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Characteristics of the coal quality and elemental geochemistry in Permian coals from the Xinjier mine in the Huainan Coalfield, north China: Influence of terrigenous inputs

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ABSTRACT

Fifty-six coals along with host rocks of Permian age (including samples from the Shanxi Formation, Lower Shihezi Formation and Upper Shihezi Formation) collected from the active Xinjier mine in the Huainan Coalfield, north China were studied in the present work. The overall object of this study was to characterize the coal quality and elucidate the possible genetic types for trace-element enrichment of Xinjier coals. Based on Chinese National Standards, all the coals can be classified as medium-high-volatile to high-volatile coal and ultra-low sulfur to low sulfur coal. The vitrinite-dominated Xinjier coals show phyiso-chemical properties difference along the coal-bearing strata. Compared to the coals of the Shanxi Formation, vitrinite contents are elevated in the coals of the Lower Shihezi and Upper Shihezi Formations, which indicates that they were probably exposed to a more reducing environment during peat accumulation. Most elements, such as Al_2O_3, K_2O, Y, Se, and Sb, are enriched compared to those of Chinese and World coals. The major-element oxides Al_2O_3 and K_2O as well as trace elements Th and Y increase from the lower to upper seams. Some elements are distinctly concentrated in host rocks (roof, floor, and parting) compared with adjacent coals. These geochemical anomalies and "increasing stratigraphically upward" ash yield trend are attributed to influence from terrigenous inputs. Elements in Xinjier coals were classified into three geochemical groups based on the statistical analysis. In particular, sequential extraction experiments of selected coals found that As, Se, and Sb predominantly occur as organic associations in coal.

1. Introduction

Coal is the major source of energy in China (Bai et al., 2017), and was responsible for 62% of China's total energy consumption in 2016 (BP Statistical Review, 2017, China's energy market in 2016). Although the Chinese government has controlled the consumption of coal in recent years, China will continue to retain its current role as the leading global producer and consumer of coal.

Coal quality characteristics and elemental geochemistry are determined via a combination of several geological factors. Many published articles have indicated that source materials, depositional environments, and climatic and hydrological conditions dominantly control these properties (Dai et al., 2012a; Dai et al., 2012b; Eskenazy, 2009; Fu et al., 2016; Sun et al., 2010a, 2010b), whereas some distinct districts could also be affected by tectonic settings, magmatic intrusion, and other factors to different extents (Chen et al., 2014; Rimmer et al., 2009; Yao et al., 2011). These factors may result in lateral and stratigraphical variations in physio-chemical properties of coal.

During the exploitation, production, transportation, and utilization of coal, some hazardous elements have drawn much more attention because they could give rise to many adverse environmental effects and contamination problems. For instance, some volatile elements are potential air pollutants, particularly toxic and highly volatile elements, such as As and Se (Kang et al., 2011; Wang et al., 2009; Yudovich and Ketris, 2005, 2006), can harm human health due to the domestic burning of coal. Although some elements, such as Sb, are less volatile, they are likely to remain in coal ash, which could erode coal-fired equipment or migrate to contaminate soil and water (Qi et al., 2008a; Tang et al., 2012). Therefore, knowledge of the abundance, distribution, and mobility of these elements in coals is essential to address

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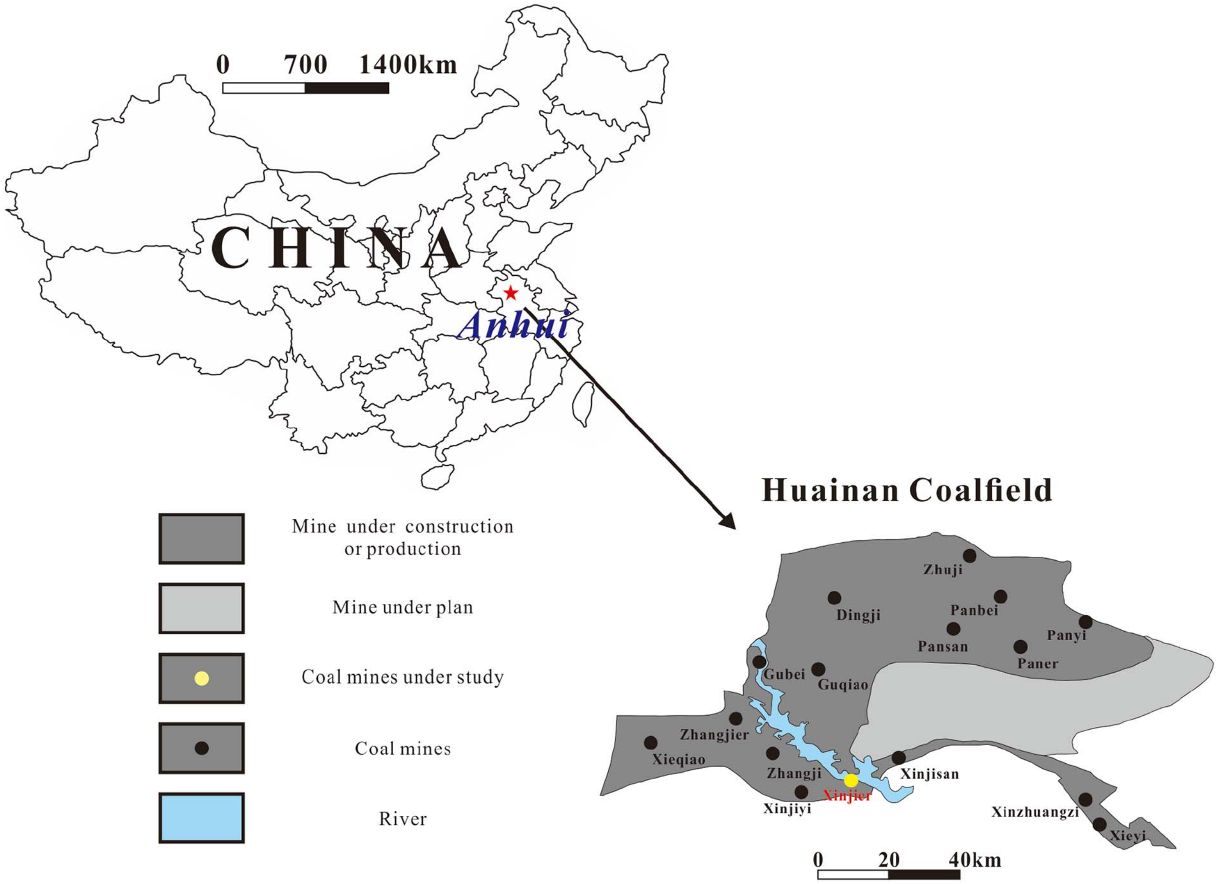

Fig. 1. Location map of the Huainan Coalfield (modified from Sun et al., 2010b).

environmental issues and minimize the damage to human health and economical production.

The Xinjier mine is located in the southwestern Huainan Coalfield of Anhui Province in China (Fig. 1). As one of the most important coal producing areas in China (Strategic Action Plan for Energy Development (2014–2020)), many studies have been conducted on coals from different mines in the Huainan Coalfield (Chen et al., 2011, 2014; Chen et al., 2016; Ding et al., 2018; Fu et al., 2016; Sun et al., 2010a, 2010b). However, there has been little determined regarding the coal quality and elemental geochemistry of Xinjier coals since the construction of this mine. Therefore, a systematic investigation was conducted based on 59 samples from the Xinjier mine to provide basic data on the characteristics of the coal quality and the geochemical composition. Meanwhile, from both a geological and environmental viewpoint, we assessed the abundances and distribution patterns of the elements in the coals, and modes of occurrence of elements were also elucidated, especially for three trace elements (As, Se, and Sb) of environmental concern.

