7). While compared to the world coals (Ketris and Yudovich, 2009), the Padhrar coals are significantly enriched in Li (6.48 ×) and slightly enriched in Be (4.55 ×), P (3.61 ×), Fe (3.13 ×), Rb (2.82 ×), V (2.79 ×), Sc (2.74 ×), Cr (2.44 ×), and B (2.16 ×) (Table 7; Fig. 8A); the Thar coals are significantly enriched in P (9.81 ×), Rb (5.82 ×), V (5.02 ×), and slightly enriched in Fe (4.23 ×) and B (2.27 ×) (Table 7; Fig. 8B); the Kotli coals are significantly enriched in P (7.03 ×), Cr (6.93 ×), and Rb (6.36 ×), and slightly enriched in V (3.83 ×), Fe (2.87 ×), Li (2.74 ×), B (2.62 ×), Cu (2.60 ×),

Table 5
Trace element concentrations (μg/g) in the Padhrar, Block 3, Block 5 Thar coalfield and Kotli coals.

	Sample No.	Li	Be	B	P	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Ba	Ti (%)	Ca (%)	Al (%)	Fe (%)	Si (%)
Padhrar coal	P-1-1	87.63	11.55	128.18	1158.47	9.48	91.56	62.06	19.69	5.61	24.97	12.66	30.60	6.92	78.15	173.36	55.55	0.36	0.47	0.49	1.57	0.61
	P-1-2	101.65	13.40	148.68	1343.83	11.00	106.21	71.99	22.83	6.51	28.97	14.68	35.49	8.03	90.66	201.10	37.48	0.14	0.37	0.60	1.64	0.74
	P-1-3	74.00	9.76	108.24	978.31	8.01	77.32	52.41	16.62	4.74	21.09	10.69	25.84	5.85	66.00	146.40	24.36	0.09	0.14	0.53	1.48	0.65
	P-2-1	88.27	10.00	195.52	1158.47	8.21	65.07	50.78	15.93	5.25	25.42	10.08	32.09	12.83	45.09	149.72	34.28	0.03	0.09	0.64	1.59	0.77
	P-2-2	91.12	10.32	201.86	1196.01	8.48	67.18	52.42	16.44	5.42	26.25	10.41	33.13	13.24	46.55	154.57	35.39	0.19	0.14	0.66	1.61	0.80
	P-2-3	110.49	9.33	120.00	672.68	16.90	87.24	57.14	34.18	9.59	30.81	14.68	37.32	10.30	46.10	132.08	166.98	0.05	0.19	0.43	1.61	0.52
	P-3-1	59.23	6.71	131.21	777.40	5.51	43.67	34.08	10.69	3.52	17.06	6.76	21.53	8.61	30.25	100.47	23.00	0.07	0.76	0.58	1.59	0.73
	P-3-2	95.25	8.04	103.45	579.90	14.57	75.21	49.26	29.46	8.27	26.56	12.66	32.17	8.88	39.74	113.87	101.52	0.08	0.57	0.80	1.58	1.00
	P-3-3	71.82	6.06	78.00	437.24	10.99	56.71	37.14	22.22	6.23	20.03	9.54	24.26	6.69	29.97	85.85	32.31	0.03	0.43	0.68	1.51	0.85
	P-4-1	106.68	8.21	89.56	869.19	9.86	92.21	95.05	14.66	6.62	40.63	16.52	24.15	10.22	46.83	129.23	26.99	0.03	0.20	0.65	1.56	0.78
	P-4-2	123.75	9.53	103.89	1008.25	11.44	106.97	110.25	17.00	7.68	47.13	19.16	28.01	11.86	54.32	149.91	89.56	0.06	1.00	0.73	1.52	0.87
	P-4-3	80.44	6.19	67.53	655.37	7.43	69.53	71.66	11.05	4.99	30.64	12.46	18.21	7.71	35.31	97.44	45.87	0.04	0.59	0.57	1.54	0.69
	Average	90.86	9.09	123.01	902.93	10.16	78.24	62.02	19.23	6.20	28.30	12.52	28.57	9.26	50.75	136.17	56.11	0.10	0.41	0.61	1.57	0.75
