



Enrichment of Nb-Ta-Zr-W-Li in the Late Carboniferous Coals from the Weibei Coalfield, Shaanxi, North China

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Abstract: Mineralogical and geochemical characteristics of coals provide crucial information on their potential clean, efficient, and integrated utilization. In this paper, the mineralogical and geochemical behaviors of the No. 5 coals of the Taiyuan Formation in the Weibei Coalfield, North China, were investigated, and their geological controlling factors were subsequently discussed. The minerals in the Weibei coals mainly consist of kaolinite (8.3%), calcite (5.0%), and pyrite (3.1%), with minor proportions of tobelite (2.9%), dolomite (1.7%), quartz (1.8%), and traces of siderite (0.4%) and gypsum (0.6%). Several critical elements, including Nb (19.8 mg/kg), Ta (3.6 mg/kg), Zr (71.0 mg/kg) and Li (32.3 mg/kg), occur at concentrations higher than those averages for world hard coals, making the Weibei coals potential sources of these critical elements. Several factors, terrigenous material, seawater invasion, and hydrothermal fluids are responsible for these mineralogical and geochemical characteristics. The L-type rare earth elements and yttrium (REE-Y) enrichment in the roofs and partings, Al₂O₃-TiO₂ and Zr/TiO₂-Nb/Y plots, and negative Eu and weak negative Ce anomalies in the Weibei coals indicate a felsic-intermediate dominated sediment provenance primarily derived from the Qilian-Qinling Oldland on the South. Marine bioclastic limestone, negative Ce and positive Y anomalies in coals imply the influence of seawater on the Weibei coals. Last but not least, the cleat-infilling and/or fracture-infilling calcite, pyrite, barite, and tobelite as well as the positive Eu and Gd anomalies, H-type, and M-type REE-Y enrichment patterns suggest the influence of hydrothermal fluids, which lead to re-distribution of some critical elements from roof and parting to the underlying coal seam.

Keywords: critical elements; mineralogy; geochemistry; hydrothermal fluids; Weibei coalfield

1. Introduction

As the development of western regions in China, Shaanxi Province is becoming one of the most significant bases for resource exploitation. Shaanxi Province is the fourth largest coal producing province in China, with estimated coal reserves of 4143Gt [1,2]. According to the geological age and the geographic distribution, there are primarily five important coalfields in Shaanxi province,



including Weibei (Permo-Carboniferous), Huanglong (Jurassic), and the three Shanbei (Trassic, Jurassic, and Permo-Carboniferous)coalfields (Figure 1a,b). The Weibei Permo-Carboniferous Coalfieldis the fourth largest coalfield in Shaanxi (up to 83 GT) [3]. Geochemical patterns, especially those related with the concentrations of hazardous elements in coal have been studied, and abnormal concentrations of hazardous elements in the Weibei coalfield, such as As, Se, Hg, and F have caused serious endemic diseases induced by coal utilization as fuel [1,4,5]. Moreover, the enrichment of some critical metals, such as Ga, Ce, and Y have also been found [6], which has a potential interest from a potential exploitation point of view.



Figure 1. Geological location of the Weibei Coalfield, southeastern Ordos Basin (**a**,**b**) and distributions of different mining districts and sampling sites (**c**).

Geochemical characteristics of coals, especially those enriched in criticalelements, including Ge, Ga, U, Li, and rare earth elements and yttrium (REE-Y), have attracted much attention in recent years due to their high potential as raw materials for criticalelement recovery [7–16]. The modes of occurrence, geological controlling factors as well as enrichment mechanism of criticalelements in coals have also been investigated by a number of researches [14,17–22]. However, geochemical characteristics, modes of occurrence, origin, and enrichment mechanism of elements in the Weibei coals were few studied in the literature [6,23], which restrict the clean and efficient utilization of these coals.

On the basis of these preliminary understandings, this paper aims to investigate the mineralogical and geochemical characteristics of coals from the Weibei Coalfield, with special emphases on the environmentally-relevant and valuable elements (eg., Nb, Ta, Zr, Hf, and Li), and subsequently expound the implications of possible geological factors, e.g., sediment source region, sea water, and hydrothermal fluids.

2. Geological Setting

The Weibei Permo-Carboniferous Coalfield is geographically located in central Shaanxi Province, and tectonically situated in the Weibei uplift area at the southeastern corner of the Ordos Syneclise

(Figure 1a,b), and is subdivided into Hancheng, Chenghe, Pubai, and Tongchuan mining districts from east to west (Figure 1c). The Weibei coalfield has undergone at least two structural changes of different properties, modes, and directions, resulting in a complex structural pattern with early compression and late extension [24,25]. The tectonic structures trend approximately northeast–southwest and faults are well developed in this coalfield [6,26].

The Early Permian Shanxi Formation and the Late Carboniferous Taiyuan Formation are the major coal bearing strata in the Weibei Coalfield (Figure 2). The former was formed in a continental environment and is composed of sandstone, mudstone, and four thin and discontinuous coal seams (Nos. 1–4 coals), among which the No. 3 coal seam is the most economically significant (2.9 m thick on average) and thins out from east to west [6,26]. The latter was deposited in a marine-continental transitional environment where episodic transgressions formed marine carbonate beds [26], and it mainly consists of sandstones, mudstones, limestones, muddy limestones, sideritic shales, claystones, and coal seams (Nos. 5 to 11), among which the No. 5 coal seam is the major minable and 2.5 m thick on average. It is worth noting that the bottom of the Shanxi Formation is usually characterized by a marker bed that is composed of quarzitic sandstone and/or sandy conglomerate.



Figure 2. Stratigraphic columnof Permo-Carboniferous coal-bearing strata in the Weibei Coalfield and sampling distributionin the No. 5 coal seam of the Dongdong and Jinhuashan underground coal mine.

3. Methodology

3.1. Sample Collection

Twenty-five bulk samples, including seven coal samples, one roof, and two parting samples from the Jinhuashan mine, and thirteen coal samples, one roof and one parting samples from the Dongdong mine, were collected from underground coalfaces of the No. 5 coal seam in the Jinhuashan and Dongdong coal mines, which are respectively located in the Tongchuan and Chenghe coal mining districts of the Weibei Coalfield (Figure 1c). The roof sample for the Jinhuashan andDongdong coals are named as JHS-R and DD-R, respectively. The coal samples for the Jinhuashan and Dongdong coals are respectively numbered as JHS-1 toJHS-7and as DD-1 to DD-13from top to bottom. The partings are numberedasJHS-P1 to JHS-P2 and DD-P1 from top to bottom, respectively for Jinhuashan and

Dongdong coals (Figure 2). Note that the No. 5 coal seam was being mined at the sampling time, so the lower portion of the No. 5 coal seam in both coal mines could not be accessed for safety reasons.

3.2. Analytical Methods

Proximate analysis was performed according to ASTM Standards D3173-11 (2011); D3175-11 (2011), and D3174-11 (2011) [27–29]. The total sulfur and forms of sulfur were determined following ASTM Standards D3177-02 (2002) and D2492-02(2005), respectively [30,31].

