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Mode of Occurrence and Distribution of Critical Metal Lithium and Other Trace Elements during Coal Preparation from Jiashun High-Sulfur Coal in Guizhou Province, China

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Abstract: During the Late Permian period, the coal from the Jiashun Mine in Xingren City, Guizhou Province, China, is characterized by a high sulfur (5.84%) and lithium (Li) (94.5 μg/g) content. Lithium is a critical metal in the context of global energy transition. Considering the importance of environmental protection and resource utilization, the mode of occurrence and distribution of trace elements in different coal preparation products were investigated. The obtained results indicated the following: (1) The minerals in Jiashun coal were mainly composed of veined and epigenetic pyrite, quartz, and kaolinite. Most of the minerals could be effectively removed from the cleaned coal through gravity separation. (2) The mode of occurrence of rare earth elements and yttrium (REY) in the coal was relatively complex, and they were mainly found in middlings from gravity separation and in flotation tailings. (3) The mode of occurrence of the trace elements in the coal significantly influenced their removal rate. The removal rate was significantly higher for trace elements removed through gravity separation compared to those removed using flotation. The trace elements mainly found in fine-grained minerals wrapped by organic matter or combined with organic portions had better removal results through flotation. The trace elements that occurred both in the minerals and organic matters had low removal rates (<25%) using two coal preparation methods. (4) Li was more enriched in the middlings from gravity separation (98 μg/g) and in flotation tailings (102 μg/g), reaching the marginal grade (80 μg/g) of Li in coal. (5) Li in Jiashun coal may be derived from intermediate-felsic rocks at the top of the Kangdian Upland and late hydrothermal solutions.

Keywords: critical metal in coal; lithium; mode of occurrence; coal preparation; economic evaluation

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1. Introduction

China is one of the world's largest producers and consumers of coal [1]. However, the distribution of coal resources is uneven, with the majority located in the north rather than the southern [2,3]. Guizhou Province, located in Southwest China, is one the richest provinces in terms of coal resources, contributing 50% of the total coal production [3]. Most coals from Southwestern China have high sulfur contents [4]. Consequently, their direct combustion will result in the release of sulfur and other toxic elements into the air, potentially causing a series of environmental problems and affecting human health [5–7]. In addition, as a special sedimentary organic mineral resource, coal is endowed with properties of reduction and acts as an adsorption geochemical barrier. Coal can become enriched in critical metal and develop into large or super-large metal deposits under specific geological conditions. High-sulfur coal should be prepared before use to remove sulfur and toxic trace elements, thereby reducing their release during the coal combustion process. In addition, the preparation holds great significance for the recycling of critical metals contained in high-sulfur coal.

Gravity separation and flotation are the most commonly used methods in the preparation of industrial coal. Gravity separation can be used to separate minerals from coal, deriving profit from their density difference [8]. Flotation is a highly efficient and economic technology for separating minerals from coal based on the difference in their surface properties [9]. Previous studies in this area have focused on the removal of sulfur from high-sulfur coal [8–10]. Some studies have also explored the distribution and geochemical control factors of trace elements during coal preparation [10–13]. However, there are relatively few studies on the distribution and evaluation of the economic potential of critical metals in coal preparation products [3,14].

Jiashun coal, located in Guizhou Province, is characterized by a high sulfur content and enrichment in the critical metal Li. In this study, Jiashun hard coal was selected, and the distribution of its trace elements was studied after its preparation using gravity separation and flotation. The genetic type, mode of occurrence, geochemical control factors influencing the removal performance of Li and other trace elements in coal were also analyzed. Moreover, the economic potential of Li in coal preparation products was evaluated. The findings from this study could provide a theoretical basis for pollution prevention when using high-sulfur coal and for recycling the critical metals contained in coal.

2. Geological Setting

The Jiashun Mine is located in Panjiazhuang Town, Xingren City, Guizhou Province, Southwestern China (Figure 1). Xingren City lies at the Southwestern Margin of the Yangtze Plate, with the southern region adjacent to the South China fold belt, known for its developed folds. The western Guizhou Province has a complex geological background due to extensive faults [15].

Figure 1. Location of the Jiashun Mine.

There was a large-scale eruption of Emeishan basalt magma between the Early and Late Permian due to the strong activity of the Emeishan mantle plume, which resulted in the widespread distribution of Emeishan basalt in Western Guizhou [16]. Above the basalt, there is the Longtan Formation coal-bearing series [17]. The exposed strata in and around the study area include Permian, Triassic, and Quaternary layers. The coal-bearing stratum in the mine field is composed of the Upper Permian Longtan Formation, which has a disconformity contact with the underlying Middle Permian Maokou Formation. The Longtan Formation is mainly composed of siltstone, chert, limestone, mudstone, shale, and coal seams, and contains fossils including brachiopods, pteridophyte, and ferns [18].

In the early Late Permian, due to the regression of most areas of South China, the coal accumulation process occurred in marine–terrigenous facies depositional environment [19], including lagoon facies, delta facies, tidal flat facies, and distributary channel facies. Most of the coal seams formed through marine–terrigenous facies sedimentation, leading to high sulfur content due to the marine influence on their formation process.

3. Samples and Analytical Procedures

One coal sample from the Late Permian Longtan Formation was taken from the mine face at the Jiashun Mine. The sample was crushed using a grinding mill to reduce the particle size to <0.5 mm. For float–sink experiments, 500 g of the coal was used, while 150 g was chosen for flotation experiments. A centrifuge was used for the float–sink experiments. Two heavy liquids (benzene, carbon tetrachloride and tribromethane), with specific gravities of 1.5 and 1.8 kg/L, respectively, were used in float–sink experiment in order to separate each coal sample into three subsplits following Chinese national standard GB/T478-2008 [20]. Two float fractions (cleaned coal and middlings) and one sink fraction (tailings) were obtained for densities of <1.5, 1.5–1.8 kg/L, and >1.8 kg/L, respectively. As for the coal flotation experiment, the procedure followed the Chinese national standard GB/T 4757-2013 [21]. In order to pre-wet samples, water and 50 g of coal were added into a 1.5-L single flotation cell (XFD-63) and stirred for 3 min to prepare a uniformly mixed coal slurry. Subsequently, collector (diesel), and frother (octanol) were added in sequence to the prepared coal slurry. After 30 s of aeration, the flotation process began. The froth was then scraped for 3 min. Both cleaned coal and tailings were collected, filtered, and dried.

Proximate analyses, including moisture, ash, and volatile matter, were performed in accordance with ASTM D3173-11, D3174-11, and D3175-11 (2011) [22–24], respectively. The total sulfur content was determined according to GB/T214-2007 [25]. The iodine generated through electrolysis of KI solution was used to titrate the SO_2 produced by combustion. The total sulfur content in the coal was calculated based on the electricity consumption of electrolysis. The forms of sulfur were determined according to ASTM D2492-02 (2002) [26]. Sulfate sulfur was extracted from the analysis sample using dilute hydrochloric acid. The pyritic sulfur was calculated as a stoichiometric combination with iron. The percentage of organic sulfur was obtained by subtracting the sum of the percentages of sulfate sulfur and pyritic sulfur.

