

Article

Enrichment Factors and Metallogenic Models of Critical Metals in Late Permian Coal Measures from Yunnan, Guizhou, and Guangxi Provinces

Bo Cao ^{1,2,3}, Xuehai Fu ^{3,*}, Junqiang Kang ³, Pan Tang ² and Hui Xu ¹

¹ China National Administration of Coal Geology, Jiangsu Mineral Resources and Geological Design and Research Institute, Xuzhou 221006, China; caobo187@163.com (B.C.)

² Jiangsu Collaborative Innovation Center for Building Energy Saving and Construction Technology, Jiangsu Vocational Institute of Architectural Technology, Xuzhou 221116, China; tangpan0513@163.com

³ Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process (Ministry of Education), School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, China; kshif@cumt.edu.cn

* Correspondence: fuxuehai@cumt.edu.cn

Abstract: The Late Permian coal measures in eastern Yunnan, western Guizhou, and central Guangxi are significantly enriched in critical metals that could serve as important supplements to conventional critical metal deposits in China. This study collected previous geochronological and geochemical data from the Late Permian coal measures to evaluate the distribution characteristics and enrichment factors of critical metals. Moreover, metallogenic models for critical metals were also developed. The results showed that Late Permian coal measures in Yunnan, Guizhou, and Guangxi provinces exhibited abnormal enrichment in Nb, Zr, and rare earth elements (REY, or REE if Y is excluded). The Emeishan mafic rocks and intermediate-felsic volcanic ash from the Truong Son orogenic belt underwent chemical weathering, with Nb and Zr selectively preserved in situ in the form of heavy minerals (e.g., rutile, zircon, and anatase), which subsequently led to the enrichment of Nb and Zr in bauxite and Al-claystone at the bottom of the Late Permian coal measures. Intermediate-felsic volcanic ash from the Emeishan large igneous province (ELIP) and the Truong Son orogenic belt supplied Nb, Zr, and REY for the middle and upper parts of the Late Permian coal measures. The intermediate-felsic mineral material of the coal measures in the intermediate zone, outer zone, and outside zone of ELIP are derived mainly from the ELIP, the mixture from ELIP and the Truong Son orogenic belt, and the Truong Son orogenic belts, respectively. Nb, Zr, and REY were leached by acidic aqueous solutions and from the parting and roof into underlying coal seams, where they deposited as authigenic minerals or adsorbed ions on organic matter during early coalification.

Keywords: critical metals; the Late Permian coal measures; enrichment factor; material sources; metallogenic model



Citation: Cao, B.; Fu, X.; Kang, J.; Tang, P.; Xu, H. Enrichment Factors and Metallogenic Models of Critical Metals in Late Permian Coal Measures from Yunnan, Guizhou, and Guangxi Provinces. *Minerals* **2024**, *14*, 206. <https://doi.org/10.3390/min14020206>

Academic Editor: Stavros Kalaitzidis

Received: 2 November 2023

Revised: 29 January 2024

Accepted: 12 February 2024

Published: 17 February 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Coal, an organic rock, has the capability to accumulate a large amount of Ge, Ga, Al, Li, V, Ti, W, Ba, REY, and other metal elements under certain geological conditions [1,2]. The content of metal elements in coal, especially in coal ash, could reach the grade of these conventional metal deposits and, thus, coal or its combustion wastes might have economic value for extraction and utilization [3]. The distribution characteristics, modes of occurrence, and enrichment factors of critical metals in coal measures determine the difficulty of exploration, mining, and metallurgy, which are important for the extraction of critical metals from coal measures.

The Late Permian is the most important coal-forming period in southwest China [4]. The Late Permian coal measures (including coal, bauxite, and claystone) in eastern Yunnan,

western Guizhou, and central Guangxi contain significant amounts of critical metals (e.g., Li, Nb, Ta, Zr, Hf, Ga, Al, U, and REY) [5–7]. A new type of Nb(Ta)-Zr(Hf)-REE-Ga polymetallic deposit was discovered in the Late Permian coal-bearing sequences in the lower part of Xuanwei Formation in eastern Yunnan [8]. These metal elements derived from ELIP alkaline rocks and intermediate-felsic magmatic rocks of the Paleo-Tethys arc and were enriched and precipitated in coal-bearing strata after acidic hydrothermal leaching and water–rock interactions [7,9]. Zr, Nb, La, Y, and Ce are significantly enriched in the Late Permian coal from the Qiandongbei coalfield, which derived from peralkaline rhyolite and ELIP basalt. In addition, the distribution of metal elements is influenced by felsic volcanic ash and acidic aqueous solutions [10]. The upper Permian Heshan Formation in Pingguo is strongly enriched in Li and Nb, and the average content of Li_2O and Nb_2O_5 is 0.56 wt.% and 0.035 wt.%, respectively, exceeding the cut-off grades for independent Li and Nb deposits (Li_2O = 0.5 wt.% and Nb_2O_5 = 0.016–0.02 wt.%). Li and Nb occur mainly in cookeite and anatase, respectively [11]. The heavy rare earth oxide (HREO) content (HREO = 0.5 wt.%) in carbonaceous mudstone at the bottom of the Upper Permian Heshan Formation in Shanglin approaches the cut-off grade for ion-adsorbed rare earth deposits (HREO = 0.3–0.5 wt.%). The detrital material in this mudstone is mainly derived from felsic magmatic rocks of the Paleo-Tethys arc, with a minor contribution from the Emeishan felsic rocks [5].

Recent studies have focused on the critical metal content [12–14], occurrence modes [6,15,16], and material source [10,17–19] in the Late Permian coal measures in southwest China. However, the material source of critical metals remains controversial because of the different rock types and research methods. The discovery of alkalic tonsteins in coal measure indicates that critical metals are derived from the Emeishan alkaline volcanic ash [13,20]. Geochemical characteristics and the detrital zircon U-Pb age of bauxites at the bottom of coal measures indicate that the origin of bauxite is related to the Emeishan flood basalt [11]. The evidence based on Lu-Hf isotopes and trace elements of detrital zircon indicate that material sources of the critical metals include ELIP basalt, ELIP intermediate-felsic magmatic rocks, and Truong Son orogenic magmatic rocks [17,20,21]. Therefore, the comprehensive study of critical metals in the different rock types of the coal measure at different temporal and spatial scales is an effective approach to solve the above problems.

In this study, major elements, trace elements, detrital zircon U-Pb ages, and Lu-Hf isotopes of Late Permian coal measures in southwest China are systematically collected, and the enrichment factors, including the material source, occurrence modes, acidic solution, and organic matter, are evaluated. Furthermore, a metallogenic model of critical metals in the Late Permian coal measures is established.

