Geological Controls on Enrichment of Rare Earth Elements and Yttrium (REY) in Late Permian Coals and Non-Coal Rocks in the Xian’an Coalfield, Guangxi Province

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Abstract: The highly elevated concentrations of the rare earth elements and yttrium (REY), U, Mo, Se, and Pb in late Permian coals in some coalfields in Guangxi Province, South China, have been widely investigated; however, the mode of occurrence and enrichment mechanism of these critical elements are still under debate. This study investigates the mineralogical and geochemical compositions of coals and non-coal rocks from the Xian’an Coalfield in Guangxi Province to discuss the geological factors influencing the distribution of critical elements. The mineral in the studied coals consists mainly of quartz, and to a lesser extent, muscovite and kaolinite, with a trace amount of anatase. The coals are significantly enriched in REY, Pb, Se, Mo, and U and display the REY–U–Se–Mo–Pb-enrichment horizon (Horizon I) and U–Mo-enrichment horizon (Horizon II) adjacent to the host rocks or partings. The REY, U, Se, and Pb show organic association while Mo is primarily hosted by Fe-sulfides within Horizon I. The U and Mo have a phosphate affinity within Horizon II. Both the input of pyroclastic and epiclastic materials and the leaching of acidic solutions jointly govern the distribution of the REY–U–Se–Mo–Pb-enrichment horizon (Horizon I) and the U–Mo-enrichment horizon (Horizon II). The concentrations of REY in Horizon I exceed the cutoff grade of REY, and, therefore, the coals in the Horizon I can be regarded as promising raw materials of REY.

Keywords: rare earth element and Y (REY); Yunkai Upland; Heshan Formation; late Permian coal; Guangxi province

1. Introduction

Rare earth elements and yttrium (REY) in coals have attracted increasing attention in recent years [1–5], mainly due to the concentrations of REY in some coals close to or exceeding the cutoff grade of REY in coal ashes [6–8] and the supply shortage of conventional types of REY ore since 2009 [7]. Moreover, the REY-rich coals are mostly enriched in critical REY (Nd, Eu, Tb, Dy, Y, and Er), which could alleviate the raw materials crisis of critical REY in the near future [7]. Therefore, the REY-rich coals can be regarded as alternative REY raw materials [1,7].

REY-rich coals and host rocks are extensively investigated in some coalfields worldwide, mainly in China [1,2,5,9–22], Russia [6,7,23–26], and America [4,27–31]. The highly elevated concentrations of REY in these coals are commonly caused by the input of epiclastic materials, pyroclastic materials, groundwater, and hydrothermal fluids [7,8]. In most cases, multiple geological factors jointly govern the abnormal enrichment of REY in the REY-rich coals [5,7,18,32].
The late Permian is an important coal-forming period in Guangxi Province, South China. The mineralogy and geochemistry of the late Permian coals in Guangxi Province have been investigated mainly in Heshan Coalfield [33–35], Yishan Coalfield [1], and Fusui Coalfield [33]. The coals present in these coalfields are superhigh-organic-sulfur coals and are enriched in Mo, U, Se, and V [1,2,33–35]. The influx of hydrothermal fluids is considered as a possible geological factor responsible for the Mo–U–Se–V enrichment in the coals [1,2]. Moreover, the highly enriched REY concentrations were also found in the coals from the Yishan Coalfield and are attributed to the injection of high-temperature solutions [1]. The Xian’an Coalfield contains relatively abundant coal resources, but the geochemical compositions of the coals from this coalfield are rarely investigated. Whether or not the rare metals are enriched in the coals in the Xian’an Coalfield is still unclear. This study investigates the mineralogy and geochemistry of the late Permian coals and non-coal rocks in the Xian’an Coalfield, Guangxi Province, China, with an emphasis on the geological controls on the geochemical anomaly in the coals. It also provides an opportunity to determine whether the coals in the Xian’an Coalfield can be considered as promising raw materials for certain rare metals.

2. Geological Setting

The late Permian is an important coal-forming period in Guangxi Province, China (Figure 1A). The late Permian coalfields in Guangxi Province mainly include the Heshan, Fusui, Yishan, Xian’an, Baiwang, and Qianjiang coalfields. The Xian’an coalfield is located in the middle part of Guangxi Province, southern China (Figure 1B). The coalfield covers an area about 8 km wide (W–E direction) and 35 km long (N–S direction) and includes Beigeng, Wanfu, Qianxian, and Mushan exploration regions (Figure 1C).

During the early–middle Permian, South China including Guangxi Province was covered by thick marine deposits of carbonate strata such as the Maokou Formation [36]. Due to crustal uplift caused by the arrival of the Emeishan mantle plume [37], the Maokou Formation is subjected to different degrees of weathering, leaching, and erosion, thereby leading to the development of claystone or bauxite at the top of the Maokou Formation. Subsequently, the marine transgression occurred during the late Permian and deposited carbonate rocks, epiclastic rocks, and coal seams. During the doming of the Emeishan mantle plume, the Yunkai Upland and Daxin Upland began to uplift and ultimately evolved into a topographic highland during the late Permian (Figure 1D) [36,38]; the Yunkai Upland provides the predominant detrital materials into the late Permian coalfields including the Yishan, Heshan, Xian’an, and Fusui coalfields, which are located in eastern Guangxi Province [1,33,36].