2. Geological setting

The Huainan Coalfield, which is a main Late Paleozoic coal deposition basin in China, is situated in the southeastern rim of the North China Plate. The coalfield covers a total area of 2000 km^{2}with 80 km in mean length and 25 km in mean width. The Xinjier mine, which is located on the southern border of the Huainan Coalfield, covers an area of 30 km^2 and has an estimated available coal reserve of 415Mt.

The coal-bearing sequences in the Huainan Coalfield are mainly composed of the late Carboniferous Taiyuan Formation, the early Permian Shanxi and Lower Shihezi Formations, and the late Permian Upper Shihezi Formation. However, all coals from the Taiyuan Formation are not thick enough to be mineable. Therefore, samples were collected from the main mineable coal-bearing sequences, specifically including coal seam 1 in the Shanxi Formation; coal seams 6, 8, and 9 in the Lower Shihezi Formation; and coal seams 11 and 13 in the Upper Shihezi Formation.

2.1. Stratigraphy

The Permian coal-bearing sequences of the Xinjier mine in the Huainan Coalfield comprise the Shanxi Formation (57 m on average), the Lower Shihezi Formation (146 m on average) and the Upper Shihezi Formation (546 m on average) with a total thickness of 749 m. Twenty five coal seams occur in these three formations, and the percentages of coal thickness are 12.2%, 11.9%, and 3.5%, respectively. The accumulative thickness of economically mineable coal seams is approximately 43.67 m. The workable coal seams of 13 and 11 in the Upper Shihezi Formation, coal seams 9, 8, and 6 in the Lower Shihezi Formation and coal seams 1 in the Shanxi Formation were sampled in this study. A detailed description of the stratigraphic and lithologic characteristics of these coal-bearing sequences is provided in Fig. 2.

2.2. Depositional environment

The depositional environment of the Permian strata in the Huainan Coalfield has been documented by many researchers. Sun et al. (2010b) elaborated on the depositional environments in the

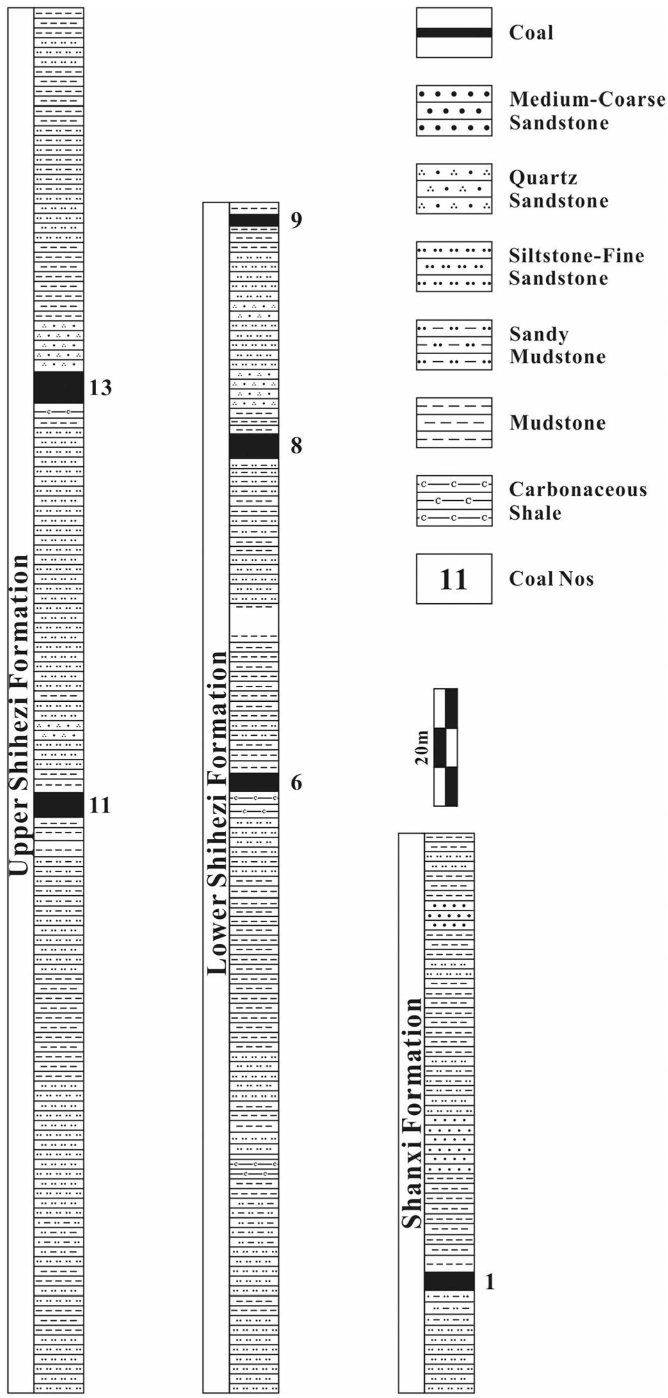

Fig. 2. Generalized stratigraphic column and lithological characteristics of coal-bearing strata in the Huainan Coalfield from Anhui, China (modified from Chen et al., 2011).

Zhuji mine using B as a significant paleosalinity indicator. The results showed that the B contents in the 11 coal seams from the Shanxi Formation to the Upper Shihezi Formation exhibited a wide range of 6–841 mg/kg with an average value of 151 mg/kg, which indicated the depositional environments had a brackish condition-orientation but fluctuated frequently. Similarly, Chen et al. (2011) inferred that there was an alternating influence of mildly brackish water and fresh water that occurred between the No. 4 and 13 coal seams in the Lower Shihezi and Upper Shihezi Formations according to the B contents due to repeated marine transgression and regression, whereas persistent brackish water influenced the No. 1 and 3 coal seams in the Shanxi Formation. Lan (1984, 1989) and Lan et al. (1988) determined the depositional environment of the coal-bearing sequences in the Huainan Coalfield from some sedimentological characteristics, such as the lithology, mineralogy, sedimentary structure, and paleontology. These studies suggested that the Shanxi Formation was developed in the subaqueous deltaic plain, coals in the Lower Shihezi Formation were accumulated in the lower deltaic plain, and the strata of the Upper Shihezi Formation was deposited in the upper deltaic plain. However, through a study of the sedimentology of the Xinji area, Zhu (1989) suggested that the strata of the Shanxi Formation was deposited in the lower deltaic plain, and the strata of the Lower Shihezi Formation was deposited mainly in the upper deltaic plain. During the Permian Period in the Huainan Coalfield, the direction of marine regression was from north to south, and the subsidence center also moved southward (Han, 1996). Therefore, these areas were situated at different locations, but there was a slight difference in the depositional environment.

3. Sample collection and analysis

During the exploration of the Xinjier mine, a total 59 samples (including coal, roof, floor, and parting samples) were collected from six mainly minable coal seams. All samples were immediately stored in polyethylene bags to prevent contamination and oxidation.