	Min.	59.23	6.06	67.53	437.24	5.51	43.67	34.08	10.69	3.52	17.06	6.76	18.21	5.85	29.97	85.85	23.00	0.03	0.09	0.43	1.48	0.52
	Max.	123.75	13.40	201.86	1343.83	16.90	106.97	110.25	34.18	9.59	47.13	19.16	37.32	13.24	90.66	201.10	166.98	0.36	1.00	0.80	1.64	1.00
Block 3 coal	3S-1-1	37.52	2.24	173.87	2074.42	5.73	68.85	33.71	13.44	6.25	24.98	18.59	72.81	5.67	115.75	150.08	198.13	0.24	0.54	0.79	2.59	1.13
	3S-1-2	43.52	2.60	201.69	2406.33	6.65	79.87	39.11	15.59	7.25	28.97	21.57	84.46	9.37	134.27	174.09	229.83	0.16	0.98	0.86	2.56	1.54
	3S-1-3	18.95	1.13	87.84	1047.96	2.89	34.78	17.03	6.79	3.16	12.62	9.39	36.78	4.08	58.48	75.82	100.09	0.12	0.38	0.69	2.28	1.35
	3S-2-1	40.77	2.70	248.19	1707.74	8.02	78.30	31.70	19.85	8.18	32.26	95.76	70.60	8.73	141.65	135.67	141.45	0.35	0.95	0.92	2.66	1.57
	3S-2-2	36.41	2.41	221.68	1525.35	7.16	69.94	28.31	17.73	7.30	28.81	85.53	63.06	15.81	126.52	121.18	126.34	0.33	0.59	0.73	2.48	1.24
	3S-2-3	23.67	1.57	144.09	991.48	4.66	45.46	18.40	11.52	4.75	18.73	55.60	40.99	10.27	82.24	78.77	82.12	0.19	0.86	0.76	2.43	1.74
	3S-3-1	35.17	1.90	145.13	5225.19	5.11	51.75	25.54	14.34	5.41	28.56	24.64	69.00	5.92	220.90	165.76	185.56	0.26	0.50	0.72	2.40	1.08
	3S-3-2	51.81	2.80	213.80	7697.75	7.52	76.24	37.62	21.12	7.97	42.07	36.30	101.65	17.70	325.42	244.20	273.37	0.46	1.74	1.02	2.68	1.36
	3S-3-3	33.68	1.82	138.97	5003.54	4.89	49.55	24.45	13.73	5.18	27.35	23.59	66.07	8.08	211.53	158.73	177.69	0.31	0.57	0.87	2.17	1.41
	Average	35.72	2.13	175.03	3075.53	5.85	61.64	28.43	14.90	6.16	27.15	41.22	67.27	9.51	157.42	144.92	168.29	0.27	0.79	0.82	2.47	1.38
	Min.	18.95	1.13	87.84	991.48	2.89	34.78	17.03	6.79	3.16	12.62	9.39	36.78	4.08	58.48	75.82	82.12	0.12	0.38	0.69	2.17	1.08
	Max.	51.81	2.80	248.19	7697.75	8.02	79.87	39.11	21.12	8.18	42.07	95.76	101.65	17.70	325.42	244.20	273.37	0.46	1.74	1.02	2.68	1.74
Block 5 coal	5S-1-1	18.43	1.27	61.75	1315.00	6.86	176.19	24.53	3.86	1.99	14.00	40.07	43.90	2.88	57.72	90.05	211.68	0.20	0.38	0.84	1.83	1.24
	5S-1-2	29.13	1.48	71.63	1525.40	7.96	204.37	28.45	4.47	3.07	16.24	46.48	50.93	3.34	66.96	104.46	245.55	0.20	1.06	2.46	1.87	0.89
	5S-1-3	24.23	0.96	46.56	991.51	5.18	132.84	18.49	2.91	2.64	10.56	30.21	33.10	2.17	43.52	67.90	159.61	0.15	0.37	0.54	1.23	0.79
	5S-3-1	21.38	1.03	62.92	1680.12	4.43	149.77	41.23	2.92	2.13	11.27	19.68	36.99	3.01	40.88	58.84	153.75	0.17	1.55	0.60	1.91	1.92
	5S-3-2	13.90	1.53	93.58	2498.64	6.59	222.73	61.32	4.34	1.90	16.76	29.26	55.01	4.48	60.80	87.50	228.66	0.27	0.57	2.43	1.92	1.89