Scanning electron microscopy (SEM, FEI Quanta™ 250, Thermal Fisher, Waltham, MA, USA), in conjunction with EDAX energy-dispersive X-ray spectrometry (EDAX), was used to determine the morphology of the minerals and their chemical compositions. The working distance of the SEM-EDS was set between 10 and 20 mm, with a beam voltage of 25 or 30 kV, aperture of 6, and micron spot size of 3.5–5.0.

X-ray fluorescence spectrometry (XRF, S8 TIGER, Bruker Corporation, Billerica, MA, USA) was used to determine the major-element oxides in the coal ash (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, MnO, Na_2O, and K_2O). Inductively coupled plasma mass spectrometry (X series II ICP-MS, Thermal Fisher, Waltham, MA, USA) was used to assay trace elements in the samples. Coal samples were dissolved through acid digestion (5 mL 65% HNO_3 and 2 mL 40% HF). The ICP-MS analysis and sample microwave digestion program for coal were conducted following reference [27].

4. Results and Discussion

4.1. Coal Chemistry

The results from the coal the analyses are given in Table 1. The coal from the Jiashun Mine was classified as low-ash (dry basis) based on the Chinese National Standard GB 15224.1-2018 [28]. The coal from the Jiashun Mine consisted of a low-ash (dry basis) type. Indeed, for low-ash coal, the yield typically falls between 10.00% and 20.00% [28]. As for volatile matter yield (i.e., 17.17% on a dry and ash-free basis), the investigated sample was classified as a low-volatile bituminous coal, according to the ASTM classification (ASTM D 388-2012) [29].

Table 1. Proximate analysis (%), total sulfur, and forms of sulfur (%) from the Jiashun Mine.

Proximate Analysis (%)			Forms of Sulfur (%)			
M_{ad}	A_d	V_{daf}	$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$
3.36	13.57	17.17	5.84	0.71	2.56	2.57

M, moisture; A, ash yield; V, volatile matter; S_t, total sulfur; S_p, pyritic sulfur; S_s, sulfate sulfur; S_o, organic sulfur; ad: air dried basis; d: dry basis; daf: dry and ash-free basis.

The total sulfur content in the coal sample was 5.84%, indicating that was made of a high-sulfur coal, as per the Chinese National Standard GB/T 15224.2-2021 [30] and Chou [31] (coals with a total sulfur content > 3% are considered high-sulfur coal). in terms of the sulfur distribution, it was predominantly in the sulfate, pyritic, and organic forms, accounting for 43.8%, 12.2%, and 44%, respectively, of the total sulfur content. It was assumed that the weathering or oxidation of pyrite resulted in a large sulfur content as sulfate.

4.2. Geochemistry

4.2.1. Major Element Oxides

Table 2 presents the oxides of the major elements found in the Jiashun coal. When compared to the average content of the major element oxides commonly found in Chinese coals, only the content of Na_2O was higher. As for oxides of other major elements, their contents were lower. The oxides of the major elements were composed of SiO_2, Al_2O_3, and Fe_2O_3, revealing that clay minerals and pyrite were the main components of the Jiashun coal.

Table 2. Percentages of major-element oxides (%) in the Jiashun coal sample (based on a whole-coal air-dried basis).

Element Oxides (%)	**SiO_2**	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**SiO_2/Al_2O_3**
JS	4.375	0.211	2.899	4.399	0.003	0.038	0.109	0.22	0.096	0.017	1.51
China *	8.47	0.33	5.98	4.85	0.015	0.22	1.23	0.16	0.19	0.092	1.42

JS, Longtan Formation coals from Jiashun Mine; *, the average values of major-element oxides for Chinese coals from Dai et al. [32].

The SiO_2/Al_2O_3 ratio of the coal (1.51 on average) was higher than the theoretical ratio of SiO_2/Al_2O_3 in kaolinite (1.18). This ratio was even higher than that of other Chinese coals (1.42) [32], demonstrating that the aluminon–silicate minerals were dominated by kaolinite [27] and quartz in the coal. Sodium was mainly found in the coal as illite or as mixed layers of illite/smecctite minerals and feldspar [33]. The Na_2O content was also found to be higher in the coal. These findings suggest the possibility that the Jiashun coal might contain sodium illite and feldspar. Anatase was the primary form of TiO_2 found in the analyzed coal [34].

4.2.2. Trace Elements

The concentrations of trace elements in the Jiashun coal are given in Table 3. Based on the enrichment classification proposed by [35], the concentrations of trace elements in coal can be classified into six categories (based on a whole-coal basis): unusually enriched (concentration coefficient CC > 100, where CC is the ratio of trace elements in samples investigated to the averages for world hard coals), significantly enriched (10 < CC < 100), enriched (5 < CC < 10), slightly enriched (2 < CC < 5), normal (0.5 < CC < 2), and depleted (CC < 0.5). The concentration coefficient is used to assess the availability or potential value of trace elements in coal mine samples. Trace elements with a high concentration coefficient may have higher economic value, as they can be more easily extracted and utilized during mining and processing operations.

Table 3. Concentrations of trace elements (μg/g) in the Jiashun and world coals (based on a whole-coal air-dried basis).

Elements (μg/g)	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga
JS	94.5	0.85	5.2	24.3	17.1	6.11	4.99	9.61	9.94	4.26
World *	14.0	2.0	3.7	28	17	6.0	17	16	28	6.0
CC	6.75	0.43	1.41	0.87	1.01	1.02	0.29	0.60	0.36	0.71
	Rb	Sr	Zr	Nb	Mo	Cd	In	Cs	Ba	Hf
JS	9.94	60.9	71.1	7.25	5.45	0.22	0.042	0.54	27.4	2.19
World *	18	100	36	4.0	2.1	0.2	0.04	1.1	150	1.2
CC	0.55	0.61	1.98	1.81	2.60	1.10	1.05	0.49	0.18	1.83
	Ta	W	Tl	Pb	Bi	Th	U			
JS	0.53	2.13	0.4	5.52	0.2	7.96	3.49			
World *	0.3	1.2	0.58	6.6	1.1	3.2	1.9			
CC	1.77	1.78	0.69	0.84	0.18	2.49	1.84			

*, the concentration of trace elements for world hard coals are from Ketris and Yudovich [36]; CC, concentration coefficient, the ratio of Jiashun samples vs. world hard coals.