Each sample was air-dried, split, and ground to pass through a 200-mesh sieve for chemical analysis. Coal proximate analysis, including the determination of the ash yield and volatile matter was performed according to Chinese National Standard GB/T-212 (2008), and total sulfur was determined according to Chinese National Standard GB/T-214 (2007).

The maceral compositions of the coal samples were determined by point counting the polished coals under a reflecting microscope according to Chinese National Standard GB/8899-1998, and vitrinite reflectance was analyzed using a Leitz MPV-III photometer system according to Chinese National Standard GB/T 8899-1998. Mineralogical analysis of the coal was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical microscopy using reflected light.

The high-temperature ash was prepared at 815 °C in an electric furnace. All samples were digested in an acid mixture (HNO_3:HCl:HF = 3:1:1) in a microwave oven (from room temperature to 120 °C for 10 min and kept for 10 min; then increased to 160 °C for 5 min and kept for 10 min; finally increased to 180 °C for 5 min and kept for 15 min). The major elements (Al, K, and Ti in the coal, and Si, Al, Fe, Ca, Mg, S, Ti, K, Na, and Mn in the ash) were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Additionally, the trace elements (Li, Sc, V, Cr, Ni, Zn, As, Sb, Se, Ga, Sn, Pb, Th, and Y) in the coal were determined using inductively coupled plasma mass spectrometry (ICP-MS). The accuracy of the elemental compositions was evaluated using standard reference materials, NIST-1632b (coal) and GBW07406 (GSS-6, soil). The relative standard deviation was ± 5% for most of the determined elements.

The sequential extraction procedure for determining the forms of As, Se, and Sb in coals was revised, based on a previous analysis for As, Se, and Sb in coals developed in our laboratory (Kang et al., 2011; Qi et al., 2008a; Qi et al., 2008b; Wang et al., 2009). Six coal samples were selected for this study. The six-step sequential extraction procedure is outlined in Table 1. The chemical forms of these three elements in Xinjier coals were defined as water-leachable, ion-exchangeable, organic matter-associated, carbonate-associated, silicate-associated, or sulfide-associated. The recovery of the sequential extraction was calculated by dividing the sum of the elemental masses in six forms by the total elemental mass in the coal.

Table 1
Sequential extraction procedures.

Chemical speciation	The main step
Water leachable	The sample of 5 g was treated with 20 ml of Milli-Q water at room temperature for 24 h; suspension was then centrifuged at 3500 rpm for 20 min. The residue was dried at 40 °C.
Ion exchangeable	Add 30 ml of $NH_4C_2H_3O_2$ to the residue, stirring for 24 h at room temperature; suspension was then centrifuged at 3500 rpm for 20 min. The residue was dried at 40 °C.
Organic matter-associated	The residue was treated with 20 ml of $CHCl_3$ (1.47 g/cm^3), stirring for 24 h at room temperature, a float-sink separation was performed by centrifugation (3500 rpm for 20 min). The float fraction (< 1.47 g/cm^3) of the sample was dried at 40 °C and then treated with 12 ml of an oxidizing mixture (HNO_3:HCl = 3:1) and 3 ml HF in a Telfon crucible put in a microwave oven (600 W, 30 min; 1200 W, 25 min; 1200 W, 30 min).
Carbonate-associated	Add 20 ml of HCl (0.5%) to the sink fraction (> 1.47 g/cm^3) dried at 40 °C from last step, suspension was then centrifuged at 3500 rpm for 20 min. The residue was dried at 40 °C.
Silicate-associated	The residue was treated with 20 ml of $CHBr_3$ (2.89 g/cm^3), stirring for 24 h at room temperature, a float-sink separation was performed by centrifugation (5000 rpm for 20 min). The float fraction (< 2.89 g/cm^3) was digested.
Sulfide-associated	The sink fraction (> 2.89 g/cm^3) dried at 40 °C from last step was digested.

Table 2
Main coal quality parameter values of coal seams in the Xinjier mine in the Huainan Coalfield.

Coal-bearing strata	Coal seams	Thickness (m)	A_d (%)	$S_{t,d}$ (%)	V_{daf} (%)	C_{daf} (%)	R^0_{max}
		Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max
		Ave	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)
Upper Shihezi Formation	13	1.51–12.79	14.89–22.25	0.16–0.50	38.55–44.29	83.20–84.94	0.79–0.91
		4.69	17.57(9)	0.31(9)	41.63(9)	84.01(9)	0.85(9)
	11	1.55–6.43	14.55–30.18	0.31–0.67	34.36–41.58	83.77–84.62	0.80–0.91
		3.58	21.40(10)	0.48(10)	35.99(10)	84.25(10)	0.88(10)
Lower Shihezi Formation	9	0–3.48	18.72–31.88	0.26–0.50	36.17–38.78	84.31–84.83	0.91–0.93
		1.76	27.38(10)	0.40(10)	37.50(10)	84.54(10)	0.92(10)
	8	1.52–4.73	11.86–23.24	0.21–0.89	34.95–40.59	83.62–84.81	0.88–1.02
		3.41	16.84(10)	0.39(10)	37.22(10)	84.44(10)	0.93(10)
	6	1.02–8.19	15.73–32.67	0.26–0.85	35.35–39.85	83.82–85.95	0.74–0.97
		3.11	23.38(9)	0.53(9)	37.10(9)	84.78(9)	0.87(9)
Shanxi Formation	1	0.73–5.81	9.07–19.47	0.18–0.59	32.06–38.76	82.68–86.69	0.76–0.90
		3.31	12.44(8)	0.32(8)	34.74(8)	85.54(8)	0.85(8)

Abbreviations: N: number of the samples; Min: minimum; Max: maximum; Ave: average; A: ash yields; d: dry basis; S_t: total sulfur; V: volatile matter; daf: dry and ash-free basis; C: carbon contents; R^0_{max}: maximum vitrinite reflectances.

Table 3
Ash chemical composition (%) of the coal seams in the Xinjier mine in the Huainan Coalfield.

Coal seam	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	K_2O	Na_2O	MnO_2
	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max
	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)	Ave (N)
13	48.48–54.27	30.65–38.20	2.40–4.72	1.08–5.65	0.46–1.38	0.003–2.43	1.28–1.89	0.40–4.77	0.21–0.95	0.000–0.040
	50.61(9)	33.93(9)	3.77(9)	3.15(9)	0.71(9)	0.91(9)	1.70(9)	1.64(9)	0.58(9)	0.021(9)
11	51.49–56.48	29.28–34.67	3.09–5.98	1.07–3.90	0.47–2.14	0.60–2.88	1.43–2.16	1.02–3.03	0.39–0.80	0.0035–0.050
	54.09(10)	31.50(10)	3.91(10)	2.23(10)	0.95(10)	1.38(10)	1.73(10)	1.76(10)	0.55(10)	0.029(10)
9	54.53–57.66	28.89–30.70	3.08–4.42	1.76–4.71	0.80–1.42	0.69–2.50	1.15–1.71	0.65–1.11	0.25–0.55	0.000–0.036
	56.26(10)	29.53(10)	3.90(10)	3.02(10)	0.99(10)	1.49(10)	1.38(10)	1.05(10)	0.42(10)	0.012(10)
8	48.61–52.99	32.02–38.43	2.86–6.74	0.38–5.08	0.39–0.86	0.21–2.11	1.49–2.62	0.00–0.16	0.00–0.82	0.000–0.026
	50.96(10)	35.68(10)	4.72(10)	1.58(10)	0.61(10)	0.96(10)	2.08(10)	0.74(10)	0.46(10)	0.005(10)
6	40.51–52.59	24.35–35.45	3.34–9.50	2.96–18.79	0.84–2.51	1.90–5.15	1.05–1.58	0.00–1.14	0.00–0.96	0.000–0.030
	45.91(9)	30.18(9)	5.32(9)	8.39(9)	1.55(9)	3.41(9)	1.30(9)	0.55(9)	0.60(9)	0.014(9)
1	43.00–55.36	24.54–31.46	3.44–5.82	3.60–13.42	0.63–2.23	2.39–5.09	1.25–2.13	0.00–0.96	0.00–0.93	0.000–0.052
	50.53(8)	27.77(8)	4.67(8)	7.02(8)	1.30(8)	3.46(8)	1.52(8)	0.58(8)	0.55(8)	0.030(8)

Abbreviations: N: number of the samples; Min: minimum; Max: maximum; Ave: average.