2. Geological Setting

The South China Block is bounded to the southwest by the Truong Son orogenic belt, to the southeast by the Yunkai massif, and to the north by the Emeishan large igneous province (Figure 1). During the Permian, the South China Block and Indochina Block drifted northward, and were subducted near the equator (paleolatitude: 0–10°), forming the Permian Island arc igneous rocks, which eventually coalesced into the Truong Son orogenic belt at the end of the Triassic [22]. The Truong Son orogenic belt extends in a NW–SE direction and is composed of Neoproterozoic to Carboniferous metasedimentary rocks and Carboniferous to Triassic intermediate-felsic magmatic rocks [23,24]. The early Late Permian (~260 Ma) intermediate-felsic magmatic rocks are mainly distributed in the Dien Bien, Xam Nua, Phonsavin, and Vinh areas. The Truong Son orogenic belt is adjacent to the north by the Song Ma suture zone, which is considered as the relic of a Paleotethyan back-arc basin (BAB) or branch [25].

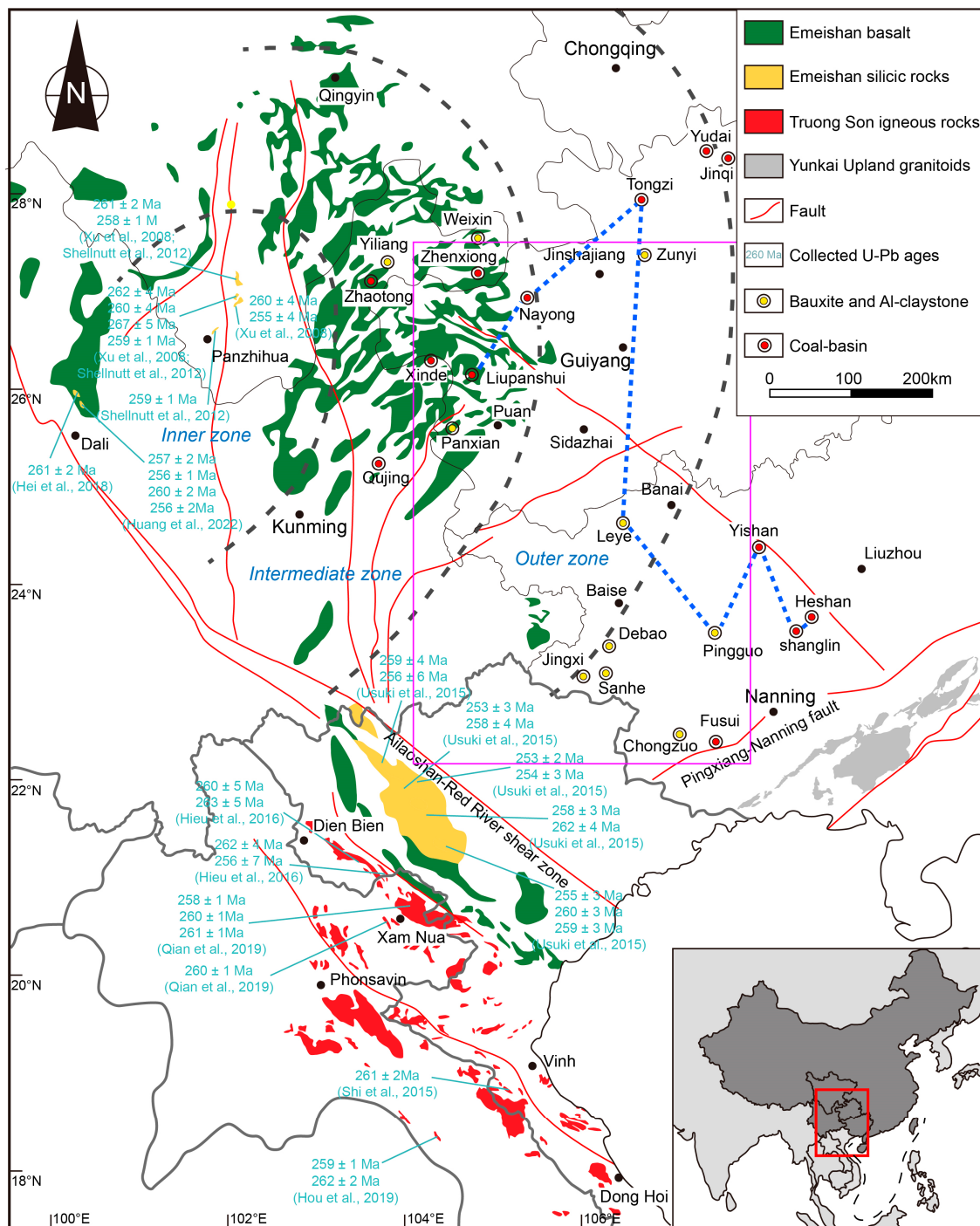


Figure 1. Simplified geological map of the Emeishan large igneous province and Truong Son orogenic belt, showing distributions of Emeishan basalt, silicic rocks, and Truong Son igneous rocks, with a summary of in situ zircon geochronology [23–31].

The ELIP covers an area of $\sim 0.3 \times 10^6 \text{ km}^2$ extending across southwestern China and northern Vietnam (Figure 1), and mainly consists of mafic lava, volcanoclastic rocks, and ultramafic-felsic intrusions [32]. In the center of ELIP, Emeishan basalts directly cover the Maokou Formation limestone. The high-precision data confirm that the Emeishan lavas erupted over a period of at least 6 m.y. (263–257 Ma) [33]. Detrital material from the ELIP was deposited in nearby basins of different environments. The ELIP is structurally divided into three zones (inner, intermediate, and outer) that broadly correspond to crustal thickness estimates [32,33]. The inner zone of the ELIP volcanic rocks has not been completely eroded

by runoff because of its considerable thickness (maximum of >5000 m). The intermediate zone of the ELIP volcanic rocks was completely eroded in some areas, and the outer zone of the ELIP volcanic rock was completely eroded [11].

In the Middle Permian, the study area was extensively covered by a restricted carbonate platform in the southwest of the South China Block, which is composed of the Maokou Formation bioclastic limestone and siliceous limestone [34]. At the end of the Middle Permian, the carbonate platform was exposed by rapid differential crustal uplift during the Dongwu movement, resulting in denudation of the Middle Permian Maokou Formation limestone and formation of paleokarst landforms [17,35,36]. With sea level rise in the Late Permian, the coal-bearing sequence formed in terrestrial, transitional, and marine environments, respectively, from northwest to southeast [35] (Figure 2). In the intermediate zone of the ELIP, the Longtan and Wuchiaping Formations unconformably overlie the Emeishan igneous rocks and the Maokou Formation limestone, respectively [7]. The Longtan Formation, a major Late Permian coal-bearing strata in western Guizhou, is divided into upper and lower segments. The upper segment is mainly composed of fine sandstone and siltstone, including 6–19 coal seams. The lower segment mainly consists of siltstone and mudstone, with occasional coal seams, which are relatively rare and have poor stability [4]. In the outer zone of the ELIP, the Heshan Formation unconformably overlies the limestone of the Maokou Formation [11]. The Heshan Formation is divided into upper and lower sections. The lower section of the Heshan Formation is mainly composed of claystone, limestone with siliceous nodules, bioclastic limestone, and a coal seam. The upper section mainly consists of limestone with siliceous nodules interbedded with mudstones, coal seams, and sandstones [14].