Compared to average values for world hard coals [36], Li was enriched; molybdenum (Mo) and thorium (Th) were slightly enriched; and beryllium (Be), nickel (Ni), zinc (Zn), cesium (Cs), barium (Ba), and bismuth (Bi) were depleted in the Jiashun coal. Scandium (Sc), vanadium (V), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), rubidium (Rb), strontium (Sr), zirconium (Zr), niobium (Nb), cadmium (Cd), indium (In), hafnium (Hf), tantalum (Ta), tungsten (W), thallium (Tl), lead (Pb,) and uranium (U) were close to their average values in the world hard coals (Figure 2).

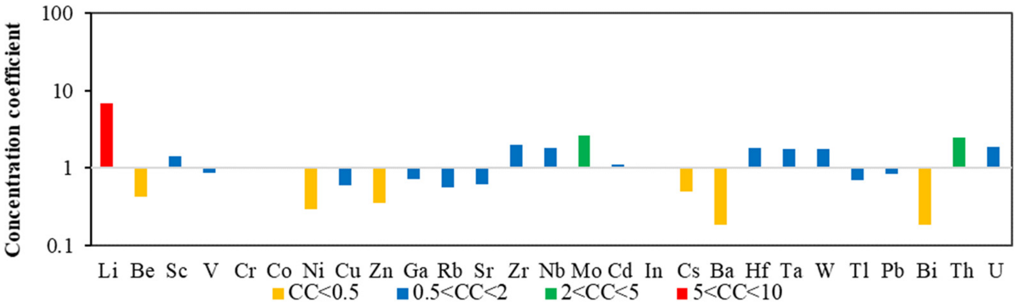

Figure 2. Concentration coefficients (CC) of the trace elements in the coal from the Jiashun Coal Mine. Average concentrations of trace elements for world hard coals are from Ketris and Yudovich [36].

4.3. Mineralogy

Figure 3 shows SEM images of the Jiashun coal, in which minerals were observed through scanning using a back-scattered electron beam. The SEM analyses revealed the presence of a large amount of pyrite of both syngenetic and epigenetic nature in the coal. In the SEM images, the syngenetic pyrite mainly appeared in a framboidal form (Figure 3a–c) with particles sizes varying from a few microns to tens of microns. The size of the fine-grained pyrite was usually less than 10 μm [37]. The coarse-grained pyrite was found to be easier to remove from the coal than the fine-grained pyrite [38]. The epigenetic pyrite was found in fractures with a vein style (Figure 3d). According to [3], the epigenetic pyrite from Xingren coal, located in Guizhou Province, originated from low-temperature hydrothermal fluids. The presence of veined pyrites suggests that Jiashun coal was influenced by hydrothermal fluids after diagenesis.

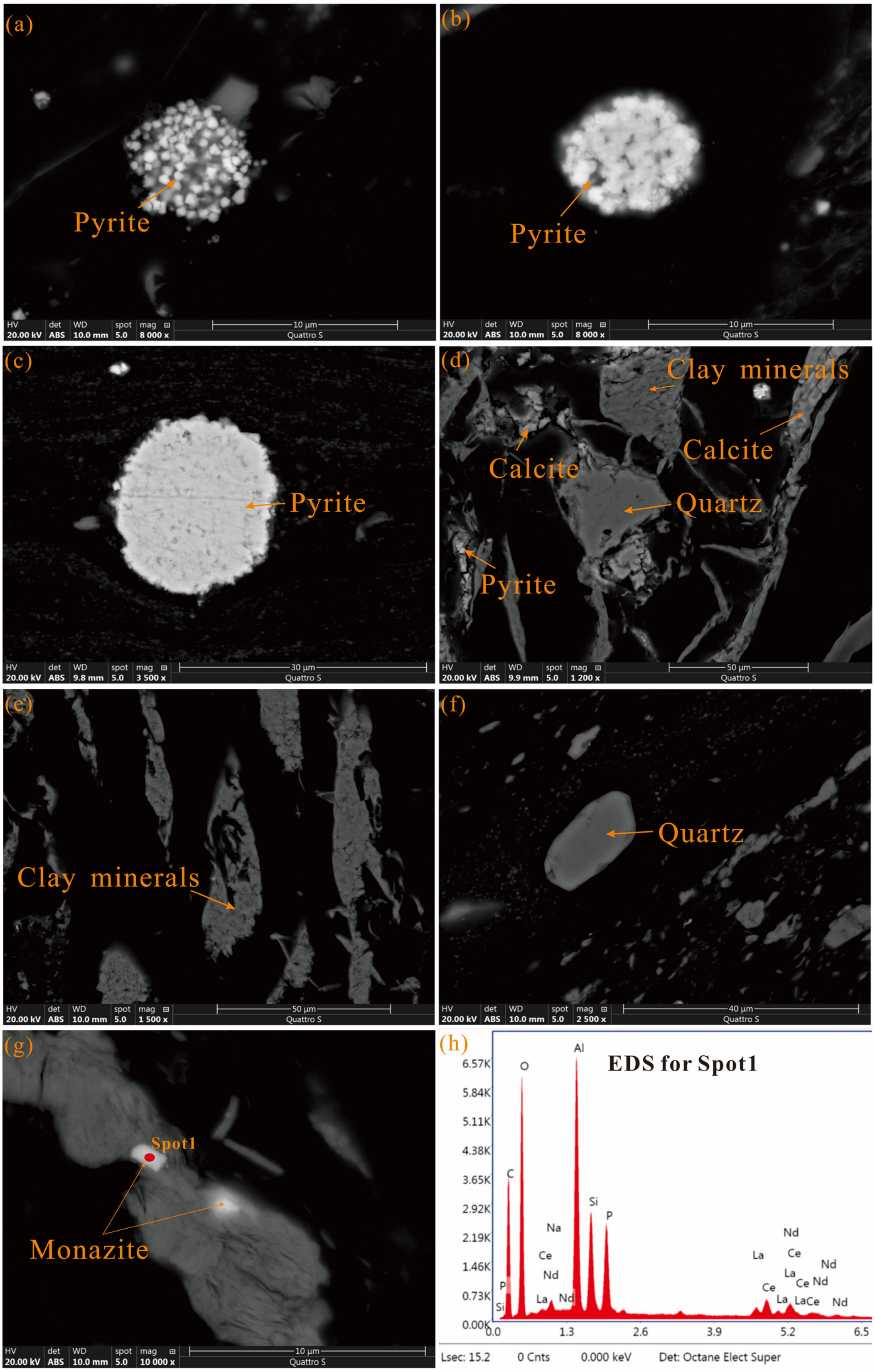

Figure 3. SEM back-scattered electron images and EDS data for Jiashun coal: (**a**–**c**), framboidal pyrite; (**d**), clay minerals in lump forms, laminar calcite, granular quartz enwrapped in clay minerals and fine-grained pyrite disseminated in clay minerals; (**e**) banded clay minerals; (**f**) clastic quartz with good abrasion; (**g**) cavity-filling monazite in clay mineral; (**h**) EDS spectrum of spot 1 in (**g**).