Mineralogical compositions of the collected samples were determined by powder X-ray diffraction (XRD) using a Bruker D8 A25 Advance diffractometer with monochromatic Cu K α 1 radiation($\lambda = 1.5405$ Å) from 4 to 60° of 2 θ range, a step size of 0.019°, and a counting time of 0.1 s/step. A semi quantitative XRD mineral analysis was carried out using the internal reference method devised by Chung (1974) [32]. In addition, morphology, and modes of occurrence of minerals and specific elements were evaluated by means of a Field Emission-Scanning Electron Microscope (FE-SEM, FEI QuantaTM 650 FEG) with an Energy Dispersive X-Ray Spectrometer (EDS; Genesis Apex 4). The sampleswere not coated for low-vacuum SEM working conditions (60 bars). The working distance of the FE-SEM-EDS was 10 mm, beam voltage20.0 kV, aperture 6, and spot size 5. Images were captured via a retractablesolid state back-scattered electron detector.

The concentrations of major and selected trace elements (Ti, Mn, P, B, Ba, Cu, Ni, Sr, Zn, and V) were determined by inductively coupled plasma atomic-emission spectrometry (ICP-AES, Iris Advantage TJA Solutions), and those of most trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS, X-Series II Thermo). Prior to determination, each sample was digested using a two-step acid-digestion method (first with HNO₃to dissolve the most volatile elements, and subsequently with a full HF: HNO₃: HClO₄ digestion reagents,) [17]. International reference material (South African coal reference material, SARM-19) and blank samples were treated in the same way to subtract blanks and controlling the quality of the analysis. The analytical precision wasbetter than $\pm 2.5\%$ for Si, Al, K, Cr, Ba, Pr, Gd, and Th; better than $\pm 5.0\%$ for Ca, Fe, Be, V, As, Y, Nd, Dy, Er, and Pb; and better than $\pm 10.0\%$ for theremaining major and trace elements.

Because most Si is lost by the HF digestion (forming the highly volatile SiF6), Si contents were not determined by ICP-AES, but calculated through a mass balance method [12,21]. To further check the accuracy of the above calculated method, Si contents of the Jinhuashan coal and rock samples were also measured by X-ray fluorescence (XRF) and correlated with the calculated Si contents.

For the identification of the elemental affinities, the Pearson's correlationanalysis was applied to illustrate the correlations betweenelement concentrations in the studied samples, especially the correlationsbetween trace element concentrations and ash yields/common majorelement oxide concentrations (e.g., Al_2O_3 and SiO_2). In the presentresearch, with a statistical sample numbers of 24, the Pearson's correlation coefficients are significant at a level of 0.01 (p < 0.01). The interpretation of the origin of elemental affinities always subjective, but was based on the typical geochemicaloccurrence of the elements with the highest loading factors (e.g., S-Fe, sulfide affinity; Al-Ti-Rb-K, clay minerals; and Ca-Mg-Mn, carbonate minerals) [13].

4. Results

4.1. Coal Chemistry

The No. 5 coal seam from the Weibei coalfield has extremely low moisture contents (0.08–0.5%, avg. 0.3%, air dry basis, Appendix A Table A1) according to Chinese Standard MT/T 850-2000, which classifies coal with moisture content <6.0% as extremely-low-moisture coal [33]. The high temperature ash (HTA) yields (7.1–32.9%, avg. 18.7%, dry basis, Appendix A Table A1), point to classification of Weibei coals as medium-ash coal (ash yield of 16.01–29.00% for medium-ash coal) [34]. The similar HTA yields of Dongdong and Jinuashan coals (avg. 18.1% and 19.6% db, respectively) indicate similar terrigenous detrital supply during peat accumulation. The volatile matter yields

(15.7–27.54%, avg.19.7%, dry ash free basis) indicate that the Weibei Coals fall within the rank of low volatile bituminous coals (Appendix A Table A1) [35]. The average total sulfur content of No. 5 coal seam in the Weibei coals is from 1.0% to 9.0% (avg. 3.0%, Appendix A Table A1), belonging to group of high-sulfur coal [36]. However, there are differences in sulfur contents and types at different regions in the Weibei Coalfield (averages 3.6 and 2.0% db, respectively, in Dongdong and Jinhuashan Mine). Higher S content in Weibei coal is probably ascribed to high marine influence during peat deposition and coal formation. The sulfur in coals includes pyritic sulfur, organic sulfur, and trace proportions of sulfate. In the Dongdong coal, the average pyritic S prevails over the organic one (1.9 vs. 1.2% db, respectively), while the opposite occurs in the Jinhuashan (0.7 and 1.0% db, respectively). Despite differences in sulfur contents and types at different regions in the Weibei coalfields (Figure 3), pyritic sulfur is the primary form of sulfur in the roof and parting samples of both coals (Appendix A Table A1).



Figure 3. Variations of forms of sulfur through the studied coal seams.

4.2. Coal Mineralogy

The minerals occurring in the coal samples from Weibei Coalfield are mainly represented by kaolinite (0.3–30.6%, avg. 8.3%), calcite (0.7–24.0%, avg. 5.3%), and pyrite (0.2–13.4%, avg. 3.1%), along with minor proportions of tobelite (0.3–11.6%, avg. 3.0%), dolomite (0.2–5.4%, avg. 1.7%) and quartz (0.7–2.7%, avg. 1.8%), and traces of siderite (0.1–1.0%, avg. 0.4%) and gypsum (0.3–1.0%, avg. 0.6%, Appendix A Table A2). Anatase also occurs in trace amount in the lower portion of the coal seam (DD-13) beneath coal parting. Although below the detection limit of the XRD techniques, barite, rutile, apatite, and chalcopyrite have been occasionally observed by SEM-EDS techniques (Figure 4). In contrast, mineral occurring in the roof and parting sample of Weibei coals varies from place to place, which is dominantly kaolinite, calcite, and quartz, along with minor amounts of dolomite, pyrite, and tobelite (Appendix A Table A2).



Figure 4. SEM back-scattered electron images of minerals in the Dongdongcoals (sample DD-3). (a) Lens-like or banded kaolinite infusinitecell fillings. (b) Dispersed and lens-like kaolinite in fusinite cell fillings. (c) Massive kaolinite and fracture-filling pyrite. (d,e) Massive pyrite, possibly as cleat infilling. (f) Syngenetic kaolinite and rutile as infillings of fusinite cells. (g) Microcrystal of apatite as infilling of fusinite cells. (h) Aggregates of chalcopyrite as infilling of fusinite pores.

4.3. Coal Geochemistry

As shown in Appendix A Tables A3 and A4, the contents of all the major element oxides in the Weibei coals are either similar to or lower than the corresponding averages for common Chinese coals [5]. The higher proportion of CaO in the Jinhuashan coals is probably caused by the higher calcite content. The average value of SiO_2/Al_2O_3 ratio in the Weibei coals is 0.9 (0.9 and 1.1, respectively, in Dongdong and Jinhuashan coal), lower than that of other Chinese coals (1.4) [5], and even lower than the theoreticalSiO₂/Al₂O₃ ratio of kaolinite (1.2).

 SiO_2 content inferred from the XRD analysis is highly correlated with that determined by XRF analysis (r = 0.99, Table A4), suggesting the accuracy of XRD data-based semi-quantification method in the present study.