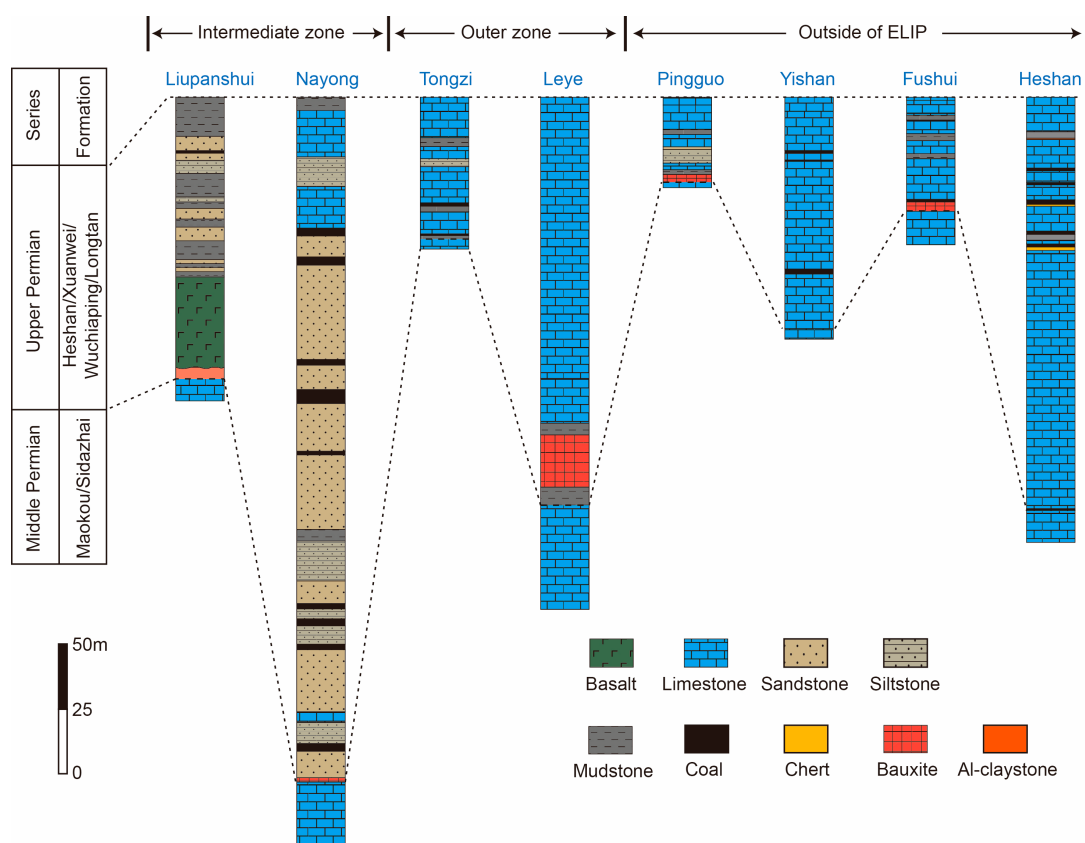


Figure 2. Stratigraphic column of the Late Permian coal measure.

The Late Permian coal in southwestern China underwent strong coalification, which resulted in anthracite predominating [37]. The coal seams commonly contain thinly bedded

pyrite nodules, with thin beds of calcite in some coal seams [38]. The composition of maceral is mainly vitrinite, with inertinite being the secondary component.

3. Sources of Data

The Late Permian coal measures (including bauxite, claystone, and coal) in the study area showed anomalous enrichment of critical metals (e.g., Nb, Zr, and REY). Recent studies have focused on the petrological, mineralogical, and geochemical features, U-Pb age, and Lu-Hf isotopes of detrital zircon in the coal measures, and numerous data were obtained. The data types, sampling locations, rock types, and data sources used in this study are listed in Table 1. The actual major elements, trace elements, U-Pb age, and Lu-Hf isotopes data used in this article are listed in Supplementary Tables S1 and S2.

Table 1. Summary of location, data type, and sample number of Late Permian coal measures in the study area.

Location	Lithology	Stratigraphy	Sample Number	Data Type and References
Fusui	coal, parting, bauxite	Heshan	38	Major elements, trace elements [39,40]
Banai	volcanoclastic rock	Shaiwa	3	Major elements, trace elements, U-Pb [41]
Chongzuo	bauxite	Heshan	8	Major elements, U-Pb, Lu-Hf [20]
Pingguo	clastic rock, bauxite	Heshan	54	Major elements, U-Pb, Lu-Hf [11,17,20]
Sanhe	bauxite	Heshan	23	Major elements, trace elements [42]
Jinshajiang	clastic rock	Longtan	30	Major elements, trace elements [43]
Panxian	mudstone, bauxite	Longtan	11	Major elements, trace elements [44]
Sidazhai	siltstone	Shaiwa	12	Major elements, U-Pb, Lu-Hf [45]
Tongzi	coal	Wujiaping	14	Major elements, trace elements [16]
Heshan	coal, floor, roof, claystone	Heshan	50	Major elements, trace elements [46,47]
Jingxi	bauxite	Heshan	4	Major elements, U-Pb, Lu-Hf [20,21]
Jinqi	coal, floor	Longtan	10	Major elements, trace elements [10]
Yudai	coal, floor, roof	Longtan	10	Major elements, trace elements [10]
Leye	Al-claystone, bauxite	Heshan	6	Major elements, trace elements [21]
Liupanshui	Al-claystone, coal, floor, roof	Heshan	20	Major elements, trace elements [35,48]
Nayong	coal, claystone	Longtan	20	Major elements, trace elements [49]
Shanglin	coal, claystone	Heshan	41	Major elements, trace elements [5,14]
Qinyin	claystone	Xuanwei	14	Major elements, U-Pb, Lu-Hf [50]
Weixin	Al-claystone	Xuanwei	10	Major elements, trace elements [7]
Yiliang	Al-claystone	Xuanwei	17	Major elements, trace elements [7]
Yishan	coal	Heshan	23	Major elements, trace elements [19]
Xinde	coal	Xuanwei	18	Major elements, trace elements [51]
Zunyi	Al-claystone	Heshan	20	Major elements, trace elements [35]
Puan	claystone	Longtan	12	Major elements, U-Pb, Lu-Hf [52]
Qujing	coal	Xuanwei	14	REY, Zr, Nb [8]
Zhenxiong	coal	Xuanwei	43	REY, Zr, Nb [8]
Zhaotong	coal	Xuanwei	5	REY, Zr, Nb [8]
Debao	bauxite	Heshan	2	U-Pb, Lu-Hf [20,21]