A large number of clay minerals were also found in Jiashun coals, with particles sizes ranging from a few microns to tens of micron sand, mostly in lumps (Figure 3d), as well as in banded (Figure 3e) or fine-grained particles (Figure 3e) with developed fractures or pits. These clay minerals can aggregate and disperse into micron-sized crystalline layer particles in water, with an impact on coal flotation efficiency [39].

The quartz observed in the Jiashun coal was of two genetic types: autogenetic and terrigenous. Authigenic quartz mainly existed in an irregularly granular form with a large grain size, and it was filled with clay minerals in organic cell cavities (Figure 3d). This type of authigenic quartz is generally found in the Late Permian coals of Eastern Yunnan Province and Western Guizhou Province. It is associated with weathering products of felsic volcanic rocks at the top of the Emeishan basalt sequence [40]. The terrigenous quartz had a clastic shape, with good abrasion resistance and a particle size of more than ten microns (Figure 3f), indicating that it experienced long-distance transportation.

The carbonate mineral calcite was also observed in the coal, appearing as a vein (Figure 3d), which confirmed its epigenetic origin. The REY- bearing mineral monazite (Figure 3g,h) was also detected as clastic filling matter in the cell cavity of the clay minerals.

4.4. Distribution of Li and Other Trace Elements during Coal Separation

4.4.1. Distribution of Li and Other Trace Elements during Flotation

The ash yield, content of sulfur and concentration of trace element in the flotation products are shown in Table 4. The ash yield and total sulfur content of the coal cleaned through flotation were 8.38% and 2.81%, respectively. The ash yield and total sulfur content of the cleaned coal were low compared to those of the feed coal. The content of sulfur as sulfate and pyrite substantially decreased, whereas the content of organic sulfur changed only slightly. This indicates that, unlike organic sulfur, ash and inorganic sulfur can be effectively removed from coal through flotation.

Table 4. Percentages of ash (%) and sulfur (%, on a whole-coal dry basis) and concentrations of trace elements (μg/g, on a whole-coal air-dried basis) in coal separation products for coal and feed coal.

Separation Products (%, μg/g)	**Method**	A_d	$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$	**Li**	**Be**	**Sc**	**V**	**Cr**	**Co**
Cleaned coal	Flotation	8.38	2.81	0.28	0.17	2.36	70.8	0.75	3.88	22.4	18.1	0.81
Tailings		21.23	13.76	6.50	0.58	6.69	102	0.83	3.56	23.1	17.8	1.13
Cleaned coal	Gravity Separation	8.79	1.82	0.06	0.35	1.41	58.35	0.79	3.48	26.39	18.77	3.15
Middlings		16.96	3.75	0.27	2.55	0.93	98.03	0.86	3.42	22.32	17.99	17.78
Tailings		38.52	15.99	3.82	11.72	0.45	69.45	0.44	1.60	12.53	7.20	16.86
Feed coal	/	13.57	5.84	0.71	2.56	2.57	94.5	0.85	5.20	24.3	17.1	6.11
		Ni	Cu	Zn	Ga	Rb	Sr	Zr	Nb	Mo	Cd	In
Cleaned coal	Flotation	4.82	4.70	8.59	3.56	1.78	74.5	72.1	8.28	4.62	0.08	0.025
Tailings		3.65	7.64	11.6	4.71	3.19	73.5	73.1	9.17	5.25	0.15	0.024
Cleaned coal	Gravity Separation	3.66	6.11	10.46	3.73	1.64	83.66	78.89	9.18	4.89	0.12	0.03
Middlings		5.32	18.75	15.22	4.50	3.46	78.91	73.04	8.41	3.45	0.15	0.05
Tailings		7.43	24.75	15.91	2.90	2.94	60.69	33.43	4.75	/	0.71	0.08
Feed coal	/	4.99	9.61	9.94	4.26	9.94	60.9	71.1	7.25	5.45	0.22	0.042
		Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U	
Cleaned coal	Flotation	0.20	14.8	2.25	0.51	1.13	0.36	3.63	0.11	3.62	2.75	
Tailings		0.27	36.5	2.14	0.55	4.36	0.50	4.90	0.23	3.95	2.30	
Cleaned coal	Gravity Separation	0.19	10.80	2.22	0.50	1.32	0.24	2.17	0.14	3.40	3.09	
Middlings		0.35	27.85	2.09	0.52	7.27	0.62	8.42	0.33	4.08	2.99	
Tailings		0.19	29.17	0.98	0.27	8.00	1.66	9.84	0.37	2.05	1.28	
Feed coal	/	0.54	27.4	2.19	0.53	2.13	0.40	5.52	0.20	7.96	3.49	

The concentration of Li and other trace elements assayed in the coal cleaned through flotation were lower than those in the treated coal (Figure 4). This suggests that most trace elements can be removed from the feed coal through flotation. However, the concentration of Be, V, Ni, Mo, Ta, Tl, and U did not significantly change when compared to the feed coal concentration. It can be concluded that these elements were evenly distributed in the minerals and the organic portions, such that their removal through flotation was difficult. In addition, the concentration of chemical elements (Cr, Sr, Zr, Nb, and Hf) in the coal preparation product (cleaned coal and tailings) was higher than in the feed coal, showing that they were mainly present in the organic portions. Furthermore, this study also showed that some elements (Co, Cu, Rb, Cs, Pb and Th) were enriched or deficient in both the cleaned coal and tailings. This could be the result of an ion exchange process with the flotation medium [13].

