Geochemistry and Mineralogy of Paleocene Coal from the Padhrar and Darra Adam Khel Coalfields of Pakistan

1922—2022

Muhammad UMAIR[1, 2, 3], YANG Ruidong[1, 2, *], CHENG Wei[4] and Salman Ahmed KHATTAK[5, 6]

[1] *College of Resources and Environmental Engineering, Guizhou University, Guiyang 550025, China*
[2] *Key Laboratory of Karst Georesources and the Environment, Ministry of Education, Guizhou University, Guiyang 550025, China*
[3] *The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*
[4] *Mining College of Guizhou University, Guiyang 550025, China*
[5] *Department of Earth Sciences, University of Haripur, Haripur 22620, KP, Pakistan*
[6] *The State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*

Abstract: Pakistan is rich in coal resources, which amount to around 186 billion tons. The Paleocene Padhrar and Darra Adam Khel coalfields are located in the Central Salt Range Punjab Province and the Khyber Pakhtunkhwa Province, Pakistan, respectively. Padhrar coal has not been studied in detail and the Darra Adam Khel coalfields are newly-discovered, so no research has been done, due to security considerations. In this study, an attempt has been made to study the geochemical and mineralogical characteristics of the Padhrar and Darra Adam Khel coals, in order to learn about the coal quality, element enrichment mechanism, sedimentary medium conditions and potentially valuable elements for coal utilization. The Padhrar and Darra Adam Khel coals are low to medium ash, low moisture content, high in volatiles and high total sulfur coal. The vitrinite reflectance in Darra Adam Khel coal is higher than in Padhrar coal, indicating either a greater burial depth or the effects of Himalayan tectonism. The vitrinite content is dominant in the Padhrar and Darra Adam Khel coals, followed by inertinite and liptinite, the major minerals including quartz, clay minerals, calcite and pyrite. The trace elements Ni, As, Be Zn, Ge, Mo, Ta, W, Co and Nb, Sn, Hf, Ta, Pb, Th, Cd, In, Be, V, Cr, Zr, Ag, Li, W and Co are concentrated in some of the Padhrar and Darra Adam Khel coal samples, respectively. The Padhrar coal shows positive Ce, Eu and Gd anomalies, with most of the Darra Adam Khel coal showing negative Ce, Eu and positive Gd anomalies with high LREE. The Al_2O_3/TiO_2 values indicate that the sediment source of the Padhrar and Darra Adam Khel coals is mostly related to intermediate igneous rocks. The Sr/Ba, $SiO_2 + Al_2O_3$, $Fe_2O_3 + CaO + MgO/SiO_2 + Al_2O_3$ and high sulfur content in the Padhrar and Darra Adam Khel coals indicate epithermal and marine water influence with a tidal flat, coal-forming environment and a deltaic coal-forming environment, respectively.

Key words: mineral, trace elements, Paleocene, Padhrar coal, Darra Adam Khel coal, Pakistan

Citation: Umair et al., 2022. Geochemistry and Mineralogy of Paleocene Coal from the Padhrar and Darra Adam Khel Coalfields of Pakistan. Acta Geologica Sinica (English Edition), 96(6): 2056–2073. DOI: 10.1111/1755-6724.14953

1 Introduction

Coal is primarily used as an energy source for electricity generation and provides 41% of global energy requirements (World Coal Association, 2017) in domestic and industrial usage. Coal is also known as an economical source of critical elements, including Li, Ge, Ga, U, V, Se, rare earth elements and Y, Sc, Nb, Au, Ag, platinum group elements (PGEs), as well as some base metals, such as Al and Mg (Massari and Ruberti, 2013; Hower et al., 2016). The critical elements are important in world economies that are directly connected with technological advancement and energy efficiency (Massari and Ruberti, 2013; Hower et al., 2016). As these elements are used in greater quantities, so the conventional sources are becoming much scarce, with demand growing rapidly, due to their wide range of applications (Massari and Ruberti, 2013; Hower et al., 2016). Furthermore, many of these critical elements are only provided by a very few specific sources, i.e., specifically China and Russia, so they also become more expensive. Therefore, to meet the current global demands for such elements, it is important to find alternative sources. Coal has received much attention as a potential source of valuable elements, such as Li and Ge, that are used in the production of advanced materials and in the semiconductor industry. Ge and Li are currently utilized from Ge and Li-rich coals in China and Russia (Dai et al., 2014c). For example, China controls about 85% of world REE production (U.S. Geological Survey, 2017)

* Corresponding author. E-mail: rdyang@gzu.edu.cn

and is also the leading global producer of Ge (U.S. Geological Survey, 2016). The Shengli Coalfield is China's largest Ge-coal deposit, containing a total Ge reserve reaching 3431 tons (Dai et al., 2012c). Sun et al. (2002) were the first to demonstrate proved that Li is highly enriched and forms coal-associated Li ore deposits in the Jungar Coalfield, Mongolia, China. The Spetzugli high-Ge coal deposit is in the Pavlovka Coalfield of the southern Russian Far East (Dai et al., 2014c). The Lincang high-Ge coal deposit of Neogene age is situated in Yunnan Province, southwestern China (Dai et al., 2015b).

Pakistan has abundant coal resources, with its coal reserves being discovered in all provinces of Pakistan. Globally, Pakistan is ranked 6th in coal reserves after discovering Thar coal (Jaleel et al., 2002; Rafique et al., 2008). The country's total coal reserves are 186 billion tons (Fasset and Durrani, 1994). Declared measured reserves were 7775 million tons; indicated reserves were 19412.5 million tons; inferred reserves were 44524 million tons and 114293 million tons of hypothetical reserves. The total coal reserves in Punjab Province are 235 million tons, while Khyber Pakhtunkhwa Province’s total coal reserves are 90 million tons. The Khyber Pakhtunkhwa Province coalfields are Hangu-Orakzai, Cherat, along with some new coalfields, such as Gulakhel-Karak-Laki Marwat, Darra Adam Khel, Bagnotar-Kala Pani and Shirani, while Punjab reserves are in the east and the central Salt Range and Makarwal area of the Surghar range, with reserves of about 213 and 90 million tons, respectively. The Darra Adam Khel coalfields in Akhorwal town alone are estimated to be greater than those in the rest of Khyber Pakhtunkhwa Province. Ali and Khan (2015) and Malkani (2012) studied the properties of Padhrar coal, however, the analysis was minimal with regard to trace elements, mineralogy and coal-forming environment, while Darra Adam Khel is a newly-developed coalfield; however, due to security reasons, no comprehensive research has been conducted in these regions on coal geochemistry, mineralogy and the coal-forming environments. Therefore, to understand the depositional environment, coal quality, comprehensive utilization and economic importance, the current study aims to analyze the mineralogical, geochemical proximate and petrological characteristics of Padhrar and Darra Adam Khel coal.

2 Geological Setting

Tectonically, the study area is part of the Himalayan sequence, formed due to the collision of the Indian and Eurasian plates during the Eocene (Aitchison et al., 2007). The Himalayas consists of several major thrust faults, namely Salt Range Thrust (SRT), Main Boundary Thrust (MBT), Main Mantle Thrust (MMT) and Main Karakorum Thrust (MKT) (Gansser, 1964). These major thrust faults have divided the Himalayas into three parts: Sub-Himalayas, Lesser Himalayas and Higher Himalayas; the Sub-Himalayas lie between SRT and MBT, the Lesser Himalayas lie between MBT and MMT, with the Higher Himalayas lying between MMT and MKT. The study area includes the Padhrar and Darra Adam Khel coalfields, located in the Sub-Himalayas and Lesser Himalayas, respectively (Fig. 1). The foothills of the Himalayan Mountain range constitute the Sub-Himalayas. The MBT and SRT demarcate the Sub-Himalayas to the north and south, respectively (Yeats and Hussain, 1987). The Salt Range and Potwar region belong to the Sub-Himalayas. Towards the east of the Sub-Himalayas sits Azad Kashmir and westward the

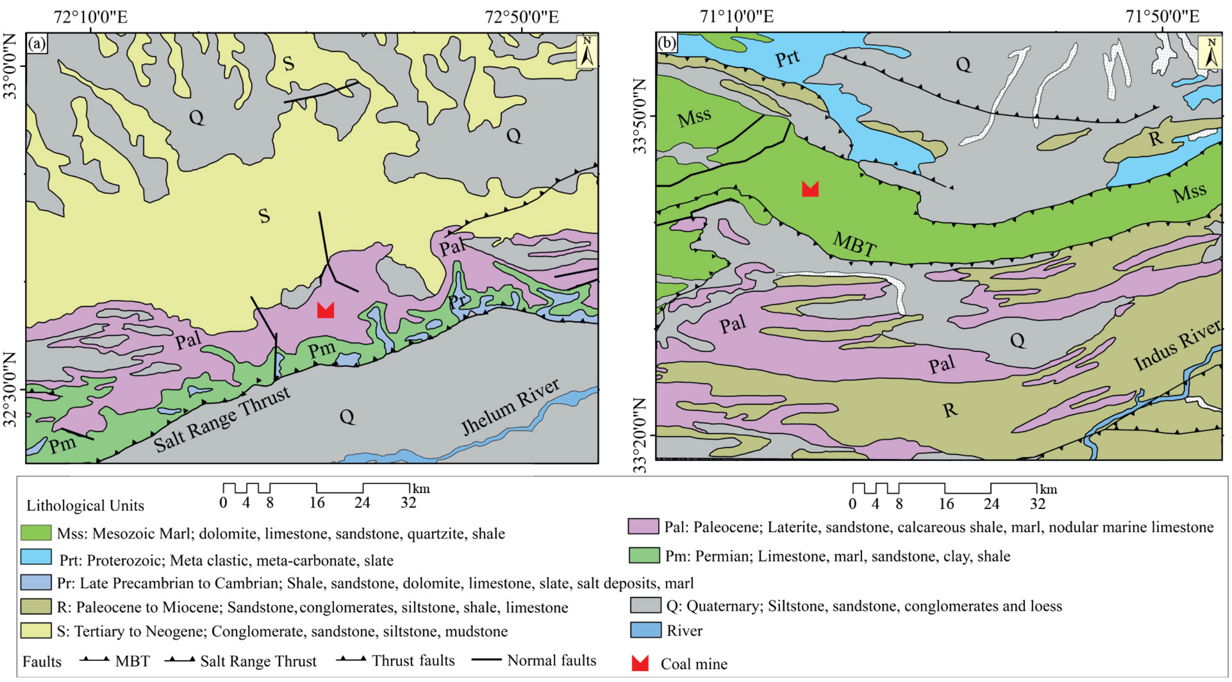

Fig. 1 Geological map of study area (a) Padhrar coal; (b) Darra Adam Khel coal.

Punjab zone is present, while the Punjab plain is located towards the south. The Sub-Himalayas is comprised of sedimentary rocks of Precambrian to recent age. MCT and MBT mark the limit of the Lesser Himalayas to the north and south, respectively (Khattak et al., 2017). The Lesser Himalayas consists of different structural blocks/ elements such as the Kala Chitta, Attock Cherat Ranges Hill Ranges, Peshawar Basin, Plio-Pleistocene basin and Southern Kohistan (Seeber and Armbruster, 1979; Seeber et al., 2013). The Lesser Himalayas comprises sedimentary, meta-sediments, metamorphic and volcanic rocks, representing Precambrian to Cenozoic ages (Sinha, 2013).

Stratigraphically, the Upper Indus Basin consists of sedimentary sequences ranging from the Precambrian to recent (Shah, 2009). The Paleocene age rocks, called the Makarwal Group in the Salt Range and F.R Peshawar area, are of primary focus. The Makarwal Group consists of the Hangu, Lockhart and Patala formations; out of these three, the Hangu and Patala formations have coal deposits (Shah, 2009). The Padhrar coalfield from the Patala Formation is located in the Central Salt Range, Punjab Province, while the Darra Adam Khel coalfield from the Hangu Formation, Khyber Pakhtunkhwa Province is also selected. These two coalfields have different geological settings with different environments of deposition. The Patala Formation in the Padhrar coalfield has an upper contact and a lower contact with the Nammal Formation and the Lockhart Formation, respectively (Fig. 2) (Ali, 2018). The lithology of the Patala Formation is carbonaceous shale with alternating coal beds and carbonate units (Ali, 2018). According to previous studies (Warwick and Shakoor, 1988; Gee and Gee, 1989; Warwick and Javed, 1990), the paleoenvironment of the Patala Formation in the Central and Eastern Salt Range is back-barrier and other freshwater to near-marine environments, as indicated by the presence of the coal beds. The Hangu Formation represents the Paleocene coal in the Darra Adam Khel coalfield (Malkani, 2012). The Darra Adam Khel coalfield is located in the vicinity of the Kohat-Peshawar Road, south of Peshawar. The lithology of the Hangu Formation is continental sandstone with interbedded shale, coal, carbonaceous clay and limestone (Shah, 2009). Danilchik and Shah (1987) suggested that the paleoenvironment of the Hangu Formation is shallow marine and deltaic settings.