	5S-3-3	19.59	1.27	77.86	2078.87	5.48	185.31	51.02	3.61	1.58	13.94	24.35	45.77	3.73	50.59	72.80	190.24	0.26	1.06	2.37	1.59	1.88
	5S-4-1	11.46	2.38	114.74	2188.00	6.23	310.17	54.10	2.88	1.84	21.84	37.52	34.50	7.38	51.32	95.31	236.70	0.26	2.29	2.31	1.79	0.88
	5S-4-2	8.64	2.76	133.10	2538.08	7.23	359.80	62.75	3.34	1.28	25.33	43.53	40.02	8.56	59.54	110.56	274.57	0.35	1.55	2.41	2.02	0.90
	5S-4-3	13.30	1.79	86.52	1649.75	4.70	233.87	40.79	2.17	1.38	16.47	28.29	26.01	5.57	38.70	71.87	178.47	0.18	0.52	2.31	1.68	0.88
	Average	17.78	1.61	83.19	1829.49	6.07	219.45	42.52	3.39	1.98	16.27	33.27	40.69	4.57	52.23	84.36	208.80	0.23	1.04	1.81	1.76	1.25
	Min.	8.64	0.96	46.56	991.51	4.43	132.84	18.49	2.17	1.28	10.56	19.68	26.01	2.17	38.70	58.84	153.75	0.15	0.37	0.54	1.23	0.79
	Max.	29.13	2.76	133.10	2538.08	7.96	359.80	62.75	4.47	3.07	25.33	46.48	55.01	8.56	66.96	110.56	274.57	0.35	2.29	2.46	2.02	1.92
Kotli coal	K-1-1	27.90	2.84	64.34	1589.00	8.18	127.66	94.08	5.21	3.11	8.78	47.49	60.74	2.50	63.96	226.60	79.12	0.19	0.25	2.34	1.42	0.89
	K-1-2	32.37	3.30	74.63	1843.24	9.49	148.08	109.13	6.04	3.61	10.19	55.09	70.46	2.90	74.19	262.85	91.78	0.22	0.40	2.39	1.39	0.91
	K-1-3	47.85	2.64	128.18	1433.00	9.62	171.97	394.24	4.79	3.34	11.98	60.84	68.80	2.76	63.02	262.66	144.48	0.25	0.26	2.41	1.57	0.92
	K-2-1	55.51	3.06	148.68	1662.28	11.16	199.48	457.32	5.55	3.87	13.90	70.58	79.81	3.20	73.11	304.69	167.60	0.22	0.20	2.33	1.54	1.56
	K-2-2	49.37	2.24	312.47	2788.66	6.48	36.17	63.27	18.06	8.87	23.13	23.39	109.55	6.08	262.82	90.26	185.79	0.26	0.28	2.19	1.55	1.47
	K-2-3	42.56	1.93	269.37	2404.02	5.59	31.19	54.54	15.57	7.65	19.94	20.16	94.44	5.24	226.57	77.81	160.16	0.23	0.29	2.23	1.26	1.49
	K-3-1	36.08	1.99	96.64	1080.48	7.25	129.66	297.26	3.61	2.52	9.04	45.88	51.88	2.08	47.52	198.05	108.94	0.29	0.57	2.16	1.46	1.45
	K-3-2	21.04	2.14	48.51	1198.11	6.17	96.25	70.94	3.93	2.35	6.62	35.81	45.80	1.88	48.23	170.86	59.65	0.59	0.54	2.30	1.39	1.54
	K-3-3	32.09	1.45	203.10	1812.63	4.21	23.51	41.13	11.74	5.77	15.03	15.20	71.21	3.95	170.83	58.67	120.76	0.34	0.35	2.22	1.32	1.49
	Average	38.31	2.40	149.55	1756.82	7.57	107.11	175.77	8.28	4.57	13.18	41.60	72.52	3.40	114.47	183.61	124.25	0.29	0.35	2.29	1.43	1.30
	Min.	21.04	1.45	48.51	1080.48	4.21	23.51	41.13	3.61	2.35	6.62	15.20	45.80	1.88	47.52	58.67	59.65	0.19	0.20	2.16	1.26	0.89
	Max.	55.51	3.30	312.47	2788.66	11.16	199.48	457.32	18.06	8.87	23.13	70.58	109.55	6.08	262.82	304.69	185.79	0.59	0.57	2.41	1.57	1.56