4. Discussion

4.1. Enrichment Characters of Critical Metals

The ionic radii of Y^{3+} and Ho^{3+} are similar and have similar geochemical characteristics [53]. Rare earth elements and yttrium are classified into light (LREY: La, Ce, Pr, Nd, and Sm), medium (MREY: Eu, Gd, Tb, Dy, and Y), and heavy (HREY: Ho, Er, Tm, Yb, and Lu) groups based on geochemical classification [54]. In order to assess the distribution characters of Nb, Zr, and REY in bauxite and Al-claystone, the weighted averages of Nb, Zr, and REY in sampling points in the mining are used to replace the contents of the whole mining area. Based on the Kriging interpolation method, Surfer software was used to draw the distribution maps of Nb, Zr, and REY in bauxite and Al-claystone. However, it should be noted that the model is based on only nine points of observation; hence, the

trends should only be considered as indicative. The average contents of Zr, Nb, and REY in bauxite and Al-claystone used in Figure 3 are listed in Supplementary Table S3.

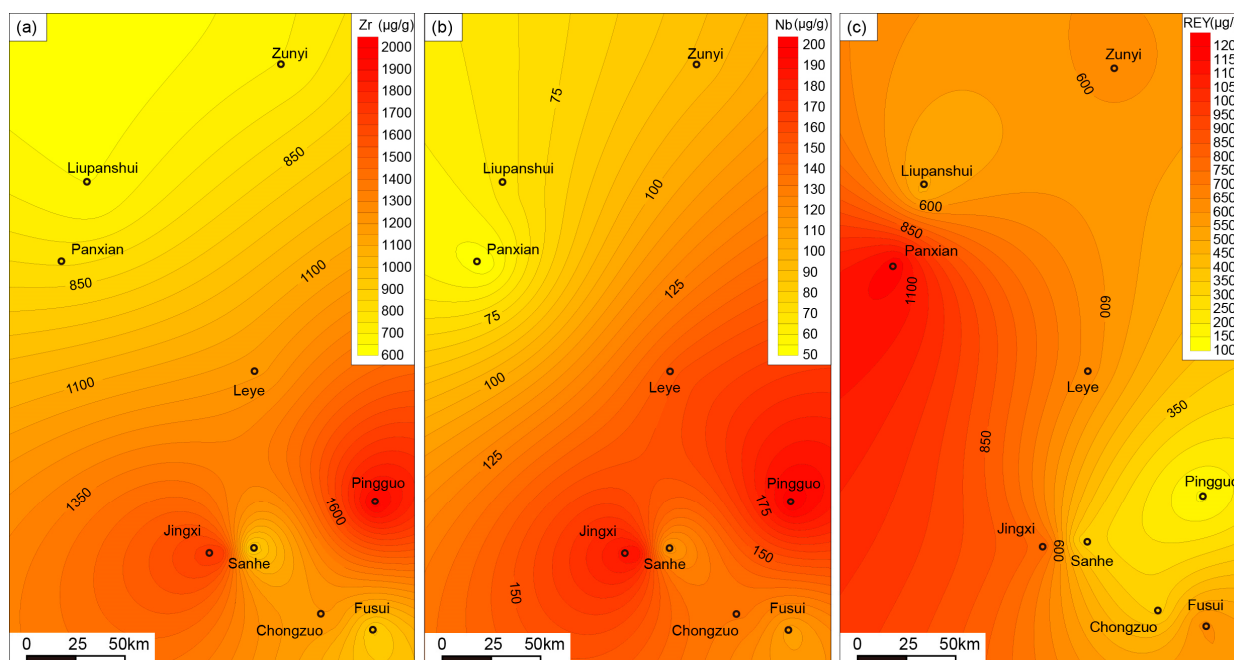


Figure 3. The distribution characters of the contents of Zr (a), Nb (b), and REY (c) in bauxite and Al-claystone, and the border is framed with purple line in Figure 1.

In the study area, numerous reports have indicated the presence of Nb-Zr-REY poly-metallic mineralization in the bauxite and Al-claystone at the bottom of the Upper Permian [6,9]. Zr contents in bauxite and Al-claystone range from 278.30 to 2790.92 $\mu\text{g/g}$, with lower contents in the northwest and higher contents in the southeast (Figure 3a). Bauxites in the Pingguo region have the highest Zr content, peaking at 1981.29 $\mu\text{g/g}$ on average [11,17,20]. The contents of Nb in bauxite and Al-claystone range from 7.40 to 279.00 $\mu\text{g/g}$, and the distribution character of Nb is similar to that of Zr (Figure 3b). Nb (Ta) is abnormally enriched in bauxite and Al-claystone in the Chongzuo, Fusui, Sanhe, Jingxi, Leye, Pingguo, and Zunyi areas, with $(\text{Nb,Ta})_2\text{O}_5$ average contents of 0.020 wt.%, 0.015 wt.%, 0.017 wt.%, 0.028 wt.%, 0.023 wt.%, 0.029 wt.%, and 0.015 wt.%, respectively, which is higher than the industrial utilization standard of Specifications for Nb (Ta) Mineral Exploration ($(\text{Nb,Ta})_2\text{O}_5 > 0.008$ wt.%, DZ/T 0203-2020) [55]. REY contents in bauxite and Al-claystone range from 22.18 to 4491.46 $\mu\text{g/g}$, and the distribution character is different to that of Zr and Nb, with higher contents in the northwest and lower contents in the southeast (Figure 3c). LREY is abnormally enriched in bauxite and Al-claystone in Fusui, Tianyang, Jingxi, Leye, and Zunyi, with the average LERY oxide (LERO) contents of 0.057 wt.%, 0.200 wt.%, 0.066 wt.%, 0.053 wt.%, and 0.052 wt.%, respectively, which is higher than the industrial utilization standard of Specifications for Rare Earth Mineral Exploration ($\text{LREO} > 0.05$ wt.%, DZ/T 0204-2002) [56]. The weathering intensity of parent rocks could be an important reason for the different distribution characteristics of Zr, Nb, and REY in bauxite and Al-claystone [57,58]. With the intensification of weathering, where the parent rock gradually transforms into bauxite, mobile elements, such as K, Na, Ca, Mg, and part of Si, are migrated, while immobile elements, such as Al, Ti, and Fe, are accumulated in situ [58,59]. Therefore, the $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)/\text{SiO}_2$ ratio could represent, to some degree, the intensity of weathering during bauxite formation. The contents of Nb and Zr in bauxite and Al-claystone are significantly positively correlated with the $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)/\text{SiO}_2$ ratios (Figure 4a,b), whereas the contents of REY in bauxite and Al-claystone are negatively correlated with the $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)/\text{SiO}_2$ ratios (Figure 4c), indicating that Zr and Nb pref-

entially accumulate in the weathering crust, with increasing weathering during bauxite formation, whereas REY is more likely to be removed from parent rocks.