3 Sampling and Analytical Methods

To study the geochemical and mineralogical composition, 37 coal channel samples were collected from floor to roof from two different coalfields, i.e.,

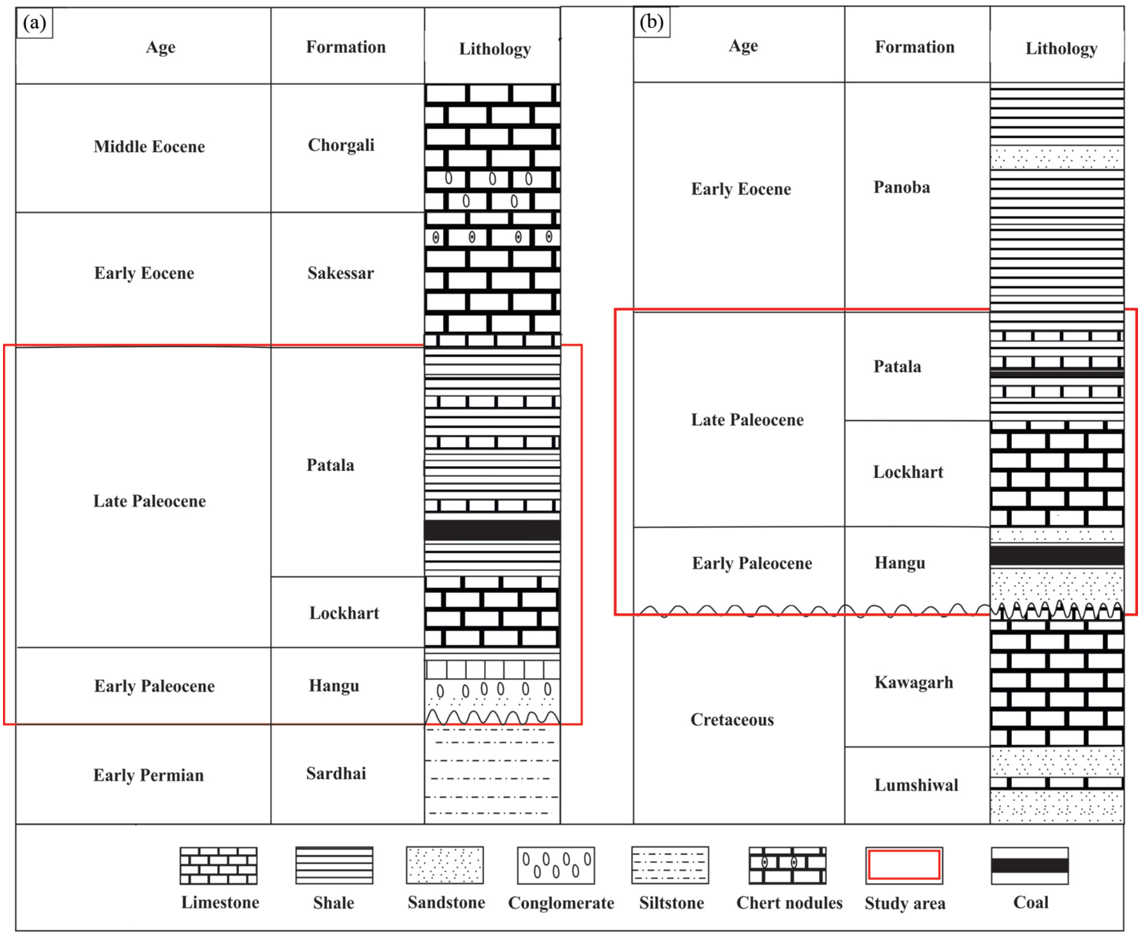

Fig. 2. Generalized stratigraphic column of the study area (a) Padhrar coalfield; (b) Darra Adam Khel coalfield.

Padhrar coal from the central Salt Range, Punjab Province and Darra Adam Khel coal, Khyber Pakhtunkhwa Province, Pakistan (Figs. 1 and 2). The samples were collected from the mining seams and packed in plastic bags to avoid moisture and contamination from the air after collection. A total of 12 coal channel samples (A1, A2, A3, A4, A5, A6, B1, B2, B3, B4, B5 and B6) were collected from 2 mines of Padhrar and 25 coal channel samples (M1S1SK, M1S2SK, M1S3SK, M1S4SK, M1S5SK, M2S1MB, M2S2MB M2S3MB, M2S4MB, M2S5MB, M2S1NM, M2S2NM, M2S3NM, M2S4NM, M2S5NM, M4S1AC, M4S2AC, M4S3AC, M4S4AC, M4S5AC, M11S1SK, M11S2SK, M11S3SK, M11S4SK and M11S5SK) were collected from 5 different mines of Darra Adam Khel coal.

The samples were collected and prepared according to the Chinese National [(GB 482-1995), ASTM D4596-09 (2015)] and GB 474-1996 (based on international standard ISO 1988:1975, ASTM D2013/D2013M-20) standards and then transported to Guizhou University, China, for laboratory analysis. The samples were crushed to 80 mesh to analyze coal quality parameters such as moisture (M_{ad}), ash (A_d), volatile (V_{daf}) according to the Chinese National Standard GB/T 212-2008 (based on international standard ISO 11722:1999). Total sulfur (S_{tad}) content in coal was measured by Coulomb sulfur meter according to GB/T 214-2007 (based on international standard ISO 334:1992, ISO 351:1996) and vitrinite reflectance was determined through the Leica DM-4500P microscope.

Major, minor and trace elements in coals and ashes have detecSuppl. Table concentrations by most modern analytical techniques (Zhu, 2004). A variety of instrumental methods have been applied to analyse ashes and ash deposits (Zhu, 2004). These are commonly based on atomic absorption/emission spectroscopy (AAS/AES), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectroscopy (ICP-MS), atomic fluorescence spectroscopy (AFS), X-ray fluorescence spectroscopy (XRF) or a combination of these techniques (Zhu, 2004). The current research determined trace elements in the powdered samples using inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Fisher, X series II), according to the method described by Dai et al. (2014a) and Li et al. (2014). XRF was used to determine the major element oxides.

The mineral phases were studied through X-ray diffraction (XRD) analysis and the polished pellets examined via optical microscopy (Leica DM4500P, Leica Microsystems, Wetzlar, Germany). Coal samples with a grain size of less than 1.0 mm were used to make coal pellets and observe the mineralogical morphology. The X-ray diffraction (XRD) analysis was carried out in the School of Mining, Guizhou University, using a X-ray Diffractometer (PANalytical, X'Pert Pro). Macerals were analyzed through oil immersion reflected light microscopy and over 500 particles were measured for each polished pellet. Vitrinite reflectance, minerals and maceral constituents were determined in the Guizhou Bureau of Coal Geology, according to Chinese National Standard GB/T 6948–2008 [based on international standard ISO 7404–5:1994, ASTM Standard D2798–20 (2020)], GB/T 8899–2013 (based on international standard ISO 7404–3–2009), [(MT/T 1158-2011), ASTM D2799–13 (2021) e1], respectively and maceral classification was based on (GB/T 15588–2013, ASTM D388–19a). The laboratory work was performed jointly in the College of Resources and Environment Engineering and Mining College, Guizhou University, Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou Aose Analysis and Testing Group.

4 Results

4.1 Proximate analysis of coal

The moisture (M_{ad}), volatile (V_{daf}), total sulfur content (St_{ad}) and ash yield (A_d) of Padhrar and Darra Adam Khel coals are tabulated in (Supp. Table 1). The moisture content in the Padhrar coal varies from 4.08%–7.90%, 5.86% on average, with the ash yield being 10.07%–22.80%, 16.71% on average (Fig. 3), while the moisture content in Darra Adam Khel coal ranged from 0.76%–2.95%, 1.91% on average, the ash yield being 5.31%–26.15%, 10.68% on average. The volatile matter in the Padhrar coal is 32.03%–41.21%, 36.97% on average, with maximum vitrinite reflectance (*R*o max %) of 0.48%–0.50%, 0.49% on average, with Darra Adam Khel coal being 9.41%–36.50%, 17.78% on average for volatiles and 0.43%–1.06%, 0.79% on average for maximum vitrinite reflectance. The maximum vitrinite reflectance (*R*o max %) value is an important parameter that reflects the degree of coal metamorphism. The total sulfur content value in Padhrar coal is 4.42%–13.73%, 7.85% on average, while for Darra Adam Khel coal it is 0.55%–4.23%, 2.27% on average.

4.2 Maceral composition

The maceral composition (vitrinite, inertinite and liptinite), V/I and O.I. indices in Padhrar and Darra Adam Khel coal are presented in Supp. Table 2. Vitrinite contents are dominant in Padhrar (85%–91%, 88% on average) and Darra Adam Khel coal (37%–68%, 57% on average), followed by inertinite (7%–11%, 9% on average and 24%–55%, 37% on average) and liptinite (3%–4%, 3% on average and 5%–8%, 7% on average). The vitrinite contents in the Padhrar coal are higher than the Darra Adam Khel coal; however, the inertinite and liptinite content in the Darra Adam Khel coal is higher than in the Padhrar coal (Fig. 4).

The vitrinite macerals in Padhrar coal are grey and greyish to light grey under reflected light. They include collodetrinite, thin banded telocollinite, with a small amount of telinite, vitrodetrinite and often corpogelinite. The vitrinite macerals in Darra Adam Khel coal are grey and greyish to light grey under reflected light, including vitrodetrinite, lenticular collodetrinite and thin banded telocollinite (Fig. 5c). The vitrodetrinite macerals in Darra Adam Khel also indicate that these coals are deposited in tidal lagoons. The secondary inertinite macerals in Padhrar coal are lenticular or irregular semifusinite, oxyfusinite, inertodetrinite. A small amount of micrinite and macrinite

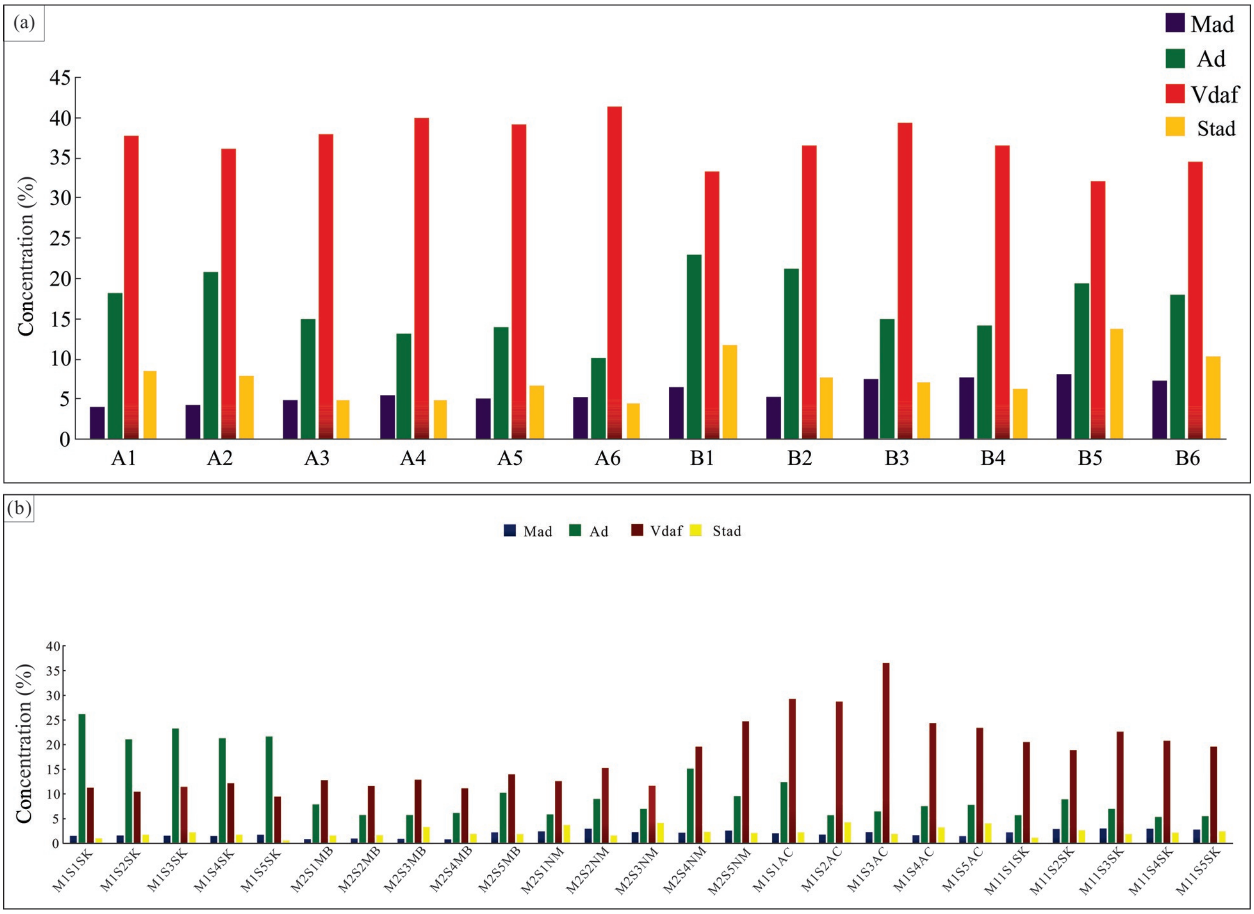

Fig. 3. Proximate analysis of the Padhrar and Darra Adam Khel coals (%) (a) Padhrar coal; (b) Darra Adam Khel coal).
M, Moisture; A, ash; V, volatile matter; St, total sulfur; ad, air dry base; d, dry base; daf, dry and ash-free base (Dai et al., 2007).