Table 4
Average proportions (%) of macerals and minerals in the coal seams in the Xinjier mine in the Huainan Coalfield.

Coal seams	Vitrinite	Inertinite	Liptinite	Organic matter	Clay	Sulfide	Carbonate	Oxides and others	Mineral matter
13	58.76	17.77	18.11	94.64	5.16	0.05	0.05	nd	5.26
11	59.91	18.12	10.57	88.60	10.69	0.34	0.35	0.02	11.40
9	63.60	16.74	9.71	90.05	9.48	nd	0.47	nd	9.95
8	62.17	17.32	15.07	94.56	5.18	0.03	0.23	nd	5.44
6	53.61	20.79	14.14	88.54	11.07	0.09	0.24	0.06	11.46
1	55.32	30.94	9.94	96.20	2.98	0.10	0.66	0.06	3.80

nd means not detected.

4. Results and discussion

4.1. Coal quality

4.1.1. Volatile matter and total sulfur content

The coals in the Xinjier mine belong to the bituminous rank based on the maximum vitrinite reflectances (0.74–0.97%) and C_{daf} (82.68–86.69%) (Table 2).The range of volatile matter content is 32.06–44.29%. According to Chinese National Standards MT/849-2000 (coals with volatile matter content of 28–37% are medium-high-volatile coals and those with 37–50% are high-volatile coals), the studied coals were classified as medium-high-volatile to high-volatile coals. The mean value of volatile matter in the Lower Shihezi (37.23%) and Upper Shihezi (37.87%). Formations were slightly higher than that of the Shanxi Formation (34.74%). Sun et al. (2010a) ascribed a similar low value of volatile matter to the activity of igneous intrusions in the Zhuji mine in the Huainan Coalfield. However, an igneous intrusion in the Xinjier mine has still not been reported.

The total sulfur content of the coals ranged from 0.16% to 0.89%, with a mean value of 0.40% (Table 2), which was lower than that of average Chinese coals (1.32%) (Yuan, 1999). According to Chinese National Standard GB/T 15224.2-2010 (coals with a total sulfur content of ≤ 0.50% are ultra-low sulfur coals and those with 0.51–1.00% are low sulfur coals), coals from the Xinjier mine were classified as ultra-low sulfur to low sulfur coals. In addition, the mean value of total sulfur was comparatively higher in coal seam 6 (0.53%) and 11 (0.48%) than that of other seams, which indicates that both coal seams may experience more influence from marine water (Dai et al., 2002, 2003).

4.1.2. Ash yield and chemical composition

The ash yields of coals ranged from 9.07% to 32.67%, with an average value of 18.87% (Table 2). According to Chinese National Standards GB/T 15224.1-2010 (coals with an ash yield of ≤ 10% are ultra-low-ash coals, those with 10.01–20.00% are low-ash coals, those with 20.01–30.00% are middle-ash coals, and those with 30.01–40.00% are medium-high-ash coals), most coals from the study area were classified as ultra-low-ash to medium-high-ash coals. This large variation is significant for the utilization of Xinjier coals. The average ash yield of coal seams in the Shanxi Formation (12.44%) were considerably lower than coals from the Lower Shihezi (21.27%) and Upper Shihezi (20.12%) Formations. This variation in ash yield, so-called "increasing stratigraphically upward", generally occurs in the Huainan Coalfield (Chen et al., 2011; Fu et al., 2016; Sun et al., 2010a). According to many detailed research studies of the depositional environment, this consistent trend is mainly due to the weaker influence of marine water and increasing terrigenous inputs from the Shanxi Formation to the Lower Shihezi and Upper Shihezi Formations. As Table 3 shows, the chemical composition of coal ash consist mainly of SiO_2 and Al_2O_3; lesser proportions of Fe_2O_3, CaO, and SO_3; and minor amounts of MgO, TiO, K_2O, and other oxides. The contents of SiO_2 and Al_2O_3 make up 76.09–86.64% of the total ash. The ash belongs to the SiO_2-Al_2O_3-Fe_2O_3-CaO type, indicating that more terrestrial minerals were transported to the Xinjier area and deposited on the coastal deltaic plain with large amounts of clastics.

4.1.3. Minerals and macerals

Table 4 shows the proportions of macerals and minerals in the coal samples. Macerals account for > 88% of the entire coal composition, whereas minerals only account for 3.8–11.46%.

Vitrinite is the most abundant and liptinite is the least abundant among the macerals. The major macerals of the vitrinite group are telocollinite and desmocollinite, along with traces of corpocollinite and vitrodetrinite in a few coal seams. Macrinite, fusinite, and semifusinite dominate inertinites; while microsporinite, suberinite, and cutinite are the main liptinites. The fraction of vitrinite in the Shanxi Formation coals (average = 55.32%) is significantly lower than in the Lower Shihezi (average = 59.79%) and Upper Shihezi (average = 59.33%) Formations; this trend also occurs in the Zhangji mine (Fu et al., 2016). This suggests that the peat in the Lower Shihezi and Upper Shihezi Formations was probably formed in a more-reducing coal-forming palaeo-environment with a high water level (Suárez-Ruiz et al., 2012).

The major minerals were identified via XRD and SEM in Xinjier coal samples. Clay minerals were the major minerals, ranging from 2.98–11.07%, followed by carbonate minerals and sulfide minerals, which were scarce and only abundant in the No. 11 coal seam. Clay minerals mainly occur as disseminated or lineate distributions. Carbonate minerals occur usually as an agglomerated distribution or fracture-filling. Additionally, sulfide minerals occur in the form of scattered specks. The concentrations of clay minerals in the Lower Shihezi and Upper Shihezi Formations coals were relatively higher than in the Shanxi Formation, which also suggests more terrigenous inputs occurred in the Lower Shihezi and Upper Shihezi Formations.

4.2. Coal geochemistry

4.2.1. Elemental abundances

The arithmetic means and ranges for the 18 major and trace elements in the coals of six mineable coal seams from the Xinjier mine are provided in Table 5. It also contains the statistical values for northern China, Chinese, and World coals for comparison (Table 6).

