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Geochemical Characteristics of Trace Elements in the No. 6 Coal Seam from the Chuancaogedan Mine, Jungar Coalfield, Inner Mongolia, China

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Abstract: Fourteen samples of No. 6 coal seam were obtained from the Chuancaogedan Mine, Jungar Coalfield, Inner Mongolia, China. The samples were analyzed by optical microscopic observation, X-ray diffraction (XRD), scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF) methods. The minerals mainly consist of kaolinite, pyrite, quartz, and calcite. The results of XRF and ICP-MS analyses indicate that the No. 6 coals from Chuancaogedan Mine are higher in Al_2O_3, P_2O_5, Zn, Sr, Li, Ga, Zr, Gd, Hf, Pb, Th, and U contents, but have a lower SiO_2/Al_2O_3 ratio, compared to common Chinese coals. The contents of Zn, Sr, Li, Ga, Zr, Gd, Hf, Pb, Th, and U are higher than those of world hard coals. The results of cluster analyses show that the most probable carrier of strontium in the coal is gorceixite; Lithium mainly occurs in clay minerals; gallium mainly occurs in inorganic association, including the clay minerals and diaspore; cadmium mainly occurs in sphalerite; and lead in the No. 6 coal may be associated with pyrite. Potentially valuable elements (e.g., Al, Li, and Ga) might be recovered as byproducts from coal ash. Other harmful elements (e.g., P, Pb, and U) may cause environmental impact during coal processing.

Keywords: mode of occurrence; cluster analysis; minerals in coal; Jungar Coalfield

1. Introduction

Coal is the main fossil fuel resource and energy source in China. China's energy consumption has grown and will continue to grow along with its economic growth [1]. In the process of coal utilization, the recovery of valuable elements from fly ash, as well as the impact on environment from harmful trace elements, have become important research topics [2,3]. In some cases, Ge, Ga, Li and U can be enriched to higher levels than usual economic grades [4], while As, Pb, Hg, and F are potentially toxic. Furthermore, the modes of occurrence of trace elements in coal control the stratus of their emission in coal combustion processes [5]. Moreover, Sr, Ba, B, and V have great significance to the environment regarding coal formation [5].

The valuable trace elements associated with Jungar coal have been reported by many authors [1,6–12], and the toxic trace elements have been investigated by several researchers [13–16]. However, these previous studies were essentially focused on the northern and central parts of the Jungar Coalfield, such as the Heidaigou Opencut Mine, the Haerwusu Opencut Mine, and the Guanbanwusu Mine (Figure 1) [4,5,7,17,18].

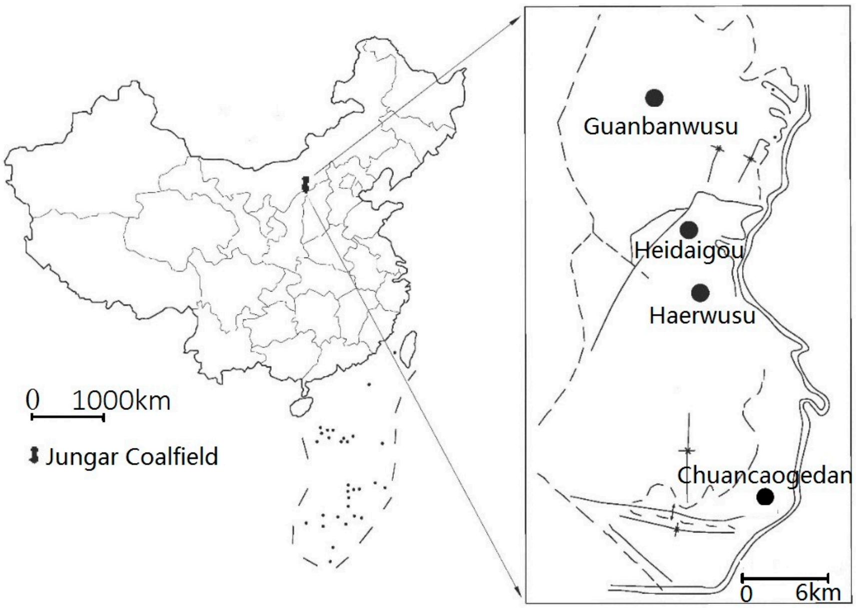

Figure 1. Locations of the Chuancaogedan Mine, Guanbanwusu Mine, Heidaigou Opencut Mine, and Haerwusu Opencut Mine in the Jungar Coalfield.

In this study, the No. 6 coal seam from the Chuancaogedan Mine was chosen because this mine is located on the southern edge of the Jungar Coalfield (Figure 1). Compared with the northern and central parts, Chuancangedan is further away from the provenance—the Yinshan Upland [4,17,18]. In this paper, the concentrations and modes of occurrence of the trace elements of No. 6 coal from the Chuancaogedan Mine are reported. The results provide new data on trace element enrichment in coal.

2. Geological Setting

The Jungar coalfield is located in the southern Yinshan Oldland (Figure 1), and is one of several Late Palaeozoic coal-bearing basins in this region [19]. The Jungar coalfield is ~64 km long (N–S) by ~26 km wide (W–E), with a total area of 1700 km^2. This coalfield was sustained by dynamic tectonic activities, and the formation, sedimentation, and evolution of the Jungar coalfield was controlled by the tectonic processes of the Central Asian Orogenic Belt (CAOB) [20,21]. The Permo-Carboniferous denudation processes of the basin development started from the Cambrian-Ordovician periods, then gradually progressed to the Middle and Late Palaeozoic [22]. During the period from the end of the Early Permian to the Late Permian, intermediate-felsic lavas erupted in the CAOB and this lava sequence might have provided an important source of minerals to the coal formations in the region.