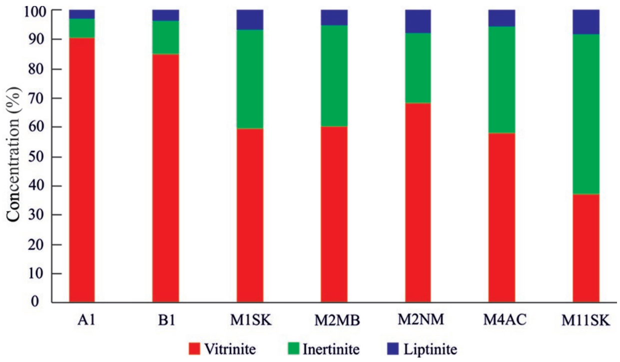

Fig. 4. Macerals identified in Padhrar coal (A1, B1) and Darra Adam Khel coal (M1SK, M2MB, M2NM, M4AC, M11SK) (%).

is distributed in the collodetrinite, occasional secretinite, fuginite, pyrofusinite (Fig. 5a, b, d). The secondary inertinite macerals in Darra Adam Khel coals are lenticular or irregular semifusinite, oxyfusinite and inertodetrinite. In Darra Adam Khel coal, a small amount of micrinite and macrinite can be identified that are distributed in collodetrinite and occasionally in some secretinite. The liptinite maceral in Padhrar coal includes sporinite, cutinite and liptodetrinite. The liptinite maceral in Darra Adam Khel coals includes liptodetrinite, with a small amount of sporinite.

The VI index of Padhrar coal in samples A1 and B1 is 13 and 8, respectively. The O.I. index of Padhrar coal for both samples A1 and B1 are 0.1. The VI index for Darra Adam Khel coal of M1S1SK, M2S1MB, M2S1NM, M4S1AC, M11S1SK is 1.8, 1.7, 2.8, 1.6, 0.7, respectively. The O.I. index of Darra Adam Khel coal for M1S1SK and M2S1MB is 0.5, with M2S1NM, M4S1AC, M11S1SK being 0.3, 0.6, 1.2, respectively.

4.3 Mineralogical composition

The mineralogical composition of the Padhrar and Darra Adam Khel coals is primarily quartz, clay minerals, calcite and pyrite (Fig. 6). The quartz mineral identified in the Padhrar and Darra Adam Khel coals had a flat surface and clear outline with a fine granular dispersion in collodetrinite; some are identified as fine inter-granular phase aggregations and appear as irregular granules (Fig. 7e). The quartz was observed in a fine intergranular form with a smooth surface and clear outline in Padhrar and Darra Adam Khel coals. The clay minerals in the Padhrar and Darra Adam Khel coals are mostly lumpy (nodules), a disseminated occurrence being subdivided in the dispersed form. Calcite in the Padhrar and Darra Adam Khel coals are observed as having rhomboid cleavage and mostly occurring as vein-like filling in fissures, cracks or pores,

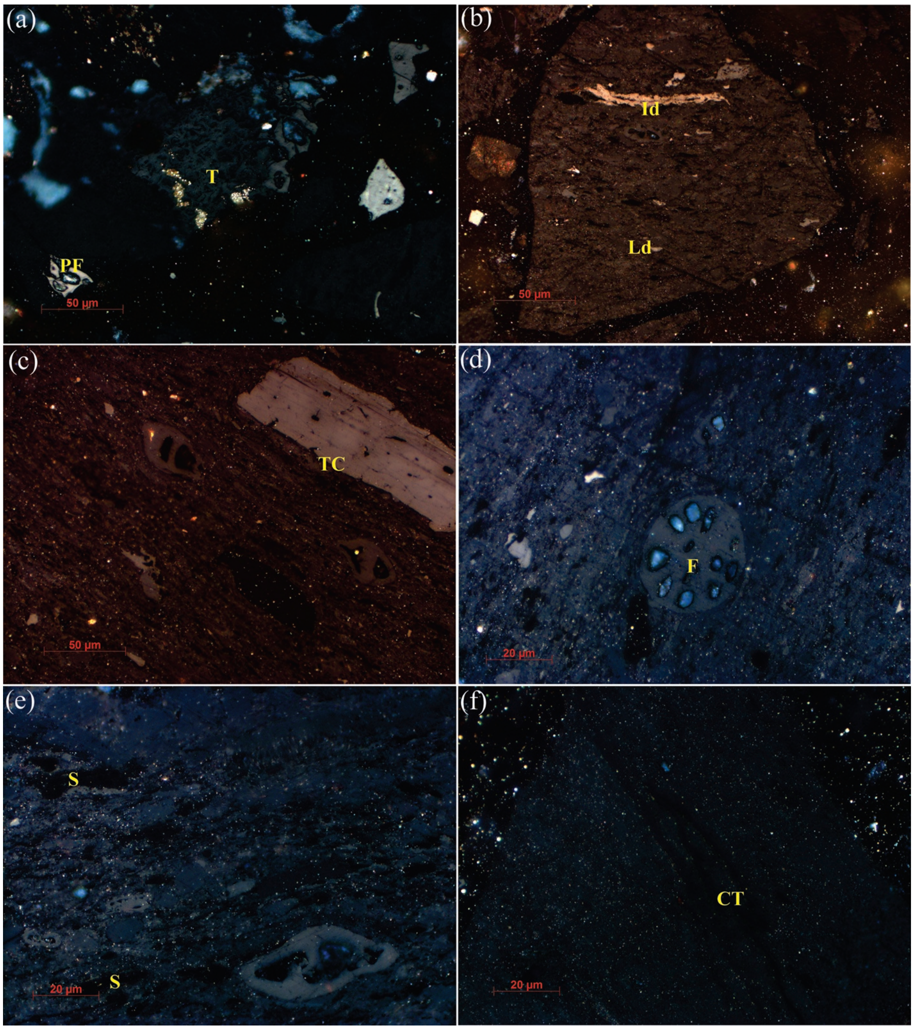

Fig. 5. Oil immersion reflected light photomicrographs of macerals in the studied samples of Padhrar coal.
(a–f) Telinite (T), pyrofusinite (PF), inertodetrinite (Id), liptodetrinite (Ld), telocollinite (TC), funginite (F), sporinite (S), cutinite (CT).

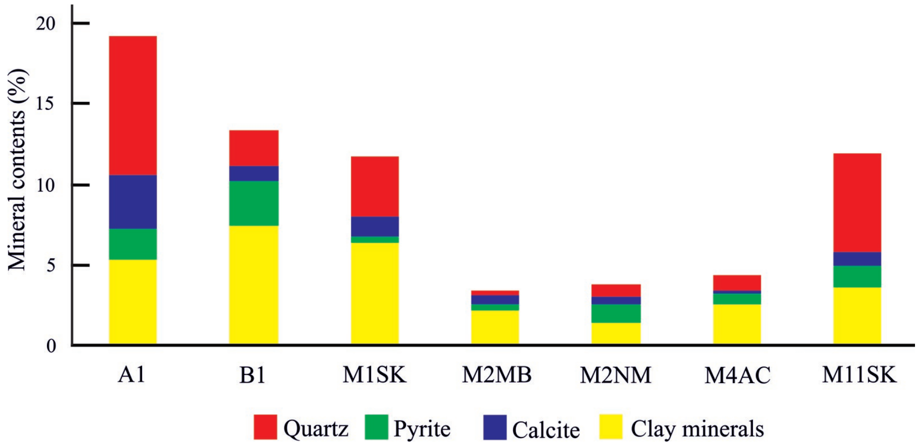

Fig. 6. Minerals identified by optical microscopy in Padhrar (A1, B1) and Darra Adam Khel. (M1SK, M2MB, M2NM, M4AC, M11SK) coal samples.

with twin crystals also being observed in Padhrar coal (Fig. 8a–d). Calcite is a common carbonate mineral in the ore-bearing rock series and generally exists in the form of veins of calcite (dolomite). Calcite is commonly found in Padhrar and Darra Adam Khel coals in the form of cell-filling and vein-filling (Fig. 8a–d). The pyrite in Padhrar and Darra Adam Khel coals are primarily fine-grained, pelletoid or spherulitic, fine-grained distribution, berry

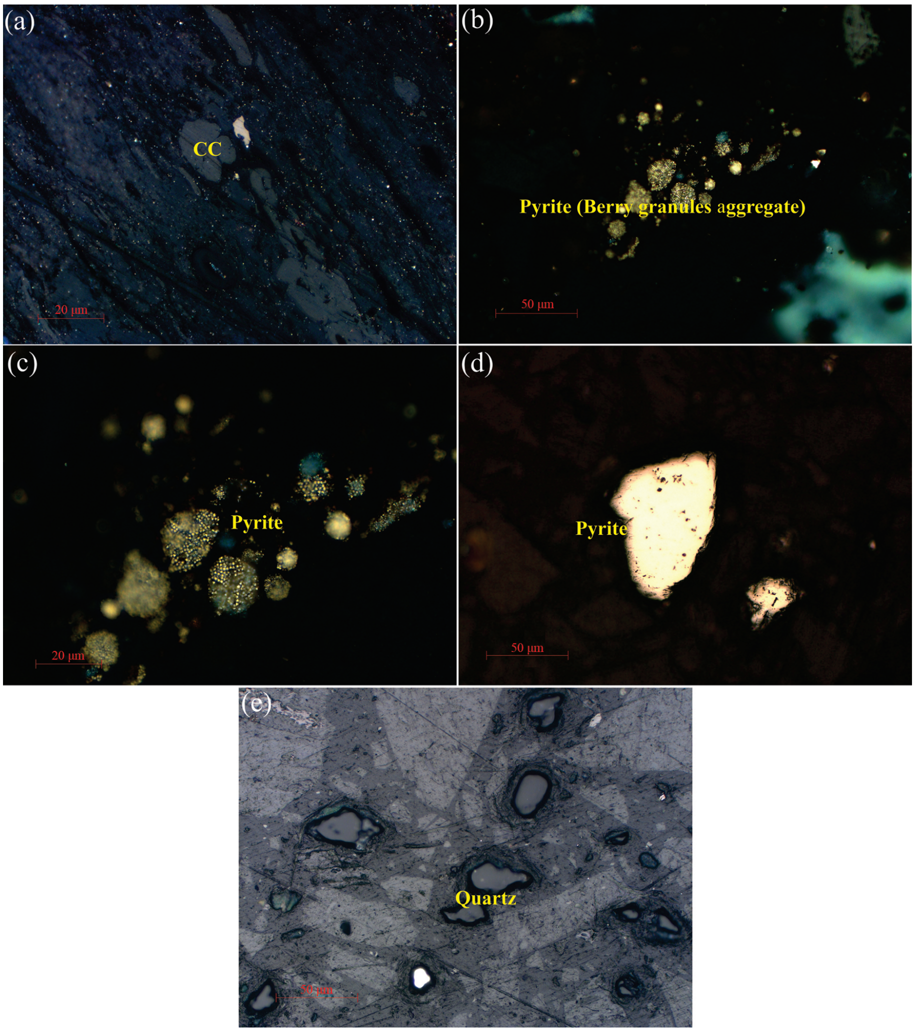

Fig. 7. Photomicrographs of minerals in the studied samples of Padhrar coal.
(a) Corpocollinite (CC); (b–d) pyrite; (e) quartz.

granular aggregates, nodular and honeycomb structure (Fig. 7b, c, d). The mineral phases identified by XRD analysis in the Padhrar coal are pyrite, quartz, coesite, magnetite, rodolicoite and hydronium jarosite (Fig. 9a, b). The minerals identified by XRD analysis in the Darra Adam Khel coal are pyrite, quartz, volborthite, magnetite, giuseppettite, eucryptite, ulvospinel, barroisite, franklinite and coesite (Fig. 9c–g).