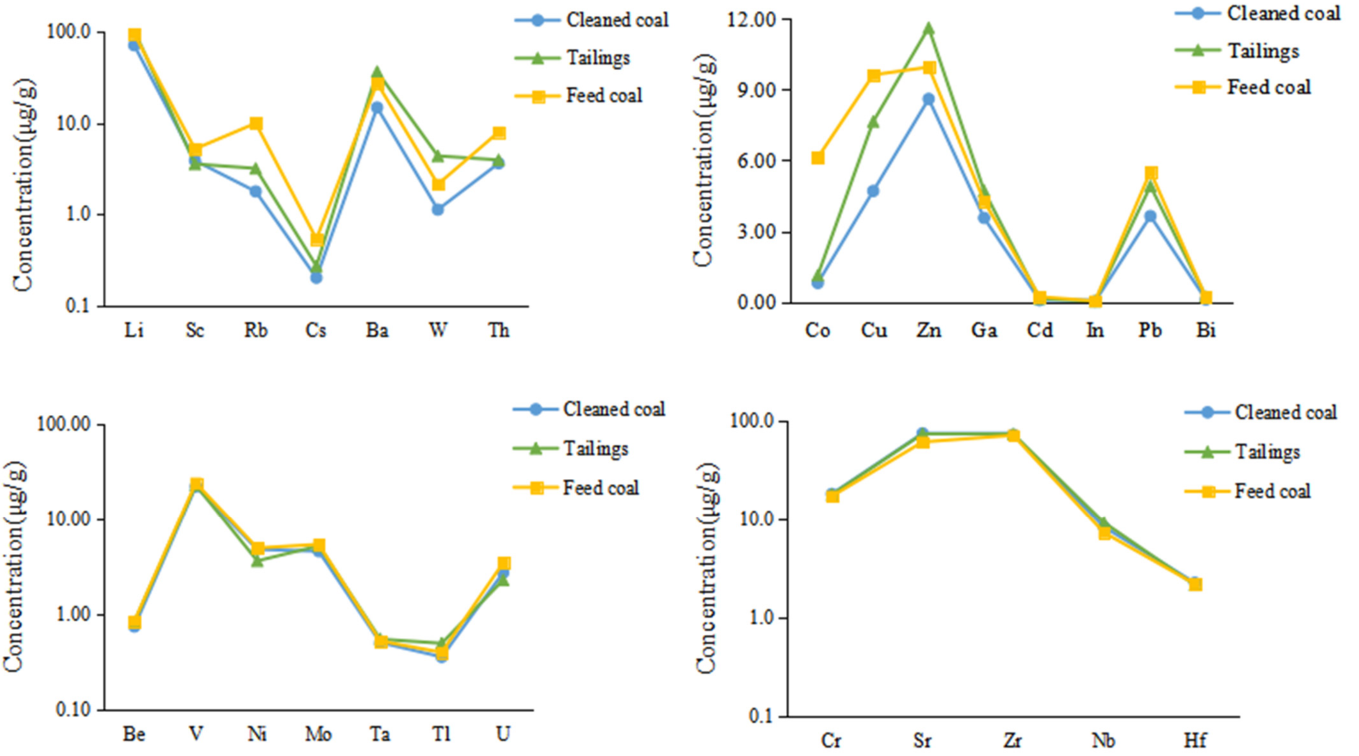

Figure 4. Partitioning of Li and other trace elements in coal separation products of flotation (μg/g).

4.4.2. Distribution Characteristics of Li and Other Elements in Gravity Separation Products

The ash yield, content of sulfur, and concentration of trace element in the gravity separation products are shown in Table 4. The ash yield and total sulfur content of the cleaned coal were 8.79% and 1.82%, respectively. Compared to values measured in the feed coal, the ash yield and inorganic sulfur (sulfate sulfur and pyrite sulfur) content of the cleaned coal through gravity separation were significantly low. Additionally, the organic sulfur content notably decreased compared to the feed coal. These findings indicate that the ash and all forms of analyzed sulfur can be effectively removed from coal through gravity separation.

Nickel, Cu, Zn, Cd, In, Tl, Pb, and Bi are sulphophile elements, and their concentrations in cleaned coal, middlings, and tailings increased with increasing of $S_{p,d}$ contents (Figure 5). This indicates that these elements mainly occurred in pyrite, which can be removed through gravity separation. However, the concentration of Zn in the coal preparation products was higher than in the feed coal. This could be explained by the adsorption of Zn ions from the washing water onto the coal [13].

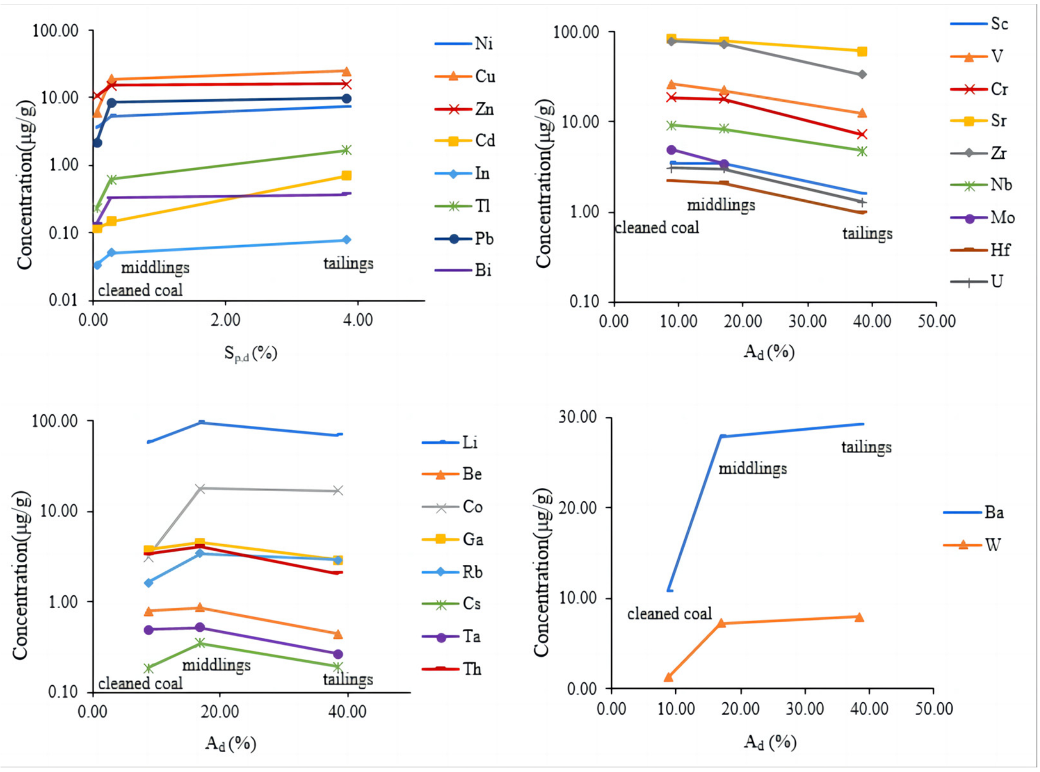

Figure 5. Partitioning of Li and other trace elements in coal preparation products of gravity separation (μg/g, results on a whole-coal air-dried basis).

The concentration of Sc, V, Cr, Sr, Zr, Nb, Mo, Hf, and U in cleaned coal, middlings, and tailings decreased when the ash yields increased. This suggests that these elements mainly occurred in the organic portions, and were difficult to remove using gravity separation.

The distribution of the lithophile elements Li, Be, Co, Ga, Rb, Cs, Ta, and Th were irregular in cleaned coal, middlings, and tailings. Therefore, they cannot be closely correlated with the ash yield, in which Al_2O_3 and SiO_2 represent the main components. This suggests that these elements may be uniformly distributed in clay minerals and organic associations. Additionally, trace elements may occur in fine-grained mineral inclusions found in the molecular voids of coal [41], which were difficult to remove during the coal gravity separation. The concentrations of Ba and W found in different coal preparation products increased with their corresponding A_d. This indicates that these two elements were mainly associated with minerals.