Based on the average concentrations of trace elements for world hard coals [37], and the enrichment classification of trace elements [19], the Weibei coals are characterized by enrichment of Ta-Nb-W-Li assemblage (Figure 5). According to Dai et al. (2015a) [19], in the Dongdong coal, tantalum is significantly enriched (10 < CC < 100) (Figure 5a), the elements Nb, and Ware enriched (5 < CC < 10), and Li, P, Se, Zr, and Th are slightly enriched (2 < CC < 5), while the remaining are depleted (CC < 0.5) or in the normal range (0.5 < CC < 2) (Figure 5a). In the Jinhuashan coal, Ta is enriched and Nb, W, Li, P, Sr, Y, La, and Ce slightly enriched, while the other elements depleted or in the normal range (Figure 5b). Furthermore, concentrations of these elevated elements are extremely higher in the non-coal rocks of the Weibei coalfield than in the corresponding coals (Figures 6 and 7). The average concentration of REE-Y is 88.0 μ g/g (from 17.7 ug/g to 264.4 ug/g) in the Weibei coals, higher than the average of world hard coals (68.6 μ g/g) but lower than that of common Chinese coals (136 μ g/g) [5,37]. Considering that coal by its nature is closer to the UCC (upper continental crust,) than to PAAS (Post-Archaean Australian shale), e.g., coal was deposited within the upper continental crust, and contains many detrital UCC contributions mixed within the peat environment [38], the REE-Y in coal are normalized to values for the UCC in the present researchas reported by Taylor and McLennan (1985) [39]. According to the classification proposed by Seredin and Dai (2012) [11], the REE-Y enrichment pattern in the Weibei coals is dominantly of H-type ($La_N/Lu_N < 1$) (from DD-3 to DD-12, JHS 1, JHS-5 to JHS-7, Appendix A Table A5), and of L-type (La_N/Lu_N > 1) or M-type in the coal samples adjacent to the roof and floor (DD-1, DD-2, and D-13, JHS-2 to JHS-4). In the roof and parting of the Weibei coals, the REE-Y enrichment pattern is characterized by an L-type (Table A5). Vertically, the REE-Y concentrations are higher in the roof and parting samples than in respective coal samples, presenting similar variation to kaolinite and also to the elevated Nb, Ta (Figures 6 and 7), and pointing to an aluminosilicate affinity. This is also evidenced by the positive correlation coefficients of REE-Ys in the Weibei coals with HTA yields (rREE-Y-HTA = 0.37-0.83), Al₂O₃ (rREY-Al₂O₃ = 0.28-0.93), and SiO₂ (rREY-Al₂O₃ = 0.35-0.94) contents on a whole-coal basis. Furthermore, the correlation coefficients are higher for light REE-Y (LREY) than heavy REE-Y (HREY), probably due to the higher inorganic affinity of LREY, and a mixed inorganic–organic affinity of HREY [19,20,40].

In order to avoid interference of the Gd anomaly with the Eu anomaly, the UCC-normalized Eu, Ce and Gd anomaly (expressed as Eu_N/Eu_N^* , Ce_N/Ce_N^* , and Gd_N/Gd_N^* , respectively) was calculated using the formula modified by Bau and Dulski (1996) and Dai et al. (2016, 2017b) [20,38,41]. Except for four coal samples (DD8 to DD11) with positive Eu anomalies (Eu/Eu_N* of 1.12 to 1.71) and obvious negative Gd anomalies (Gd/Gd_N* of 0.23 to 0.73), the Weibei coals are generally characterized by weak to pronounced negative Eu anomalies and weak negative Ce anomalies, and weak negative to positive Gd anomalies, with Eu/Eu_N^* , Ce_N/Ce_N^* , and Gd/Gd_N^* , respectively, ranging from 0.25 to 1.71 (avg. 0.78), 0.82 to 1.30 (avg. 0.96), and 0.23 to 2.19 (avg. 1.14) (Appendix A Table A5). The roof and parting of the Weibei coals have obvious negative Eu anomalies (0.18–0.84, avg. 0.48) and positive Gd anomalies (1.05–1.71, avg. 1.21). Notably, REE-Y concentrations in the four coal samples with positive Eu anomalies (DD8 to DD11) are significantly lower than in other coal and non-coal samples (Figures 6 and 7).



Figure 5. Concentration coefficients (CC) of trace elements in the coals from the Dongdong and Jinhuashan Coals. Normalized to average trace element concentration forworldwide coals [37]. (a) CC of trace elements in the Dongdong Coals; (b) CC of trace elements in the Jinhuashan Coals.







Figure 7. Vertical distribution of elevated elements through coal benches of the Jinhuashan coal mines.

5. Discussion

The mineralogical and geochemical characteristics of the Weibei Coal are mainly controlled by three factors: (1) sediment provenance, (2) marine influence during deposition, and (3) hydrothermal fluids.

5.1. Influence of Sediment Provenance

Combinations of Al₂O₃/TiO₂, Zr/TiO₂-Nb/Y, and REE-Yenrichment patterns, and/or other geochemical parameters have been widely used for a more precise sediment provenance analysis [42]. Al₂O₃/TiO₂ ratio is effectively used to identify the provenance of sedimentary rocks [43], coal seams [19,20,44,45], and altered volcanic ashes in coal-bearing sequences [16,46,47], with Al₂O₃/TiO₂ ratios of 3–8, 8–21, and 21–70, respectively for mafic-, intermediate-, and felsic-dominated provenance [43]. As illustrated in Figure 8, Al₂O₃-TiO₂ plots of the coal and host rocks in the Weibei coalfield principally fall in the felsic field, and secondarily in the intermediate field, indicate that the terrigenous materials dominantly derived from felsic-intermediate dominated sediment source region.





Figure 8. Plots of elements in the coal and non-coal samples from the Dongdong and Jinhuashan coal mines. (**A**) Plots of Al₂O₃ vs. TiO₂. (**B**) Diagram showing Zr/TiO₂ vs. Nb/Y ratios using the magma source discrimination diagram of Winchester and Floyd (1977) [48].

The elevated Ta, Nb, Zr, Li, and Win the Weibei coals exhibit high correlations and similar vertical distributions with HTA yields, Al₂O₃ and SiO₂ contents (Figures 9 and 10), which represent an obvious aluminosilicate affinity and imply the terrigenous origin of these elevated elements. The Zr/TiO₂-Nb/Y plot was widely used as an auxiliary indicator to discriminate the provenance, classification and evolution of altered volcanic ashes and associated coal bearing sequences [16,22,49,50]. The majority of the coal and non-coal rocks in the Dongdong mine fall within the trachyandesite and trachyte fields, pointing to a felsic-intermediate sediment provenance, while those in the Jinhuashan coal mine are distributed in slightly broader areas, falling within the fields of trachyandesite, trachyte, as well as rhyodacite/dacite (Figure 8B), pointing to a felsic-dominated sediment provenance. Overall, the sediment provenance of the terrigenous materials in the Weibei coalfield was characterized by felsic to intermediate chemical composition.



Figure 9. Relations between concentrations of Ta, Nb, and Zrwithhigh temperature ash (HTA) yield (whole-coal basis), Al_2O_3 (whole-coal and ash basis), and SiO_2 (whole-coal and ash basis) contents in the Dongdong coals.



Figure 10. Relations between concentrations of Ta, Nb, and ZrwithHTA yield (whole-coal basis), Al₂O₃ (whole-coal and ash basis), and SiO₂ (whole-coal and ash basis) contents in the Jinhuashan coals.