The late Permian coal-bearing stratum in the Xian’an coalfield is primarily the Heshan Formation, with a thickness ranging from 98 to 220 m. The Heshan Formation unconformably overlies the middle Permian Maokou Formation and conformably underlies the late Permian Dalong Formation (Figure 2A). Based on the lithological and coal-bearing characteristics, the Heshan Formation is subdivided into the upper and lower sections. The lower section of the Heshan Formation consists mainly of clayey stones, flint limestones, bioclastic limestones, and a coal seam, with an average thickness of 17.4 m; the upper section is primarily composed of flint limestones interbedded with mudstones, coal seams, sandstones (Figure 2A).

The Heshan Formation contains five coal seams in the Xian’an coalfield, namely K1, K2, K3, K4, and K5 (Figure 2A). Among these, the K1, K2, and K3 coals are mostly carbonaceous mudstone interbedded with a thin coal seam, and their thickness ranges from 0.1 to 0.3 m, 0.7 to 4.3 m, and 0.4 to 4.5 m, respectively; the K4 coal is the primary workable coal seam, and its thickness ranges from 0.3 to 6.2 m, with an average of 2.1 m; the K5 coal is an unworkable coal seam and is intercalated into the clayey rocks.
Figure 1. Maps of the study area: (A) Map of China showing the location of Guangxi Province, China. (B) Location of the Xian’an Coalfield. (C) Location of the coal exploration region. (D) Paleogeography of the late Permian period modified from [38]. 1—upland, 2—fluvial facies, 3—fluvial estuary facies, 4—clastic tidal facies, 5—lagoon, 6—lagoon-isolated carbonate platform, 7—isolated carbonate platform, 8—peat mire, 9—deep-water pyroclasts, siliceous rocks basin.
3. Methodology

Eighteen samples, including eight coal samples and ten non-coal samples, were collected from the outcrop section in the Qianxian exploration region of Xian’an Coalfield in Guangxi Province, SW China (Figure 1B, C and Figure 2B). The weathered layer of the outcrop section was first removed before sampling to reduce the influence of chemical weathering on mineralogical and geochemical constituents. The studied samples were cut over an area 10 cm wide and 10 cm deep, and then, were put in plastic bags to avoid contamination and oxidation.

The studied samples were ground to ≤0.2 mm and split into two representative portions. A portion of the sample (<0.2 mm) was directly used for proximate analysis based on the ASTM Standards D3173-11 (2011), D3174-11 (2011), and D3175-11 (2011) [39–41], while another representative portion was ground further to ≤0.076 mm (200 mesh) using an agate mortar and pestle for mineralogical and geochemical analysis. The total sulfur content in the studied samples was determined following ASTM Standard D3177-02 (2002) [42]. Mineralogical analyses of the sample powders were performed by powder X-ray diffraction (XRD) using a Bruker D8 A25 Advance (Bruker D8 A25 Advance, Leipzig, Germany) at the Institute of Environmental Assessment and Water Research (Spain). The detailed XRD analysis procedure and semiquantitative analysis were reported in a previous study [32].
The diffractograms were obtained at 40 kV and 40 mA by scanning at a 2θ interval of 4–60°, with a step size of 0.019° and a counting time of 0.1 s/step and the sample under rotation of 15/min. Semiquantitative XRD analysis was performed by using the matrix-flushing method devised by Chung [43] and calculating the integrated area of the main peak for the different mineral phases in each sample. This method first requires the calculation of the XRD constants for each crystalline phase by applying the Klug and Alexander equation [44]. Subsequently, the material under study is spiked with the internal standard and analyzed by XRD to obtain the proportions of each crystalline phase of the sample.

Approximately 0.1 g of coal sample was weighed and digested based on the method proposed by Querol et al. [45] for geochemical analysis. Major elements (Al, Ti, Fe, Mg, Ca, Na, K, and P) and trace elements were identified by inductively coupled plasma–atomic-emission spectrometry (ICP-AES, Iris Advantage TJX Solutions, Thermo Fisher Scientific, Waltham, MA, USA) and inductively coupled plasma–mass spectrometry (ICP-MS, X-Series II Thermo, Thermo Fisher Scientific, Waltham, MA, USA). Silicon content was measured by wavelength-dispersive X-ray fluorescence spectrometry (XRF; ZSX Primus II) following the methods for chemical analysis of silicate rocks [46].

A small portion of representative block samples was used to prepare the polished sections for the SEM-EDS analysis. The modes of occurrence of minerals were studied using a field-emission scanning electron microscope (ZEISS Sigma300, Carl Zeiss AG, Jena, Germany), equipped with an energy-dispersive X-ray spectrometer (EDS) in the State Key Laboratory of Geological Processes and Mineral Resources (China).

4. Results

4.1. Standard Coal Characteristics

The moisture contents, ash yields, volatile matter yields, and sulfur contents of the coal samples are tabulated in Table 1. The moisture contents range from 2.2% to 14.3% with an average of 10.0%. The ash yields of the coal samples vary between 36.4% and 79.7% with an average of 52.5%. The high ash yield of the coal samples is due to exposure and chemical weathering of the coals along the outcrop profile. The volatile matter yields of the coal samples range from 22.9% to 56.4%, with an average of 41.1%. The high volatile matter yields in the coal samples are ascribed to relatively high ash yields, which contribute to some proportion of volatile matter as indicated by the linear correlation of volatile matter and ash yield ($r = 0.81$) in coal samples except for sample SL-13. Previous coalfield exploration data show that the coals from the Xian’an Coalfield have 10–18% volatile matter yield, indicating low-volatile bituminous coals.