Table 6
Average contents of trace element in each location/seam (μg/g) from the Padhrar, Block 3, Block 5 of Thar coalfield and Kotli coals.

Location	Sample no.	Li	Be	B	P	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Ba	Ti (%)	Ca (%)	Al (%)	Fe (%)
Padhrar coal	P-1	87.76	11.57	128.37	1160.20	9.50	91.70	41.64	19.71	5.62	25.01	12.67	30.64	6.93	78.27	173.62	39.13	0.19	0.33	0.54	1.56
	P-2	96.63	9.88	172.46	1009.05	11.20	73.17	35.81	22.18	6.75	27.49	11.72	34.18	12.12	45.91	145.46	78.88	0.09	0.14	0.58	1.60
	P-3	75.43	6.94	104.22	598.18	10.36	58.53	26.91	20.79	6.01	21.22	9.65	25.99	8.06	33.32	100.06	52.28	0.06	0.58	0.69	1.56
	P-4	103.62	7.98	86.99	844.27	9.58	89.57	61.86	14.24	6.43	39.47	16.05	23.46	9.93	45.49	125.53	54.14	0.05	0.60	0.65	1.54
Block 3 coal	3S-1	33.33	1.99	154.47	1842.90	5.09	61.17	20.07	11.94	5.55	22.19	11.40	64.68	6.37	102.83	133.33	176.02	0.17	0.63	0.78	2.48
	3S-2	33.62	2.23	204.66	1408.19	6.61	64.57	17.51	16.37	6.74	26.60	64.38	58.22	11.60	116.80	111.87	116.64	0.29	0.80	0.80	2.52
	3S-3	40.22	2.18	165.97	5975.49	5.84	59.18	19.57	16.39	6.19	32.66	19.44	78.91	10.57	252.62	189.56	212.21	0.34	0.94	0.87	2.42
Block 5 coal	5S-1	23.93	1.24	59.98	1277.30	6.67	171.13	15.96	3.75	2.57	13.60	31.66	42.65	2.80	56.07	87.47	205.61	0.18	0.60	1.28	1.64
	5S-3	18.29	1.28	78.12	2085.88	5.50	185.94	34.30	3.62	1.87	13.99	16.86	45.92	3.74	50.76	73.05	190.89	0.23	1.06	1.80	1.81
	5S-4	11.14	2.31	111.45	2125.28	6.05	301.28	35.21	2.80	1.50	21.21	25.15	33.51	7.17	49.85	92.58	229.92	0.26	1.45	2.34	1.83
Kotli coal	K-1	36.04	2.93	89.05	1621.75	9.10	149.23	133.43	5.35	3.35	10.32	54.47	66.66	2.72	67.06	250.70	105.12	0.22	0.31	2.38	1.46
	K-2	49.15	2.41	243.51	2284.99	7.74	88.95	128.45	13.06	6.80	18.99	38.04	94.60	4.84	187.50	157.59	171.18	0.24	0.26	2.25	1.45
	K-3	29.74	1.86	116.09	1363.74	5.88	83.14	91.41	6.43	3.54	10.23	32.29	56.29	2.64	88.86	142.52	96.45	0.41	0.49	2.23	1.39
This study		45.67	3.81	132.69	1891.19	7.41	116.61	51.71	11.45	4.73	21.22	27.61	52.26	6.69	93.72	137.26	139.36	0.22	0.65	1.38	1.81
Chinese[a]		32.00	2.10	67.00	400.00	4.40	35.00	15.00	116.00	7.10	14.00	18.00	41.00	3.80	9.30	140.00	159.00	0.22	0.86	3.22	0.40
World[b]		14.00	2.00	57.00	250.00	3.70	28.00	17.00	71.00	6.00	17.00	16.00	28.00	9.00	18.00	100.00	150.00	0.58	1.56	4.01	0.50
UCC[c]		20	3	15	nd	13.6	107	85	nd	17	44	25	71	1.5	112	350	550	nd	nd	nd	nd

[a] From Dai et al. (2012b).
[b] World, world hard coals, from Ketris and Yudovich (2009).
[c] Taylor and McLennan (1985).

Zn (2.59 ×), and Sc (2.05 ×) and other trace elements in the studied coals are either close to (0.5 < CC < 2) or depleted (CC < 0.5) relative to world averages (Table 7; Fig. 8A–C).