The Taiyuan Formation, with a total thickness of 21–95 m, is mainly composed of grey and greyish-white quartzose sandstone, mudstone, siltstone, and coal which is interbedded with dark-grey mudstone, siltstone, limestone, and thin-bedded quartzose sandstone. The Taiyuan Formation was formed in paralic delta and tidal flat-barrier complex environments (Figure 2).

The No. 6 coal seam, the main minable seam, is located in the second section of the Taiyuan Formation. The thickness of the No. 6 coal varies from 0.30 to 16.80 m (11.61 m on average), with 0 to 7 partings. The partings consist mainly of mudstone. The floor and the roof are mainly composed of mudstone, sandy mudstone, and siltstone.

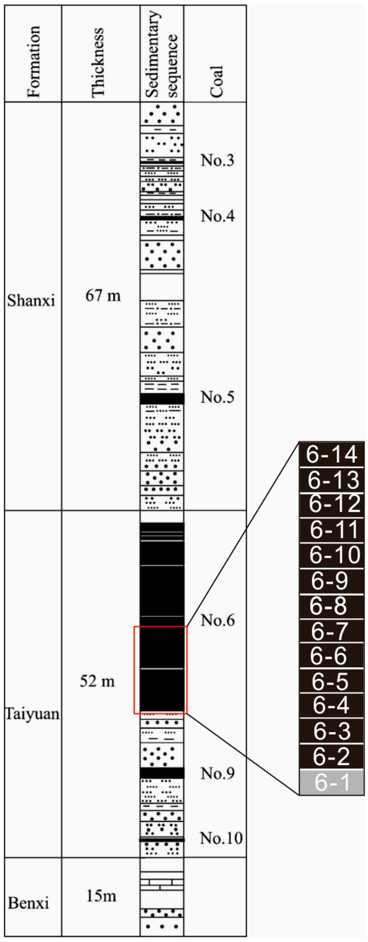

Figure 2. Lithostratigraphical column of the Jungar Coalfield and lithological column of the sampling profile.

3. Samples and Methods

Fourteen bench samples were taken from the workface at the Chuancaogedan Mine, following the Chinese Standard Method GB 482-2008 [23]. Every coal bench sample was cut over a column that was 10-cm wide, 10-cm deep, and 50-cm thick. All the collected samples were immediately stored in plastic bags to minimize contamination and oxidation. From bottom to top, the 14 bench samples were identified as 6-1 (roof) to 6-14 (Figure 2)

The mineralogical composition was determined on the raw coal samples by coal-petrography microscopy (Leica DM 4500P microscope (Leica Microsystems, Solms, Germany) (at a magnification of 500×) equipped with a Craic QDI 302™ spectrophotometer, CRAIC, San Dimas, CA, USA). Low-temperature ashing of coal was performed on an EMITECH K1050× plasma asher (Quorum, Ashford, UK). The temperature for low-temperature ashing was kept lower than 200 °C (75 W power). X-ray diffraction (XRD) analyses on the resultant low-temperature ashes and the parting samples were performed on a D/max-2500/PC powder diffractometer (Rigaku, Tokyo, Japan) with Ni-filtered Cu-Kα radiation and a scintillation detector. The XRD patterns were recorded over a 2θ interval of 2.6°–70°, with a step size of 0.01°.

A scanning electron microscope (HITACHI UHR FE-SEM, SU8220, HITACHI, Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (SEM-EDS) was used to study the distribution characteristics of the minerals, and the distribution patterns of some elements of interest in the coal.

All of the samples were crushed and ground to pass 200 mesh (75 μm) for elemental analysis. X-ray fluorescence spectrometry (XRF) was used to determine the oxides of the major elements in the coal ash (815 °C), including Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, and Fe_2O_3 [24].

Inductively coupled plasma mass spectrometry (ICP-MS) was applied to determine the trace element contents in the coal samples. For the ICP-MS analysis, microwave digestion of an approximate 200-mg sample (∅ <40 μm) was weighed into PTFE (Poly Tetra Fluoro Ethylene) vessels; 2 mL of HF (50%) + 5 mL of HNO_3 (65%) + 2 mL of H_2O_2 (30%) were added, and microwave digestion was performed for 1 h at a temperature of 210 °C. This solution was then transferred into 125-mL FEP (Fluorinated Ethylene Propylene) bottles that were filled with 100 g of deionized water [24].

4. Results and Discussion

4.1. Minerals in the Coal

The XRD results from the low temperature ashes, optical microscopic observations, and SEM-EDS data show that the minerals in the No. 6 coal from Chuancaogedan are mainly composed of clay (kaolinite) pyrite, quartz and calcite (Figures 3–6).

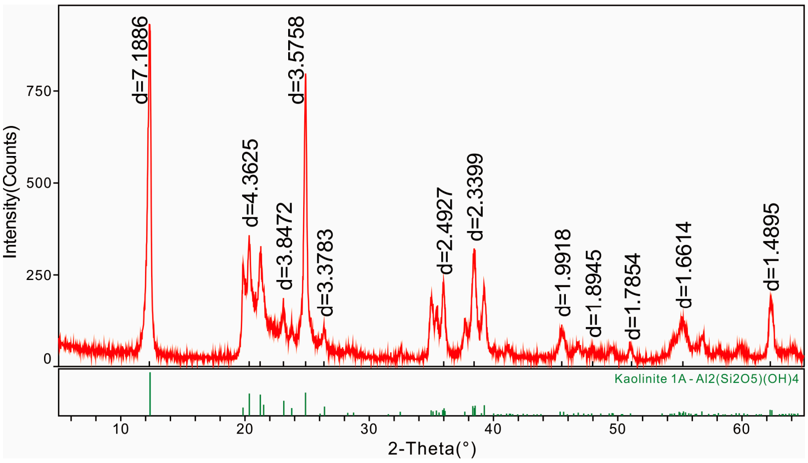

Figure 3. Identification of minerals in the X-ray diffraction (XRD) pattern of the low temperature ash (LTA) of Sample 6-10.