The total sulfur contents in the coal samples vary from 1.1% to 3.1% with an average of 1.9%, indicating medium sulfur coal (<1.0%, 1.0–3.0%, and >3.0% for low, medium, and high-S coals, respectively) [47].

| Sample | Thickness | $M_{ad}$ | $V_{daf}$ | $A_d$ | $S_{t,d}$ |
|--------|-----------|---------|----------|------|----------|
| SL-8   | 0.40      | 7.6     | 33.1     | 46.5 | 1.45     |
| SL-13  | 0.75      | 2.2     | 22.9     | 62.0 | 2.25     |
| SL-15  | 0.35      | 14.0    | 40.7     | 37.1 | 3.09     |
| SL-16  | 0.35      | 14.3    | 40.8     | 40.1 | 2.86     |
| SL-21  | 0.25      | 10.7    | 47.3     | 66.8 | 1.99     |
| SL-22  | 0.25      | 5.7     | 56.4     | 79.7 | 1.07     |
| SL-23  | 0.25      | 13.3    | 40.7     | 36.4 | 1.52     |
| SL-25  | 0.25      | 12.5    | 47.0     | 51.2 | 1.06     |

$M$, moisture; $A$, ash yield; $V_M$, volatile matter yield; $S_t$, total sulfur; $ad$, air-dry basis; $d$, dry basis; $daf$, dry and ash-free basis.
4.2. Mineralogy

4.2.1. Mineral Phases

The proportions of crystalline mineral phases in samples are summarized in Table 2. The minerals in coal samples mainly consist of quartz, and to a lesser extent, muscovite and kaolinite, with a trace amount of anatase (Figure 3). Hematite is only identified in sample SL-13. The sandstone samples, including samples SL-18, SL-20, SL-24, and SL-26, are characterized by a high level of quartz, with minor proportions of kaolinite, dickite + kaolinite, and muscovite (Figure 3). The claystone samples SL-6 and SL-7 are composed predominantly of kaolinite with minor amounts of anatase while claystone samples SL-9, SL-10, and SL-11 consist almost exclusively of dickite + kaolinite with minor amounts of anatase and pyrite (Figure 3). The minerals in mudstone sample SL-19 consist primarily of quartz, rectorite, and muscovite, with minor kaolinite and trace of anatase.

Dickite is a polytype of kaolinite and has the same chemical composition as kaolinite, but they can be distinguished by the XRD pattern. Dickite can be distinguished from kaolinite by the presence of diffraction peaks of 3.95, 3.79, and 3.43 Å (sample SL-11; Figure 4). However, relatively low intensities of 3.95, 3.79, and 3.43 Å appear to indicate a complex of dickite and kaolinite. Thus, this mineral phase is reported as dickite + kaolinite in the XRD results. Most claystone and coal samples have poorly ordered kaolinite (e.g., samples SL-6, SL-8) (Figure 4), indicating a detrital origin [48,49]. However, sample SL-7 immediately adjacent to the coal bench (sample SL-8, Figure 3) shows an increasing kaolinite crystallinity, which is characterized by the weak diffraction of (020) as well as the presence of six diffraction peaks of kaolinite from 20° to 25° (2θ) and from 35° to 40° (2θ), respectively (Figure 4); this relatively well-ordered kaolinite is most likely caused by acidic solutions from the degradation of organic matter, which allow inorganic materials to be degraded and recrystallized.

Table 2. Mineralogical proportions of the coal and non-coal samples determined by X-ray diffraction (XRD) from the outcrop profile in the Xian’an Coalfield (on whole-coal basis; unit in %).