The mean contents of Al_2O_3 (by a factor of 1.1) and K_2O (1.6 ×) were higher than the average contents for corresponding elements in Chinese coals as summarized by Dai et al. (2012a), probably indicating the abundant inputs of detrital debris, such as clay minerals. The North China Coal Basin is a stable coal accumulating basin; thus, it benefits from transportation and deposition of abundant terrigenous clastics into the coal basin (Dai et al., 2012a). Compared with Chinese coals reported by Dai et al. (2012a), the mean concentrations of most of the elements in the Xinjier coals were higher or nearly at normal levels. In particular, for Se, Sb, Sc, Cr, Ga, Sn, Th, and Y, they were obviously elevated, by approximately 2.0-times higher. The remainder elements were lower (Li, V, and Zn) than average Chinese coals. Compared with northern China coals (Tang and Huang, 2004), Xinjier coals had higher contents of Ti, Sc, Cr, Sn, Y, and Sb, whereas the remaining elements

Table 5
Numbers of samples and abundances for the 18 elements found in the coal seams.

Elements	13				11				9				8				6				1			
	AM	Max	Min	N	AM	Max	Min	N	AM	Max	Min	N	AM	Max	Min	N	AM	Max	Min	N	AM	Max	Min	N
Al_2O_3%	7.91	8.97	7.46	9	7.81	8.19	7.37	10	6.93	7.97	5.71	10	6.90	8.74	5.71	10	5.90	7.01	5.41	9	5.27	5.35	5.18	8
K_2O%	0.37	0.43	0.33	9	0.39	0.41	0.36	10	0.36	0.47	0.27	10	0.35	0.62	0.12	10	0.19	0.28	0.16	9	0.13	0.17	0.11	8
TiO_2%	0.33	0.41	0.28	9	0.41	0.45	0.35	10	0.32	0.38	0.30	10	0.32	0.39	0.27	10	0.32	0.37	0.23	9	0.41	0.50	0.37	8
Li	26.69	43.49	20.71	9	29.02	34.53	23.70	10	24.85	35.21	17.71	10	43.21	56.12	26.45	10	21.48	24.53	19.82	9	24.81	26.82	23.30	8
Sc	14.95	15.85	13.67	9	14.42	15.70	13.12	10	16.37	19.32	12.59	10	24.20	31.62	14.88	10	7.07	10.42	2.70	9	7.66	9.13	7.15	8
V	25.48	34.39	19.42	9	25.34	27.36	23.33	10	25.12	44.26	9.50	10	45.07	59.04	25.46	10	13.85	22.23	6.23	9	8.31	8.70	8.00	8
Cr	1.07	1.36	0.93	9	1.16	1.35	0.92	10	1.10	1.42	0.76	10	162.32	210.62	99.71	10	10.31	23.17	1.75	9	7.85	8.85	7.26	8
Ni	7.99	9.80	6.81	9	0.83	1.04	0.65	10	8.23	10.67	5.85	10	119.42	154.45	73.38	10	6.64	15.20	1.21	9	5.15	5.86	4.62	8
Zn	22.14	23.18	20.61	9	21.24	22.13	20.54	10	14.97	16.82	14.15	10	14.94	19.93	10.90	10	13.92	15.75	13.03	9	11.41	13.22	10.85	8
Ga	13.35	14.16	12.20	9	16.19	17.56	13.40	10	14.17	15.95	12.45	10	22.68	29.61	14.02	10	14.55	19.05	11.30	9	16.93	17.66	16.33	8
Sn	6.50	7.80	5.83	9	6.65	7.05	5.86	10	6.92	7.83	5.57	10	10.86	14.13	6.70	10	6.97	13.01	3.28	9	8.94	10.32	8.19	8
Pb	16.51	20.08	13.88	9	16.31	17.25	15.56	10	17.03	21.55	13.48	10	28.43	36.94	17.25	10	14.20	18.04	12.86	9	15.08	15.51	14.75	8
Bi	1.14	1.19	1.05	9	1.21	1.26	1.16	10	1.20	1.37	0.91	10	1.91	2.50	1.16	10	1.57	2.06	1.20	9	1.50	1.72	1.25	8
Th	15.93	17.08	15.25	9	14.46	15.85	13.77	10	11.14	12.81	9.06	10	10.81	11.98	8.47	10	10.11	12.00	9.47	9	6.96	7.73	6.59	8
Y	47.25	50.02	42.96	9	63.54	68.25	57.64	10	54.28	71.89	34.23	10	79.68	104.18	49.15	10	23.56	39.87	15.18	9	30.18	40.11	27.89	8
As	2.18	2.69	1.71	9	7.07	8.16	5.47	10	2.23	5.63	0.82	10	4.10	5.42	2.04	10	8.28	9.38	7.34	9	8.64	14.28	6.69	8
Se	9.71	11.80	8.90	9	8.39	9.01	7.97	10	9.54	11.24	7.60	10	15.80	20.50	9.74	10	9.34	9.82	8.61	9	7.30	10.06	5.54	8
Sb	5.28	5.84	4.92	9	7.46	8.15	6.67	10	5.33	5.65	4.98	10	8.55	11.18	5.29	10	5.49	5.73	5.20	9	5.91	6.87	5.09	8

AM: arithmetic average; Max: maximum; Min: minimum; N: the number of coal samples.
The units for major elements oxides from Al_2O_3 to TiO_2, and for trace elements from Li to Sb are % and mg/kg, respectively.

were lower or fairly equal. The abundances for most elements in the Xinjier coals were enriched or equivalent in comparison with the average values of World hard coals, as summarized by Ketris and Yudovich (2009), except for V, Zn, and As.

In general, comparisons with northern China, Chinese and World coals showed that most elements in Xinjier coals were higher than in Chinese and World coals. The highly elevated contents of As, Se, Sb, Cr, Sn, and Th, which are potential toxic elements, deserve more attention due to their environmental effects. For some valuable elements, including Sc, Ga, and Y, their enrichments are also particularly worth noting for utilization from a practical and economical point of view.

4.2.2. Distribution characteristics of the elements

The elemental abundances typically vary spatially in a mine or even in a coalfield. The characteristics of the vertical distribution of elements were studied under different scales of stratigraphic units in the Xinjier mine.

The average values for the elements in the coals from different formations are presented in Table 7. The contents of Al_2O_3, K_2O, and Y were obviously higher in the Lower Shihezi and Upper Shihezi Formations compared with the Shanxi Formation. The coals in the Lower Shihezi Formation were fairly enriched in V, Cr, and Ni. Remarkably, the content of As, a significant toxic element, was the highest in the Shanxi Formation. Nevertheless, only small differences in the contents of Ti, Ga, Sn, Li, Bi, and Sb appeared among these three formations.

Plots of the elemental abundances as a function of the coal seams (Fig. 3) show important variability among the different coal seams. The abundances of Al_2O_3, K_2O, and Th significantly increase from the lower to upper coal seams. The increasing trends for these lithophile elements may suggest that terrigenous inputs increased vertically towards the upper coal sequences. This is generally in agreement with previous studies (Chen et al., 2011; Sun et al., 2010b). There are significant enrichments of Ga, Sn, Pb, Bi, and Se in the No. 8 coal seam. Chen et al. (2016) specifically studied the same coal seam in the Zhuji mine in the Huainan Coalfield, and reported the average concentrations of Sn, Bi, and Se in the No.8 coal seam are higher than corresponding elements in Chinese, World coals, and Clark value of sedimentary rock. According to their study, the No.8 coal seam in the Zhuji mine was deposited in an acidic-reducing and anoxic depositional environment that was slightly influenced by seawater, which served as a favorable environment for anaerobic bacterial activities. These conditions may result in the accumulation of these elements in the No.8 coal seam. Furthermore, the significant differences in abundances of these elements could serve as useful geochemical indicators to distinguish the No.8 coal seam from adjacent coal seams.