4.4 Major elements oxides

The major element oxides present in the Padhrar and Darra Adam Khel coals are given in Supp. Table 3. In comparison with the average values of major element oxides in Chinese coals (Dai et al., 2012c), Padhrar and Darra Adam Khel coals have a lower concentration of SiO_2, TiO_2, Al_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_5 concentration and a higher concentration of Fe_2O_3 in Padhrar coal (Fig. 10). The SiO_2/Al_2O_3 values in the Padhrar (2.07–2.10, 2.08 on average) and Darra Adam Khel coals (1.10–22.31, 5.76 on average) are higher than the average SiO_2/Al_2O_3 value in Chinese coal (1.42) (Dai et al., 2012c). The contents of $SiO_2 + Al_2O_3$ in coals are usually related to the terrigenous detrital influx; therefore, the contents of $SiO_2 + Al_2O_3$ indicate the coal accumulation environment (Dai et al., 2012c). The Al_2O_3/TiO_2 ratio was used as a reliable indicator to recognize the provenance of sedimentary rocks and coals (Dai et al., 2014b), as well as the source magmas of altered volcanic ashes in coal-bearing sequences (Dai et al., 2014c). The stability of this provenance indicator is due to the immobility of the involved elements during surficial weathering, hydrothermal alteration and volcanic processes (Dai et al., 2011, 2014b, c; Shen et al., 2021). Typically, Al_2O_3/TiO_2 values of 3–8, 8–21 and 21–70 in sediments correspond to mafic, intermediate and felsic igneous source rocks, respectively (Zheng et al., 2017; Liu et al., 2020; Shen et al., 2021). In this study, the Al_2O_3/TiO_2 values for the studied samples of Padhrar and Darra Adam Khel coals range from 0.65 to 14.57 (Supp. Table 3; Fig. 11).

4.5 Trace elements

The concentration of trace elements was analyzed and compared to the world's averages of low-rank coal by

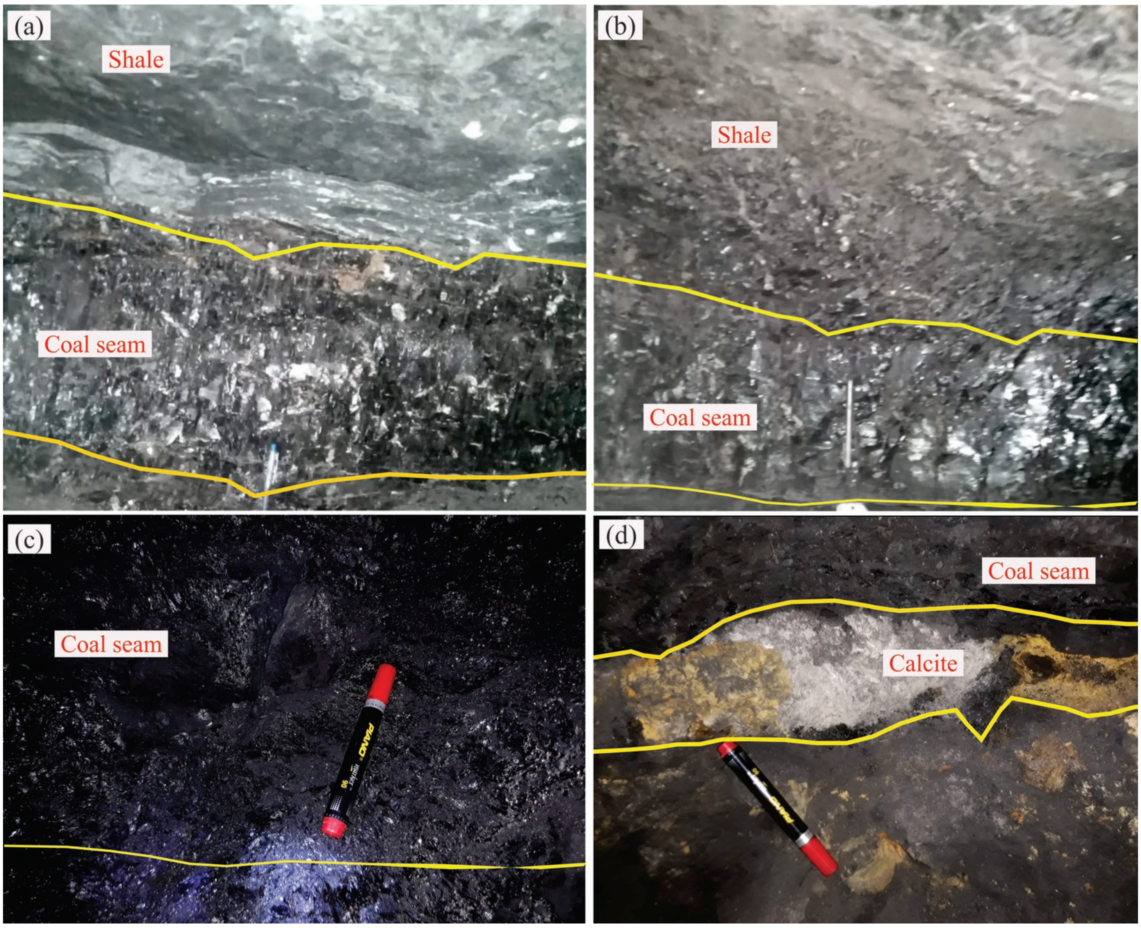

Fig. 8. Field photographs of Padhrar and Darra Adam Khel coals.
(a–b) The shale and coal seams of Padhrar coal (pen for scale, length = 6 cm); (c) the coal seam of Darra Adam Khel coal (marker pen for scale, length = 6 cm); (d) the coal seam and calcite-filled veins of Darra Adam Khel coal (marker pen for scale, length = 6 cm).

Ketris and Yudovich (2009) and are listed in figure 10. According to the value of CC, concentration coefficient (the ratio of trace element concentration in coal samples investigated vs averages for world low-rank coals) (Dai et al., 2015a) in the study area (Padhrar and Darra Adam Khel coals) vs. world coal, enriched (CC 2–5) and significantly enriched (CC > 5) trace elements were analyzed.

The significantly enriched trace elements with a CC > 5 in Padhrar coal are Be (5.11 ppm–7.16 ppm, 6.13 ppm on average), Zn (21.2 ppm–776 ppm, 165.62 ppm on average), Ge (9.15 ppm–13.1 ppm, 11.16 ppm on average), Mo (4.6 ppm–21.7 ppm, 11.18 ppm on average), Ta (0.575 ppm–4.06 ppm, 1.7 ppm on average), W (0.658 ppm–3460 ppm, 832.97 ppm on average), Co (2.3 ppm–368 ppm, 186 ppm on average) (Supp. Table 4, Fig. 12). The significantly enriched trace elements with a concentration coefficient CC > 5 in Darra Adam Khel coals are Cr (75.6 ppm–99.1 ppm, 85.5 ppm on average), Zr (171 ppm–195 ppm, 181.6 ppm on average), Ag (0.051 ppm–16.3 ppm, 2.96 ppm on average respectively), Sn (0.88 ppm–57 ppm, 11.29 ppm on average), Li (2.05 ppm –317 ppm, 87.13 ppm on average), W (18 ppm–146 ppm, 71.92 ppm on average) and Co 25.60 ppm–145 ppm, 61.94 ppm on average (Fig. 12).

4.6 Rare earth elements and yttrium (REY)

The total average REY concentration in Padhrar coal ranges from 60.39 ppm–97.12 ppm, 70.58 ppm on average and total average REY concentration in Darra Adam Khel coal ranges from 23.68 ppm–179.80 ppm, 79.38 ppm on average (Supp. Table 5). The REY in Darra Adam Khel coal M1SK ranges from 160.42 ppm to 189.59 ppm, 174.91 ppm on average, which was higher among Darra Adam Khel coal samples. The REY in Padhrar and Darra Adam Khel coals are higher than world low-rank coal REY (65.3 ppm) (Ketris and Yudovich, 2009) and about half of the Chinese coal REY concentration (135.9 ppm) (Dai et al., 2012b) except for Darra Adam Khel coal M1SK. The values of La, Ce, Pr, Nd, Sm, Gd, Dy, Y, Er and Yb in Padhrar and Darra Adam Khel coal are high, the values of Eu, Tb, Ho, Er, Tm and Lu in Padhrar and Darra Adam Khel coal being lower (Fig. 13).

In this research, the three-fold REY enrichment classification of coal was adopted (Seredin and Dai, 2012). High-REY coal ashes may be enriched in light (L-type distribution), medium (M-type distribution), or heavy REY (H-type distribution) in comparison with UCC

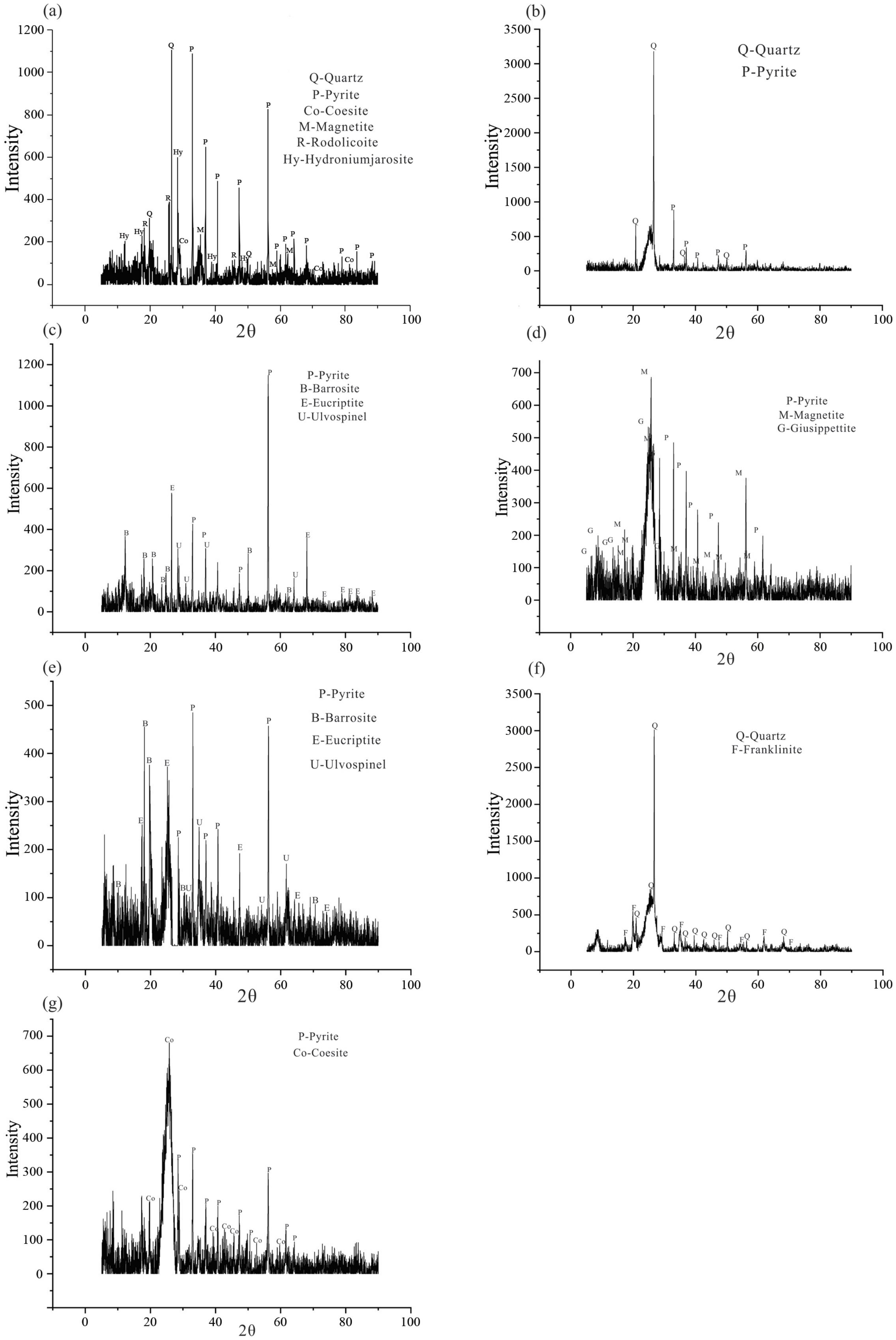

Fig. 9. X-ray diffraction (XRD) patterns of some selected coal samples.
Padhrar coal (a) A1; (b) B1; Darra Adam Khel (c) M1SK; (d) M2MB; (e) M2NM; (f) M4AC; (g) M11SK.

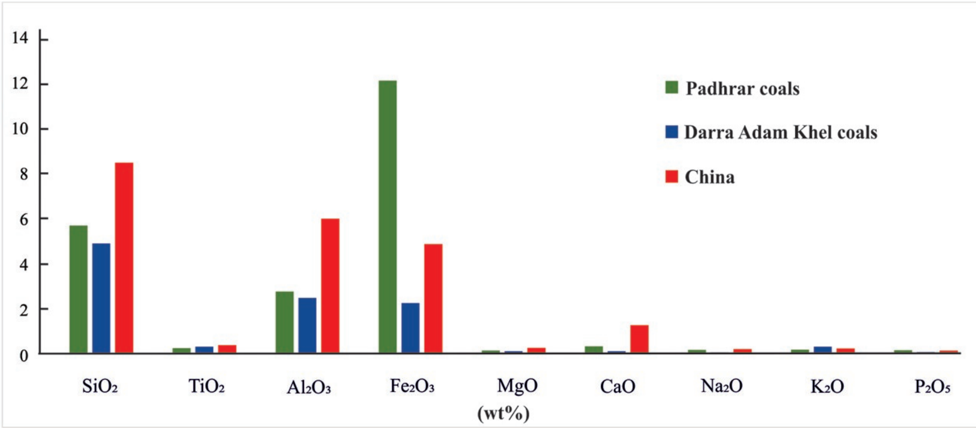

Fig. 10. Major element oxides in Padhrar and Darra Adam Khel coals in comparison with major element oxides in Chinese coal (%).