| Sample | Muscovite | Kaolinite | Dickite + Kaolinite | Rectorite | Quartz | Pyrite | Hematite | Anatase |
|--------|-----------|-----------|---------------------|-----------|--------|--------|----------|---------|
| SL-11  | <dl      | 11.8      | 89.2                | <dl       | 3.3    | 4.1    | <dl      | 1.6     |
| SL-13  | <dl      | <dl      | 91.1                | <dl       | 47.1   | 2.7    | <dl      | 0.5     |
| SL-10  | <dl      | <dl      | 88.9                | <dl       | 6.4    | 2.8    | <dl      | 1.7     |
| SL-09  | <dl      | <dl      | 86.9                | <dl       | 6.5    | 3.0    | <dl      | 1.4     |
| SL-26  | 3.2      | 16.3      | <dl                 | <dl       | 80.2   | <dl    | <dl      | 0.3     |
| SL-25  | 2.4      | 1.7       | <dl                 | <dl       | 47.1   | <dl    | <dl      | <dl     |
| SL-24  | 5.2      | 1.9       | <dl                 | <dl       | 92.8   | <dl    | <dl      | <dl     |
| SL-23  | 13.7     | 2.0       | <dl                 | <dl       | 20.3   | <dl    | <dl      | 0.5     |
| SL-22  | 1.1      | 2.9       | <dl                 | <dl       | 75.3   | <dl    | <dl      | 0.4     |
| SL-21  | 12.9     | 4.7       | <dl                 | <dl       | 49.2   | <dl    | <dl      | <dl     |
| SL-20  | <dl      | <dl      | 5.0                 | <dl       | 94.8   | <dl    | <dl      | 0.2     |
| SL-19  | 22.6     | 5.8       | <dl                 | <dl       | 32.6   | <dl    | <dl      | 0.4     |
| SL-18  | <dl      | <dl      | <dl                 | <dl       | 100.0  | <dl    | <dl      | <dl     |
| SL-16  | 13.8     | 4.0       | <dl                 | <dl       | 21.6   | <dl    | <dl      | 0.8     |
| SL-15  | 12.7     | 1.9       | <dl                 | <dl       | 22.2   | <dl    | <dl      | 0.3     |
| SL-08  | 12.2     | 17.0      | <dl                 | <dl       | 17.2   | <dl    | <dl      | 0.2     |
| SL-07  | <dl      | 98.0      | <dl                 | <dl       | <dl    | <dl    | <dl      | 2.0     |
| SL-06  | <dl      | 97.7      | <dl                 | <dl       | <dl    | <dl    | <dl      | 2.3     |

dl, below detection limit.
Figure 3. Vertical distribution of minerals throughout the outcrop profile.

Figure 4. X-ray diffraction (XRD) patterns of minerals in selected samples.
4.2.2. Mode of Occurrence of Minerals

Pyrite was identified in samples SL-9, SL-10, and SL-11 by XRD analysis. Pyrite primarily occurs as individual euhedral crystals, with eroded cavities within them (Figure 5A); this form of pyrite is considered to be formed by direct interaction of Fe$^{2+}$ with HS$^{-}$ [47]. To a lesser extent, pyrite was found as massive form (Figure 5B) and framboidal aggregates (Figure 5B) within the kaolinite matrices.

Kaolinite primarily occurs as thin layers or lenses (Figure 5C) and as a kaolinite matrix (Figure 5D), all of which indicate that kaolinite was mechanically transported as a detrital input into paleomire. The detrital kaolinite is also confirmed by the XRD patterns, which show the abundant existence of poorly ordered kaolinite (Figure 4). Moreover, vermiculate kaolinite was also observed in the studied coals (Figure 5F).

Quartz is found as cavities and fracture infillings within the organic matter (Figure 5E), and cavity infillings within the kaolinite matrix (Figure 5D), all of which indicate authigenic precipitation of Si-rich fluids. Fine-grained disseminated anatase particles were identified within the kaolinite matrix (Figure 5C), and the size of anatase was mostly <10 µm.

**Figure 5.** Scanning electron microscope (SEM) back-scattered electron images of minerals (A–F). (A) Euhedral pyrite embedded within dickite matrix (sample SL-9); (B) massive pyrite, framboidal pyrite, and kaolinite matrix (sample SL-9); (C) kaolinite layers and lenses, combined with fine-grained disseminated anatase particles (sample SL-16); (D) kaolinite matrix and quartz-filled cavities (sample SL-13); (E) fracture-filled quartz (sample SL-16); (F) vermiculate kaolinite (sample SL-25).
4.3. Geochemistry

4.3.1. Major Elements

The major elemental contents of the coal and non-coal samples collected from the outcrop profile are listed in Table 3. SiO$_2$ and to a lesser extent, Al$_2$O$_3$ are the major inorganic components in the coal samples, as would be expected from mineral assemblage (quartz–muscovite–kaolinite) (Table 2). Furthermore, the claystone samples (sample SL-6, SL-7, SL-9, SL-10, and SL-11) are dominated by SiO$_2$ and Al$_2$O$_3$ due to kaolinite- and dickite-bearing mineral fractions. SiO$_2$ is almost exclusively an inorganic constituent in the sandstone samples (sample SL-18, SL-20, SL-24, and SL-26) due to the quartz-bearing mineral fraction. Compared with Chinese coals reported by Dai et al. [10], the proportions of SiO$_2$ and K$_2$O in coal samples are evidently higher than those in Chinese coals due to the abundant occurrence of quartz and aluminosilicate minerals (e.g., muscovite); the remaining major elements are similar in abundance to those in Chinese coals.

The SiO$_2$/Al$_2$O$_3$ ratio in the coals (2.3–10.8, 5.7 on average) and sandstone samples (6.4–123.1, 40.2 on average) are significantly higher than that in claystone samples (1.2–1.4, 1.3 on average); this result is in accordance with the mineral assemblage in them. The K$_2$O/Al$_2$O$_3$ ratios in the coals (0.08–0.14, 0.11 on average) and sandstone (0.08–0.27, 0.11 on average) are higher than those in claystone (0.006–0.034, 0.018 on average) due to the presence of aluminosilicate minerals (e.g., muscovite) in the coals and sandstones.