Likewise, several REE-Y parameters, e.g., Ce, Eu, and Gd anomalies, as well as REE-Y enrichment patterns are extensively used for sediment provenance analysis [11,21,51–56]). Sediments, including coal bearing sequences, with L-type REY enrichment pattern are generally indicative of a terrigenous origin [21]. The host rocks (roofs and partings) in the Weibei coalfield and several coal samples adjacent to the partings in the Jinhuashan coal are all characterized by L-type REE-Y enrichment patterns, which are consequently inherited from the terrigenous sediment source origin. Furthermore, sediment source regions with weak negative Ce and distinct negative Eu anomalies are primarily composed of felsic or felsic-intermediate rocks, and notably, coals with terrigenous inputs from felsic-intermediate dominated provenance are expected to inherit similar negative Ce and Eu anomalies [21]. Asaforementioned, the Weibei coals and non-coal rocks mostly display negative Eu and weak negative Ce anomalies, which indicates the terrigenous input into the Weibei coalfield was largely derived from felsic or felsic-intermediate sediment source region.

Based on Al₂O₃-TiO₂ plots, Zr/TiO₂-Nb/Y plots, REE-Y distribution patterns, as well as Eu and Ce anomalies, the sediment provenance of the No. 5 coals in the Weibei Coalfield are dominantly by felsic-intermediate provenance, which probably originated from the Qilian-Qinling Old land on the south [57,58]. Wan (2011) also suggested that the Qilian-Qinling Old land is comprised of Proterozoic metamorphic rocks (e.g., quartzite, gneiss, and marble) and Proterozoic-Palaeozoic granites, metamorphic sedimentary rocks, and carbonates, which is characterized by LREY enrichment [59].

5.2. Influence of Sea Water

The coal characteristics are highly influenced by marine-influenced sedimentary environment as well, apart from the influence of sediment provenance. HREY enrichment in coals is probably caused by strong influences of HREY-rich natural waters circulating in coal basins [60], for instance, sea water [61], alkaline waters [62], high pCO₂ or other acid waters [63,64], low-temperature hydrothermal solutions [65], or volcanogenic solutions [62,66]. With exception of the roofs, partings, and coals adjacent to them, the REY enrichment patterns are dominantly of the H-type in most of the Dongdong and Jinhuashan coals, which is probably attributed to the influence of sea water. This tconclusion is further evidenced by the following distinct features of Ce, Y, and Gd anomalies.

As discussed above, coals with terrigenous inputs from felsic and/or felsic-intermediate dominated sediment source regions are characterized by weak negative Ce anomalies. Nonetheless, negative Ce anomalies are also indicative of influence of sea water [67,68], consequently, coals formed in a marine environment are also characterized by negative Ce anomalies [21,69]. The weak negative Ce anomalies of the Dongdong and Jinhuashan coals were consequently considered to be caused by the integrated influences of felsic-intermediate sediment provenance and seawater. Furthermore, the Dongdong coals (Ce_N/Ce_N* of 0.9 to 0.99, Appendix A Table A5) were formed in anoxic marine environment according to the classification with Ce_N/Ce_N* of 0.76 to 0.96) in suboxic to anoxic marine environment according to the classification with Ce_N/Ce_N* values of < 0.5, 0.6–0.9, and 0.9–1.0 respectively for oxic marine, suboxic marine, and anoxic marine environment [70]. The more anoxic marine environment in the Dongdong coals may reflect higher influence of sea water and is suggested to be responsible for the higher total S content and pyritic sulfur content in Dongdong coals with respect to the Jinhuashan coals.

In addition, felsic-intermediate rocks generally have weak or no Y anomalies, so coals with input of felsic-intermediate terrigenous materials would be expected to exhibit weak or no Y anomalies [38]. By contrast, seawater usually has positive Y and Gd anomalies [38,41,61,71,72]; hence, coals with positive Y and Gd anomalies may have been formed in a marine sedimentary environment. In the present research, the roof, partings, and coals adjacent to the roof and partings show weak Y anomalies (Appendix A Table A5), which was thought to have been inherited from the felsic-intermediate sediment provenance. However, most of the Dongdong and Jinhuashan coals dominantly show positive Y and Gd anomalies (Appendix A Table A5), which is probably indicative of the influence of sea water.

5.3. Influence of Hydrothermal Fluids

Except the sediment provenance and marine effects, hydrothermal fluids are the most important controlling factors of the mineralogical and geochemical characteristics in the Weibei coal samples.

5.3.1. Mineralogical Evidence

The influence of hydrothermal fluids has been obviously evidenced by the occurrence of cleat-infilling and/or fracture-infilling minerals, such as kaolinite, pyrite, goyazite, barite, and tobelite in coals [13,20,52,73,74].

Kaolinite in the Weibei coals occurs mainly in lens-like (Figures 4a and 11a), banded (Figure 11a,c,d and Figure 12a,b,e), and massive (Figure 11b) forms as cleat infillings, while in some cases, kaolinite occurs in banded forms as infillings of fusinite cells (Figures 11a and 12a,b), suggesting both a terrigenous origin and an authigenic origin. The cell-infilling kaolinite, to some extent, has been re-mineralized by epigenetic disseminated pyrite (Figure 12a). In a few cases, kaolinite also occurs as dispersed particle, intergrown with illite (Figure 11d), also representing its formation by authigenesis process.

Pyrite in the Weibei coals occurs as discrete crystals (Figure 12a,h), veins of very fine to large cleat infillings (Figure 12f–h), and in many cases, occurs in banded (Figures 11c and 13a–d,g) and massive forms (Figures 12f and 13a), as cleat infillings as well. The various forms of occurrence of pyrite represent anauthigenic origin for its formation and the occurrences as cleat/fracture-fillings suggest an epigenetic origin. Barite occurs as cleat-filling veins in the Jinhuashan coals (Figure 13a,b), and represents a hydrothermal origin. Moreover, the barite cross-cut the cleat-infilling pyrite (Figure 13a,b), indicating that the precipitation of pyrite was prior to that of barite. Carbonate minerals in the studied coals, principally dolomite and calcite, usually coexist with pyrite, and occur primarily as irregular fracture infillings (Figure 13c,d), indicative of an epigenetic origin.



Figure 11. SEM back-scattered electron images of kaolinite, pyrite, rutile, and goyazitein the Jinhuashancoals. (a) Lens-like and banded kaolinite as fusinite cell infillings, coexisting with rutile; (b) Massive kaolinite and goyazite particles as cleat infillings; (c) Fracture/Cleat-infilling pyrite and kaolinite intergrown with goyazite; (d) Enlargement of yellow square in (c); (e,f) EDS spectrum respectively for kaolinite and goyazite in (c,d).



Figure 12. SEMback-scattered electron images of kaolinite, pyrite, and illite in the Jinhuashancoals (sample JHS-2). (**a**) Kaolinite and pyrite as cleat infillings as well as framboidal pyrite and banded kaolinite, in some cases remineralized by disseminated pyrite; (**b**) Enlargement of yellow square in (**a**); (**c**) Pyrite veins as cleat infillings and dispersed particle of kaolinite and illite; (**d**) Enlargement of yellow square in (**c**); (**e**) Banded kaoliniteand intergrown pyrite as cleat infillings; (**f**,**g**) Fragments of banded pyrite and pyrite mineralization in very fine to large cleats, mostly in vitrinite bands; (**h**) Discreted (mostly framboidal) pyrite crystals and massive pyrite as fine cleat infillings.



Figure 13. SEM back-scattered electron images of pyrite, barite, dolomite, and calcitein the Jinhuashancoals. (a) Massive pyrite infilling of epigenetic cleats, cross-cutby cleat-filling barite veins; (b) Enlargement of yellow square in (a); (c) Cleat-filling pyrite and dolomite; and (d) Pyrite, calcite, and dolomite as cleat infillings.