To investigate the elemental variation in the individual coal seams, the following samples were systematically collected: (a) nine coals and one floor from the No. 6 coal seam, (b) ten coals and one parting from the No. 11 coal seam, and (c) nine coals and one roof from the No. 13 coal seam. The distribution patterns of some selected elements in these three coal seams are shown in Fig. 4. The elements in different coal seams show different variations. However, there is a common phenomenon in that some elements (Al_2O_3, K_2O, Zn, Th, Li, Pb, Sc, and Y) are accumulated in the floor, roof, and parting or the coal samples near them. Similar conclusions have been observed in many other studies (Chen et al., 2011; Fu et al., 2016). This noteworthy feature means that host rocks (floor, roof, and parting) significantly carry these elements, and terrigenous inputs may primarily influence the distribution of these elements in coal seams. Additionally, elemental enrichment in the coals above or beneath host rocks is also probably attributed to leaching and transportation during the rise or drop of the groundwater table and its flow through host rocks (Sun et al., 2010a, 2010b). Finally, the uniform distribution of these elements may indicate that these three seams in the Xinjier mine formed in a relatively stable depositional environment.

Table 6
Elemental abundances in coals from the Xinjier mine and comparisons with northern China, Chinese, and World coals.

Elements	This study				Northern China[a]				Chinese coals[b]		World coals (hard coals)[c]	CC
	AM	Max	Min	N	AM	Max	Min	N	AM	N	AM	
Al_2O_3%	6.84	8.97	5.18	56	nd	nd	nd	nd	5.98	1322	nd	1.1
K_2O%	0.31	0.62	0.11	56	nd	nd	nd	nd	0.19	1322	nd	1.6
TiO_2%	0.30	0.41	0.21	56	nd	nd	nd	nd	0.33	1322	0.133	0.9
Li	28.62	56.12	17.71	56	18.0	40.0	6.0	43	31.80	1274	14.00	0.9
Sc	14.45	31.62	2.70	56	6.0	20.0	0.6	172	4.38	1919	3.70	3.3
V	24.57	59.04	6.23	56	38.0	70.0	7.0	86	35.10	1324	28.00	0.7
Cr	32.34	210.62	0.76	56	16.0	60.0	2.0	206	15.40	1615	17.00	2.1
Ni	26.03	154.45	0.65	56	20.0	60.0	1.0	122	13.70	1392	17.00	1.9
Zn	16.56	23.18	10.85	56	30.0	100.0	1.0	217	41.40	1458	28.00	0.4
Ga	16.38	29.61	11.30	56	13.0	20.0	1.0	1126	6.55	2451	6.00	2.5
Sn	7.81	14.13	3.28	56	2.0	4.0	1.0	32	2.11	848	1.40	3.7
Pb	18.12	36.94	12.86	56	20.0	60.0	5.0	188	15.10	1446	9.00	1.2
Bi	1.42	2.50	0.91	56	1.6	4.8	0.7	9	0.79	856	1.10	1.8
Th	11.68	17.08	6.59	56	7.0	20.0	2.0	233	5.84	1052	3.20	2
Y	50.96	104.18	15.18	56	9.0	22.0	4.0	17	18.20	888	8.20	2.8
As	5.31	14.28	0.82	56	3.0	10.0	0.4	249	3.79	3386	9.00	1.4
Se	10.13	20.50	5.54	56	6.0	11.0	0.1	171	2.47	1537	1.60	4.1
Sb	6.38	11.18	4.92	56	0.6	7.0	0.1	172	0.84	596	1.00	7.6

AM: arithmetic average; Max: maximum; Min: minimum; N: the number of coal samples; nd: no data; CC: concentration coefficient = AM of this study/AM of Chinese coals.
The units for major elements oxides from Al_2O_3 to TiO_2, and for trace elements from Li to Sb are % and mg/kg, respectively.
[a] From Tang and Huang (2004).
[b] From Dai et al. (2012a).
[c] From Ketris and Yudovich (2009).

Table 7
Average elemental abundances in coals from the Shanxi, Lower Shihezi and Upper Shihezi Formations in the Xinjier mine in the Huainan Coalfield.

Element	Shanxi Formation	Lower Shihezi Formation	Upper Shihezi Formation
Al_2O_3%	5.27	6.60	7.86
K_2O%	0.13	0.31	0.38
TiO_2%	0.26	0.32	0.29
Li	24.81	30.13	27.92
Sc	7.66	16.19	14.67
V	8.31	28.51	25.41
Cr	7.85	59.55	1.12
Ni	5.15	46.08	4.22
Zn	11.41	14.64	21.66
Ga	16.93	17.22	14.84
Sn	8.94	8.30	6.58
Pb	15.08	20.08	16.40
Bi	1.50	1.56	1.18
Th	6.96	10.71	15.15
Y	30.18	53.50	55.83
As	8.64	4.75	4.75
Se	7.30	11.64	9.01
Sb	5.91	6.49	6.43

The units for major elements oxides from Al_2O_3 to TiO_2, and for trace elements from Li to Sb are % and mg/kg, respectively.

4.2.3. Modes of occurrence of trace elements

In the present work, a Spearman correlation analysis between the content of each element and the ash yield in 56 coal benches was conducted to preliminarily infer modes of occurrence of elements in Xinjier coals. The Spearman correlation coefficients of these elements with ash yield are tabulated in Table 8, and three groups are categorized. Group 1 elements include Sc and Y. These two elements are significantly positively correlated with ash yields ranging from 0.7 to 0.8, indicating they dominantly occur in inorganic matter. Scandium and Y are typical lithophile elements; thus, some clastic minerals of terrigenous origin are their possible host minerals (Seredin and Dai, 2012). Zinc, Li, K, Pb, Al, Ti, Sn, Th, Ga, Bi, and V are in Group 2 (r_{ash} = 0.3–0.69). The elements in this group show more organic affinity compared with Group 1 and usually have intermediate affinity. Vanadium in coal is generally associated with both organic matter and mineral matter (Liu et al., 2016b), and clay minerals were reported to be its main carriers mineral (Chen et al., 2011; Fu et al., 2013; Liu et al., 2016a). However, the correlation coefficients of V and Al were not high ($r_{V\text{-}Al}$ = 0.372), which perhaps suggests that vanadium is also related to organic matter or other minerals in Xinjier coals, but this is not the case for Al-bearing minerals. Group 3 elements include Ni, Cr, Se, Sb, and As, and their correlation coefficients with the ash yield were all below 0.3. These elements are more likely associated with organic matter or only dominant organic phases.

Arsenic, Se, and Sb have been cited as potentially hazardous elements by the U.S. Clean Air Act Amendments (Finkelman, 1994); therefore, a sequential extraction was specifically conducted to examine the detailed chemical forms of As, Se, and Sb. The fraction of different forms of As, Se, and Sb in six samples from different seams are listed in Table 9. The sum of the masses of As, Se and Sb in the six fractions are in good agreement with each total mass in the coals, with recoveries of 85.7–109.1%, 85.1–108.2%, and 73.3–100%, respectively.