Table 3. Major-element oxides (%) of the coal and non-coal samples from the outcrop profile in the Xian’an Coalfield (on whole-coal basis).

| Sample | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | CaO | Na$_2$O | K$_2$O | P$_2$O$_5$ |
|--------|---------|---------|------------|------------|-----|-----|--------|-------|----------|
| SL-6   | 45      | 1.5     | 39         | 0.67       | 0.17| 0.01| 0.1    | 0.39  | 0.01     |
| SL-7   | 44      | 1.2     | 37         | 0.81       | 0.14| 0.04| 0.1    | 0.23  | 0.02     |
| SL-8   | 28      | 0.27    | 9.2        | 2.2        | 0.25| 0.09| 0.07   | 1.2   | 0.01     |
| SL-15  | 23      | 0.31    | 9.9        | 2.4        | 0.35| 0.1  | 0.06   | 1.4   | 0.01     |
| SL-16  | 26      | 0.57    | 9.9        | 1.8        | 0.3 | 0.11| 0.06   | 1.4   | 0.02     |
| SL-18  | 96      | 0.02    | 0.78       | 2.4        | 0.03| 0.15| 0.02   | 0.04  | 0.01     |
| SL-19  | 63      | 0.32    | 23         | 3.8        | 1.3 | 0.08| 0.35   | 2.7   | 0.05     |
| SL-20  | 92      | 0.14    | 5.1        | 1.2        | 0.17| 0.14| 0.07   | 0.41  | 0.01     |
| SL-21  | 50      | 0.25    | 12         | 2.3        | 0.62| 0.12| 0.07   | 1.1   | 0.02     |
| SL-22  | 65      | 0.42    | 7.7        | 4.6        | 0.36| 0.12| 0.05   | 0.87  | 0.02     |
| SL-23  | 27      | 0.04    | 3.4        | 4.4        | 0.08| 0.06| 0.04   | 0.42  | 0.01     |
| SL-24  | 87      | 0.18    | 6.6        | 3.8        | 0.28| 0.26| 0.05   | 0.6   | 0.01     |
| SL-25  | 45      | 0.02    | 4.2        | 0.9        | 0.11| 0.08| 0.03   | 0.35  | 0.01     |
| SL-26  | 77      | 0.31    | 12         | 5.3        | 0.37| 0.26| 0.94   | 3.3   | 0.03     |
| SL-9   | 42      | 0.73    | 30         | 5.7        | 0.65| 0.02| 0.49   | 1     | 0.01     |
| SL-10  | 43      | 0.99    | 31         | 5          | 0.38| 0.02| 0.26   | 0.7   | 0.02     |
| SL-13  | 45      | 0.29    | 7.7        | 8.2        | 0.3 | 0.1  | 0.1    | 0.63  | 0.02     |
| SL-11  | 41      | 0.65    | 31         | 5.8        | 0.77| 0.07| 0.31   | 0.57  | <dl      |

4.3.2. Trace Elements

The trace element contents of the coal and non-coal samples collected from the outcrop profile are listed in Table 4. The concentration coefficient (CC) is used in the present study to conveniently describe the degree of enrichment or depletion of trace elements; the CC is a ratio of the coal samples versus world hard coals reported by [50], with CC <0.5, 0.5–2, 2–5, 5–10, and >10 indicative of depletion, similarity, slight enrichment, enrichment, and significant enrichment, respectively [51]. Compared with world hard coals [50], the studied coals are significantly enriched in V, Se, Mo, Ce, Sm, and U, enriched in As, Cs, La, Pr, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, and Pb, slightly enriched in Sc, Cu, Ga, Zr, Nb, Sn, Tm, Hf, and Th, and depleted in B, Mn, Co, Ni, Sr, and Ba; other trace elements are similar to the corresponding averages of world hard coals (Figure 6). Therefore, the studied coals contain highly elevated concentrations of the REY–V–Se–Mo–U assemblage.
Table 4. Trace element concentrations (µg/g) of the coal and non-coal samples from the outcrop profile in the Xian’an Coalfield (on whole-coal basis).