Particles of goyazite grows as cleat infillings and usually intimately associated with kaolinite in the Jinhuashan coals (JHS-2, Figure 11b,f), and in some cases, surrounded by epigenetic cleat-infilling kaolinite (Figure 11d), which reflects an authigenic, epigenetic process for its formation. Goyazite also occurs in the boehmite-rich coals from the Jungar (Guanbanwusu, Heidaigou, and Haerwusu coal mines) and DaqingshanCoalfield (Adaohai, Hailiushu, and Datanhao coal mines), in which goyazite is closely related to kaolinite, boehmite, or diaspore, and occurs in the forms of cell infillings and as massiveand discrete particles, indicating an authigenicorigin [7,8,16,75–77]. Authigenic goyazite has also been found in several other coals; for instance, in the coal-bearing strata of the Fusui Coalfield [55], and in the K2 coal of the Moxinpo coalfield [78]. Goyaziteis an important mineral indicating hydrothermal activity, which is usually formed by reaction between Al-rich hydrothermal solutions and P derived from organic matter in peat swamp [55,73].

Tobelite ((NH₄,K)Al₂(AlSi₃O₁₀)(OH)₂, a member of illite group) is another important hydrothermal indicator. As shown in Figure 14, tobelite occurs with lower amounts in the middle to the lower portion, and higher amounts in the bottom of the No. 5 coal from the Dongdong mine, obtaining the maximum content in the lower parting sample (Appendix A Table A2). By contrast, it occurs with minor amount in the parting, and higher amount in the bottom of the No. 5 coal in the Jinhuashan mine (Appendix A Table A2 and Figure 15). It has been reported that tobelite occurs in the Permo-Carboniferous coals from the Moxinpo coalfield, Chongqing, SW China [20], Daqingshan Coalfield, Inner Mongolia, NW China [18], as well as Qinshui coalfield, North China [58]. It is proved that the presence of tobelite in coals was caused by the hydrothermal alteration of existing kaolinite in coals with the active participation of NH⁴⁺ from organic matter at a relatively high temperature (e.g., >200 °C) [73,79–82].





Figure 14. Vertical variations of primary minerals expressed as percentages of each whole-coal or rock sample in the Dongdongcoal mine.



Figure 15. Vertical variations of primary minerals expressed as percentages of each whole-coal or rock sample in the Jinhuashancoal mine.

5.3.2. Geochemical Evidence

High sulfur contents (1.01–9.02%, avg. 3.01%)in the Weibei coals suggest sulfur were probably carried into the peat swamp by hydrothermal fluids and then evenly combined with Fe to form pyrite or distributed as the organic sulfur [8,55]. Although the Weibei coals were influenced by seawater,

as mentioned above, the concentration of SO_4^{2-} in paleo-seawater was in the range of 5–27.6 mmol/kg in the Phanerozoic [83,84], and it could not provide such high sulfur content (up to 9.0%) in coals. There are differences in sulfur contents and types at different regions in the Weibei coalfields. In the Dongdong coals, the average pyritic and organic sulfur content is 1.9% and 1.2%, respectively, while the counterpart in the Jinhuashan coals is 0.7% and 1.0%, respectively (Figure 3). These differences indicate the intensity of hydrothermal activity varies in the Weibei coalfield. The hydrothermal activity in the Dongdong coals is higher and responsible for the higher total sulfur content with respect to the Jinhuashan coals.

Positive Eu anomalies in coals may be ascribed to the influence of high-temperature hydrothermal fluids [54,65], which could be volcanogenic solutions [38,76], or activities of hydrothermal solutions (>200 °C) in marine environment during coal formation process [85,86]. It is worth noting that Eu obtain obvious positive anomalies (Eu_N/Eu_N* of 1.12 to 1.71) in DD-8 to DD-11 coal samples from the Dongdong coal section (Appendix A Table A5), probably caused by strong activities of high-temperature hydrothermal solution other than the aforementioned ones, which covered up the original negative Eu anomalies inherited from the felsic to intermediate dominated sediment provenance [38,63].

Furthermore, positive Gd anomalies and MREY and/or HREY enrichment are also significant indicators of activities of hydrothermal fluids [38,62,63]. The coal and non-coal rocks from the Weibei coalfield generally show positive Gd anomalies (0.23–2.19, avg. 1.14). In addition, the REY enrichment types are dominantly of H-type in most of the Weibei coals and of M- type in coals adjacent to the roof and parting, which were also probably caused by hydrothermal fluids. The most probable source of the hydrothermal solution would be derived from the volcanic/tectonic activity during accumulation of the Late Carboniferous coals in the Weibei coalfield (Nos. 5, 10, and 11 coals), which have been evidenced by occurrence of high-temperature quartz, and zircon [6].

Hydrothermal fluids were not only evidenced by some mineral and elemental enrichment as mentioned above, but also by theirdistribution among coal seam, roof, and parting. Compared to the overlying roof and parting, the critical elements (Nb, Ta, Zr, Li and HREE) enrichment and the higher Yb/La, Nb/Ta, and Zr/Hf ratios in the coal probably result from the re-deposition of these elements. Dai et al. (2013) suggested that the active leaching from roof and parting led to some elemental re-deposition in the underlying organic matter [55]. For instance, the Yb/La ratios is from 0.03 to 0.67 (avg. 0.12) in the Weibei coal seam, which is higher than the world hard coals (0.09) [37]. This kind of elemental redistribution, resulting from hydrothermal fluids, has also been reported in the Fusui and Jungar coals, China [18,55], and some US coals [87].

6. Conclusions

Based on chemical, mineralogical, and geochemical results of the No. 5 coals of the Taiyuan Formation from the Weibei coalfield, North China, the following can be concluded.

The No. 5 coals from the Weibei coalfield have extremely low moisture contents, low volatile matter yields, high sulfur contents, and medium HTA yields. The minerals in the Weibei coals mainly consist of kaolinite, calcite, quartz, pyrite, dolomite, and minor amounts of siderite and tobelite. The Weibei coals are characterized by enrichment of Ta-Nb-W-Li-P trace element assemblages, close to or higher than the respective industry cut-off grades or standards for ores containing these strategic elements, which make the Weibei coals potential sources of these critical elements.

The L-type REE-Y enrichment in the roofs and partings, as well as the Al₂O₃-TiO₂ plots, Zr/TiO₂-Nb/Y plots, and UCC-normalized negative Eu and Ce anomalies, demonstrate that the sediment provenance of the No. 5 coals from the Weibei coalfield are mainly of felsic-intermediate composition, dominantly from the Qilian-Qinling Oldland on the south. Marine bioclastic limestone, negative Ce anomalies, and positive Y anomalies in coals suggest the influence of sea water. Activities of hydrothermal fluids are evidenced by the occurrence of cleat-infilling and/or fracture-infilling minerals, HREY and MREY enrichment patterns, and positive Eu and Gd anomalies.

Overall, factors controlling the mineralogical and geochemical composition of the Weibei coalfield include the sediment provenance (Qilian-Qinling Old land), seawater invasion during deposition, and hydrothermal fluids. Although provenance and seawater invasion are partly responsible for the mineral composition, hydrothermal fluids are probably the main controlling factors of the mineralogical and geochemical characteristics in the No. 5 coals from the Weibei coalfield.