4.4.3. Distribution of REY in Coal Separation

The concentrations of REY in Jiashun feed coal and in the separation products are given in Table 5. For the purpose of comparing the variation in REY from different coal preparation products, the geochemical parameters of REY were calculated after normalizing the upper continental crust (Table 6), including ∑REY (total REY, enrichment types, La_N/Yb_N, Eu anomaly (Eu_N/Eu_N*), and Ce anomaly (Ce_N/Ce_N*). The enrichment types were classified into L-type (light-REY [LREY]: La, Ce, Pr, Nd, and Sm; $La_N/Lu_N > 1$), M-type (medium-REY [MREY]: Eu, Gd, Tb, Dy, and, Y; $La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type (heavy-REY [HREY]: Ho, Er, Tm, Yb, and Lu; $La_N/Lu_N < 1$) [42].

Table 5. Concentrations of REY (μg/g, on a whole-coal air-dried basis) in coal separation products and feed coal of Jiashun.

Separation Products (μg/g)	**Method**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Y**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Cleaned coal	Flotation	17.3	35.3	3.97	15.2	2.81	0.42	2.51	0.45	2.60	12.9	0.52	1.53	0.276	1.51	0.235
Tailings		19.1	41.1	4.73	18.2	3.57	0.59	3.31	0.58	3.18	15.9	0.59	1.68	0.284	1.63	0.238
Cleaned coal	Gravity Separation	16.29	32.01	3.64	13.93	2.55	0.39	2.42	0.41	2.48	12.87	0.49	1.42	0.26	1.43	0.22
Middlings		18.26	39.22	4.60	17.88	3.34	0.53	2.97	0.50	2.81	15.39	0.57	1.63	0.28	1.59	0.24
Tailings		10.77	24.13	2.78	10.97	2.58	0.47	2.57	0.43	2.13	11.06	0.36	0.93	0.16	0.82	0.12
Feed coal	/	16.86	33.22	3.86	14.14	2.85	0.43	2.51	0.45	2.83	14.72	0.56	1.57	0.27	1.65	0.23

Table 6. Geochemical parameters of REY in coal separation products and Jiashun feed coal.

Separation Products	**Method**	**ΣREY (μg/g)**	**Type**	**Ce_N/Ce_N^***	**Eu_N/Eu_N^***	**La_N/Yb_N**
Cleaned coal	Flotation	97.6	H	0.97	0.74	0.84
Tailings		114.7	M-H	0.99	0.81	0.86
Cleaned coal	Gravity Separation	90.80	H	0.95	0.75	0.83
Middlings		109.80	M-H	0.98	0.80	0.84
Tailings		70.28	M-H	1.00	0.88	0.96
Feed coal	/	96.1	H	0.94	0.74	0.75

REY is the total concentration of La to Lu plus Y. In order to avoid interference of the Gd anomaly with the Eu anomaly, Eu_N/Eu_N^* is calculated based on the formula $Eu_N/(Sm_N \times 0.66 + Tb_N \times 0.33)$ [43,44]; $Ce_N/Ce_N^* = Ce_N/(La_N \times 0.5 + Pr_N \times 0.5)$ [44]. Sm_N, Eu_N, Tb_N, La_N, Ce_N and Pr_N are upper continental crust (UCC) normalized values [45].

1. Distribution of REY in coal preparation products

REY-bearing minerals were embedded in the coal with small particle sizes, and flotation was revealed to be the best method for separating ultrafine particles [46]. The concentration of most REY in the cleaned coal through flotation was higher or close to that found in the feed coal (Table 5). This reveals that REY in Jiashun coal is found in organic matter rather than independent REY-bearing minerals. The result from gravity separation shows that the concentration of REY in middlings was higher (Table 5). This reveals that REY in the Jiashun coal was more complex and occurred in micro-fine minerals wrapped by organic portions or combined with organic matter, making it difficult to remove.

The cleaned coals presented H-type enrichment, while in middlings and tailings, the enrichment was of M-H type for both separation methods (Table 6). A large number of studies have shown that HREY in coal might be mainly combined with organic matter or in the form of ion adsorption, but LREY may be more easily banded to minerals [47]. This resulted in the HREY enrichment in cleaned coal and deficit in tailings, and M-H type enrichment in middlings and tailings.

The concentration of ΣREY in the feed coal was 96.1 μg/g (Table 6). This value was higher than the world average content of 69 μg/g in hard coal [36], but lower than the average (138 μg/g) found in Chinese coal [32]. ΣREY were more enriched in tailings from flotation (114.7 μg/g) and in middlings from the gravity separation (109.8 μg/g). There was not much difference in concentration found in coal preparation products, indicating that the physical coal preparation method was not very effective for the separation in Jiashun coal.

In both of the physical coal preparation methods, the ratio value of La_N/Yb_N was greater in tailings and smallest in cleaned coal, indicating that LREY was relatively enriched in tailings, whereas HREY was enriched in cleaned coal. This reflects that LREY mainly occurred in minerals, and HREY was associated with organic matter. This finding is consistent with previous conclusions.

In this study, the upper continental crust (UCC) [45] was used to normalize REY in Jiashun coal and its coal preparation products. The distribution patterns after normalization of the average REY concentration in UCC are shown in Figure 6. This showed negative Eu anomalies, with HREY slightly enriched. In general, the distribution patterns of REY in feed coal and its separation products were comparatively consistent, indicating that physical separation had almost no effect on the distribution patterns [48].

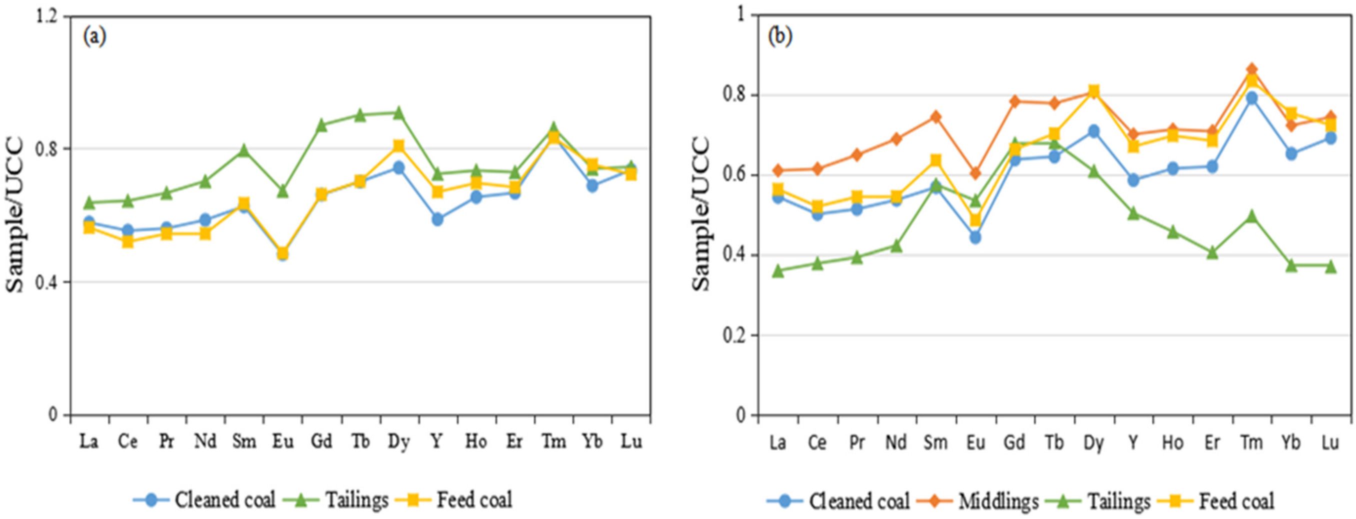

Figure 6. Distribution patterns of REY in different coal preparation methods. (**a**) Flotation; (**b**) gravity separation). Normalized to average REY concentrations in UCC [45].