| Element | SL-6 | SL-7 | SL-8 | SL-15 | SL-16 | SL-18 | SL-20 | SL-21 | SL-22 | SL-23 | SL-24 | SL-25 | SL-26 | SL-27 | SL-28 | SL-29 | SL-30 | SL-31 |
|---------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mn      | 4.0  | 2.5  | 6.9  | 8.1   | 7.0   | 67    | 11    | 29    | 18    | 88    | 18    | 44    | 18    | 76    | 25    | 11    | 11    | 26    |
| Tm      | 0.59 | 0.59 | 0.77 | 0.70  | 0.70  | <dl  | <dl  | <dl  | <dl  | 1.7   | <dl  | <dl  | <dl  | <dl  | 1.9   | <dl  | <dl  | 1.3   |
| Mo      | 6.5  | 12   | 162  | 171   | 189   | 11    | 41    | 13    | 76    | 122   | 84    | 132   | 4.8   | 27    | 16    | 5.5   | 46    | 4.5   |
| Nd      | 11   | 9.9  | 24   | 25    | 24    | <dl  | 1.7   | 28    | 27    | 177   | 111   | 264   | 65    | 199   | 98    | 13    | 12    | 19    |
| Sm      | 4.9  | 3.1  | 6.4  | 6.7   | 6.6   | <dl  | <dl  | <dl  | 49    | 33.4  | 79    | 20    | 65    | 25    | 3.5   | 3.3   | 4.5   | 2.8   |
| Nb      | 55   | 74   | 5.6  | 18    | 12    | 1.6  | 5.9   | 4.9   | 6.6  | 5.6   | 5.6   | 5.6   | 5.6   | 5.6   | 5.6   | 5.6   | 5.6   | 5.6   |
| Ho      | 1.4  | 1.5  | 1.4  | 1.2   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Eu      | <dl  | <dl  | <dl  | <dl   | <dl   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Gd      | 4.2  | 3.4  | 5.7  | 5.7   | 5.7   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Tb      | 0.82 | <dl  | 1.1  | 0.96  | 0.99  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Dy      | 6.1  | 6.2  | 7.9  | 6.7   | 6.7   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Er      | 1.4  | 3.5  | 19   | 17.7  | 17.7  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Yb      | <dl  | <dl  | <dl  | <dl   | <dl   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Lu      | <dl  | <dl  | <dl  | <dl   | <dl   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Tl      | 1.6  | 0.95 | 1.2  | 1.2   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Pb      | 1.4  | 14   | 62   | 63    | 63    | 8.5  | 47    | 100   | 115   | 83    | 213   | 58    | 65    | 58    | 58    | 58    | 58    | 58    |
| Sn      | 5.2  | 6.5  | 3.3  | 5.8   | 6.5   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Cr      | 395  | 358  | 169  | 271   | 185   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   | 32   |
| Be      | <dl  | <dl  | <dl  | <dl   | <dl   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| Zr      | 787  | 617  | 141  | 105   | 105   | 19   | 18   | 18   | 18   | 177   | 111   | 284   | 65    | 199   | 98    | 13    | 12    | 9.7   |
| La      | 13   | 20   | 40   | 34    | 34    | 21   | 13   | 9.9  | 66   | 25    | 25    | 25    | 25    | 25    | 25    | 25    | 25    | 25    |
| Ce      | 32   | 65   | 55   | 50    | 50    | 3.6  | 75   | 54   | 384   | 266   | 590   | 132   | 409   | 132   | 409   | 132   | 409   | 132   |
| Ba      | 11   | 12   | 106  | 60    | 63    | 12   | 57   | 46   | 31    | 35    | 26    | 25    | 32    | 38    | 35    | 44    | 35    | 44    |
| Th      | 1.6  | 0.95 | 1.2  | 1.2   | <dl   | <dl   | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  | <dl  |
| U       | 377  | 277  | 17   | 16    | 16    | 16   | 16   | 16   | 16   | 16    | 16    | 16    | 16    | 16    | 16    | 16    | 16    | 16    |

<dl: below detection limit.

Figure 6. Concentration coefficient (CC) of trace elements in the studied coals, normalized to the respective average of world hard coals [28].

4.3.3. Rare Earth Elements and Y (REY)

A threefold geochemical classification (LREY, MREY, and HREY) and the three enrichment types (L-type, M-type, and H-type) of REY proposed by Seredin and Dai [7] as well as the upper continental crust [52]–normalized REY pattern were used in the present study to monitor the fractionation among REY. The Upper Continental Crust (UCC)–normalized REY patterns show an H-type REY distribution pattern in coal benches SL-8, SL-15, SL-16, and SL-13 (Figure 7A) and an M-type REY pattern in coal benches SL-21, SL-22, and SL-23.
and SL-25 (Figure 7B), possibly indicating the influence of aqueous solutions [5,53]. The coal samples exhibit slightly negative Eu anomalies (Figure 7A,B), indicating contributions from felsic compositions [53]. The coal benches showing an H-type REY pattern display essentially no Ce anomalies (Figure 7A) while coal benches showing an M-type REY pattern exhibit slightly positive Ce anomalies (Figure 7B).

5. Discussion

5.1. Source of Detrital Materials

The Al$_2$O$_3$ / TiO$_2$ ratio is widely utilized to infer the geochemical composition of detrital materials transported or blown into peat mires [5,18,28,54] due to little fractionation of both elements during geological process [55], with 3–8, 8–21, and 21–70 indicative of mafic, intermediate, and felsic igneous rocks, respectively [55]. The coal and non-coal samples all fall into the field of intermediate-felsic rocks (Figure 8), indicating that detrital materials in coal-bearing basins are geochemically dominated by intermediate-felsic compositions. Moreover, the input of intermediate-felsic constituents is also further supported by the slightly negative Eu anomalies in the studied coals (0.67–0.79) (Figure 7A,B) because the UCC-normalized negative Eu anomalies in coals are thought to represent contributions from felsic constituents [15].

Figure 7. Distribution patterns of rare earth elements and yttrium (REY) in the studied coals (A,B). REY are normalized to the upper continental crust [52].