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Appendix A

Table A1. Coal bench thickness (cm), proximate analysis (%), and forms of sulfur (%) of the No. 5 coals from Dongdong and Jinhuashan coal mines, Weibei coal field.

Coal Mine	Sample No.	Thickness	M _{ad}	HTAd	V _{daf}	$\mathbf{S}_{t,d}$	S _{s,d}	S _{p,d}	S _{o,d}
	DD-R	20	1.10	61.33	41.76	8.12	0.51	7.03	0.58
	DD-1	20	0.54	27.15	21.40	2.06	0.16	0.35	1.54
	DD-2	20	0.46	25.17	20.83	2.98	0.60	1.29	1.09
	DD-3	20	0.41	25.72	22.31	9.02	1.74	6.86	0.42
	DD-4	20	0.45	14.26	18.41	3.18	0.32	1.35	1.51
	DD-5	5	0.45	14.59	17.39	2.72	0.28	1.14	1.30
	DD-6	20	0.36	10.62	17.24	2.75	0.28	1.06	1.41
Dongdong	DD-7	20	0.33	9.68	15.76	2.55	0.30	0.99	1.26
8	DD-8	20	0.32	20.81	25.54	4.76	0.99	2.82	0.96
	DD-9	20	0.40	7.61	18.35	3.39	0.63	1.30	1.46
	DD-10	20	0.33	9.00	18.66	2.81	0.35	1.07	1.39
	DD-11	20	0.34	12.62	20.14	4.50	0.89	2.43	1.18
	DD-12	10	0.38	27.75	23.27	4.47	0.42	3.14	0.91
	DD-P1	20	0.37	71.60	43.05	0.68	0.02	0.53	0.13
	DD-13	20	0.39	30.57	17.69	1.26	0.03	0.36	0.87
	Coal Av	-	0.40	18.12	19.77	3.57	0.54	1.86	1.18
	JHS-R	20	1.51	88.49	72.36	0.29	0.01	0.18	0.10
	JHS-1	20	0.26	7.13	15.67	1.45	0.03	0.13	1.29
	JHS-2	20	0.10	7.51	17.13	1.87	0.09	0.30	1.47
	JHS-P1	20	0.48	67.35	29.08	0.97	0.12	0.67	0.18
	JHS-P2	40	0.51	81.73	61.72	1.46	0.09	0.88	0.49
Jinhuashan	JHS-3	20	0.30	32.95	19.37	1.01	0.03	0.19	0.79
	JHS-4	20	0.08	16.15	18.33	3.80	0.84	1.88	1.08
	JHS-5	20	0.11	25.76	27.54	1.13	0.06	0.75	0.32
	JHS-6	20	0.30	23.84	18.15	1.56	0.03	0.43	1.10
	JHS-7	15	0.17	24.10	19.92	2.90	0.63	1.22	1.04
	Coal Av	-	0.19	19.63	19.44	1.96	0.24	0.70	1.01

M, moisture; HTA, high temperature ash yield; V, volatile matter; St, total sulfur; Ss, sulfate sulfur; Sp, pyritic sulfur; So, organic sulfur; ad, as-received basis; d, dry basis; daf, dry and ash-free basis; and Av, average.

Min

Av

1.2

2.1

0.6

8.4

1.3

7.6

Coal Mine	Sample No.	Qtz	Kln	Cal	Dol	111	Ру	Tb	Sd	Gp	Mc	Ant	Rt
	DD-R	1.1	24.5	20.7	7.9		7.2						
	DD-1	0.7	16.2	1.5	2.7		5.5			0.5			
	DD-2	1.8	13.8	2.0	2.1		4.6			0.8			
	DD-3		8.2	1.1	3.0		13.4						
	DD-4		11.0	0.7			2.5						
	DD-5		7.4	0.8			2.8	2.2	0.5	1.0			
	DD-6		4.5	1.7			1.7	2.1	0.7				
	DD-7		1.1	5.4	0.2		1.2	1.4	0.4				
Dongdong	DD-8		0.3	15.1	2.2		2.3	0.3	0.3	0.3			
00	DD-9		0.5	3.1			2.4	1.4	0.2				
	DD-10		0.4	5.9	0.3		1.1	0.7	0.1	0.3			
	DD-11		1.5	5.5	1.1		3.3	1.1					
	DD-12		16.0	2.2	2.1		3.5	4.0					
	DD-P1		47.6	0.9	0.9			18.5			0.6	2.4	0.7
	DD-13		25.6					4.2				0.7	
	Max	1.8	25.6	15.1	3.0		13.4	4.2	0.7	0.8			
	Min	0.7	0.3	0.7	0.2		1.1	0.3	0.1	0.3			
	Av	1.3	8.3	4.0	1.7		3.8	1.9	0.3	0.5			
	JHS-R	41.4	43.9			3.2							
	JHS-1	1.2	4.4	1.3	0.2								
	JHS-2		3.4	3.6			0.4						
	JHS-P1	9.9	56.7			0.4	0.4						
	JHS-P2	30.8	42.3			5.4	1.1	2.0					
	JHS-3	2.4	30.6										
Jinhuashan	JHS-4		2.7	8.9	1.8		2.5		0.2				
	JHS-5		0.6	24.0	0.9		0.2		0.1				
	JHS-6		14.7	2.7	5.4				1.0				
	JHS-7	2.7	2.2	4.9	0.4		2.2	11.6	0.2				
	Max	2.7	30.6	24.0	5.4		2.5		1.0				

Table A2. The semi-quantitative contents of main mineral phases in the studied coals (%, on whole-coal basis).

Kln, kaolinite; Qtz, quartz; Cal, calcite; Dol, dolomite; Ill, illite; Py, pyrite; Sd, siderite; Gp, gypsum; Mc, microcline; Tb, tobelite; Ant, anatase; Rt, rutlie; andnd, not detected by XRD.