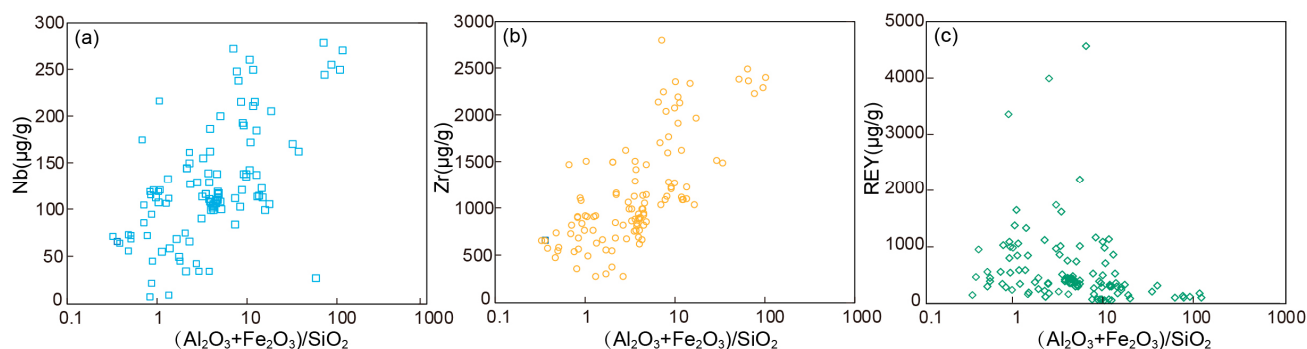


Figure 4. Relationship between Nb and $(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)/\text{SiO}_2$ (a), Zr and $(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)/\text{SiO}_2$ (b), and REY and $(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)/\text{SiO}_2$ (c) in bauxite and Al-claystone.

The contents of Zr, Nb, and REY in the Late Permian coal gradually increase from the intermediate zone to the outside zone of ELIP. The average contents of Zr, Nb, and REY in the Late Permian coal in the intermediate zone of ELIP are 99.46 µg/g, 9.92 µg/g, and 203.61 µg/g, respectively. In contrast, the average contents of Zr, Nb, and REY in the Late Permian coal from the outside zone of ELIP are 210.64 µg/g, 15.91 µg/g, and 305.54 µg/g, respectively. The migration and deposition of Zr, Nb, and REY is influenced by the material source and the mode of occurrence, which could be the main reason for the different distribution of these elements [60]. Nb(Ta) and LREY are abnormally enriched in Jingqi and Yudai coals. The average $(\text{Nb,Ta})_2\text{O}_5$ content in Jingqi and Yudai coals is 0.013 wt.% and 0.013 wt.%, respectively, which is higher than the industrial utilization standard of Specifications for Nb (Ta) Mineral Exploration ($(\text{Nb,Ta})_2\text{O}_5 > 0.008$ wt.%, DZ/T 0203-2020) [55]. The average LREO contents in Jingqi and Yudai coal are 0.053 wt.% and 0.054 wt.%, respectively, which are higher than the industrial utilization standard of Specifications for Rare Earth Mineral Exploration ($\text{LREO} > 0.05$ wt.%, DZ/T 0204-2002) [56].

4.2. Enrichment Factors

4.2.1. Material Sources

The possible provenance sources for the mineral matter of the Late Permian coal measures in the study area include: Emeishan volcanic rocks [4,12,16], arc-related intermediate-felsic rocks [17,36], Maokou Formation limestone [61,62], and mixed sources of Emeishan volcanic rocks and arc-related rocks [7,20,21,35]. The REY concentration in the Maokou Formation limestone is significantly low (about 2 ppm on average) [63], and the thickness of bauxite over the Maokou Formation ranges from 4 to 10 m, with an average REY content of about 280 ppm.

The ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2$ is widely used to infer the origin of sedimentary rocks, because Al_2O_3 and TiO_2 are relatively immobile during weathering, transport, sedimentation, diagenesis, and epigenesis [64]. Typical ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ range from 3 to 8, 8 to 21, and 21 to 70, corresponding to the parental rocks being of mafic, intermediate, and felsic composition, respectively [17,65]. Since the distribution of REY is hardly influenced by epigenetic and diagenetic processes, this is considered a crucial approach for tracing the provenance of sedimentary rocks [66]. Intermediate-felsic magmatic rocks usually show negative Eu anomalies, whereas basic magmatic rocks show positive or no Eu anomalies [53]. In the studied area, there are significant differences in $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios and δEu in the Late Permian coal measures. From the intermediate zone to the outside zone of ELIP, the minimum ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ gradually increase (Figure 5a), while the maximum δEu tends to decrease (Figure 5b). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of bauxite and Al-claystone in the bottom of Upper Permian in the intermediate zone of the ELIP range from 2.67 to 14.45 (with an average value of 5.75). The patterns of REE are similar to those of ELIP mafic

rocks (Figure 6a), showing significant LREY enrichment and no or a weak negative Eu anomaly ($\delta\text{Eu} = 0.83\text{--}0.96$), suggesting that material sources may be weathering products of Emeishan mafic rocks [4,12]. The ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ of coal measures in the middle and upper parts of the Upper Permian in the intermediate zone of ELIP are 3.19–116.00 (with average value of 22.55), and the REE patterns exhibit obvious LREY enrichment, with significant negative Eu anomalies ($\delta\text{Eu} = 0.17\text{--}0.70$), similar to the intermediate-felsic rocks in the ELIP and the Truong Son orogenic belt (Figure 6b). The ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ and REE patterns suggest that the detrital material might be derived from intermediate-felsic volcanic rocks [11]. In the outer zone of ELIP, the ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ in coal measures vary widely ($\text{Al}_2\text{O}_3/\text{TiO}_2 = 4.53\text{--}73.00$), and the REE patterns are complex (Figure 6c). The δEu of coal measures in Banai, Zunyi, Sidazhai, and Jinshajiang are 0.79, 0.75, 0.84, and 0.74, respectively, showing no or weak negative Eu anomalies, and the δEu of coal measures in Yudai and Leye are 0.32 and 0.63, respectively, showing significant negative Eu anomalies, suggesting that the detrital material is derived mainly from ELIP mafic rocks, with a minor contribution from intermediate-felsic rocks. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of coal measures in the outside zone of ELIP range from 3.13 to 135.93 (with an average value of 27.18), and the REE patterns are similar to the intermediate-felsic rocks in the ELIP and the Truong Son orogenic belt (Figure 6d), with obvious LREY enrichment and significant negative Eu anomalies ($\delta\text{Eu} = 0.35\text{--}0.53$), indicating that the detrital material is probably derived from intermediate-felsic volcanic rocks [17].