Figure 8. The plot of TiO$_2$ versus Al$_2$O$_3$ contents for the coal and non-coal samples.
The previous studies demonstrate that the Yunkai Upland is the dominant sediment-source region and provides terrigenous felsic detrital materials into the late Permian coal-bearing basin in Guangxi Province, China [1,2,33,36]. During the deposition of late Permian coal-bearing strata, the Xian’an Coalfield was located in the margin of the isolated carbonate platform and bounded to the south by a deep-water basin (Figure 1D). This appears to denote that detrital materials from the Yunkai Upland are rarely mechanically transported into the Xian’an Coalfield. Additionally, the detrital materials in the Xian’an Coalfield are possibly derived from the weathering residues (immediately above the Maokou Formation limestone) within the coastal zone, which were transported into the peat mire by seawater during the formation of the coal-bearing stratum. In this case, detrital calcite and dolomite grains are generally associated with the clay matrices [56]. However, the carbonate mineral phases cannot be identified in the coals by the XRD and SEM-EDS analysis, indicating a negligible detrital input from the adjacent weathering crust directly above the Maokou Formation limestone. Furthermore, the morphological characteristics of kaolinite matrices shown in Figure 5 are similar to those of the pyroclastic materials as reported in previous studies [57–60], appearing to indicate the pyroclastic input into the paleomires. The input of pyroclastic materials is also supported by the following evidence: (1) the presence of vermiculate kaolinite (Figure 5F), which is usually originates from the transformation of volcanic ash [5,60], and (2) the abundant occurrence of synchronous pyroclastic materials, which are deposited in the late Permian strata close to the studied region [38]. Thus, the input of pyroclastic materials is a possible source for the inorganic constituents in the late Permian Heshan Formation.

5.2. Origin of Highly Elevated Concentrations of the REY–Se–Pb–Mo–U Assemblage

There is a REY–Se–Pb–Mo–U-enrichment horizon (Horizon I) immediately overlying the sandstone throughout the outcrop section (Figure 9). In Horizon I, the REY, Se, Pb, Mo, and U contents are up to 1013, 38, 123, 72, and 81 µg/g, respectively; the REY negatively correlates with ash yield ($r = −0.99$) and show essentially no correlations with $\text{Al}_2\text{O}_3$ (Figure 9), $\text{P}_2\text{O}_5$, and Zr, thereby appearing to indicate an organic association; this result differs from previous studies showing that the REY in some REY-rich coals is mostly likely hosted by phosphates, heavy minerals, and clay minerals [5,7,56]. Moreover, Horizon I is characterized by a high degree of REY enrichment and normal levels of Zr, Hf, Nb, and Ta, appearing to exclude the possibility of the input of alkaline volcanic ash due to them being enriched in the REY–Zr (Hf)–Nb (Ta) assemblage [5,7,60–64]. Furthermore, the highly elevated concentrations of REY in Horizon I, however, are accompanied by elevated contents of Se, U, Mo, and Pb; this assemblage most commonly represents the influx of metal-bearing solutions [7]. It is noteworthy that the highly elevated REY concentrations in Horizon I are jointly controlled by both the input of felsic epiclastic and pyroclastic detrital materials, and the subsequent leaching of acidic solutions based on the following evidence. As mentioned above, the terrigenous detrital materials from the Yunkai Upland are dominated by felsic compositions, which can provide relatively high background values of incompatible elements such as REY. This result is also further substantiated by the fact that the parting (sample SL-24) and roof (sample SL-26) contain REY contents (353 and 481 µg/g, respectively) distinctly higher than the upper crust composition (UCC) (168 µg/g) [52]. Moreover, the coals from the Yishan, Heshan, and Fusui coalfields that have the same sediment source region as the studied coals, are characterized by the relatively enhanced contents of REY [2,16,33], also supporting the input of REY-rich felsic terrigenous detrital materials. Moreover, the pyroclastic input from the adjacent regions also supplies abundant inorganic constituents into the coal-bearing strata as discussed previously. Subsequently, the pyroclastic and epiclastic materials that were deposited as parting and roof were subjected to the intense leaching of acidic solutions, which causes the breakdown of REY–Se–U–Mo–Pb-bearing detrital minerals. Consequently, the leachates derived from the host rocks or parting migrate upward or downward into the adjacent coal benches and were then re-deposited as authigenic minerals or adsorbed onto
clay minerals or organic matter under anoxic conditions as reported elsewhere [56]; this process is supported by the Zr/Hf ratio, which shows a higher value in the coal benches than in the parting (sample SL-24) and roof (sample SL-26) (Figure 9), mainly because Zr is more easily mobilized than Hf during the activity of acidic solutions as reported in previous studies [5,33]. This is also supported by the cleat/fracture infilling of quartz, which most likely originates from the epigenetic precipitation of Si-rich solutions through leaching processes during coalification. Due to the low migration capacity of REY, the REY-rich leachates shortly migrate, and thus the REY-enrichment horizon is confined to Horizon I (Figure 9); this result is consistent with previous studies [5,23]. The REY displays similar distribution to that of Se, U, and Pb, which is most likely because these elements are synchronously leached from the same detrital materials (roof and parting), and then REY–Se–U–Pb-bearing leachates simultaneously precipitate into the adjacent coal benches.

| Sample  | Coal profile | Ash yield (%) | Al₂O₃ (%) | REY (µg/g) | Se (µg/g) | U (µg/g) | Pb (µg/g) | Mo (µg/g) | V (µg/g) | Cr (µg/g) | Zr/Hf |
|---------|--------------|---------------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-------|
| SL-11   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-13   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-10   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-9    |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-26   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-24   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-23   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-22   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-21   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-20   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-19   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-18   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-16   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-15   |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-8    |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-7    |              |               |           |            |           |           |           |           |           |           | 0     |
| SL-6    |              |               |           |            |           |           |           |           |           |           | 0     |

Figure 9. Vertical distribution of ash yield, selected elements, and element ratios throughout the outcrop profile.