0.2

1.7

0.2

1.3

0.1

0.4

μg/g	DD-R	DD-1	DD-2	DD-3	DD-4	DD-5	DD-6	DD-7	DD-8	DD-9	DD-10	DD-11	DD-12	DD-P	DD-13
SiO ₂	12.4	8.4	8.4	3.9	5.1	4.5	3.2	1.3	0.2	0.9	0.6	1.3	9.6	32.1	14.1
Al_2O_3	12.5	6.0	5.6	5.2	4.5	4.6	3.3	2.0	1.3	1.3	1.3	2.0	8.3	28.3	12.5
CaO	5.5	1.1	0.7	0.8	0.4	0.6	0.7	1.9	6.2	1.0	2.0	1.6	0.7	0.4	0.1
Fe ₂ O ₃	9.7	5.8	4.1	11.4	2.2	2.7	1.1	1.4	4.7	2.4	1.7	4.3	4.5	0.9	0.6
K ₂ O	0.5	0.1	0.1	0.08	0.02	0.06	0.02	0.02	0.02	0.02	0.02	0.02	0.06	0.1	0.02
MgO	1.0	0.4	0.3	0.3	0.06	0.04	0.03	0.08	0.4	0.03	0.06	0.2	0.2	0.2	0.04
Na ₂ O	0.2	0.09	0.07	0.05	0.05	0.04	0.03	0.03	0.02	0.03	0.03	0.02	0.05	0.08	0.05
Li	43	43	59	32	32	25	21	10	7	5	6	12	60	171	95
Be	1.6	1.8	2.5	1.2	1.2	1.3	1.0	0.2	0.3	0.2	0.2	0.2	1.3	3.0	2.2
В	19.3	9.1	10.3	7.9	11.8	28.2	22.3	30.4	31.7	24.5	35.6	33.9	22.7	21.6	27.0
Р	71	82	121	100	549	1388	1501	1049	1065	940	917	350	562	973	185
Sc	4.0	4.6	3.4	2.1	2.1	2.4	1.0	0.2	0.3	0.2	0.2	0.2	5.7	14.3	14.0
Ti	1511	945	1480	720	607	1165	908	494	273	246	307	252	1234	7961	4466
V	17.4	15.7	15.6	10.5	10.1	10.7	10.9	11.3	7.3	5.8	6.9	7.6	21.2	49.7	44.7
Cr	16	15	16	11	14	19	18	19	10	6	9	9	19	46	33
Mn	78	20	13	21	10	10	14	100	240	53	162	69	47	30	5
Со	1.3	1.3	0.9	1.5	1.3	0.9	0.2	0.3	0.3	0.2	0.2	0.9	1.8	0.2	0.3
Ni	5.3	3.5	2.0	2.2	1.6	1.5	1.4	1.9	2.4	1.6	1.9	2.5	4.4	5.2	4.4
Cu	8.8	12.8	11.7	18.6	8.6	21.7	7.3	6.4	13.5	3.9	4.3	7.2	18.1	40.5	29.4
Zn	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Ga	13.4	8.7	9.4	6.5	6.5	3.9	2.2	1.7	1.1	1.2	1.4	3.8	24.9	36.4	15.2
Ge	0.2	0.2	0.2	0.3	2.7	1.0	0.2	1.0	1.0	0.2	1.3	1.0	1.1	0.8	0.2
As	5.6	6.7	5.0	10.1	5.9	8.3	4.5	7.2	15.9	10.9	6.9	11.9	5.8	2.1	1.7
Se	9.5	5.6	4.4	9.7	3.3	4.0	1.0	1.8	5.8	2.7	1.7	3.4	2.7	3.3	5.1
Rb	23.1	5.7	5.2	9.7	2.0	3.8	1.3	0.2	0.3	0.2	0.2	0.2	2.4	5.2	1.7
Sr	255	74	73	69	230	469	296	230	213	167	192	109	113	497	89
Y	11.8	16.2	15.3	10.0	9.3	10.6	10.2	5.5	4.1	2.7	3.5	5.5	12.9	20.9	28.5
Zr	140	95	97	66	43	42	28	17	10	13	12	13	216	383	399
Nb	44.7	30.1	40.5	19.0	14.2	19.2	11.8	5.6	3.6	4.6	3.8	3.8	27.8	170.8	76.2
Mo	1.9	2.9	1.8	4.1	2.2	1.8	0.2	0.2	0.3	0.2	0.2	1.6	5.2	5.1	1.5
Cd	0.2	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3

Table A3. Concentrations of major element oxides (%) and trace elements (μ g/g) of the No.5 coal seam from Dongdong coalmine (on whole-coal basis).

Table A3. Cont.

μg/g	DD-R	DD-1	DD-2	DD-3	DD-4	DD-5	DD-6	DD-7	DD-8	DD-9	DD-10	DD-11	DD-12	DD-P	DD-13
Sn	2.8	2.9	2.6	2.0	1.3	1.5	1.1	1.0	1.0	0.9	0.8	0.9	4.7	7.0	4.9
Sb	1.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Cs	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Ba	89	36	39	36	79	99	57	45	37	46	49	38	86	278	91
La	28.2	24.2	14.8	6.3	20.8	18.2	11.6	8.1	2.4	3.3	5.0	2.3	9.2	44.9	14.7
Ce	54.3	54.5	36.8	15.6	34.8	37.3	24.6	16.3	4.9	6.8	9.1	5.8	21.3	92.9	35.6
Pr	6.0	5.9	4.5	2.0	3.5	4.5	3.1	1.9	0.3	0.8	1.1	0.8	2.6	10.3	4.4
Nd	20.9	20.3	16.7	8.0	11.5	17.5	12.2	7.2	3.0	3.5	3.9	3.3	10.5	37.1	17.6
Sm	3.8	3.6	3.3	1.9	1.9	2.8	2.1	1.2	0.3	0.2	0.2	0.8	2.6	6.8	4.5
Eu	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Gd	3.4	3.4	3.0	1.7	1.9	2.3	1.9	1.1	0.3	0.2	0.2	0.9	2.6	5.8	4.4
Tb	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.9	0.9
Dy	2.9	3.5	3.2	1.9	1.9	2.1	1.9	1.0	0.3	0.2	0.2	1.1	2.8	5.2	5.9
Ho	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.9	1.1
Er	1.5	2.0	1.9	1.2	1.2	1.3	1.2	0.2	0.3	0.2	0.2	0.2	1.6	2.6	3.5
Tm	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Yb	1.3	2.0	2.0	1.3	1.3	1.4	1.2	0.3	0.3	0.3	0.2	0.2	1.4	2.4	3.4
Lu	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Hf	3.8	2.4	2.5	1.7	1.1	1.1	0.2	0.25	0.3	0.2	0.2	0.2	3.7	8.3	7.5
Ta	10.2	8.6	11.2	5.7	2.2	4.9	2.4	1.3	0.3	1.1	0.8	0.2	6.4	32.9	13.4
W	7.0	4.3	8.6	5.4	10.7	4.4	6.2	8.1	7.0	7.0	10.3	11.0	9.2	23.0	10.2
Tl	1.6	2.1	1.2	1.8	0.2	1.0	0.2	0.8	1.9	0.2	0.2	0.2	0.2	0.2	0.3
Pb	112	27.0	22.9	22.9	10.2	16.1	4.3	5.0	6.8	2.8	3.1	6.0	28.6	56.2	30.1
Bi	0.2	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.2	1.6	0.8
Th	24.3	11.4	17.8	7.7	4.3	6.7	2.6	1.6	0.9	1.4	1.2	1.7	8.8	46.5	24.3
U	2.8	4.8	3.4	2.1	2.5	1.8	1.1	0.2	0.3	0.2	0.2	1.2	9.1	7.0	5.6

Table A4. Contents of major element oxides (%) and concentrations of trace elements ($\mu g/g$) of the No. 5 coal seam from Jinhuashan coal mine (on whole-coal basis).