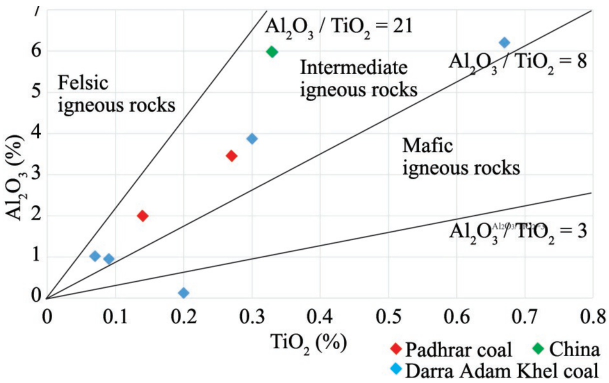

Fig. 11. Scatter diagram of Al_2O_3–TiO_2 (after Zheng et al., 2017; Liu et al., 2020), showing the comparison between the studied samples and the provenance of the Padhrar and Darra Adam Khel coals.

(upper continental crust) (Seredin and Dai, 2012). Three REY distribution patterns for high-REY coal ashes are fixed, with L-type REY ($La_N/Lu_N > 1$), M-type REY ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$) and H-type REY ($La_N/Lu_N < 1$) enrichment (Seredin and Dai, 2012). REY plots of each type may have Ce-, Eu- and Y-negative or positive anomalies of various amplitudes, as the behaviour of these elements in the environment can differ from other REY (Seredin and Dai, 2012).

The Padhrar coal shaft and Darra Adam Khel coal M2MB are characterized by H-type and M-type enrichment (Supp. Table 5, Fig. 13). Darra Adam Khel coal M1SK, M2NM and M4AC are characterized by L-type and M-type enrichment, while M11SK are characterized by L-type enrichment (Supp. Table 5, Fig. 13). Compared with the MREE and HREE, the LREE in Padhrar and Darra Adam Khel coals are higher. The Ce (Ce_N/Ce_N^*), Eu (Eu_N/Eu_N^*), and Gd (Gd_N/Gd_N^*) anomalies are determined using the formula by Dai et al. (2016). The Padhrar coal shows positive cerium (Ce), europium (Eu) and gadolinium (Gd) anomalies and most of the Darra Adam Khel coal samples show negative Ce, Eu and positive Gd anomalies. There is a positive Ce_N/Ce_N^* value of 0.9–1.0 in the Padhrar coal, while the negative Ce_N/Ce_N^* values in most Darra Adam Khel coal samples are 0.6–0.9.

5 Discussion

5.1 Depositional environment and provenance

Based on proximate analysis, the Padhrar coal has low to medium moisture content and the Darra Adam Khel coal is characterized by low moisture content. The Padhrar and Darra Adam Khel coal are both low to medium ash coal, according to Chinese National Standard GB/T 15224.1–2010 [ASTM Standards D3173–11 (2011), D3174–12 (2018)]. According to the U.S coal Classification System (also compared with the International Classification of In-Seam Coals, Economic Commission for Europe Committee on Sustainable Energy, 1998), the coal is classified based on volatile matter and maximum vitrinite reflectance. The volatile matter of the Padhrar coal indicates medium rank, high volatile bituminous coal and maximum vitrinite reflectance values, suggesting that the Padhrar coal is low-rank sub-bituminous coal (Stach et al., 1982; Bustin et al., 1995; ASTM, 2013). The volatile matter of Darra Adam Khel coal indicates medium rank, low to medium volatile bituminous coal and maximum reflectance values suggesting that the Darra Adam Khel coal is high volatile low rank sub-bituminous to medium rank bituminous coal (Jackson, 1997; ASTM, 2013). The vitrinite reflectance in Darra Adam Khel coal is higher than Padhrar coal (Supp. Table 2), indicating that Darra Adam Khel coal has higher temperature and pressure conditions compared to Padhrar coal, which can be attributed to greater burial depth or can also be linked with the Himalayan Orogeny which has the Main Boundary Thrust fault (MBT) in the vicinity of the Darra Adam Khel area, thus indicating intense collision. The sulfur content indicates that the Padhrar and Darra Adam Khel coals are high sulfur coals (GB/T 15224.2–2010, ASTM Standards D4239–18a). Sulfur is the principal element reflecting the depositional environment, but its concentration can be caused by various processes (e.g., seawater- or fresh-water influenced peat swamp), so

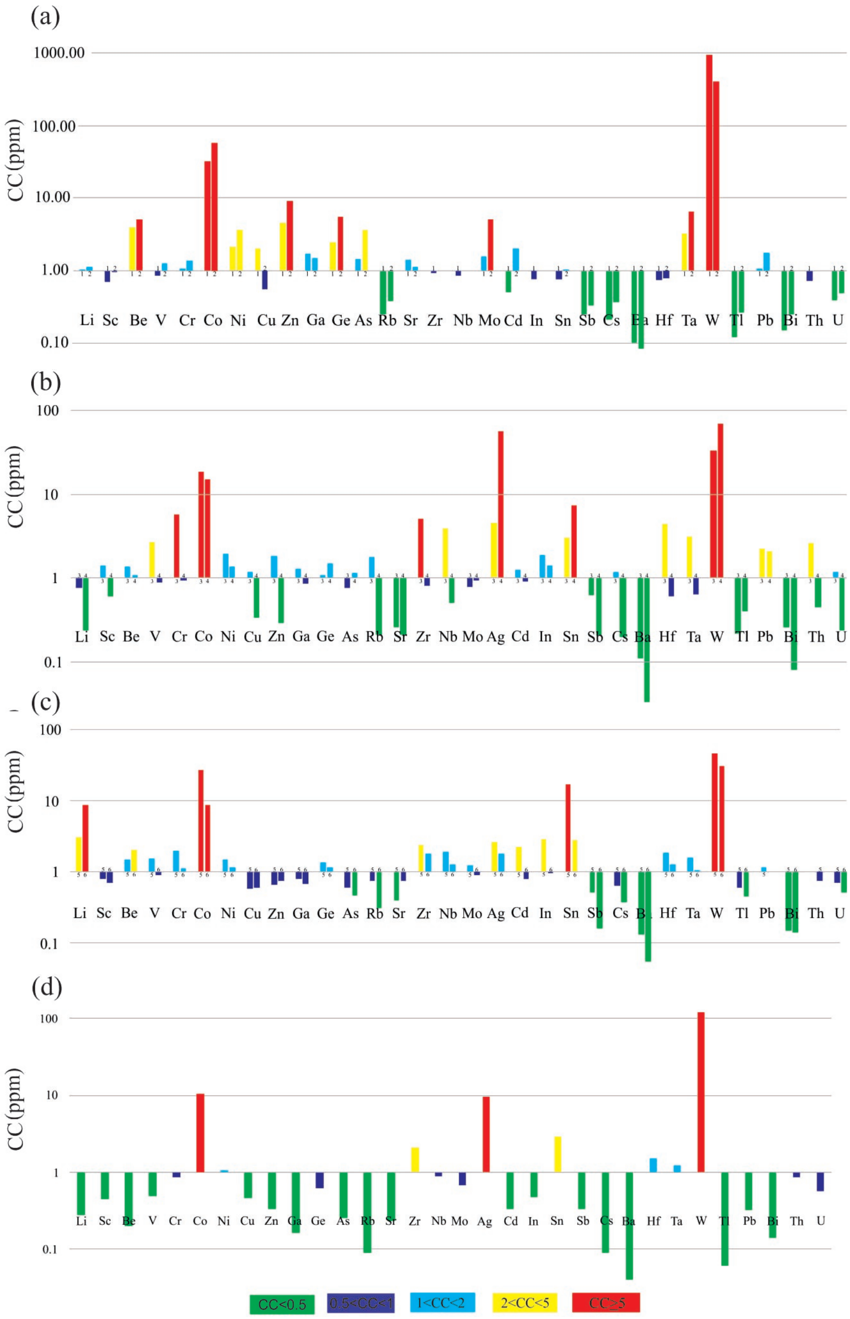

Fig. 12. Trace elements concentration (CC) in studied coal sample, Padhrar coal (a) Shaft A, Shaft B; Darra Adam Khel coal (b) M1SK, M2MB; (c) M2NM, M4AC; (d) M11SK; normalized by average trace elements concentration in world low coal, as reported by Ketris and Yudovich (2009).

a detailed study is required to precisely interpret the environment (Dai et al., 2020). Based on the analysis, Padhrar and Darra Adam Khel are high sulfur coals, which may indicate seawater influence, but the sulfur content of Padhrar coal is higher than Darra Adam Khel coal which shows that Padhrar coal has been more strongly influenced by seawater than Darra Adam Khel coal. The high sulfur is described as possibly indicating regional activity, peat environment, alkaline, sedimentary environment, as well as an alkaline, sedimentary environment with massive sulfide mineralization. The main sulfur in Padhrar and Darra Adam Khel coal is pyritic. In addition to seawater, the elevated concentrations of sulfur in these coals may also be caused by epithermal, hydrothermal, or sulfate-rich waters, which can happen at all stages of coal formation from peat accumulation through diagenetic to later epigenetic processes (Chou, 2012; Dai et al., 2020). The moisture, sulfur, volatile matter content and ash yield in the Padhrar coal were all higher than Darra Adam Khel coal. The high moisture content in the Padhrar coal shows that the water was high during the formation of peat and the high sulfur content indicates the seawater and

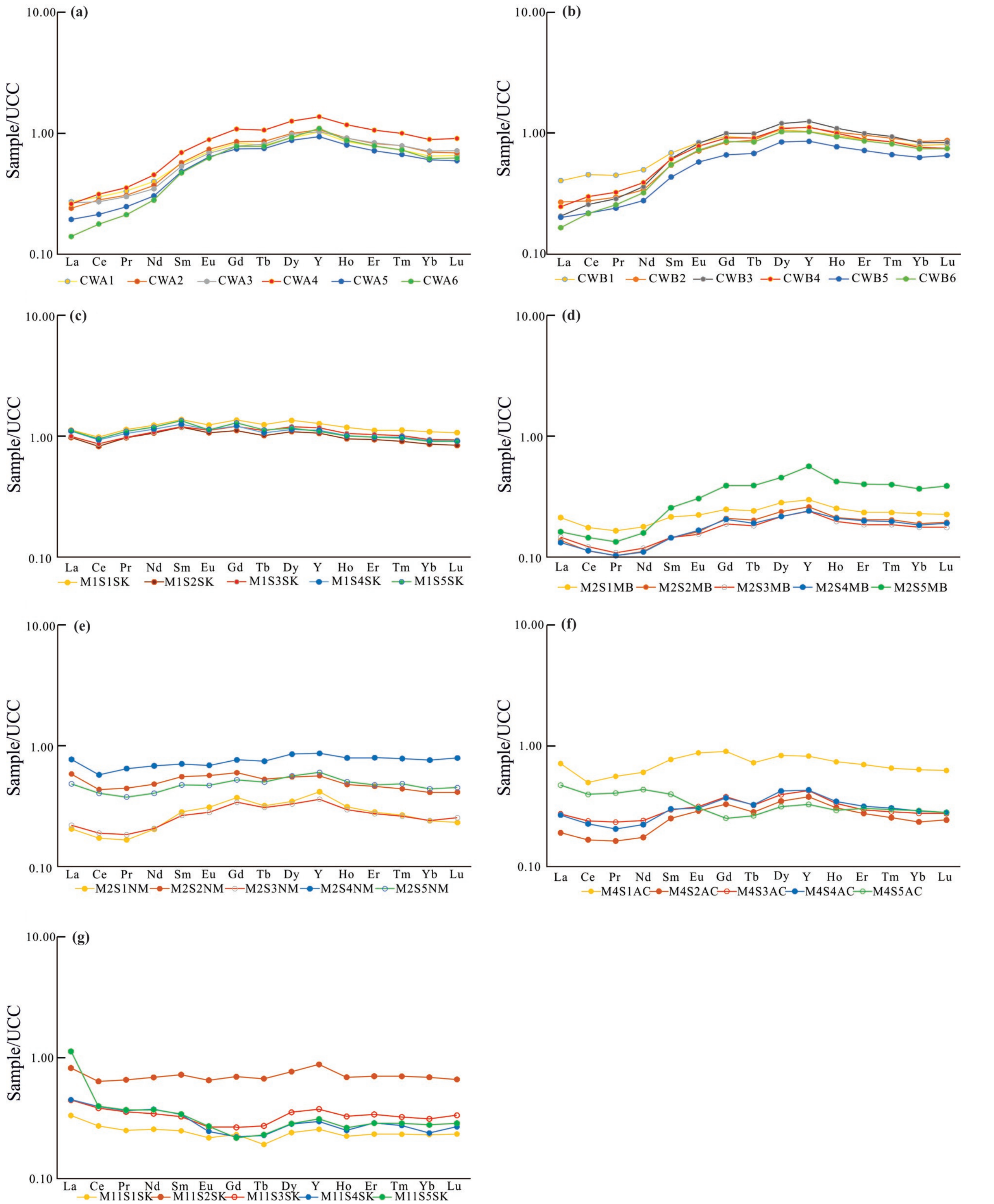

Fig. 13. Rare earth yttrium (REY) distribution patterns in studied coal samples, normalized to Upper Continental Crust (UCC) by Taylor and McLennan (1985).
Padhrar (a) Shaft A; (b) Shaft B; and Darra Adam Khel (c) M1SK; (d) M2MB; (e) M2NM; (f) M4AC; (g) M11SK.

epithermal influence, the high sulfur content in the Padhrar coal showing high seawater and epithermal influence compared with Darra Adam Khel coal (Dai et al., 2020). Based on the ash yield results in Padhrar coal and Darra Adam Khel coal, M1SK shows the influence of land-based debris and the invasion of basin seawater. The ash yield in coal also comes from coal-forming plants. When the action of seawater is intense, the river's carrying capacity will be restrained, thus affecting the ash yield of the coal seam; therefore, there may be a specific relationship between the ash yield of coal and the marine regression and transgression.