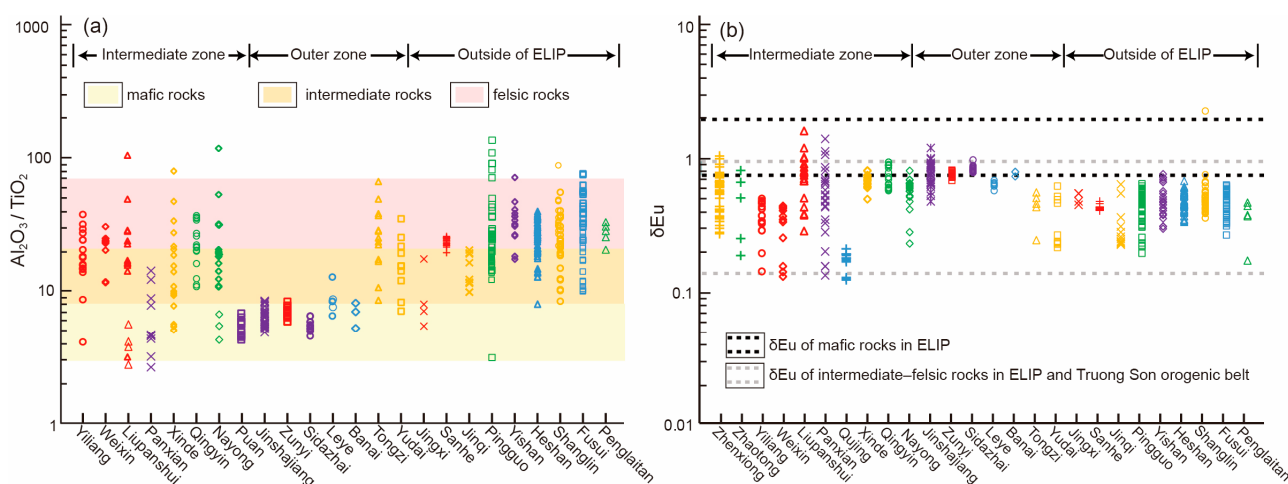


Figure 5. (a) Spatial change of $\text{Al}_2\text{O}_3/\text{TiO}_2$ and (b) spatial change of δEu .

In addition, high-precision U-Pb dating and Lu-Hf in situ isotopic analysis of detrital zircon grains are important methods for determining the provenance of sedimentary rocks [7,52]. Zircon U-Pb dating shows that the age of the Late Permian coal measures (263–257 Ma) is consistent with that of ELIP intermediate-felsic volcanic rocks (267–255 Ma) and Truong Son intermediate-felsic island arc rocks (263–256 Ma; Figure 1). The $\epsilon\text{Hf}(t)$ values of zircon (with U-Pb ages of 251–269 Ma) from the Late Permian in Qingyin, Puan, Sidazhai, Jingxi, Pingguo, and Chongzuo are $-1.85\text{--}11.50$, $-14.60\text{--}14.40$, $-14.27\text{--}5.50$, $-7.69\text{--}11.17$, $-10.23\text{--}17.88$, $-26.70\text{--}12.60$, and $-6.88\text{--}17.87$, respectively. The $\epsilon\text{Hf}(t)$ values of zircon in ELIP intermediate-felsic rocks exhibit positive values, whereas the $\epsilon\text{Hf}(t)$ values of zircon in Truong Son medium-acid island arc magmatic rocks show negative values [17]. From the intermediate zone to the outside zone of ELIP, the $\epsilon\text{Hf}(t)$ peak values gradually change from positive values to negative values (Figure 7). According to the Hf/Th–Th/Nb discrimination diagram of detrital zircons (Figure 8), the detrital zircons in the intermediate zone of the ELIP mostly fall into the within-plate/anorogenic region, whereas those in the outside of ELIP mostly fall into the arc-related/orogenic region, with those in the outer zone of ELIP falling into the region between arc-related/orogenic and within-plate/anorogenic. The zircon U-Pb ages and Lu-Hf isotope data indicate that the

intermediate-felsic components of the coal measures in the intermediate zone, outer zone, and outside zone of ELIP are derived mainly from intermediate-felsic volcanic rocks from the ELIP, the mixture from ELIP and the Truong Son orogenic belt, and the Truong Son orogenic belts, respectively [4,21].