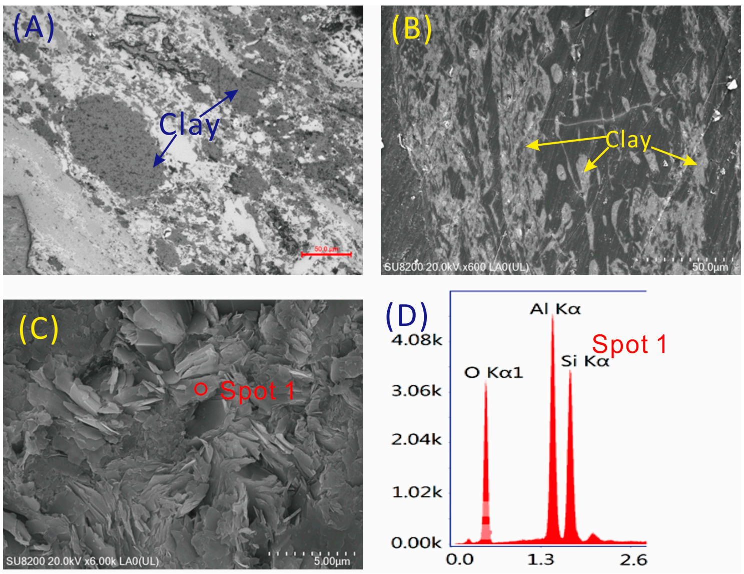

Figure 4. Clay minerals in Sample 6-1. (**A**) Lumpy clay with microgranular texture (reflected light); (**B**) Cell-filling clay minerals (scanning electron microscopy, SEM); (**C**) Crystalline kaolinite (SEM) and energy-dispersive X-ray spectrometry (EDS) spectrum from Spot 1 (**D**).

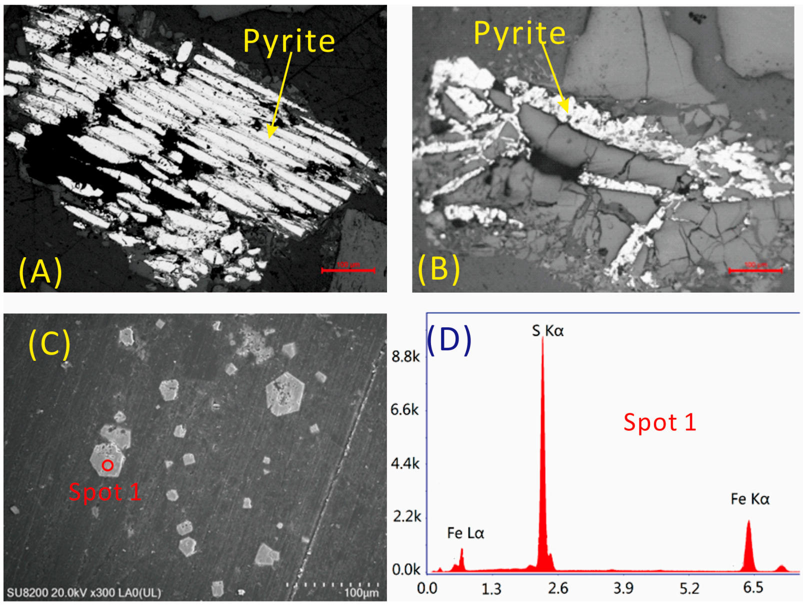

Figure 5. Pyrite in the Sample 6-13. (**A**) Pyritized cell filling (reflected light); (**B**) Fracture-filling pyrite (reflected light); (**C**) Crystals of pyrite (SEM) and EDS spectra of it (**D**).

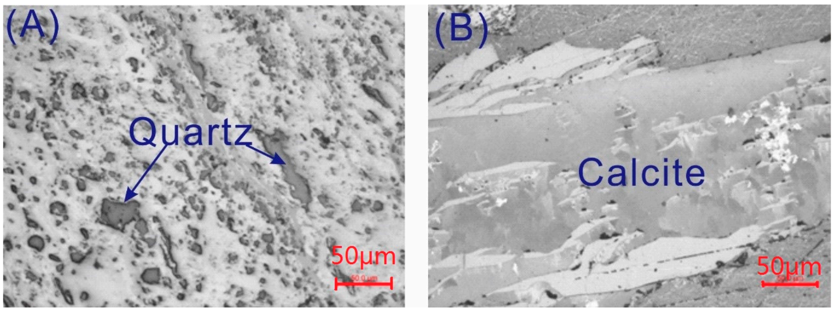

Figure 6. Quartz (**A**) and calcite (**B**) in the Sample 6-3 (reflected light).

The clay minerals mainly occur as lumps and cell-fillings with microgranular surfaces (Figure 4A) in telinite and fusinite (Figure 4B). This is common in many other coals and closely associated strata, and may indicate formation by authigenic processes. The results from XRD (Figure 3) and SEM-EDS studies (Figure 4C,D) show that the clay minerals consist mainly of kaolinite. Moreover, the data also indicates that kaolinite is well crystallized.

Pyrite is one of the most common sulfides occurring in coal, especially in coals formed in marine influenced depositional environments. Pyrite in the No. 6 coal predominantly occurs in pyritized cells (Figure 5A) and as fracture-fillings (Figure 5B); euhedral pyrite crystals are also found in the coal (Figure 5C,D), showing that pyrite can be of both syngenetic and epigenetic origin.

Quartz is commonly distributed in the macerals as irregular particles (Figure 6A) in this coal, suggesting a terrigenous detrital origin. Calcite mainly occurs as fracture-infillings (Figure 6B) in the No. 6 coal, indicating an epigenetic origin.