5. Discussion

5.1. Depositional environment

The high sulfur coals (Banerjee and Goodarzi, 1990; Dai et al., 2012a, 2012b, 2013; Greb et al., 1999), boron contents (Alastuey et al., 2001; Du et al., 2009), k-value (Dai et al., 2013; Fu et al., 2012; Hower et al., 2002; Querol et al., 2008), and Sr/Ba ratio (Dai et al., 2016; M. Sun et al., 2012; Y. Sun et al., 2012; Li et al., 2013) are effective indexes for depositional environment. Generally sulfur contents are accumulated in a marine-influenced depositional environment. Based on the distribution of sulfur contents, coal samples from Padhrar and Kotli coal mines have higher contents of total sulfur, may have been significantly affected by marine water (Table 1). While Blocks 3 and 5 of Thar coalfield exhibit lower sulfur contents, compared to Kotli and Padhrar coals (Table 1). The ratio of Sr/Ba is another effective index for the depositional environment, all the Thar coal seams bear Sr/Ba ratios < 1 (Fig. 10C, D) suggesting the influence of brackish water during coal accumulation, while the Kotli and Padhrar coals bear Sr/Ba ratios higher than 1 indicative of marine water influence (Fig. 10A, B). Additionally, an alternative geochemical indicator for depositional environments is boron contents in coals, proposed by Goodarzi and Swaine (1994), for fresh water (< 50 μg/g), moderately brackish-water influences as (50–110) μg/g and brackish water-influenced (> 110 μg/g), is commonly adopted in other coals (Dai et al., 2012a; Ren et al., 2006; Singh and Siddique, 2015; M. Sun et al., 2012; Y. Sun et al., 2012). The boron content in the Padhrar and Kotli coals fluctuates between the coal samples (Tables 5, 6). This may result from an alternate influence of mildly brackish water and fresh water from repeated marine transgression and regression. While boron contents in the Block 3 coals are higher than 110 μg/g (Table 5) indicative of brackish water-influenced coals and Block 5 coals have B contents (50–110) μg/g (Tables 5, 6) suggesting moderately brackish-water influences.

5.2. Sediment source region

The Al_2O_3/TiO_2 ratio of coals can be used to indicate the parent rocks of sedimentary rocks and sediments (Chen et al., 2014; Dai et al., 2013). Sedimentary rocks and sediments derived from felsic have ratio ranges (21 to 70), mafic (3 to 8), and intermediate (8 to 21). The average Al_2O_3/TiO_2 ratios of Padhrar coals (on average 50.37), Block 3 coals (on average 29.05), Block 5 (89.80) and Kotli coals (60.09), indicates a parent material of felsic igneous rock (Table 2; Fig. 4). Most of the major elements in coals are present in the minerals rather than in the organic matter. The major elemental geochemistry may therefore be used to document the mineralogical variation and thus to establish the trace element–mineral associations (Querol et al., 1997; Radenovic, 2006; Spears et al., 1999; Spears and Zheng, 1999; Ward, 2002; Zhang et al., 2002). The relation between total sulfur and Fe are given in Fig. 6(A–D). In general, the correlation coefficient between total sulfur and Fe for all coal samples is positive (Fig. 6), but stronger correlations are determined in the Padhrar (r = 0.83) and Block 5 (r = 0.95) coals (Fig. 6A, D). The relatively high Fe content of Padhrar and Block 5 coals can be attributed to high pyrite in coal (Dai et al., 2006; Gürdal, 2011). The positive linear correlations of K_2O-Al_2O_3, TiO_2-Al_2O_3, MgO-Al_2O_3 and Na_2O-Al_2O_3 in the Padhrar, Blocks 3 and 5 coals indicate that these major-element oxides mainly occur in alumino-silicate phases (Table 8). According to the statistical data (Table 8), positive correlation coefficients between the major elements and the ash yields were determined, e.g., Al, Si, and Ti in the Blocks No. 3 and 5 coals strongly correlate with ash yields (Table 8; Figs. 12, 13), indicating that these

Table 7
Concentration coefficients of Padhrar salt range, Thar Coalfield and Kotli coals Pakistan.

Elements	Chinese				World			
	Padhrar coal	Thar coal	Kotli coal	This study	Padhrar coal	Thar coal	Kotli coal	This study
	CC	CC	CC	CC	CC	CC	CC	CC
Al	0.19	0.41	0.71	0.43	0.15	0.33	0.57	0.34
As	2.44	1.85	0.89	1.76	1.03	0.78	0.38	0.74
B	1.84	1.93	2.23	1.98	2.16	2.27	2.62	2.33
Ba	0.35	1.19	0.78	0.88	0.37	1.26	0.83	0.93
Be	4.33	0.89	1.14	1.81	4.55	0.94	1.20	1.90
Ca	0.48	1.06	0.41	0.75	0.26	0.59	0.22	0.42
Co	0.87	0.57	0.64	0.67	1.03	0.68	0.76	0.79
Cr	2.77	1.58	7.85	3.45	2.44	1.40	6.93	3.04
Cu	0.70	1.56	2.31	1.53	0.78	1.76	2.60	1.73
Fe	3.91	5.29	3.58	4.52	3.13	4.23	2.87	3.62
Li	2.84	0.84	1.20	1.43	6.49	1.91	2.74	3.26
Mn	0.17	0.08	0.07	0.10	0.27	0.13	0.12	0.16
Ni	2.02	1.55	0.94	1.52	1.66	1.28	0.78	1.25
P	2.26	6.13	4.39	4.73	3.61	9.81	7.03	7.56
Rb	5.46	11.27	12.31	10.08	2.82	5.82	6.36	5.21
Sc	2.31	1.35	1.72	1.68	2.74	1.61	2.05	2.00
Sr	0.97	0.82	1.31	0.98	1.36	1.15	1.84	1.37
Ti	0.44	1.12	1.31	1.00	0.17	0.43	0.50	0.38
V	2.24	4.02	3.06	3.33	2.79	5.02	3.83	4.16
Zn	0.70	1.32	1.77	1.27	1.02	1.93	2.59	1.87