Vitrinite macerals were formed in a slightly reducing environment, the inertinite macerals being formed in an oxidizing environment (Stach et al., 1982; Lin and Tian, 2011). Therefore, the vitrinite/inertinite (V/I) index may indicate an oxidizing reduction environment. According to Xu and Fang (2005) and Lin and Tian (2011), V/I > 4 indicates strong overlying water environments; V/I values between 1 and 4 indicate overlying water environments; V/I values between 0.25 and 1 indicate wet or weak overlying water environments; and V/I < 0.25 indicates dry or strongly dry environments. The V/I value of the Padhrar coal is greater than 4, thus indicating an overlying water environment (Supp. Table 2), i.e., 2 samples represent strong overlying water environments. The V/I value of Darra Adam Khel coal for 4 samples is between 1 and 4, thus indicating an overlying water environment, while in 1 sample, the V/I value is between 0.25 to 1, thus indicating wet or weak overlying water environment. The oxidizing index (OI) was calculated (Supp. Table 2). OI > 1 values may indicate dry environments; OI values between 0.5 and 1 may indicate wet environments; OI < 0.5 values may indicate overlying water environments (Lin and Tian, 2011). According to the standard, both the samples of Padhrar coal have OI value less than 0.5, thus indicating an overlying water environment. In Darra Adam Khel coal 4 samples have OI value between 0.5 and 1 thus indicate a wet environment while 1 sample is having OI value less than 0.5 thus indicating an overlying water environment.

As has been noted, the mineral composition of the Padhrar and Darra Adam Khel coals is mainly quartz, clay minerals, calcite and pyrite (Fig. 6). The distribution of quartz may be controlled by two geological factors, one being the increase in the supply of clastic materials in the source area during the process of peat accumulation, the other being the mixed accumulation of underlying sediments and peat during the process of peat formation. The mode occurrence of quartz indicates its terrigenous detrital origin. Calcite in cell-filling and vein-filling calcite minerals can be authigenic and/or epigenetic. Calcite may be formed due to the influence of groundwater activity or the invasion of low-temperature hydrothermal fluid rich in calcium. The iron ion in pyrite mainly comes from the parent rock in the source area, the sulfur ion coming from the sulfate ion in seawater, the reaction of Fe^{2+} and H_2S then producing pyrite (Dai et al., 2002; Chou, 2012). The modes of occurrence indicate the syngenetic origin of the pyrite, which may be related to the activity of algae and bacteria (Dai et al., 2002; Chou, 2012). Pyrite is composed of microcrystalline (colloidal, dispersed) or fine crystalline (spherulitic) forms, the colloidal and fine-grained pyrite being the product of syngenetic sedimentation of sediments in the early diagenetic stage, representing an anoxic environment (Dai et al., 2002; Chou, 2012). Spherulitic pyrite may be the result of filling holes with colloidal pyrite, which is embedded in organic matter pores under the action of surface tension; the colloid crystallizes into an approximate spherulite structure (Dai et al., 2002; Chou, 2012). The berry granular aggregate pyrite may be the product of early diagenesis, which is formed by replacing or filling bacterial reservoir residues with colloidal and fine-grained pyrite. The berry granular aggregate pyrite reflects an anoxic environment. In coal, it is distributed in the form of nodules, veins and lumps, some being filled in vitrinite (Dai et al., 2002; Chou, 2012). In this study, pyrite is mostly tuberculous, occasionally filled with cells. Pyrite forms in the diagenetic process i.e., nodular pyrite and cell-filled pyrite form in the early diagenetic stage and late diagenetic stage, respectively (Dai et al., 2002; Chou, 2012).

The Sr/Ba ratio is widely used as an indicator for marine/freshwater influences for coals (Wei et al., 2018; Spiro et al., 2019). Sr/Ba values greater than 1 indicate the marine environment, less than 1 indicating the terrestrial environment (Spiro et al., 2019). The Sr/Ba values in Padhrar coal vary from 6 to 44.8, with an average of 14.6. In Darra Adam Khel coal, the Sr/Ba values vary from 1.51 to 14.42 with an average of 5.29, greater than 1, indicating a marine environment. Padhrar coal has a comparatively high Sr/Ba ratio, so that the peat-deposition environment may belong to the tidal flat. However, Darra Adam Khel coal may belong to a marine deltaic, peat-deposition environment (Fig. 14). The high Sr/Ba value in Padhrar coal indicates a strong seawater influence relative to Darra Adam Khel coal.

The $(Fe_2O_3 + CaO + MgO)/(SiO_2 + Al_2O_3)$ in coal is significant in the study of peat-forming environments. Ren and Dai (2009) noted that peat influenced by

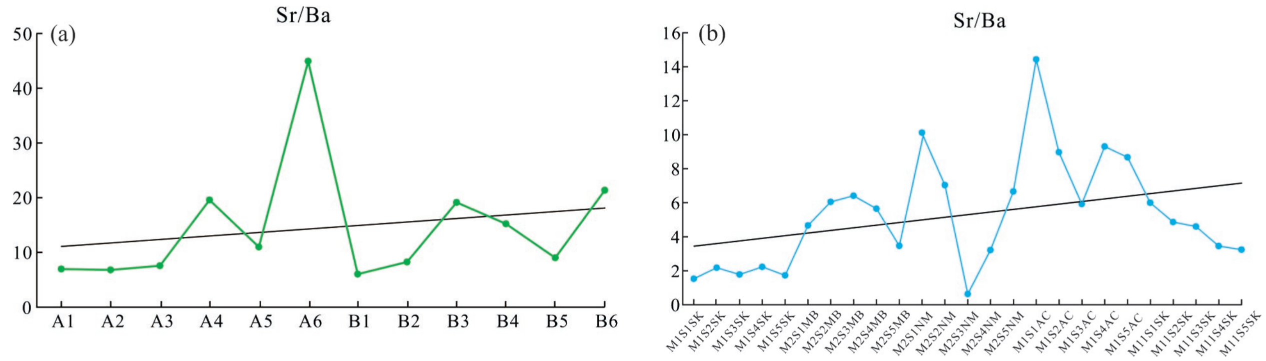

Fig. 14. Sr/Ba values in the studied coal samples (a) Padhrar coal; (b) Darra Adam Khel coal.

seawater had a $SiO_2 + Al_2O_3$ value less than 75% and $Fe_2O_3 + CaO + MgO/SiO_2 + Al_2O_3$ greater than 0.23. This parameter indicates the depositional environment of peat formation, including marine (>0.23), terrestrial (<0.23) and marine−terrestrial deposits (Dai et al., 2018). The SiO_2/Al_2O_3 values in the Padhrar (2.07–2.10, 2.08 on average) and Darra Adam Khel coals (1.10–22.31, 5.76 on average) are higher than the average SiO_2/Al_2O_3 value in Chinese coal (1.42). The $SiO_2 + Al_2O_3$ value in Padhrar and Darra Adam Khel coals are < 75%, the average of the $(Fe_2O_3 + CaO + MgO)/(SiO_2 + Al_2O_3)$ parameter is 1.36, indicating that the Padhrar and Darra Adam Khel coals were mainly influenced by seawater. The Al_2O_3/MgO values in some studied samples are high, reflecting warm and humid desalination. The values of V/Cr less than 2, Ni/Co less than 5 and U/Th less than 0.75 in the Padhrar and Darra Adam Khel coal samples show that the coal formed in an oxidizing environment. The Cu/Zn ratio in Padhrar coal shows reductive oxidation and reduction, while Darra Adam Khel coal shows oxidizing to weak oxidizing.

The Al_2O_3/TiO_2 ratio is a good diagnostic indicator of sedimentary rock origins (Hayashi et al., 1997) and sediments associated with coal deposits (Dai et al., 2015a). It is proposed that the ranges of Al_2O_3/TiO_2 ratios, 3–8, 8–21 and 21–70 for sediment and sedimentary rocks, refer to mafic, intermediate and felsic igneous rocks, respectively (Hayashi et al., 1997; Zheng et al., 2017; Liu et al., 2020). The Al_2O_3/TiO_2 value in the studied coal samples refers to the weathered parent intermediate igneous rocks, which also explains the high content of W and Co in Padhrar and Darra Adam Khel coal. Co is mainly derived from fine-grained sulfides or sulfide minerals in clay or organic materials in coal (Goodarzi, 2002). The high content of W, Co may be related to the addition of weathering material from the surrounding granite. The Al_2O_3/TiO_2 values indicate that Padhrar coal and Darra Adam Khel coal M1SK, M2MB, M2NM, M4AC were initially sourced from intermediate igneous rocks and the Darra Adam Khel coal M11SK is related to ultramafic rocks (Supp. Table 3, Fig. 11) (Zheng et al., 2017; Liu et al., 2020; Shen et al., 2021). Furthermore, on the Al_2O_3/TiO_2 diagram, the studied samples all fall in a similar distribution area to those widespread around Southern China, indicating that they have a common volcanic source (Supp. Table 3, Fig. 11) (Zheng et al., 2017; Liu et al., 2020; Shen et al., 2021).

The study shows that the distribution patterns of REEs of Padhrar and Dara Adma Khel coals are similar, except for slight variations in a few samples of Darra Adam Khel coal, indicating a similar depositional environment and epigenetic evolution of coals and that the REEs fractionation was not influenced during diagenesis. The Ce and Eu anomalies in coal are generally inherited from terrigenous materials within the sediment source region (Shenjun et al., 2018). A positive Ce_N/Ce_N^* value in Padhrar coal shows anoxic marine water and negative Ce_N/Ce_N^* values in most Darra Adam Khel coal shows suboxic marine water (Alibo and Nozaki, 1999; Wang et al., 2008; Shenjun et al., 2018). The Eu anomalies in sediments could not have developed in a peat-forming environment that is not influenced by high temperature (> 200°C) hydrothermal solutions (Dai et al., 2016). Based on the distribution pattern of REY with negative Ce−Eu anomalies, the sediment source region for the Darra Adam Khel coal is considered to be basaltic. These weak negative Ce and Eu anomalies in Darra Adam Khel coal are probably due to the combined influence of marine and basaltic sediment source regions. In Padhrar and Darra Adam Khel coals, the M-type enrichment and positive Gd anomaly may be attribu to the influence of terrestrial acidic waters, while the H-type enrichment indicates some contribution from alkaline waters (Shen et al., 2021).

5.2 Padhrar and Darra Adam Khel coal comparison with other coalfields of Pakistan

The world's highest percentage of lignite coal is found in Asia, with a significant portion in the Thar Parker area of Sindh Province, Pakistan. The Padhrar and Darra Adam Khel coal characteristics were compared with Pakistan's largest Thar coal and the other coalfields of Pakistan. Petrographically, the Pakistan coals are vitrinite rich, the primary maceral in Darra Adam Khel, Lakhra, Sonda, Thar and Padhrar coal was vitrinite with a gradual increase, i.e., 56.68% in Darra Adam Khel, 63.4% in Lakhra, 73.8% in Sonda, 85.2% in Thar and 87.78% Padhrar coal. The inertinite content was 36.7% in Darra Adam Khel, 17.3% in Lakhra, 14.7% in Sonda, 7.4% in Thar and 8.97% in Padhrar. The liptinite content was 3.2% in Padhrar, 6.6% in Darra Adam Khel and 7.4% in Thar coal. The macerals content shows that Thar coal was formed from herbaceous plants. The low inertinite macerals content in Balochistan's, Thar's, and Padhrar's coal indicates not that much fluctuation in the water, compared to Darra Adam Khel coal, indicating these coal were formed under humid conditions.