4.2. Major Element Contents in the No. 6 Coal

The contents of major oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, and Fe_2O_3, on dry coal basis) in the No. 6 coal from Chuancaogedan Mine, in comparison to the average values of coals from Guanbanwusu, Haerwusu, Heidaigou and averages for Chinese coals, are listed in Table 1. Although the oxides of major elements in the No. 6 coal from the Chuancaogedan Mine are dominated by SiO_2 (8.09% on average) and Al_2O_3 (6.76% on average) (Table 1), the SiO_2/Al_2O_3 ratio of the No. 6 coal (1.20 on average) is lower than the common values of Chinese coals. Because quartz is virtually absent, the clay minerals are the major carrier of Si in the coal [25].

Table 1. Contents of major elements (re-calculated as oxides; in %, on dry coal basis) and total sulfur in No. 6 coal from Chuancaogedan.

Sample	LOI	Na_2O	MgO	Al_2O_3	SiO_2	SiO_2/Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	St
6-1 (roof)	20.24	0.008	0.000	34.98	43.30	1.24	0.025	0.072	0.06	0.85	0.0000	0.18	0.07
6-2	95.21	0.008	0.013	1.96	2.29	1.17	0.004	0.019	0.06	0.07	0.0001	0.29	0.60
6-3	89.53	0.004	0.029	2.45	2.24	0.91	0.011	0.004	0.09	0.04	0.0005	5.48	4.37
6-4	96.00	0.002	0.013	1.64	1.87	1.14	0.005	0.004	0.08	0.07	0.0003	0.25	0.64
6-5	93.09	0.003	0.024	2.84	2.89	1.02	0.253	0.012	0.21	0.08	0.0003	0.23	0.75
6-6	91.29	0.003	0.011	3.69	4.23	1.15	0.125	0.003	0.10	0.09	0.0003	0.31	0.34
6-7	94.56	0.002	0.013	2.22	2.54	1.14	0.043	0.003	0.10	0.04	0.0005	0.41	0.74
6-8	76.45	0.010	0.069	9.10	13.91	1.53	0.006	0.077	0.06	0.13	0.0005	0.16	1.16
6-9	84.03	0.006	0.033	6.78	7.93	1.17	0.037	0.019	0.21	0.16	0.0004	0.62	0.73
6-10	85.25	0.003	0.019	6.24	6.96	1.12	0.389	0.007	0.23	0.14	0.0004	0.54	0.81
6-11	84.12	0.003	0.016	6.68	7.59	1.14	0.265	0.021	0.12	0.27	0.0010	0.66	0.87
6-12	87.32	0.002	0.019	4.69	4.79	1.02	0.796	0.005	0.76	0.10	0.0006	1.06	1.43
6-13	88.58	0.002	0.013	4.77	5.16	1.08	0.368	0.010	0.19	0.16	0.0003	0.50	1.00
6-14	82.97	0.006	0.024	6.57	7.57	1.15	0.038	0.038	0.15	0.29	0.0010	2.26	2.30
Av.	81.47	0.004	0.021	6.76	8.09	1.20	0.169	0.021	0.17	0.18	0.0004	0.93	1.13
Guanbanwusu [17]	nd	0.020	0.110	9.34	6.97	0.74	0.126	0.120	0.83	0.43	0.0140	0.73	nd
Haerwusu [17]	nd	0.070	<0.110	8.89	6.19	0.70	0.100	0.100	1.33	0.47	0.0100	0.56	nd
Heidaigou [17]	nd	0.010	3.660	10.56	8.04	0.76	0.016	0.210	0.44	0.74	0.0060	0.93	nd
China [26]	nd	0.160	0.220	5.98	8.47	1.42	0.090	0.190	1.23	0.33	0.0200	4.85	nd

Av., average; St, total sulfur; LOI, loss on ignition; nd, no data.

The average content of Al_2O_3 is higher than that in other Chinese coals, because abundant kaolinite and boehmite are present in these coals. In addition, Chuancaogedan coal displays higher SiO_2, P_2O_5, and Fe_2O_3 contents than those of Guanbanwusu, Haerwusu, and Heidaigou coals; this is maybe due to higher quartz and pyrite contents in the former than in the latter coal.

4.3. Trace Elements in the No. 6 Coal

The contents of trace elements in the coal samples, in comparison to the average values for Guanbanwusu, Haerwusu, and Heidaigou coals, as well as other Chinese coals [26] and world hard coals [27], are listed in Table 2. The abundance of trace elements in the No. 6 coal from the Chuancaogedan Mine, in comparison to the average values for Chinese and world hard coals, is shown in Figure 7.

Compared to world hard coals (Figure 7A), the only trace element with a CC > 5 (the CC (concentration coefficient) which is the ratio of the element concentration in Chuancaogedan and world hard coals) in the coals is Sr. Elements with a weak enrichment (2 < CC < 5) include Li, Ga, Zn, Zr, Gd, Hf, Pb, Th and U. Co, Ni, Rb, and Cs, which have lower concentrations than those of world hard coals (CC < 0.5). Beryllium, Sc, V, Cr, Nb, Mo, Ba, Ta, W, and Bi (0.5 < CC < 2) are close to the levels of abundance found in average world hard coals.

Compared to Chinese coals (Figure 7B), only Sr has a CC > 5, and Zn shows a weak enrichment (2 < CC < 5). Caesium is lower compared to world hard coals (CC < 0.5). The concentrations of the remaining elements are close to those found in average world hard coals.

Compared to the Chinese coals [28] (Table 2), Lithium, Sr, and Bi are enriched in the No. 6 Coal, Sc, Co, Ni, Cu, Rb, Nb, Cs, Ba, and Ta are depleted.

The coals from Chuancaogedan Mine contain more Zn, Sr, Cd, and Ba than Guanbanwusu, Haerwusu and Heidaigou coals. The remaining elements in the Chuancaogedan Mine samples display lower contents compared to the coals from Guanbanwusu, Haerwusu and Heidaigou Mines.

Table 2. Concentrations of trace elements in the No. 6 coal from Chuancaogedan (μg/g, on dry coal basis).