2. Geochemical characteristics of REY

The Jiashun feed coal enrichment was of H-type. In general, terrestrial sediments are enriched in LREY while marine sediments are enriched in HREY [49], indicating that Jiashun coal was influenced by the marine environment. The La_N/Yb_N ratio can reflect the fractionation between LREY and HREY [8], if the ratio is close to 1, the fractionation of LREY and HREY is not obvious. The La_N/Yb_N ratio of feed coal was approximately 0.75, suggesting a significant LREY deficit.

Ce and Eu are more sensitive to the changes in the redox environment and are commonly used to analyze the sedimentary environment of coal seams [50]. Several studies have shown that coals formed in a marine environment have a negative Ce anomaly [51]. It is generally believed that $Ce_N/Ce_N{}^*$ ratios are <0.5 in oxic water, 0.6–0.9 in suboxic water, and 0.9–1.0 in anoxic water [52]. The Ce anomaly value in the Jiashun feed coal was 0.94, which indicates a weak negative anomaly, suggesting that the formation of Jiashun coal was affected by anoxic water.

Eu anomaly in coal is usually considered to be inherited from rocks within the sediment source region [53]. Europium usually exhibits a negative anomaly in coals with input of felsic rocks and felsic-intermediate terrigenous material [44]. The Eu anomaly value in the feed coal was approximately 0.74, showing an obvious negative anomaly. Therefore, it was considered that a felsic or felsic-intermediate sediment source region contributed to the Jiashun coal. Overall, the formation of Jiashun coal was influenced by both seawater and terrigenous deposition.

4.5. Removal Rate of Trace Elements

To study the reduction degree of the elements during coal preparation, the following Equation [14] was used to calculate the removal rate.

$$R = (1 - ci/Ci) \times 100\% \tag{1}$$

where R is the removal rate, ci is the content of element i in the cleaned coal, and Ci is the content of element i in the feed coal.

The removal rates of ash, sulfur, and trace elements achieved using different coal preparation methods are given in Table 7 and depicted in Figure 7. It was found that there was little difference in the removal of ash and sulfate sulfur through flotation and gravity separation. However, the removal rate of total sulfur, pyrite sulfur, and organic sulfur using gravity separation was significantly higher than that of flotation.

Table 7. Removal rate (%) of ash, sulfur, and trace elements in coal cleaned using different preparation methods.

Coal Preparation Products (%)	**A_d**	**$S_{t,d}$**	**$S_{p,d}$**	**$S_{s,d}$**	**$S_{o,d}$**	**Li**	**Be**	**Sc**	**V**	**Cr**	**Co**	**Ni**
Gravity separation	34.21	68.76	91.39	86.37	44.91	38.27	6.75	33.14	−8.56	−9.57	48.38	26.65
Flotation	37.27	51.87	61.24	93.18	8.13	25.07	12.20	25.38	7.75	−5.46	86.82	3.39
	Cu	Zn	Ga	Rb	Sr	Zr	Nb	Mo	Cd	In	Cs	Ba
Gravity separation	36.39	−5.26	12.48	83.55	−37.33	−10.92	−26.53	10.18	48.03	20.01	65.65	60.53
Flotation	51.14	13.55	16.60	82.07	−22.29	−1.33	−14.11	15.29	64.14	40.52	62.43	46.07
	Hf	Ta	W	Tl	Pb	Bi	Th	U				
Gravity separation	−1.01	5.70	38.28	41.20	60.71	31.95	57.31	11.28				
Flotation	−2.50	3.40	47.18	10.46	34.10	46.91	54.51	21.11				

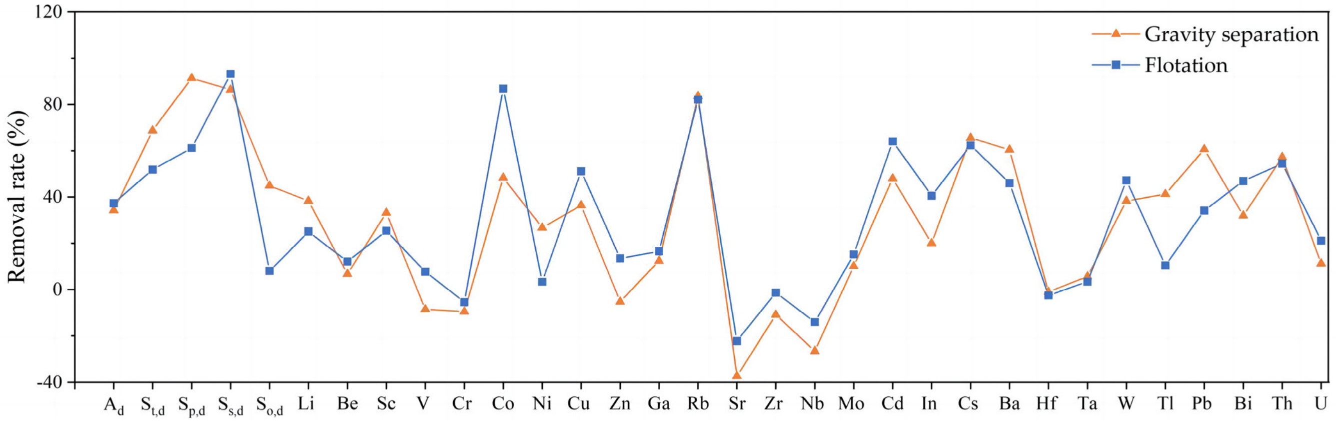

Figure 7. Removal rate of ash and elements in coal cleaned using different preparation methods.

As shown in Figure 7, the removal rates of Cr, Sr, Zr, Nb, and Hf in gravity separation and flotation cleaned coal were all negative. This indicates that these elements were enriched in cleaned coal, suggesting that they occurred within organic portions, making them difficult to remove.

The removal rate of Li, Ni, Ba, Tl, and Pb using gravity separation for cleaned coal was significantly higher than that of flotation-cleaned coal. These elements were mostly combined with minerals that were easily removed using gravity separation due to their greater density compared to coal.