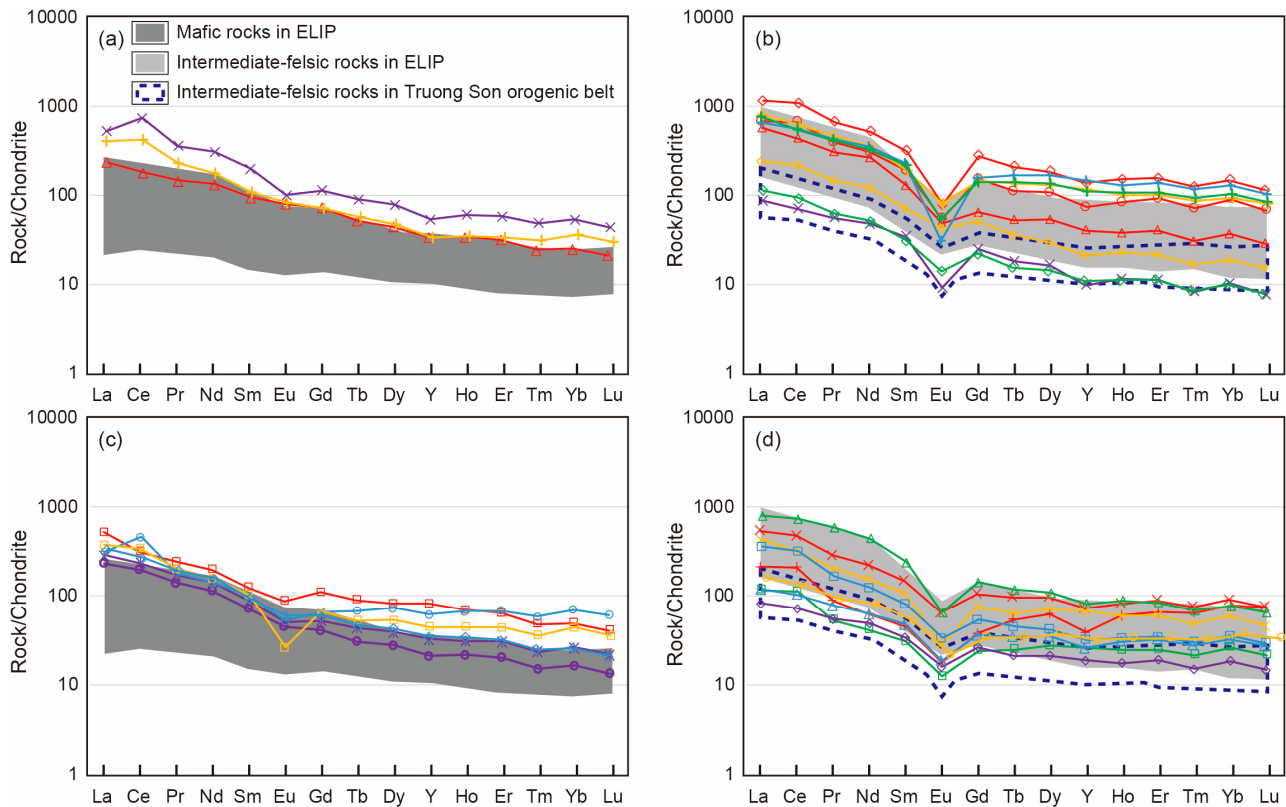


Figure 6. Chondrite-normalized REE pattern distributions: (a) bauxite and Al-claystone in the intermediate zone of ELIP, (b) claystone and coal in the intermediate zone of ELIP, (c) coal measure in the outer zone of ELIP, and (d) coal measure in the outside zone of ELIP. The symbols and lines represent rocks in different areas, corresponding to the horizontal coordinates of Figure 5.

4.2.2. Modes of Occurrence

It is generally accepted that zircon, the major host mineral of Zr and Hf, is one of the most stable heavy minerals in the process of supergenesis [36]. There is a strong positive correlation between Zr and Hf ($R^2 = 0.95$, Figure 9a) in the Late Permian coal measures. The ratios of Zr/Hf ranged from 19.43 to 77.55, with an average ratio of 39.65, which is close to the theoretical Zr/Hf ratio of zircon (~40) [67], providing further evidence that zircon is the main carrier mineral of Zr (Hf). It is generally believed that Nb and Ta in coal measures occur by absorption in the clay minerals, by constituent admixture in zircon, and by isomorphic replacement of Ti in Ti-bearing minerals (e.g., rutile and anatase) [3,8,68]. Nb content is positively correlated with Zr content in the Late Permian coal measures ($R^2 = 0.87$, Figure 9b), probably suggesting that zircon is also the main carrier mineral of Nb. Nb-bearing rutile and anatase were detected by SEM-EDS in the Late Permian coal measures from Shanglin [5], Yiliang [7], Xuanwei [18], and Tongzi [16], indicating that rutile and anatase are also carriers of Nb (Ta) in certain coal measures.

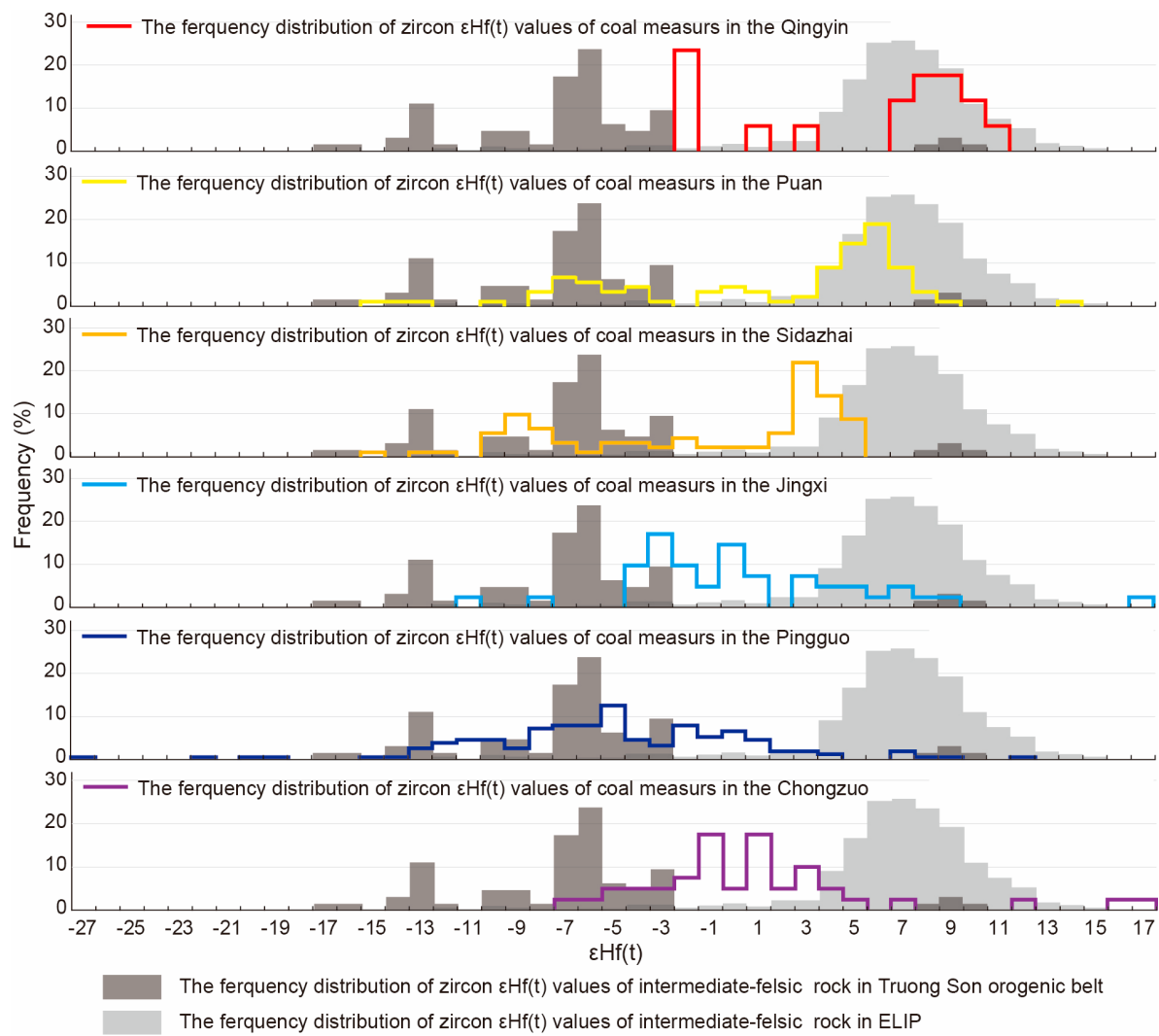


Figure 7. The frequency of $\epsilon\text{Hf}(t)$ values of zircon.