μg/g	JHS-R	JHS-1	JHS-2	JHS-P1	JHS-P2	JHS-3	JHS-4	JHS-5	JHS-6	JHS-7
SiO ₂ ^a	63.2	3.3	1.6	36.7	54.8	16.8	1.3	0.3	6.9	9.7
SiO ₂ ^b	54.3	3.5	2.4	36.7	47.4	17.6	3.1	1.7	11.6	9.1
Al_2O_3	16.9	2.3	2.2	15.0	15.0	9.0	2.9	1.7	6.4	5.8
CaO	0.2	0.3	1.1	0.1	0.09	0.07	2.8	15.4	0.6	2.3
Fe ₂ O ₃	0.9	0.1	0.4	1.3	2.3	0.3	3.3	0.9	0.5	2.4
K ₂ O	1.4	0.02	0.02	0.4	1.2	0.07	0.02	0.02	0.3	0.2
MgO	0.4	0.05	0.05	0.2	0.3	0.04	0.3	0.5	0.06	0.2
Na ₂ O	0.3	0.02	0.02	0.1	0.2	0.04	0.02	0.02	0.06	0.04
Li	112	11.5	12.4	215	119	57.6	16.7	16.4	71.2	53.4
Be	3.7	3.8	3.1	5.3	4.5	2.5	2.1	0.2	1.5	1.0
В	36	26	34	22	44	25	28	36	102	101
Р	196	47	845	377	202	128	1655	888	1004	815
Sc	11.1	3.4	0.2	9.3	7.5	5.6	1.4	0.2	2.1	3.0
Ti	5723	550	248	4240	5003	1683	1520	205	1770	1384
V	99	29	15	119	85	24	17	7	32	23
Cr	56	9	8	61	57	20	12	5	15	14
Mn	19	6	25	13	20	5	48	396	16	66
Co	10.6	4.0	4.9	24.8	12.5	1.5	4.3	4.4	2.5	3.0
Ni	21.2	6.8	8.5	39.3	22.2	4.1	4.9	2.8	3.9	4.1
Cu	22	16	10	50	38	17	27	8	9	16
Zn	37	7	6	92	148	19	26	4	11	11
Ga	28.1	6.3	3.6	26.2	26.7	11.8	8.2	4.0	11.2	10.0
Ge	2.1	0.2	1.9	1.9	1.8	0.2	0.2	0.2	0.9	0.2
As	3.1	1.2	2.1	10.0	6.0	1.9	5.1	1.5	3.3	3.3
Se	0.2	0.2	0.2	2.8	4.2	1.1	4.4	1.3	0.2	4.2
Rb	89.0	0.2	0.2	21.9	62.8	3.1	0.2	0.2	11.7	7.1
Sr	96	76	412	98	73	37	1088	424	126	155
Y	29.8	18.9	21.4	34.5	27.6	36.5	25.6	10.9	6.4	6.3

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μg/g	JHS-R	JHS-1	JHS-2	JHS-P1	JHS-P2	JHS-3	JHS-4	JHS-5	JHS-6	JHS-7
Zr	154	23	15	173	184	93	49	18	77	93
Nb	67.9	7.9	4.7	63.5	68.0	27.5	22.6	3.8	37.8	30.8
Мо	0.8	1.5	1.7	3.3	1.8	0.9	2.2	0.9	1.4	1.5
Cd	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Sn	4.1	0.9	0.9	5.0	5.4	2.7	2.5	0.8	2.0	2.4
Sb	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Cs	10.7	0.2	0.2	2.0	5.0	0.2	0.2	0.2	1.2	0.2
Ba	307	51	712	241	331	64	64	35	124	76
La	57	3	47	55	62	47	73	10	13	11
Ce	102	9	67	98	95	94	100	19	22	22
Pr	13.1	1.3	6.3	13.8	12.9	11.2	9.6	2.2	2.7	2.5
Nd	48.1	5.9	20.3	54.0	44.4	42.1	31.9	8.9	9.3	8.9
Sm	7.6	1.5	3.0	10.0	6.8	7.7	4.6	1.7	1.6	1.6
Eu	1.2	0.2	0.2	1.6	0.3	0.9	0.2	0.2	0.2	0.2
Gd	6.8	1.8	3.5	8.2	5.8	7.0	4.9	1.6	1.4	1.5
Tb	1.0	0.2	0.2	1.2	0.9	1.1	0.2	0.2	0.2	0.2
Dy	6.1	2.5	2.7	7.0	5.6	6.6	4.4	1.4	1.4	1.4
Но	1.1	0.2	0.2	1.4	1.1	1.3	0.8	0.2	0.2	0.2
Er	3.4	1.9	1.7	4.0	3.5	4.2	2.5	0.9	0.9	0.9
Tm	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Yb	3.2	2.0	1.4	3.8	3.6	4.4	2.2	0.8	0.9	1.0
Lu	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Hf	3.7	0.2	0.4	4.1	4.5	2.3	1.2	0.2	2.0	2.3
Ta	6.4	0.2	0.2	7.1	7.5	3.4	2.2	0.2	4.3	3.1
W	9.6	2.4	7.2	8.1	11.0	3.8	3.9	3.5	5.2	3.8
Tl	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Pb	15.6	2.4	3.0	30.8	35.3	17.0	16.9	7.0	5.6	14.9
Bi	0.2	0.2	0.2	1.1	0.9	0.2	0.2	0.2	0.2	0.2
Th	16.6	1.7	1.1	22.6	24.7	15.6	4.4	1.3	10.6	7.4
U	5.8	1.3	0.2	4.9	5.1	5.0	3.1	0.8	1.9	2.5

Table A4. Cont.

 Si^{a} and Si^{b} is Si content derived from the aforementioned calculation method and the XRF analysis data, respectively.

 Table A5. Total REY concentrations and elemental pairs and anomalies of typical rare earth elements.

Coal Mine	Sample No.	REY	La _N /Lu _N	La _N /Sm _N	Gd_N/Lu_N	Eu _N /Eu _N *	Ce _N /Ce _N *	Gd_N/Gd_N^*	Y_N/Ho_N
	DD-R	135	1.26	1.10	1.22	0.39	0.95	1.71	1.81
	DD-1	137	1.06	1.01	1.16	0.42	1.04	1.71	2.41
	DD-2	103	0.64	0.67	1.01	0.45	1.02	1.56	2.25
	DD-3	51	0.27	0.49	0.58	0.69	0.99	1.13	1.45
	DD-4	89	0.96	1.60	0.69	0.64	0.92	1.29	1.47
	DD-5	99	0.76	0.99	0.76	0.54	0.94	1.29	1.50
	DD-6	71	0.52	0.84	0.69	0.62	0.94	1.28	1.58
Dongdong	DD-7	44	0.35	1.02	0.39	0.92	0.94	0.86	0.81
	DD-8	17	0.10	1.39	0.08	1.71	1.30	0.23	0.57
	DD-9	19	0.15	2.15	0.08	1.71	0.92	0.23	0.43
	DD-10	25	0.23	3.26	0.08	1.71	0.90	0.23	0.55
	DD-11	22	0.10	0.43	0.30	1.12	0.98	0.73	0.84
	DD-12	69	0.43	0.54	0.94	0.52	0.99	1.58	2.06
	DD-P1	231	2.08	0.99	2.11	0.18	0.98	1.05	0.86
	DD-13	125	0.63	0.49	1.51	0.25	1.00	0.95	0.93
	JHS-R	281	2.58	1.13	2.41	0.80	0.85	1.11	0.95
	JHS-1	49	0.14	0.32	0.65	0.79	0.96	1.35	2.92
	JHS-2	175	2.07	2.33	1.22	0.48	0.85	1.94	3.20
	JHS-P1	293	2.42	0.82	2.87	0.84	0.82	1.10	0.92
Jinhuashan	JHS-P2	269	2.59	1.36	1.92	0.20	0.76	1.07	0.89
Jinnaashan	JHS-3	264	2.08	0.91	2.43	0.57	0.93	1.09	1.00
	JHS-4	260	3.19	2.40	1.69	0.34	0.82	2.19	1.10
	JHS-5	58	0.43	0.87	0.56	0.73	0.93	1.12	1.65
	JHS-6	61	0.59	1.19	0.52	0.73	0.87	1.04	1.01
	JHS-7	58	0.52	1.07	0.53	0.75	0.94	1.07	0.99

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