The removal rate of sulphophile elements (Co, Cu, Cd, In, W, and Bi) through flotation was significantly higher than the rate achieved using gravity separation. This higher removal rate could be explained by the fact that these elements were mostly in fine-grained minerals in Jiashun coal. Therefore, the gravity separation method did not succeed in achieving their effective removal. On the contrary, flotation succeeded removing those elements by taking advantage of the difference between the surface properties of their bearing minerals and coal. The above findings show that flotation was more effective and appropriate for the removal of trace elements contained in fine-grained minerals, in contrast to gravity separation [8].

The removal rate of several lithophile elements (Sc, Rb, Cs, Th) through both gravity separation and flotation showed no significant difference (<10%). However, the removal rate of Be, V, Zn, Ga, Mo, Ta, and U through the coal preparation using both methods was low (<25%). This may be due to fact that these elements were mainly bound to organic matter, with only a small amount associated with minerals. Tantalum might be adsorbed by the organic matter under the action of a hydrothermal solution [44], resulting in a low removal rate.

Previous studies on the mode of occurrence of Li in coal have concluded that it is mainly found in clay minerals or closely related to organic matter [54–58]. In the Jiashun coal, Li was more obviously enriched in flotation tailings and middlings from the gravity separation. This suggests that Li was mainly bound to minerals, with a small amount combined to organic matter. These findings are consistent with previous studies.

4.6. Economic Potential Evaluation and Enrichment Genesis of Li

4.6.1. Economic Potential Evaluation of Li in Jiashun Coal and Its Preparation Products

The concentration of Li in Jiashun coal was assayed to be 94.5 μg/g, which was higher than the value of 14 μg/g for the world coal [36] and the average concentration (31.8 μg/g) in Chinese coal [32] (Table 8). It is worth noting that the marginal grade and industrial index for recyclable utilization of Li are set at 80 μg/g and 120 μg/g, respectively [59]. The marginal grade of Li_2O in clay-based Lithium deposits is usually 0.1%, with a minimum industrial grade of 0.2% [60]. Li_2O (HTA based) > 0.08% represents the marginal grade of Li [61]. Based on the theoretical value of Li_2O (HTA-based) calculated from the concentrations of Li and ash yield, it can be stated that Jiashun feed coal, tailings from flotation coal, and middlings from the coal gravity separation succeeded achieving the marginal grade (Table 8). Cleaned coal obtained through flotation also reached the marginal grade for Li_2O (HTA-based) > 0.08%. However, none of them reached the minimum industrial grade.

Table 8. The concentration of Li (μg/g, on a whole-coal air-dried basis) and Li_2O (%) in feed coal and various coal preparation products.

Method	/	Flotation		Gravity Separation			/	/
Coal preparation products	Feed coal	Cleaned coal	Tailings	Cleaned coal	Middlings	Tailings	World	China
Li (μg/g)	94.53	70.83	102.42	58.35	98.03	69.45	14.0	31.8
A_d (%)	13.36	8.38	21.23	8.79	16.96	38.52		
Li_2O (%)	0.07	0.085	0.05	0.07	0.06	0.02		

World, Li for world hard coals is from Ketris and Yudovich [36]; China, the average value for Chinese coals is from Dai et al. [32].

4.6.2. Origin of Li in the Jiashun Mine

The enrichment of trace elements in coal is a long-term and complex process. Various coal-forming environments and geological movements will affect the distribution of trace elements [62,63]. The input of terrestrial materials plays an important role in the enrichment of trace elements in coal-bearing strata. The terrigenous materials of most Late Permian coals in Southwestern China derive from basalt [64]. However, it has also been shown that the terrigenous materials of some Late Permian coals likely derived from felsic-intermediate rocks at the top of the Kangdian Upland [65]. When the terrigenous materials are from felsic-intermediate rocks, they feature low contents of transition metal elements, Sc, V, Cr, Co, Ni, Cu, Zn and Eu, showing obvious negative anomalies [44]. Jiashun coal exhibits obvious negative anomalies in Eu (0.74), and its content of transition metal elements, Sc (5.2 μg/g), V (24.3 μg/g), Cr (17.1 μg/g), Co (6.11 μg/g), Ni (4.99 μg/g), Cu (9.61 μg/g), and Zn (9.94 μg/g), was close to or lower than the average content of the world hard coals [36]. This suggests that the terrestrial inputs of the Jiashun coal mainly derive from the felsic-intermediate rocks at the top of the Kangdian Upland.

Previous studies have also shown that the influence of hydrothermal solutions was the main cause of mineralogical and geochemical anomalies in Late Permian coals in Southwestern China [61,66,67]. Veined pyrite and layered calcite were observed in Jiashun coal (Figure 3d), providing evidence that the Jiashun coal was influenced by late hydrothermal fluids. In summary, the input of felsic-intermediate terrigenous materials from the top of the Kangdian Upland and late hydrothermal fluids may be responsible for the enrichment of Li in the Jiashun coal.

5. Conclusions

Based on flotation and gravity separation, the mode of occurrence and distribution of Li and other trace elements in different coal preparation products were investigated. The data obtained from geochemical, mineralogical, and coal preparation experiments suggest the following:

(1) The Late Permian coal from the Jiashun Mine in southwestern China is characterized by high sulfur content (5.84%) and a high concentration of Li (94.5 μg/g). The minerals in Jiashun coals mainly consist of pyrite, quartz, and clay minerals, with kaolinite being the predominant clay mineral. In addition, common carbonate mineral calcite and REY-bearing mineral monazite are also present.

(2) Ni, Cu, Zn, Cd, In, Ba, W, Tl, Pb, and Bi are primarily distributed in the tailings, which may mainly occur in the minerals. Sc, V, Cr, Sr, Zr, Nb, Mo, Hf, and U are distributed in the cleaned coals, likely combining with the organic portions. Li, Be, Co, Ga, Rb, Cs, Ta, Th, and REY are distributed in the middlings, with these elements being uniformly distributed in minerals and organic components or in fine-grained minerals wrapped by organic matter.

(3) The removal rate of trace elements occurred in minerals obtained through gravity separation is significantly higher than the rate obtained using flotation. The trace elements mainly occurred in fine-grained minerals wrapped by organic matter or combined to organic portions exhibit better removal efficiency through flotation. Elements occurring in both minerals and organic matter have a low removal rate (<25%) with both preparation methods.

(4) Li is more enriched in flotation tailings (102 μg/g) and middlings (98 μg/g) obtained through gravity separation. The values reached the marginal grade (80 μg/g). The reason for the enrichment of Li in Jiashun coal may be the input of felsic-intermediate terrigenous materials from the top of the Kangdian Upland and late hydrothermal fluids.

Author Contributions: P.D. and W.W. conceived and designed the experiments; P.D. initiated the project and performed the experiments; Y.Z. analyzed the data, collected the literature, and created the figures; P.D. and A.K. revised the manuscript; Y.Z. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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