Sample	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Zr	Nb	Mo	Cd	Cs	Ba	Hf	Ta	W	Pb	Bi	Th	U
6-1	253	0.7	3.2	24.5	6.5	0.4	0.8	16.3	13.5	30.4	4.7	80.3	209	34.4	2.2	0.1	0.60	19.3	7.4	2.45	5.8	19.2	1.0	12.5	6.1
6-2	28.9	2.2	3.0	19.4	6.8	0.9	1.2	5.1	24.3	8.8	0.4	31.3	192	3.0	1.3	0.2	0.02	27.2	4.4	0.19	0.4	5.40	0.2	15.3	3.6
6-3	16.8	1.5	<0.5	9.12	5.2	1.6	1.5	16.9	83.1	4.5	0.2	48.4	48.7	1.6	7.7	0.1	0.02	32.0	1.2	0.08	1.4	122	0.2	2.8	0.9
6-4	23.1	1.5	<0.5	9.00	6.0	0.6	1.0	4.1	26.2	3.3	0.2	47.7	39.7	1.5	1.0	0.1	0.01	5.08	0.9	0.10	0.6	3.51	0.2	2.0	0.4
6-5	34.2	1.5	2.2	30.0	10.5	1.0	1.9	10.8	125	15.2	0.7	1623	407	11.3	3.0	0.7	0.04	112	9.9	0.27	0.9	15.2	0.3	23.8	5.2
6-6	33.2	1.5	0.2	11.7	6.4	1.0	2.1	7.5	160.5	8.7	0.4	759.7	7.6	56.7	3.1	1.2	0.5	0.0	60.1	30.3	54.1	5.5	17.8	3.0	0.5
6-7	23.1	1.3	<0.5	12.6	6.2	1.6	3.7	4.6	159	8.9	0.5	309	21.5	1.1	1.4	0.3	0.01	25.0	0.6	0.07	1.2	7.16	0.2	1.1	0.4
6-8	88.6	2.0	5.2	33.8	8.9	2.0	5.3	19.2	83.6	13.1	1.6	5737	186	17.8	2.7	0.2	0.13	377	4.9	1.13	2.1	36.1	0.8	17.2	7.9
6-9	57.9	1.1	3.1	20.1	6.0	1.5	2.3	8.3	180	18.0	1.0	375	161	8.2	3.2	0.2	0.10	46.2	3.4	0.44	2.1	14.2	0.3	8.6	7.6
6-10	72.9	2.0	2.4	18.2	7.5	1.5	3.3	15.2	217	13.1	0.3	920	123	4.1	2.1	0.1	0.04	34.8	2.9	0.27	0.6	18.8	0.4	7.0	4.5
6-11	49.1	2.5	2.0	17.0	8.8	1.2	3.5	11.3	102	12.9	1.2	1075	104	7.7	2.0	0.1	0.19	212	3.0	0.68	1.4	14.4	0.6	15.2	3.6
6-12	33.9	1.5	1.4	26.0	8.0	2.0	6.4	19.7	561	19.4	0.4	1759	122	5.9	4.4	2.7	0.03	90.9	3.0	0.21	0.8	27.4	0.6	8.4	5.6
6-13	40.4	2.3	1.5	21.1	12.8	1.3	4.8	9.7	81.1	13.8	0.5	1915	88.7	3.8	2.1	0.2	0.04	73.9	2.3	0.25	0.6	14.1	0.3	8.8	2.8
6-14	60.6	1.5	0.9	39.0	22.6	2.7	11.2	28.6	37.2	13.9	1.8	108	160	7.7	4.2	0.2	0.17	39.8	3.8	0.48	1.0	25.3	0.6	8.9	2.5
Av.	56.6	1.6	2.1	20.2	8.6	1.3	3.4	12.3	134.2	12.8	1.0	1037	132	7.6	2.7	0.4	0.10	81.0	3.4	0.47	1.4	23.1	0.4	9.3	3.6
Guanbanwusu [17]	175	1.64	6.87	38.3	16.2	1.28	2.76	13.3	29.1	12.9	2.99	703	143	11.1	1.83	0.11	0.15	62	3.96	0.85	1.1	26.5	0.49	12.9	3.74
Haerwusu [17]	116	2.8	7	27	10	1.3	2.3	13	40	18	1.3	350	268	13	1.6	0.06	0.07	41	7.2	0.9	1.7	30	0.5	17	3.7
Heidaigou [17]	38	2.3	8.4	32	15	2.1	5.6	16	17	45	2	423	234	13	3.1	0.13	0.35	56	8	1	1.8	36	0.8	18	3.9
Clarke value [28]	20	2.8	22	135	100	25	75	55	70	15	90	375	165	20	1.5	0.2	3	425	3	2	1.5	12.5	0.17	9.6	2.7
China [26]	31.8	2.1	4.2	35.1	15.4	7.1	13.7	17.5	41.4	6.6	9.3	140	89.5	9.4	3.1	0.3	1.1	159	3.7	0.6	1.1	15.1	0.8	5.8	2.4
World [27]	14	2	3.7	28	17	6	17	16	28	6	18	100	36	4	2.1	0.2	1.1	150	1.2	0.3	0.99	9	1.10.8	3.2	1.9

Av., average.