CC; concentration coefficient.

elements are predominantly associated with the clay minerals in the Thar coals. While Al, Ti, and Si weekly or negatively correlate with ash yield in the Padhrar and Kotli coals (Table 8). The concentration of SiO_2 is higher than Al_2O_3 in the Kotli and Thar coal samples, probably due to the presence of quartz. The strong correlation coefficient of Ti–Al in the Block 3 ($r = 0.68$) and Block 5 ($r = 0.75$) (Fig. 4) indicated a clay association. The other major elements (Ca, Al, Fe, Si, and P) in the Thar coals also showed positive correlations with ash yields (Table 8; Figs. 12, 13) may be present in clay minerals (illite and mixed-layer clays) and feldspars in the coal. Iron and sulfur exhibit a significant positive correlation in the Padhrar ($r = 0.76$) and Kotli ($r = 0.52$) samples (Table 8), suggesting that both are associated with pyrite, as evidenced by significantly positive correlations of S-pyrite in the (Padhrar; $r = 0.62$; Kotli; r = 0.75) and Fe-pyrite in the (Padhrar; $r = 0.49$; Kotli; $r = 0.55$) coals. The correlation coefficient between CaO and MnO in the Padhrar, Kotli, Block Nos. 3 and 5 coals is (0.67, −0.75, 0.04, and −0.12), respectively, suggesting that Mn doesn't occurs in the calcite in the Kotli and Thar coals.

5.3. Affinity of the elements

The correlation of element concentrations with ash yield may provide statistical evidence for the determination of their inorganic or inorganic affinity (Eskanazy et al., 2010; Dai et al., 2012a, 2013), and may use to discuss the affinity, genesis and occurrence of elements in coal (Ali et al., 2017; Chen et al., 2015; Dai et al., 2015, 2016; Suárez-Ruiz et al., 2006; Wang et al., 2008; Zhaoet al., 2014).

5.3.1. Padhrar coals

The ash content of the Padhrar samples is positively correlated with Zn, Li, Sr, Be, As, P, B, V ($r = 0.61$–0.80), with Cu, Fe, Ni, Rb, Co, Cr ($r = 0.40$–0.60), suggesting an inorganic affinity of these elements (Table 8; Fig. 11A). While Mn, Sc, and Ba occurred in both organic and inorganic form ($r = -0.30$-0.30) (Table 8; Fig. 11A). Boron, Be, P, Rb, Sr in the Padhrar coals are significantly correlated to Al_2O_3 (Table 8). In view of the mineral compositions these elements might occur in kaolinite and/or montmorillonite (Eskenazy, 2009; Huggins et al., 2009; Suárez-Ruiz et al., 2006). While Li, Sc, V, Cr, Co, Cu, and Zn are related to CaO, indicating an association with calcite in the Padhrar coals (Chen et al., 2015; Li et al., 2012; Zhuang et al., 2012; Životić et al., 2008). Arsenic and Cr in the Padhrar coals are correlated to Fe_2O_3 (Table 8), suggesting a pyrite affinity (Cutruneo et al., 2014; Dai et al., 2014; Fu et al., 2013; Riley et al., 2012; Tian et al., 2013; Wang et al., 2008).