Table 9 shows that As is mainly mixed with organic matter (35.4%) and sulfide (39.5%). Silicate-associated As is almost equal to carbonate-associated As, accounting for 11.1% and 7.8%, respectively. Many studies have showed that As in coal mineral matter commonly occurs in Fe-sulfides (pyrite and marcasite) (Finkelman, 1994; Hower et al., 2008; Kang et al., 2011; Yudovich and Ketris, 2005). Direct methods, such as micro-PIXE techniques (Hower et al., 2008), have demonstrated that As in some bituminous coal occurs primarily as a substitutional replacement for S in coal in the Fe-sulfide structure, and have wide variations in the concentrations of different size and genetic types of iron disulfides (Hower et al., 2008). Additionally, arsenic has also been found as arsenate (As^{5+}) and arsenite (As^{3+}) in associated organics (Kang et al., 2011).

The leading chemical forms of Se in Xinjier coals include organic matter-associated (40.9%), followed by an equal amount in of sulfide-associated (24.5%) and silicate-associated (22.5%) forms. These three forms account for 87.9% of the total. Based on several previous studies, the organic constituents of Se in most coals are generally indicated.

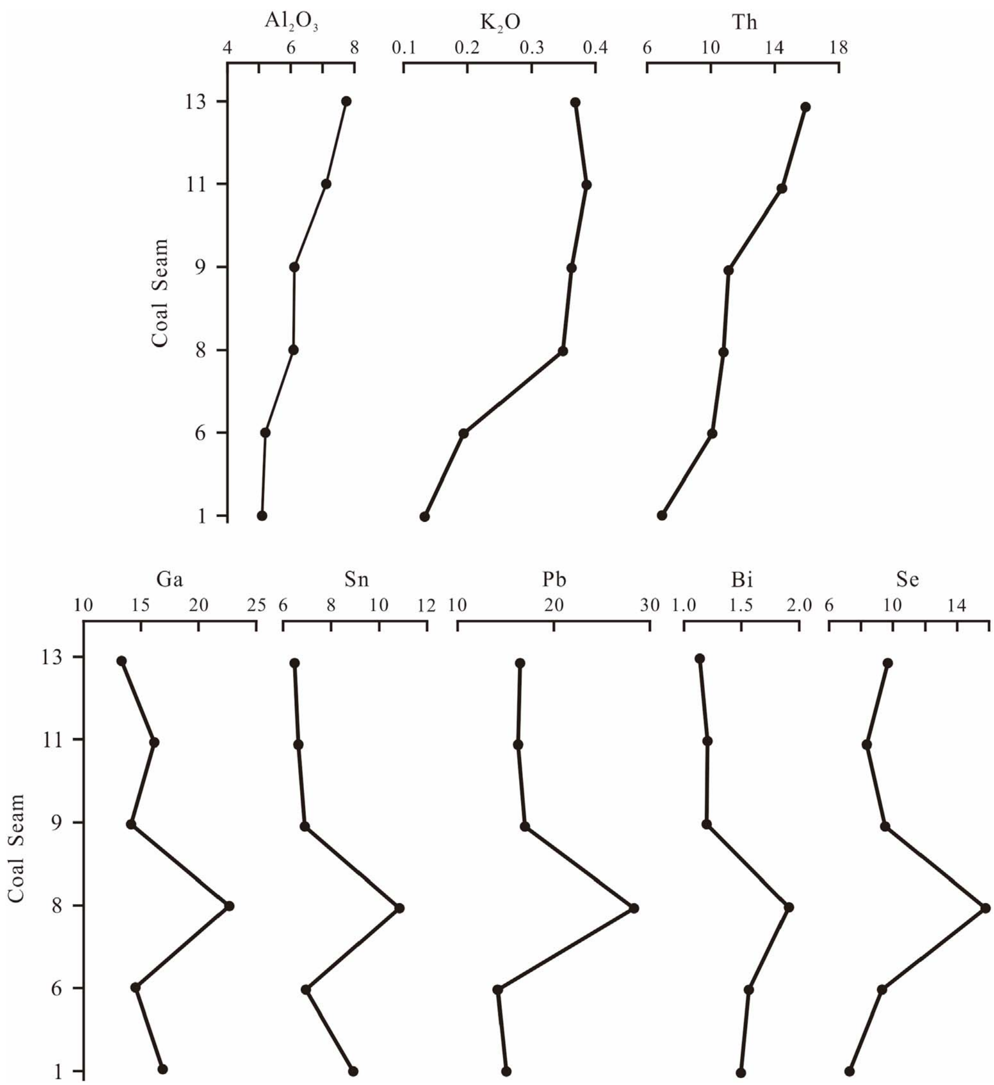

Fig. 3. Distributions of selected elements among different seams in the Xinjier mine in the Huainan Coalfield.

Other important mixtures with Se include those associated with Fe-sulfides and some accessory sulfide minerals (especially galena), possibly with selenide substitution in the sulfide structure. It was also detected in several other forms, such as PbSe minerals and aluminosilicate minerals (Finkelman, 1994; Hower and Robertson, 2003; Liu et al., 2007; Wang et al., 2009; Yudovich and Ketris, 2006; Zhang et al., 2007).

The large fraction of Sb forms are also organic matter–associated (60.5%), and sulfide-associated Sb is the second most abundant form, which accounts for 32.6%. Most studies have suggested that modes of occurrence of Sb in coal are still ambiguous (Eskenazy, 1995; Finkelman, 1994; Qi et al., 2008a; Qi et al., 2008b). Antimony may be present in solid solution in pyrite and may also be associated with organic matter (Qi et al., 2008a). However, Finkelman (1994) suggested that some tiny accessory sulfide (e.g. stibnite, Sb_2S_3) particles finely dispersed in the organic matrix may be mistaken for organic matter-associated, but direct evidence is still lacking.

From the above observation, the water-leachable and ion-exchangeable As, Se, and Sb in Xinjier coals are all insignificant. Arsenic, Se, and Sb were all negatively correlated with the ash yield, suggesting their predominant organic affinity. This is in accordance with the result from sequential extraction in which organic matter-associated As, Se, and Sb account for approximately 40–60% of the total As, Se, and Sb in coals. These data are significant for potential environmental impacts on the utilization of Xinjier coals. During coal cleaning, the sulfide-associated fraction can be easily removed from coals, leading to less emission of these hazardous elements. However, the organic-associated fraction is difficult to clean, and these elements need to be captured after use.

5. Conclusions

This research suggests that the coals collected from six major minable coal seams in the Xinjier mine in the Huainan Coalfield are medium-high-volatile to high-volatile bituminous coals. They have ultra-low to low sulfur contents and ultra-low to medium-high ash yield. The vitrinite contents and ash yield all increased in the coals of the Lower Shihezi and Upper Shihezi Formations, which indicates that the Lower Shihezi and Upper Shihezi Formations were deposited in a more reducing environment and received abundant terrigenous inputs during peat accumulation relative to the Shanxi Formation.