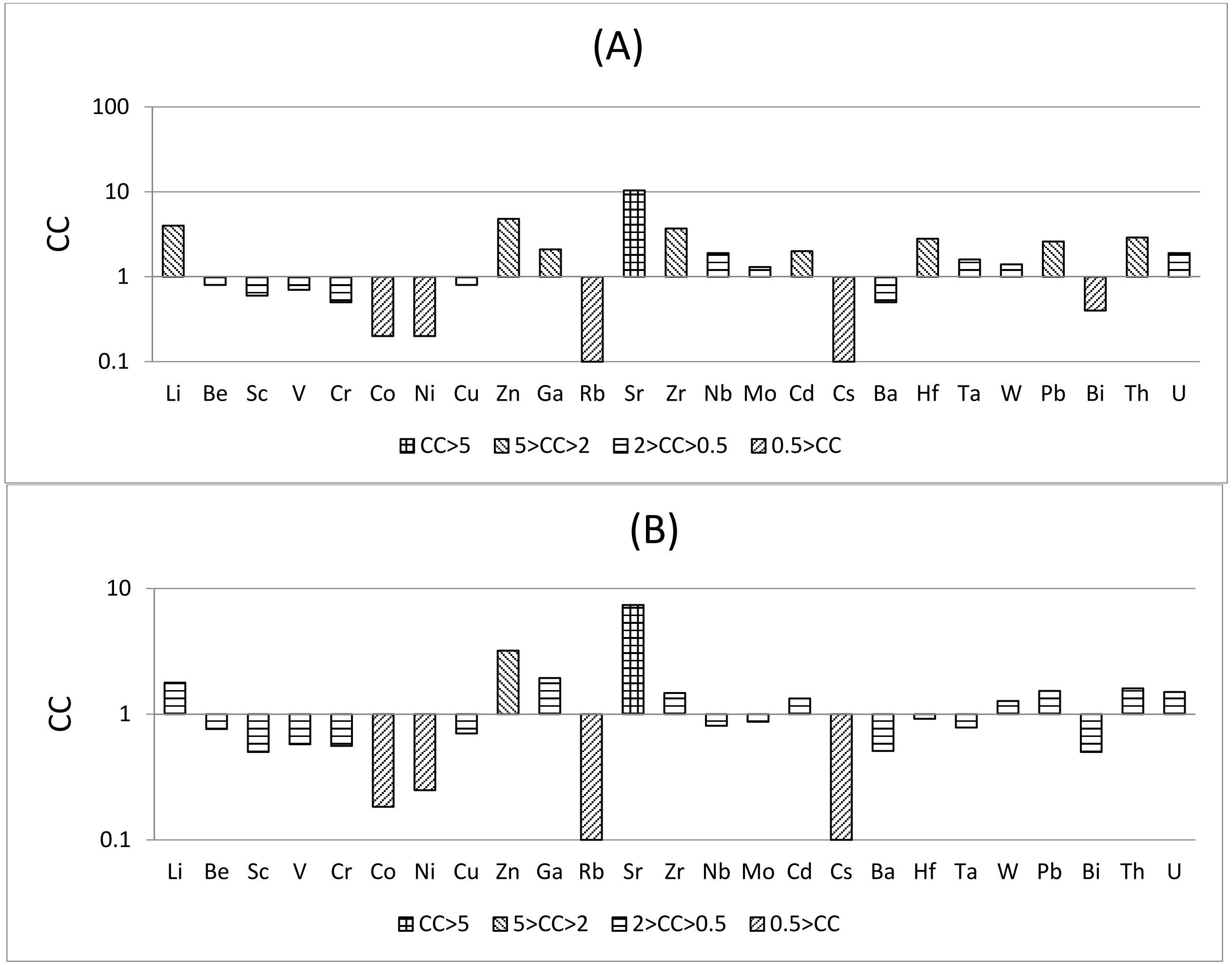

Figure 7. (**A**) Concentrations coefficients (CC) of elements in the Chuancaogedan coal *vs.* world coals; (**B**) CC of elements in the Chuancaogedan coals *vs.* Chinese coals.

4.4. Paragenetic Association of Trace Elements in the No. 6 Coal

4.4.1. Affinity of the Elements

Trace elements bound in the organic matter of coal volatilize more easily during combustion than these bound in the inorganic matter, which tend to remain in the ash. Therefore, ash yield and trace element contents in coal often display a close relationship [29–31].

Four groups (Groups 1 to 4) of elements have been identified in the No. 6 coal from the present based on their correlation coefficients with ash yield (Table 3).

Table 3. Element affinities between the concentration of each element in the coal and ash yield or selected elements.

Correlation With Ash Yield	
Group 1:	r_{ash} = 0.8–1.0 Li (0.99), Ta (0.85), Bi (0.85), Al_2O_3 (0.99), SiO_2 (0.99), TiO_2 (0.96)
Group 2:	r_{ash} = 0.5–0.8 Sc (0.59), V (0.59), Co (0.67), Ni (0.56), Cu (0.69), W (0.65), U (0.66) Na_2O (0.5), Cs (0.76), Ga (0.53), Rb (0.75), Sr (0.63), Nb (0.73), Ba (0.69), K_2O (0.74)
Group 3:	r_{ash} = 0.3–0.5 Cr (0.35)
Group 4:	r_{ash} = −0.3–0.3 Zn (0.11), Fe_2O_3 (−0.12), MnO (−0.29), CaO (−0.14), Pb (0.19), Th (0.27), SO_3 (−0.17), P_2O_5 (−0.15), MgO (−0.17), Hf (0.14), Zr (0.11), Mo (0.28), Cd (−0.02), Be (0.22)
Aluminosilicate Affinity	
$r_{Al–Si}$ > 0.8 TiO_2, Li, Ga, Rb, Nb, Cs, Ta, W	
$r_{Al–Si}$ = 0.5–0.8 K_2O, Bi, Na_2O	
$r_{Al–Si}$ = 0.3–0.5 Sc, Cu, Hf, U	
Correlation Coefficients Between Selected Elements	
V-Cr 0.7, V-Co 0.5, V-Ni 0.7, V-MnO 0.27, V-Cu 0.7 Cr-Co 0.6, Cr-Ni 0.8, Cr-MnO 0.54, Cr-Cu 0.6 Co-Ni 0.88, Co-MnO 0.5, Co-Cu 0.70 Ni-MnO 0.71, Ni-Cu 0.73, MnO-Cu 0.5, Sr-Ba 0.90 Li-K_2O 0.77, Li-Bi 0.77, Li-W 0.93, Li-Ta 0.97, Li-Nb 0.94, Li-Rb 0.95, Li-Ga 0.81 Th-Sc 0.68, Th-V 0.64, Th-Zr 0.89, Th-Hf 0.87, Cd-SO_3 0.5 Ga-S −0.25, Cd-Zn 0.90	

r_{ash}: correlation of elements with ash yield; figures in the brackets: correlation coefficients.