5.3.2. Thar coals

In detail, Ni, Li, Mn, Zn, Be, Sr, Co, Sc, Rb, Al, Cr, V, Ba, B, Ca, Ti, P, Si, As, and Fe in the Block 3 coals and P, B, Ba, Ni, V, Cr, Be, As, Al, Sr, Fe, Ti, Rb, Sc, Ca, Zn, and Cu in the Block 5 coals are positively correlated with ash yields, suggesting an inorganic affinity of these elements (Table 8; Figs. 12, 13). Only Cu in the Block 3 coals and Co and Li in the Block 5 coals are negatively correlated with ash yield and (Table 8). Arsenic, Ti, Mn, Ni, Rb, Sc, Co, Al, Sr, Ca, and Zn in the No. 3 coals and only Ca in the No. 5 coals are significantly correlated to Al_2O_3 (Table 8), indicating an association with kaolinite and/or montmorillonite in the Thar coalfield (Dai et al., 2012a; M. Sun et al., 2012; Y. Sun et al., 2012; Wang et al., 2005, 2016). Vanadium in the Block 3 coals and Cu and Sc, in the Block 5 coals positively correlated with CaO (Table 8). In view of the mineral compositions V, Cu, and Sc indicating an association with calcite in the No. 3 and No. 5 coals. Phosphorus, Rb, Sr, Ni, Zn, Li, Ti, and Ba in the Block 3 coals and P, Cr, Ti, B, Ni, V, As, Be, Ba, and Fe in the Block 5 coals strongly correlated with Fe_2O_3 suggesting a pyrite affinity (Cutruneo et al., 2014; Dai et al., 2014; Fu et al., 2016; Riley et al., 2012; Tian et al., 2011; Wang, 2009).

Boron, Sc, Co, B, Be, Mn, V, Li, Ni, Cr, Fe, Zn, and Ti in the Block 3 and P, Cr, Ti, B, Ni, V, As, Be, Ba, Al, and Fe in the Block 5 coals are strongly correlated with SiO_2 (Table 8), indicating an association with silicate and/or aluminosilicate minerals in the Block 3 and Block 5 coals (Chen et al., 2015; Eskenazy, 2009Huggins et al., 2009; Suárez-Ruiz et al., 2006; Tian et al., 2014). However, Sr may be also associated with organic matter in the Block 5 coals because a negative correlation between Sr and sulfur ($r = -0.29$) and a weak correlation between Sr and ash yield ($r = 0.05$) were determined. Cobalt and Li in the Block 5 coals are negatively correlated with ash yield but positively correlated with sulfur (Table 8), indicating a sulfur (pyrite) affinity. It is worth noting that Rb, Li, Co, and Ti present intermediate associations with both clay, calcite, and pyrite (Table 8).

Table 8
Pearson correlation coefficients between ash yields, major element oxides, and trace elements in the Padhrar, Kotli and Blocks 3 and 5 coals from the Thar Coalfield.

Items	Padhrar	Kotli	Block 3	Block 5
Ash yield	Zn (0.79), Li (0.78), Sr (0.74), Be (0.74), As (0.74), P (0.68), B (0.65), V (0.61), Cu (0.54), Fe (0.53), Ni (0.52), Rb (0.46), Co (0.46), Cr (0.45), Sc (0.36), Mn (− 0.29)	P (0.63), Be (0.52), Zn (0.48), As (0.40), Co (0.37), Mn (0.07), Rb (0.33), Al (0.31), Ni (0.28) B (0.16), Sc (0.15), Ba (0.03), Sr (0.02), Li (− 0.02), Cu (− 0.04), Fe (− 0.09), V (− 0.11), Ti (− 0.35), Ca (− 0.39), Si (− 0.39), Cr (− 0.47)	Be (0.90), Sc (0.86), Mn (0.96), As (0.60), Co (0.88), Cu (− 0.67), V (0.80), Cr (0.81), Ni (0.99), Li (0.91), B (0.78), Rb (0.83), Fe (0.64), Sr (0.61), P (0.70), Ti (0.72), Ca (0.75), Al (0.81), Si (0.68)	Be (0.79), Sc (0.61), Mn (0.39), As (0.77), Co (0.12), Cu (0.41), V (0.81), Cr (0.84), Ni (0.81), Li (− 0.61), B (0.94), Rb (0.63), Fe (0.69), Sr (0.05), P (0.91), Ti (0.67), Ca (0.48), Al (0.77)
Al_2O_3	B (0.85), Be (0.85), P (0.95), (0.65), Sr (0.89), TiO_2 (0.81), K_2O (0.71), MgO (0.72), Na_2O (0.69)	As (0.91), Be (0.65)	As (0.73), Ti (0.94), Mn (0.90), Ni (0.89), Rb (0.79), Sc (0.77), Co (0.74), Al (0.69), Sr (0.67), Ca (0.66), Zn (0.66), TiO_2 (0.93), K_2O (0.51), MgO (0.32), Na_2O (0.56)	Ca (0.60), TiO_2 (0.37), K_2O (0.61), MgO (0.62)
CaO	Li (0.75), Sc (0.60), V (0.94), Cr (0.55), Co (0.62), Cu (0.74), Zn (0.68)	Sr (0.66), Rb (0.93), Ni (0.84)	V (0.71), Cu (− 0.12),	Cu (0.58), Sc (0.53)
Fe_2O_3	As (0.84), Cr (0.58)	B (0.62), Mn (0.74)	P (0.92), Rb (0.98), Sr (0.94), Ni (0.94), Ti (0.84), Ba (0.81)	P (0.99), Cr (0.96), B (0.90), Ni (0.81), V (0.82), As (0.79), Be (0.76), Ba (0.71), Fe (0.65)
S_{td}	Mn (0.70), Ba (0.78), Sc (0.81)	Zn (0.80), Li (0.62), As (0.60), Ba (0.60), Cu (0.68), Ni (0.60), Be (0.58)	Li (0.73), Co (0.70), Ca (0.35), Cu (− 0.20)	Li (0.73), Co (0.70), Sr (− 0.39)
SiO_2	Li (0.42), Be (0.96), Ni (0.31)	Sc (0.81), Al (0.77)	Sc (0.99), Co (0.99), B (0.98), Be (0.98), V (0.94), Li (0.88), Ni (0.87)	