The drying and wetting cause the oxidation of the peat and thus forms the inertinite macerals; the rarity of sclerotia (an inertinite maceral) in Balochistan's coals indicates anaerobic environments. The Padhrar coal is characterized by low to medium moisture content, low and medium ash yield, high volatile matter content and high sulfur content. The Darra Adam Khel coal is low moisture content, low ash yield, high sulfur and high volatile matter. The high sulfur content in Padhrar and Darra Adam Khel coals indicates a strong marine influence. The low ash and sulfur contents of Thar coal indicate that it was formed in raised peat bogs and a predominantly acidic environment. At the time of Thar coal formation, the sea was to the west, the shoreline transgressing and regressing. The trend of the thickest Thar coal bed with low ash and sulfur contents suggests that the coal was deposited in an upper delta environment, where the formation of peat bogs continued for a much longer time, without any disturbances in the basin configuration. The Thar coal has a Sr/Ba value of less than 1, indicating a brackish water influence during coal accumulation. In contrast, Padhrar and Darra Adam Khel coal has a Sr/Ba value greater than 1, indicating marine water influence. Padhrar coal has a comparatively high Sr/Ba ratio, so the coal-forming environment may belong to the tidal flat coal

-forming environment; however, Darra Adam Khel coal may belong to a deltaic coal-forming environment. The Sr/Ba value in Padhrar coal shows a stronger marine influence than the Darra Adam Khel coal.

5.3 Potentially valuable elements

The critical elements are important in world economies that are directly connected with technological advancement and energy efficiency (Massari and Ruberti, 2013; Hower et al., 2016). As these elements are used in greater amounts, the conventional sources are becoming scarce, with demand growing rapidly due to the breadth of their application (Massari and Ruberti, 2013; Hower et al., 2016). Also, these critical elements are provided by particular sources, i.e., China and Russia, making them expensive. Therefore, to meet the global demands of such elements, it is important to seek alternative sources. Coal has received much attention as a potential source of valuable elements, such as Li and Ge, used in the production of advanced materials as well as in the semiconductor industry. Ge and Li are currently utilized from Ge and Li-rich coals in China and Russia (Dai et al., 2014c).

The average value of lithium (Li) in common Chinese coals and world coals is 31.80 ppm and 10 ppm, respectively (Ketris and Yudovic, 2009; Dai et al., 2012a). Li is significantly enriched (2.05 ppm to 317 ppm, 87.13 ppm on average) in Darra Adam Khel coal samples (M4S1AC-M4S5AC) and enriched (12.6 ppm to 63 ppm, 30.56 ppm on average) in other Darra Adam Khel coal samples (M2S1NM-M2S5NM) (Fig. 15, Supp. Table 4). Sun et al., 2012 analyzed the Li value in many Chinese coals and proposed that 80 ppm Li was reasonable to be taken as the minimum mining grade, with 120 ppm as the economic or industrial grade (Sun et al., 2012, 2013). The Li concentration in Darra Adam Khel coal (samples M4S1AC-M4S5AC) is a mining grade. There are several sources and occurrences of Li and Ge in the coal of the current study for the following possible reasons. The main Li carriers in the coal deposits are Li-bearing clay minerals (Vladimir et al., 2013). The high Li contents in the Russian Far East coal deposits most likely have an epigenetic hydrothermal origin (Vladimir et al., 2013). These Li accumulations are similar to hydrothermal clayey ores of some volcanogenic Li deposits, with respect to their mineralogical and geochemical relationships (high Be, Zn, Pb, and Ag contents) (Vladimir et al., 2013). Li accumulation may have occurred during the peat bog stage, along with surface water from Li-bearing bauxites and with basin brines. However, epigenetic hydrothermal Li supply is another possible carrier of Li, rather than detrital material of terrigenous origin, as Li-bearing chlorite occurs as cell-filling in the coal (Vladimir et al., 2013).

In past research, the value of Ge in coal varied from 10 to 100 and could be considered industrially viable (DZ/T, 0203-2002, 2003). The value of germanium in Padhrar coal Shaft A ranges from 3.0 ppm to 7.1 ppm, 4.9 ppm on average (with the highest value in sample A1, i.e., 7.1 ppm) and Shaft B 9.2 ppm to 13.1, 11.2 ppm on average (with highest in sample B6, i.e., 13.1 ppm) which are higher than those of the Chinese coals (2.78 ppm) and world hard coals (2.0 ppm) (Ketris and Yudovic, 2009; Dai et al., 2012a), indicating that Ge in some Padhrar coal has commercial value (Fig. 15, Supp. Table 4). Several studies have confirmed that the Ge in coal-hosted ore deposits occurs predominantly as an organic association (Dai et al., 2015a, b; Etschmann et al., 2017). A recent study by Wei and Rimmer (2017) showed that Ge is bonded (but only weakly) to organic matter, possibly occurring in the form of chelates, thus allowing them to be removed from the raw coal by HCl-HF. The Ge was derived from Ge-rich granites (either the basement of coal-bearing sequences or occurring in an area adjacent to the coal deposits) leached by hydrothermal solutions (Dai et al., 2015a, b). Based on the published literature on high-Ge coals, prospecting coal-hosted Ge deposits should focus on those with a low-rank (lignites and subbituminous coals) and with low calorific values, with high-Ge granitoids as the basement of coal-bearing sequences or occurring in the area surrounding the coal deposits (Dai et al., 2015a). Well-developed faults, either within or in the area adjacent to the coal deposit, are important for Ge enrichment in coal deposits, because they serve as the channels for Ge-rich solutions injected to the peat mire. The elevated Ge is

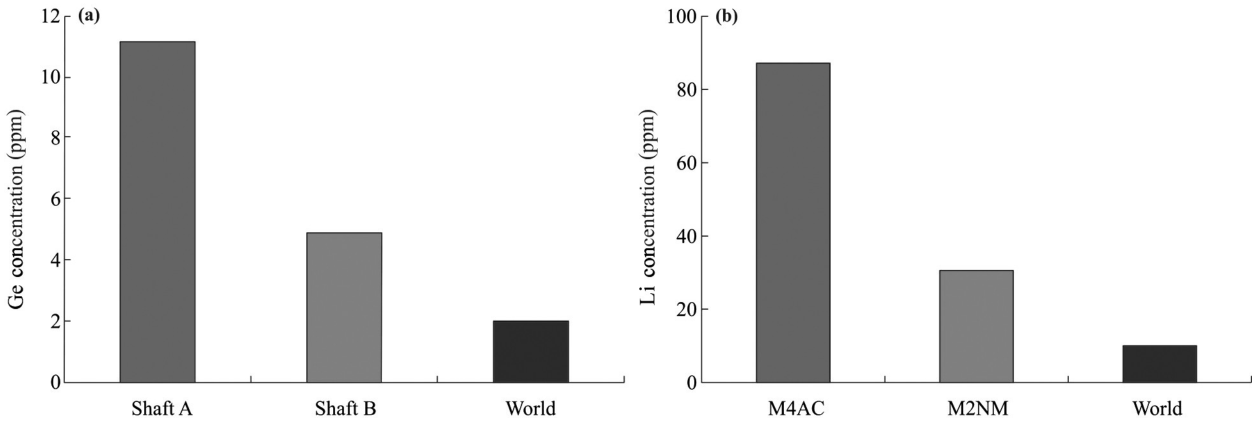

Fig. 15. Valuable elements in the studied coal samples (a) Ge in Padhrar coal shaft A and shaft B; (b) Li in Darra Adam Khel coal M4AC and M2NM.

mainly distributed in coal on the margin of the coal basin, if the faults developed in the adjacent area to the coal deposit (Dai et al., 2015).

6 Conclusions

The conclusions drawn, based on mineralogical and geochemical investigation of the Padhrar and Darra Adam Khel coals are given as follows.

(1) Based on the proximate analysis, the Padhrar coal is classified as high volatile low-rank sub-bituminous to medium rank bituminous coal and Darra Adam Khel coal as low to high volatile low-rank sub-bituminous to medium rank bituminous coal.

(2) The depositional environment was analyzed on the basis of several parameters; the Sr/Ba (>1), $SiO_2 + Al_2O_3$ (<75%), Fe_2O_3 + CaO + MgO/$SiO_2 + Al_2O_3$ (≥0.23) and high sulfur content in Padhrar and Darra Adam Khel coals indicate marine water and epithermal influence. The Ce_N/Ce_N^* values in Padhrar coal show anoxic marine water, most Darra Adam Khel coal samples showing suboxic marine water. The values of V/Cr less 2, Ni/Co less than 5 and U/Th less than 0.75 in the Padhrar and Darra Adam Khel coal samples show that the coal formed in an oxidizing environment. The Cu/Zn ratio in Padhrar coal shows reductive oxidation and reduction, while Darra Adam Khel coal shows oxidizing to weak oxidizing.

(3) The Al_2O_3/TiO_2 values indicate the sediment source of the Padhrar and Darra Adam Khel coals, mostly related to intermediate rocks, some of the Darra Adam Khel coal being related to ultramafic rocks.

(4) The potentially valuable element lithium (Li), with significantly enriched (2.05 ppm to 317 ppm, 87.13 ppm on average) and enriched (12.6 ppm to 63 ppm, 30.56 ppm on average) concentrations in Darra Adam Khel coal, are of a mining grade. The germanium (Ge) value in Padhrar coal (9.15 ppm to 13.1 ppm, 11.16 ppm on average, and 2.98 ppm to 7.12 ppm, 4.9 ppm on average) is higher than Chinese coals (2.78 ppm) and world coals (2.0 ppm). Therefore, the large local coal reserves have enormous potential and need to be utilized to meet the country's rising energy requirements.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. U1812402) and the project of the scientific and technological innovation team of sedimentary deposits in Guizhou Province (No. 2018-5613).

Manuscript received Jun. 17, 2021
accepted Mar. 02, 2022
associate EIC: FEI Hongcai
edited by Jeffery J. LISTON and FEI Hongcai

Supplementary data to this article can be found online at https://doi.org/10.1111/1755-6724.14953.

References

Ali, M., 2018. Pakistan's quest for coal-based energy under the China-Pakistan Economic Corridor (CPEC): Implications for the environment. Environmental Science & Pollution Research, 25(32): 31935–31937.

Ali, H.M.Z., and Khan, S., 2015. Ranking of Paleocene age coal Salt Range, Punjab and its application in coal-fired power plants. Science International, 27(2): 1243–1246.

Alibo, D.S., and Nozaki, Y., 1999. Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation. Geochimica et Cosmochimica Acta, 63(3–4): 363–372.

Aitchison, J.C., Ali, J.R., and Davis, A.M., 2007. When and where did India and Asia collide. Journal of Geophysical Research, 112(5): B05423.

ASTM, 2013. Annual Book of ASTM Standards, Vol. 05.06, ASTM International, West Conshohocken, PA, 2013.

Bustin, R.M., Ross, J.V., and Rouzaud, J.N., 1995. Mechanisms of graphite formation from kerogen: experimental evidence. International Journal of Coal Geology, 28(1): 1–36

Chou, C.L., 2012. Sulfur in coals: A review of geochemistry and origins. International Journal of Coal Geology, 100: 1–13.

Dai, S., Ren, D., Tang, Y., Shao, L., and Li, S., 2002. Distribution, isotopic variation, and origin of sulfur in coals in the Wuda coalfield, Inner Mongolia, China. International Journal of Coal Geology, 51: 237–250.

Dai, S., Zhou, Y., Ren, D., Wang, X., Li, D., Zhao, L., 2007. Geochemistry and mineralogy of the Late Permian coals from the Songzao Coalfield, Chongqing, southwestern China. Science in China Series D: Earth Sciences, 50(5): 678–688.

Dai, S., Wang, X., Zhou, Y., Hower, J.C., Li, D., Chen, W., and Zou, J., 2011. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. Chemical Geology, 282(1–2): 29–44.

Dai, S., Ren, D., Chou, C.L., Finkelman, R.B., Seredin, V.V., and Zhou, Y., 2012a. Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization. International Journal of Coal Geology, 94: 3–21.

Dai, S., Zou, J., Jiang, Y., Ward, C.R., Wang, X., Tian, L., Xue, W., Liu, S., Tian, H., Sun, X., and Zhou, D., 2012b. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Adaohai mine, Daqingshan coalfield, Inner Mongolia, China: Modes of occurrence and origin of diaspore, gorceixite, and ammonian illite. International Journal of Coal Geology, 94: 250–270.

Dai, S., Wang, X., Seredin, V.V., Hower, J.C., Ward, C.R., O'Keefe, J.M., Huang, W., Li, T., Li, X., Liu, H., Xue, W., and Zhao, L., 2012c. Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: New data and genetic implications. International Journal of Coal Geology, 90: 72–99.