Group 1 includes Al_2O_3, SiO_2, TiO_2, Li, Ta, and Bi, which are strongly correlated with the ash yield (r_{ash} = 0.8–1.0). Silicon and Al are major constituents of the aluminosilicate minerals (kaolinite) [11]. The correlation coefficient between ash yield and Al_2O_3, SiO_2 is 0.99. Li, TiO_2, Ta, and Bi have high correlation coefficients with SiO_2 and Al_2O_3.

Group 2 includes elements with a relatively high inorganic affinity. The elements in this group (Sc, V, Co, Ni, Cu, W, U, Na_2O, Cs, Ga, Rb, Sr, Nb, Ba, and K_2O) are strongly correlated with the ash yield, with correlation coefficients between 0.50 and 0.80.

Group 3 includes only Cr, which has a correlation coefficient with the ash yield of 0.35.

Group 4 includes Fe_2O_3, MnO, CaO, Pb, Th, SO_3, P_2O_5, MgO, Hf, Zr, Mo, Cd, and Be. These elements have correlation coefficients with the ash yield that range from −0.30 to 0.30, indicating an intermediate affinity.

4.4.2. Cluster Analysis

The elemental associations in the Chuancaogedan coals were studied by cluster analysis. Four groups of elemental association were identified (Figure 8), referred to as Groups 1, 2, 3 and 4.

Group 1. This group includes Al_2O_3, SiO_2, Li, Rb, TiO_2, Cs, Nb, and Ta (Figure 8). All of the elements in this group have high positive correlation coefficients with the ash yield, ranging from 0.53 to

0.99 (Table 3). SiO_2 and Al_2O_3 are major constituents of the ash-forming minerals (clay minerals) [18]. All of the elements in Group 1 are lithophile elements that probably occur in aluminosilicate minerals.

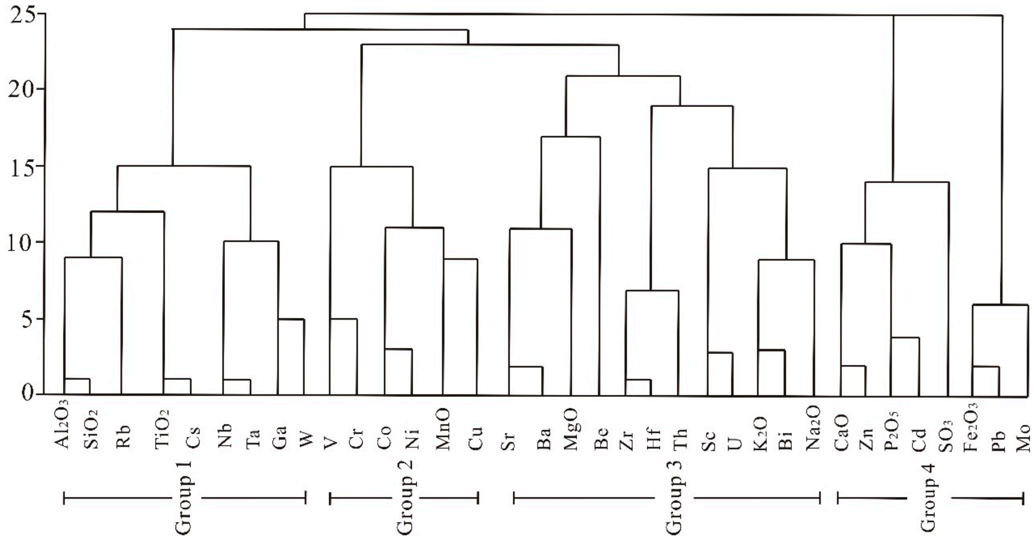

Figure 8. Cluster analyses of analytical results on 14 samples.

Group 2. This group includes the elements V, Cr, Co, Ni, MnO, and Cu. All of the elements in this group, except MnO, have relatively high correlation coefficients with the ash yield, ranging from 0.34 to 0.67. With the exception of V-MnO (0.27), the correlation coefficients between the pairs of elements in this association are higher than 0.50. The elements in this group, except Cu, are lithophile elements that are probably associated with the clay minerals.

Group 3. This group consists of Sr, Ba, MgO, Be, Zr, Hf, Th, Sc, U, K_2O, Bi, and Na_2O. With the exception of K_2O, Bi, and Na_2O, they have low correlation coefficients with the ash yield (Table 3), and these elements are probably associated with unidentified traces of sulfide minerals. K_2O, Bi, and Na_2O have high correlation coefficients with SiO_2 and Al_2O_3, and these elements probably occur in clay minerals and diaspore.

Group 4. This group includes CaO, Zn, P_2O_5, Cd, SO_3, Fe_2O_3, Pb, and Mo. All of these elements have negative correlation coefficients with the ash yield, possibly because they occur in phosphate minerals (gorceixite and fluorapatite).

4.5. Elevated Trace Elements in the Coal

4.5.1. Strontium

The concentration of Sr in the samples varies considerably, from 31.3 to 1915 μg/g, with a weighted average of 1037 μg/g. This level is much higher than that in common Chinese coals (140 μg/g on average) [26] and world hard coals (114 μg/g on average) [27]. The correlation coefficient between Sr and Ba is high at 0.90 (Table 3). The most probable carrier of Ba in the coal is gorceixite, so Sr may be also contained in this mineral [18].