5.3.3. *Kotli coals*

The modes of occurrence of trace elements in the Kotli coals are slightly different than Padhrar and Thar coals. Only Be is positively correlated with ash yield in the Kotli coals and Zn, As, Co, Mn, Rb, Al, P, and Ni are weakly correlated with ash yield (r = 0.50–0.15), indicating both organic and inorganic affinities (Table 8; Fig. 11B). However the negative correlation between ash yield and B, Sc, Ba, Sr, Li, Cu, Fe, V, Ti, Ca, Si, and Cr is probably of organic affinity in the Kotli coals. It is worth mentioning that the correlation coefficient of Zn, P, Li, As, Ni, Be, Co, and Fe with Sulfur in the Kotli coals is significantly higher (Table 8; Fig. 11B), indicating that Zn is mostly associated with sulphides, e.g., pyrite (Cutruneo et al., 2014; Dai et al., 2014; Fu et al., 2016; Riley et al., 2012; Tian et al., 2011; Wang, 2009). The elements which have the lower correlation coefficients (r < 0.49) with ash content in the Kotli coals are positively correlated with total sulfur content (db) or Ca (Table 8). It was observed that organic matter has significant amounts of Ca and S elements. Therefore, Ba, Li, Zn, Ni, B, As, Co, P, Rb, and Mn that have positive correlation with Ca indicating that these elements can be associated with organic materials in the coals, besides the carbonate, sulphide and sulfate minerals (Sutcu and Karayigit, 2015).

6. Conclusion

Based on a preliminary mineralogical and geochemical investigation of the Padhrar, Thar, and Kotli coals, the conclusions are summarized below.

The medium volatile sub-bituminous coals from Padhrar coal mine, Punjab and low volatile sub-bituminous coals from Kotli, AJK are characterized by medium ash yields and high total sulfur contents. The marine water-influenced Padhrar and Kotli coals show high boron concentration and bear Sr/Ba ratios higher than 1. The presence of high sulfur content in coal is attributed to the peat environment and regional activity as well as to alkaline depositional environments with intensive sulphide mineralization. While Thar coals are medium-high volatile lignite to sub-bituminous coals characterized by low-medium ash yields coals. The brackish water-influenced Block 3 coals are medium sulfur coals show high boron contents and bear Sr/Ba ratio < 1 and Block 5 coals of Thar coalfield are moderately brackish-water influenced coals with low B contents and Sr/Ba ratio.

The major minerals in the studied coals include quartz, pyrite, kaolinite, illite, along with calcite, siderite and, in some samples, trace amounts of montmorillonite bassanite, gypsum, and dolomite. The concentrations of most trace elements, including Li, Be, P, Fe, Rb, V, Sc, Cr, and B in the Padhrar; P, Rb, V, Fe, and B in the Thar; and P, Cr, Rb, V, Fe, Li, B, Cu, Zn, and Sc in the Kotli coal samples are enriched than average world coals. While other elements, Al, Mn, Ca, As, Ti, Co, Ni, and Ba are either close to or depleted relative to world averages in the studied coals. Overall, the trace element assemblages of the Blocks 3 and 5 are similar, and are characterized by enrichment in B-P-Rb-Fe-Cr. Most of the trace elements, excluding Cu in the Block 3 coals and Li in the Block 5 coals, correlate positively with ash yields and sulfur contents, demonstrating an association with inorganic matter in the coal seam. The enrichment of trace elements in the Thar coals is dominantly influenced by sediment source region. It should also be noted that the samples with the highest trace element contents are also the samples that contain the highest ash yield and/or sulfur.

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