Dai, S., Li, T., Seredin, V.V., Ward, C.R., Hower, J.C., Zhou, Y., and Zhao, C., 2014a. Origin of minerals and elements in the Late Permian coals, tonsteins, and host rocks of the Xinde Mine, Xuanwei, eastern Yunnan, China. International Journal of Coal Geology, 121: 53–78.

Dai, S., Luo, Y., Seredin, V.V., Ward, C.R., Hower, J.C., Zhao, L., Liu, S., Tian, H., and Zou, J., 2014b. Revisiting the late Permian coal from the Huayingshan, Sichuan, southwestern China: Enrichment and occurrence modes of minerals and trace elements. International Journal of Coal Geology, 122: 110–128.

Dai, S., Seredin, V.V., Ward, C.R., Jiang, J., Hower, J.C., Song, X., Jiang, Y., Wang, X., Gornostaeva, T., Li, X., Liu, H., Zhao, L., and Zhao, C., 2014c. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. International Journal of Coal Geology, 121: 79–97.

Dai, S., Liu, J., and Ward, C.R., 2015a. Petrological, geochemical, and mineralogical compositions of the low-Ge coals from the Shengli Coalfield, China: A comparative study with Ge-rich coals and a formation model for coal-hosted Ge ore deposit. Ore Geology Reviews, 71: 318–349.

Dai, S., Wang, P., Ward, C.R., Tang, Y., Song, X., Jiang, J., Hower, J.C., Li, T., Seredin, V.V., Wagner, N.J., Jiang, Y., Wang, X., and Liu, J., 2015b. Elemental and mineralogical

anomalies in the coal-hosted Ge ore deposit of Lincang, Yunnan, southwestern China: Key role of N_2–CO_2-mixed hydrothermal solutions. International Journal of Coal Geology, 152: 19–46.
Dai, S., Graham, I.T., and Ward, C.R., 2016. A review of anomalous rare earth elements and yttrium in coal. International Journal of Coal Geology, 159: 82–95.
Dai, S., Ward, C.R., French, D., and Hower, J.C., 2018. Geochemical characteristics of rare-metal, rare-scattered, and rare-earth elements and minerals in the Late Permian Coals from the Moxinpo mine, Chongqing, China. Energy & Fuels, 32: 8891–8894.
Dai, S., Bechtel, A., Eble, C.F., Flores, R.M., French, D., Graham, I.T., Hood, M.M., Hower, J.C., Korasidis, V.A., Moore, T.A., Püttmann, W., Wei, Q., Zhao, L., and O'Keefe, J.M.K., 2020. Recognition of peat depositional environments in coal: A review. International Journal of Coal Geology, 219: 103383.
Danilchik, W., and Shah, S., 1987. Stratigraphy and coal resources of the Makarwal area, Trans-Indus Mountains, Mianwali District, Pakistan. United States Geological Survey Professional Paper, 38(4): 1341.
Economic Commission for Europe Committee on Sustainable Energy, 1998. International Classification of In-Seam Coals, United Nations, Geneva.
Etschmann, B., Liu, W., Li, K., Dai, S., Reith, F., Falconer, D., Kerr, G., Paterson, D., Howard, D., Kappen, P., Wykes, J., and Brugger, J., 2017. Enrichment of germanium and associated arsenic and tungsten in coal and roll-front uranium deposits. Chemical Geology, 463: 29–49.
Fassett, J.E, and Durrani, N.A., 1994. Geology and Coal Resources of the Thar Coal Field, Sindh Province, Pakistan. U.S. Department of the Interior, U.S. Geological Survey Open -File Report, 94–167.
Gansser, A., 1964. Geology of the Himalayas. London and New York: John Wiley, Interscience Publishers,1– 289.
Gee, E.R., and Gee, D.G., 1989. Overview of the geology and structure of the Salt Range, with observations on related areas of northern Pakistan. Special Paper of the Geological Society of America, 232: 95–112.
Goodarzi, F., 2002. Mineralogy, elemental composition and modes of occurrence of elements in Canadian feed-coals. Fuel, 81(9): 1199–1213.
Hayashi, K.I., Fujisawa, H., Holland, H.D., and Ohmoto, H., 1997. Geochemistry of 1.9 Ga sedimentary rocks from northeastern Labrador, Canada. Geochimica et Cosmochimica Acta, 61(19): 4115–4137.
Hower, J.C., Granite, E.J., Mayfield, D.B., Lewis, A.S., Finkelman, R.B., 2016. Notes on contributions to the science of rare earth element enrichment in coal and coal combustion by-products. Minerals, 6: 32. http://dx.doi.org/10.3390/min6020032.
Jackson, J.A. (ed.), 1997, Glossary of Geology. American Geological Institute, Fourth edition, 769 p.
Jaleel, A., Alam, G.S., and Hussain, M., 2002. Coal resources of four blocks in Thar coalfield, Sindh, Pakistan. Records of the Geological Survey of Pakistan, 1154–1157.
Ketris, M., and Yudovich, Y.E., 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. International Journal of Coal Geology, 78(2): 135–148.
Khattak, S. A., Rehman, G., Ahmad, S., Jan, M. F., Khurshid, S., and Ghani, A., 2017. Deformational style and hydrocarbons trapping mechanism of the sub-Himalayan frontal ranges near Fateh Jhang, Punjab, Pakistan. Journal of Himalayan Earth Sciences, 50(2): 1–13.
Li, X., Dai, S., Zhang, W., Li, T., Zheng, X., and Chen, W., 2014. Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS). International Journal of Coal Geology, 124: 1–4.
Lin, M., and Tian, L., 2011. Petrographic characteristics and depositional environment of the No. 9 Coal (Pennsylvanian) from the Anjialing Mine, Ningwu Coalfield, China. Energy Exploration & Exploitation, 29(2): 197–204.
Liu, J., Nechaev, V.P., Dai, S., Song, H., Nechaeva, E.V., Jiang, Y., Graham, I.T., French, D., Yang, P., and Hower, J.C., 2020. Evidence for multiple sources for inorganic components in the Tucheng coal deposit, western Guizhou, China and the lack of critical-elements. International Journal of Coal Geology, 223: 103468.
Malkani, M.S., 2012. A review of coal and water resources of Pakistan. Journal of Science, Technology and Development, 31(3): 202–218.
Massari, S., and Ruberti, M., 2013. Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resources Policy, 38: 36–43.
Rafique, T., Naseem, S., Bhanger, M.I., and Usmani, T.H., 2008. Fluoride ion contamination in the groundwater of Mithi sub-district, the Thar Desert, Pakistan. Environmental Geology, 56 (2): 317–326.
Ren, D., and Dai S., 2009. Potential co-associated mineral resources in coal and coal-bearing rock series: a problem worthy of attention. Coal Geology of China, 21(10): 1–4.
Seeber, L., Armbruster, J.G., and Quittmeyer, R.C., 2013. Seismicity and continental subduction in the Himalayan Arc. In: Gupta, H.K., and Delany, F.M. (eds.), Zagros Hindu Kush Himalaya geodynamic evolution. American Geophysical Union, 215–242.
Seeber, L., and Armbruster, J., 1979. Seismicity of the Hazara arc in northern Pakistan: decollement versus basement faulting. In: Farah, A., and DeJong, K.A. (eds.), Geodynamics of Pakistan. Geological Survey of Pakistan, Quetta, 131–142.
Seredin, V.V., and Dai, S., 2012. Coal deposits as potential alternative sources for lanthanides and yttrium. International Journal of Coal Geology, 94: 67–93.
Shah, S.M.I., 2009. Stratigraphy of Pakistan. Memoirs of the Geological Survey of Pakistan, 22: 482.
Shen, M., Dai, S., Graham, I.T., Nechaev, V.P., French, D., Zhao, F., Shao, L., Liu, L., Zuo, J., Zhao, J., Chen, K., and Xie., X., 2021. Mineralogical and geochemical characteristics of altered volcanic ashes (tonsteins and K-bentonites) from the latest Permian coal-bearing strata of western Guizhou Province, southwestern China. International Journal of Coal Geology, 237: 103707.
Sinha, A.K., 2013. Geology and tectonics of the Himalayan region of Ladakh, Himachal, Garwhal–Kumaun and Arunachal Pradesh: a review. In: Gupta, H.K., and Delani, F.M. (eds.), Zagros Hindu Kush Himalaya geodynamic evolution. American Geophysical Union, 122–148.
Spiro, B.F., Liu, J., Dai, S., Zeng, R., Large, R., and French, D., 2019. Marine derived $^{87}Sr/^{86}Sr$ in coal, a new key to geochronology and palaeoenvironment: Elucidation of the India-Eurasia and China-Indochina collisions in Yunnan, China. International Journal of Coal Geology, 215: 103304.
Stach, E., Mackowsky, M., Teichmüller, M., Taylor, G.H., Chandra, D., and Teichmüller, R., 1982. Coal Petrology. Gebrüder, 1–535.
Sun, Y., Püttmann, W., Kalkreuth, W., and Horsfield, B., 2002. Petrologic and geochemical characteristics of seam 9-3 and seam 2, Xingtai Coalfield, Northern China. International Journal of Coal Geology, 49: 251–262.
Sun, Y., Zhao, C., Zhang, J., Yang, J., Zhang, Y., Yuan, Y., Xu, J., and Duan, D., 2013. Concentrations of valuable elements of the coals from the Pingshuo Mining District, Ningwu Coalfield, northern China. Energy Exploration & Exploitation, 31(5): 727–744.
Sun, Y., Zhao, C., Li, Y., Wang, J., and Liu, S., 2012. Li distribution and mode of occurrences in Li-bearing coal seam 6 from the Guanbanwusu Mine, Inner Mongolia, Northern China. Energy Exploration & Exploitation, 30(1): 109–130.
Taylor, S.R., and McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution, Blackwell Scientific, 312.
U.S. Geological Survey, 2016 https://minerals.usgs.gov/minerals/pubs/commodity/germanium/ mcs-2016-germa.pdf.
U.S. Geological Survey, 2017, Mineral Commodity Summaries, Rare Earths, https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/mcs-2017-raree.pdf.
Vladimir, V.S., Dai, S., Yuzhuang, S., and Igor, I. C., 2013. Coal

deposits as promising sources of rare metals for alternative power and energy-efficient technologies. Applied Geochemistry, 31: 1–11.
Wang, W., Qin, Y., Sang, S., Zhu, Y., Wang, C., and Weiss, D.J., 2008. Geochemistry of rare earth elements in a marine influenced coal and its organic solvent extracts from the Antaibao mining district, Shanxi, China. International Journal of Coal Geology, 76(4): 309–317.
Warwick, P.D., and Javed, S., 1990. Quality and character of Pakistan coal. Geological Survey of Pakistan, 127–135.
Warwick, P., and Shakoor, T., 1988. Controls on the distribution and lithofacies of marginal marine Paleocene formations of the Salt Range, Pakistan. Geological Society of America, 20 (7): A90.
Wei, Q., and Rimmer, S., 2017. Acid solubility and affinities of trace elements in the high-Ge coals from Wulantuga (Inner Mongolia) and Lincang (Yunnan Province), China. International Journal of Coal Geology, 178: 39–55.
Wei, W., Algeo, T.J., Lu, Y., Liu, H., Zhang, S., Peng, L., Zhang, J., and Chen, L., 2018. Identifying marine incursions into the Paleogene Bohai Bay Basin Lake system in northeastern China. International Journal of Coal Geology, 200: 1–17.
World Coal Association, 2017. https://www.worldcoal.org/coal/uses-coal/coal-electricity.
Xu, F.M., and Fang, A.M., 2005. The coal facies study of Coal Seam 16 in Yanzhou coal mine. Coal Geology and Exploration, 33(4): 10–15 (in Chinese with English abstract).
Yeats, R.S., and Hussain, A., 1987. Timing of structural events in the Himalayan foothills of northwestern Pakistan[J]. Geological Society of America Bulletin, 99(2): 161–176.
Zheng, X., Wang, Z., Wang, L., Xu, Y., and Liu, J., 2017. Mineralogical and geochemical compositions of the Lopingian coals and carbonaceous rocks in the Shugentian coalfield, Yunnan, China: With emphasis on Fe-bearing minerals in a Continental-Marine Transitional Environment. Minerals, 7: 170. doi: 10.3390/min7090170.
Zhu, Q., 2004. Coal sampling and analysis standards. IEA Clean Coal Centre Park House, 14.

About the first author

Muhammad UMAIR, male, born in 1993 in Swabi, Khyber Pakhtunkhwa Province, Pakistan; graduated from the College of Resources and Environmental Engineering, Guizhou University, Guiyang, China. Engages in the study of sedimentary deposits. Currently a Ph.D. student at The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. E-mail: umaikh745@hotmail.com.

About the corresponding author

YANG Ruidong, male, born in 1963 in Dali, Yunnan Province; Professor of the College of Resources and Environmental Engineering of Guizhou University; doctoral advisor; graduated from Nanjing University; currently engaged in research on geochemistry and mineral deposits. E-mail: rdyang@gzu.edu.cn.