4.5.2. Lithium

The arithmetic average lithium content reaches 56.6 μg/g in the No. 6 coal, and is much higher than that in common Chinese coals and world hard coals. The highest content of Li is 253 μg/g (Table 2). Sun *et al.* suggest that the cut-off grade of Li for economic recovery should be 120 μg/g [32]. However, the Li content of the coal from the Chuancaogedan Mine does not reach this level.

The modes of occurrence of lithium in coal have not been fully studied. Li mainly occurs in granite pegmatite deposits, alkali feldspar granite deposits and salt lake deposits [23,25,32]. Researchers thought that Li in coal generally occurred in clay minerals and partially in mica and tourmaline [33,34]. The high correlation coefficient between Li and ash indicates that a large proportion of the Li occurs in the inorganic matter [18]. Lithium is positively correlated with Al_2O_3, SiO_2, and K_2O, with correlation coefficients of 0.99, 0.99 and 0.77, respectively (Table 3), indicating that Li may also be associated with kaolinite, chlorite, and possibly with illite.

Lithium is also positively correlated with some lithophile elements, including Rb, Nb, Bi, Ga, Ta, and W (Table 3), with correlation coefficients of 0.95, 0.94, 0.77, 0.81, 0.97, and 0.93, respectively, and it is further confirmed that Li occurs in aluminosilicate minerals. The distribution of the Li content in the coal benches, except sample 6-1, is uniform. The high content of Li in sample 6-1 may be caused by a parting within the seam.

4.5.3. Gallium

Gallium in coal is generally related to clay minerals [35–40]. The Ga content of the Chuancaogedan coals (12.8 μg/g) is much higher than that of other Chinese coals and world hard coals.

It can be deduced that the Ga mainly occurs in inorganic association, including the clay minerals and diaspore, based on the positive correlations of Ga-ash (r = 0.81), Ga-Al_2O_3 (r = 0.82), and Ga-SiO_2 (r = 0.80). Gallium may replace Zn in sphalerite, but the low-sulfur content and the negative correlation coefficient of Ga-S ($r = -0.25$) indicate that Ga is not related to sulfide in the Chuancaogedan coals.

4.5.4. Zirconium

The average concentration of Zr is 132 μg/g, which is higher than that of common Chinese (89.5 μg/g) [26] and world coals (36 μg/g) [27]. The correlation coefficients of Zr-Al_2O_3 and Zr-SiO_2 are relatively low, 0.24 and 0.25, respectively. Dai *et al.* found that the content of Zr in the coals from the northern and central Jungar Coalfield is higher than that of common Chinese coals, and pointed out that the major carrier of Zr is zircon [18].

4.5.5. Cadmium

Cadmium is one of the toxic trace elements in coal. The average Cd content of the No. 6 coal (0.4 μg/g on average) is higher than that of common Chinese coals and world hard coals. Cd is a chalcophile element. Cd is positively correlated with S and Zn (Table 3), with correlation coefficients of 0.5 and 0.9, respectively, indicating that the Cd in the No. 6 coal mainly occurs in sphalerite.

4.5.6. Lead

The average concentration of Pb is 23.1 μg/g, which is higher than that of common Chinese (15.1 μg/g) [26] and world coals (7.8 μg/g) [27].

Pb in coal mainly occurs in galena or is associated with other sulfide minerals. The relationships between Pb and Al_2O_3 and SiO_2 in the No. 6 coal are poor, with correlation coefficients of 0.05 and 0.10, respectively. The correlation coefficient with Fe_2O_3 is high, suggesting that the occurrence of Pb in the No. 6 coal may be associated with pyrite.

4.5.7. Thorium

The average Th content of the No. 6 coal (9.3 μg/g) is higher than that of common Chinese coals and world hard coals. Thorium in the Chuancaogedan coals has high correlation coefficients with Sc (0.68), V (0.64), Zr (0.89), and Hf (0.87), probably indicating the same source for these elements. The relatively low correlation coefficients of Th-Al_2O_3 (0.21), Th-SiO_2 (0.23), and Th-ash (0.20) indicate that Th may occur in accessory minerals in the coal and probably in the organic matter as well.

5. Conclusions

1. The No. 6 coal from Chuancaogedan Mine is significantly enriched in Zn and Sr and is slightly enriched in Li, Ga, Zr, Gd, Hf, Pb, Th, and U compared with world hard coals. The major elements exhibit enrichment in Al_2O_3 (6.76%) and P_2O_5 (0.169%), but with a lower SiO_2/Al_2O_3 ratio (1.20), compared to Chinese hard coals. The contents of Zn, Sr, Li, Ga, Zr, Gd, Hf, Pb, Th, and U are higher than those of world hard coals. Aluminum, Li, and Ga could be recovered as the byproducts from coal ash, and P, Pb, and U may be harmful to the environment during coal processing.
2. The elements in the No. 6 coal may be classified into four groups of association according to their modes of occurrence. Group 1 includes Al_2O_3, SiO_2, Li, Rb, TiO_2, Cs, Nb, and Ta. Group 2 includes the elements V, Cr, Co, Ni, MnO, and Cu. Group 3 consists of Sr, Ba, MgO, Be, Zr, Hf, Th, Sc, U, K_2O, Bi, and Na_2O. Group 4 includes CaO, Zn, P_2O_5, Cd, SO_3, Fe_2O_3, Pb, and Mo. Most of the elements in Group 1 and Group 2 are strongly correlated with the ash yield, but the elements of the remaining two associations have negative or weak correlation coefficients with the ash yield.
3. The most probable carriers of Sr in the coal are barite and gorceixite. Lithium is mainly associated with kaolinite and possibly with illite. Gallium mainly occurs in inorganic association, including the clay minerals and diaspore, but is not related to sulfide. Zirconium occurs in association with sulfide minerals. Cadmium mainly occurs in sphalerite. Lead in the No. 6 coal may be associated with pyrite. Thorium may occur in accessory minerals in the coal and probably in the organic matter as well.

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