The comparison with northern China, Chinese, and World coals showed that most elements (such as Al_2O_3, K_2O, Y, Se, and Sb) in Xinjier coals are higher than in Chinese and World coals, whereas only Ti, Sc, Cr, Sn, Y, and Sb are more enriched than in coals from northern China. The vertical elemental variations are distinct among different formations and coal seams, and the vertical elemental variations within individual coal seams suggest that host rocks (including roof, floor, and

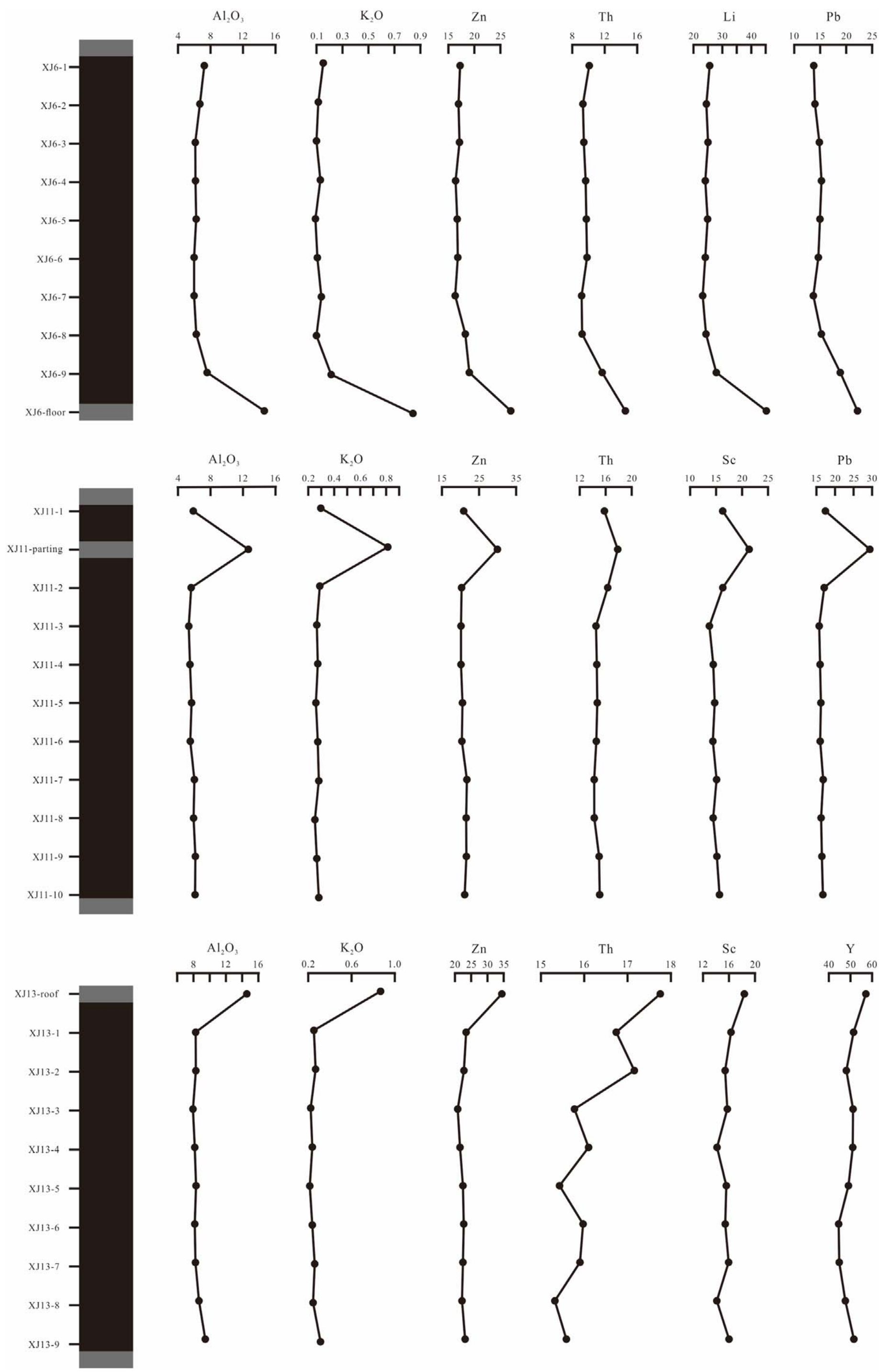

Fig. 4. Distributions of selected elements in the No. 6, 11, and 13 seams in the Xinjier mine in the Huainan Coalfield.

Table 8
Elemental affinities deduced from the Spearman's correlation coefficients between individual elements and the ash yield.

Group 1: r_{ash} = 0.7–0.8	Sc, Y
Group 2: r_{ash} = 0.3–0.69	Zn, Li, K, Pb, Al, Ti, Sn, Th, V, Ga, Bi
Group 3: r_{ash} < 0.3	Ni, Cr, Se, Sb, As

Correlation is significant at 0.05 level (2-tailed).

partings) are significant carriers of some elements in coal. Three groups (r_{ash} = 0.7–0.8, 0.3–0.69, < 0.3) of modes of elemental occurrence were classified based on the correlation coefficients of the elemental abundances with ash yield. Using six-step sequential extraction, the chemical forms of As, Se, and Sb in Xinjier coals were determined, and the results showed that there exists a substantial portion of these elements in organic matter, whereas the sulfide-associated form is also important for As.

Table 9
Fraction (%) of As, Se, and Sb in six selected samples from different seams as defined by the sequential extraction experiment.

Coal seam	As	Water leachable	Ion exchangeable	Organic matter bound	Carbonate bound	Silicate bound	Sulfide bound	Recoveries
1	XJ1–4	bdl	6.7	53.3	bdl	13.3	26.7	107.1
6	XJ6–4	bdl	bdl	50	bdl	16.7	33.3	85.7
8	XJ8–4	bdl	4.2	37.5	4.2	8.3	45.8	100
9	XJ9–4	8.3	5.6	8.3	5.6	13.9	58.3	109.1
11	XJ11–4	bdl	bdl	32	12	8	48	92.6
13	XJ13–4	bdl	12.5	31.3	25	6.3	25	106.7
	Average fraction	1.4	4.8	35.4	7.8	11.1	39.5	

Coal seam	Se	Water leachable	Ion exchangeable	Organic matter bound	Carbonate bound	Silicate bound	Sulfide bound	Recoveries
1	XJ1–4	2.6	5.1	51.3	bdl	23.1	17.9	85.1
6	XJ6–4	4.2	8.3	8.3	12.5	29.2	37.5	88.9
8	XJ8–4	3.7	3.7	47.6	6.1	22	17.1	103.8
9	XJ9–4	0.8	1.2	49.2	3.6	24.9	20.3	104
11	XJ11–4	1	2.1	47.7	10.4	13.9	24.9	97.4
13	XJ13–4	2	4.6	41.1	1	21.8	29.4	108.2
	Average fraction	2.4	4.2	40.9	5.6	22.5	24.5	

Coal seam	Sb	Water leachable	Ion exchangeable	Organic matter bound	Carbonate bound	Silicate bound	Sulfide bound	Recoveries
1	XJ1–4	2.8	2.8	63.9	5.6	8.3	16.7	92.3
6	XJ6–4	bdl	bdl	75	bdl	bdl	25	75
8	XJ8–4	bdl	bdl	54.5	bdl	bdl	45.5	100
9	XJ9–4	bdl	9.1	45.5	bdl	bdl	45.5	73.3
11	XJ11–4	bdl	bdl	65.2	4.3	8.7	21.7	85.2
13	XJ13–4	bdl	bdl	58.8	bdl	bdl	41.2	89.5
	Average fraction	0.5	2	60.5	1.7	2.8	32.6	

bdl, below detection limit.

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