In Horizon I, U, Se, and Pb significantly positively correlate with each other, possibly reflecting that they have the same carrier; however, they show essentially no correlations with S and Fe₂O₃ but strongly negative correlations with ash yield (Figure 9), apparently pointing to an organic association. As reported above, the U–Se–Pb-bearing solutions, which are leached from the host rocks and partings, flow and ultimately precipitate into coal benches due to the reduction of organic matter during coalification. This process can better explain why the U-enrichment horizons are closely adjacent to the host rocks and parting throughout the outcrop profile (Figure 9). By contrast, the distribution of Mo differs from that of U, Se, and Pb, indicating various carriers; Mo is positively correlated with Fe₂O₃ (r = 0.90), appearing to indicate that the Fe-sulfides are the major host of Mo. Fe-sulfides (e.g., pyrite) predominantly occur as euhedral crystals, indicating a syngenetic origin. Thus, Mo involved within pyrite is most likely hosted during peat accumulation or
the early diagenetic stage under anoxic conditions. The contents of V and Cr are strikingly higher in the host rocks (samples SL-26 and SL-20) compared to that in the coal benches in Horizon I, suggesting a detrital input, which is consistent with the previous studies [56].

There is a Mo–U-enrichment horizon (Horizon II) below the sandstone layer (Figure 9). In Horizon II, the contents of Mo and U are up to 174 and 98 µg/g, respectively. The U and Mo display a similar distribution and an increasing, upward tendency toward the roof rocks (sample SL-18). The U (r = 0.99) and Mo (r = 0.99) significantly positively correlate with CaO, and CaO and P2O5 significantly correlate with each other. This appears to denote that the U and Mo are hosted by the phosphate phases (e.g., apatite), and their derivation is possibly from the leaching of pyroclastic materials within the roof rocks (sample SL-18).

5.3. Potential Economic Significance of REY in the Coals and Non-Coal Rocks

Total REY contents and individual REY compositions in coals are important for evaluating the economic recovery of REY. Seredin and Dai [7] proposed that the cutoff grade of REY oxides (REO) in coal ashes is 1000 µg/g. For REY-rich coal ashes, the outlook coefficient (Ccoeff) was used to determine the economic potential of REY, and its calculation follows Equation (1), with >2.4, 0.7–2.4, and <0.7 indicative of highly promising, promising, and unpromising REY raw materials, respectively [1,7,16]. Moreover, the Ccoeff-REO graph was also utilized to evaluate the REY economic potential [15].

\[
C_{\text{coeff}} = \frac{(\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y}) / \Sigma \text{REY}}{(\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu}) / \Sigma \text{REY}}
\]  

(1)

The REO concentrations in coal ashes and non-coal rocks are plotted as a function of Ccoeff in Figure 10, where the REO contents of coal ashes in Horizon I (samples SL-21, SL-22, SL-23, and SL-25) range from 899 to 4503 µg/g and their average (2398 µg/g) exceeds the cutoff grade (1000 µg/g; Seredin and Dai, 2012), indicating that the coals in Horizon I can be regarded as promising raw materials of REY (Figure 10). However, the REO concentrations of other coal seams (samples SL-8, SL-13, SL-15, and SL-16) (320–613 µg/g) and non-coal rocks (11–567 µg/g) are much lower than the cutoff grade of REY in coal ash, suggesting that these coals and non-coal rocks are not seen as raw materials of REY.

Although the investigated coals are highly enriched in U, Mo, Se, and V, the concentrations of U (68–302 µg/g, 184 µg/g on average), Mo (9–472 µg/g, 233 µg/g on average), Se (9–157 µg/g, 46 µg/g on average), and V (361–1128 µg/g, 629 µg/g on average) in coal ashes are much less than the suggested cutoff grade of U (1000 µg/g), Mo (1000 µg/g), Se (500–800 µg/g), and V (1000 µg/g) [1], suggesting these critical elements cannot be economically extracted from the coals.

![Figure 10. Evaluation of REY in coal ash and non-coal rocks from the Xian’an Coalfield.](image-url)
6. Conclusions

The coals from the outcrop profile in the Xian’an Coalfield, Guangxi Province, South China, show the REY (1013 µg/g)–Se (38 µg/g)–Pb (123 µg/g)–Mo (72 µg/g)–U (81 µg/g)-enrichment horizon (Horizon I) and Mo (174 µg/g)–U (98 µg/g)-enrichment horizon (Horizon II). In Horizon I, REY, Se, Pb, and U are intimately associated with organic matter while Mo is hosted by Fe-sulfides (e.g., pyrite). In Horizon II, the Mo and U are hosted within phosphate phases. The highly elevated concentrations of REY, Se, Pb, Mo, and U are derived from the input of pyroclastic and epiclastic materials. However, the leaching of acidic solutions allows the inorganic materials to be degraded and soluble REY, Se, Pb, Mo, and U to be migrated and redistributed, leading to higher contents of REY, Se, Pb, Mo, and U in the coal benches immediately adjacent to the roof and partings. The coals in Horizon I can be regarded as promising raw materials of REY.

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