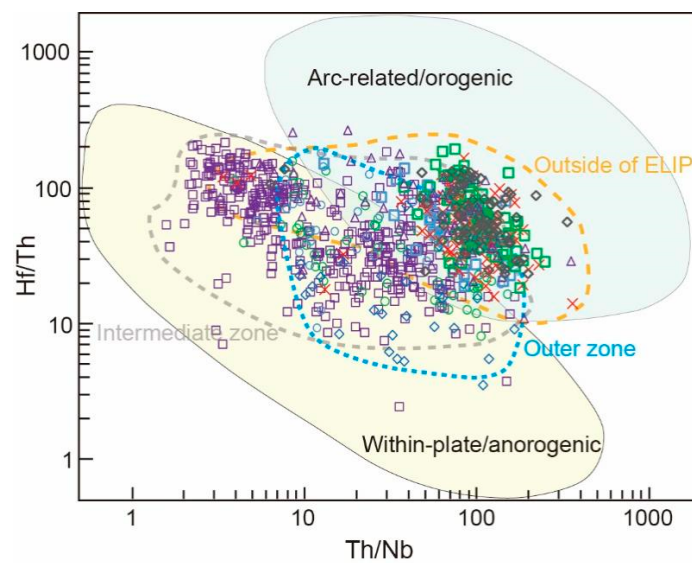


Figure 8. Discriminating diagrams of Hf/Th - Th/Nb . Symbol explanations are the same as in Figure 5.

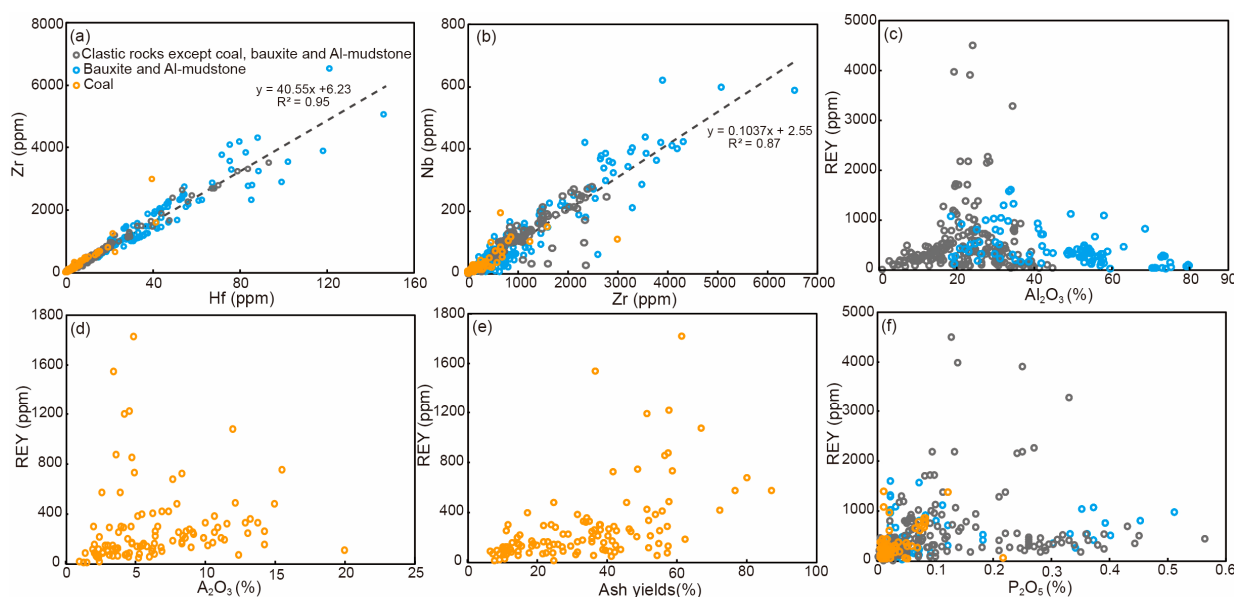


Figure 9. Relationship between Zr and Hf in coal measures (a), Nb and Zr in coal measures (b), REY and Al_2O_3 in bauxite and Al-mudstone (c), REY and Al_2O_3 in coal (d), REY and ash yields in coal (e), and REY and P_2O_5 in coal measures (f).

REY commonly occurs in coal measures in the following three forms: (1) as REY primary or REY-bearing minerals, including detrital minerals and authigenic minerals [3,69], (2) as organic association [70,71], and (3) as ion absorbed on the clay minerals [72]. REY correlates negatively with Al_2O_3 in the Late Permian bauxite and Al-claystone (Figure 9c), showing that most of the REY migrated during the bauxite formation process. REY correlates weakly positively with Al_2O_3 and ash yields in the Late Permian coal (Figure 9d,e), indicating that clay minerals are important carrier minerals of REY in the Late Permian coal. Although there is no obvious correlation between REY and P_2O_5 in the Late Permian coal measures (Figure 9f), REY-bearing phosphate minerals, including monazite, florencite, and rhabdophane, have been found in Yiliang, Liupanshui, Yudai, and Xinde coalfields [7,10,18,49,51], which indicates that a small amount of REY occurs in REY-bearing phosphate minerals.

In bauxite and Al-claystone, the detrital material from Emeishan basalt gradually decreased, and the clastic material from intermediate-felsic volcanic rocks from Truong Son orogenic belt gradually increased from the intermediate zone to the outside zone of ELIP. The contents of main carrier minerals of Nb and Zr (e.g., zircon and rutile) in intermediate-felsic volcanic rock are higher than those in Emeishan basalt. With the weathering, zircon and rutile preferentially accumulate in situ, whereas part of REY tended to transport away from the parent rocks. In conclusion, the material source, modes of occurrence, weathering, and transportation together lead to the increase in Zr and Nb content and the decrease in REY content from the northwest to southeast (Figure 3).

4.2.3. Acidic Aqueous Solution and Organic Matter

Mineral dissolution, element migration, and redistribution are induced by acidic aqueous solutions, affecting the enrichment and mineralization of REY, Zr, Nb, and other critical metal elements. Kaolinite is very stable under acidic conditions (pH = 3.0–6.0). In addition, other aluminosilicates (e.g., feldspar, illite, and smectite) are more susceptible to leaching by acid solution and are eventually converted to kaolinite [73]. Kaolinite is the most abundant clay mineral (more than 50%) in the Late Permian coals in Tongzi [16], Shanglin [14], Panxian [74], Fusui [39], Xinde [75], Yudai, and Jinqi [10], indicating that the critical metals in the Late Permian coal measures were probably affected by acidic aqueous solutions during coalification. Ti minerals (e.g., anatase and rutile) can corrode and

mobilize under highly acidic conditions ($\text{pH} < 3$), although they are very resistant [76,77]. The phenomenon of anatase corrosion was found in Yudai and Jinqi coals, indicating the activity of strongly acidic solutions. Emeishan eruptions released $\sim 1 \times 10^{17}$ g bulk sulfur into the higher atmosphere. The S gasses would be emitted in the form of both H_2S and SO_2 , and converted into sulfate aerosols, leading to cooling of the surface climate and formation of acid rain [46], which is confirmed by tuff and tuffaceous clayrock widely exposed in eastern Yunnan and western Guangxi, as the roof and floor of coal measures [7,41,44]. The dominance of the inertinite content over vitrinite in Yudai and Jinqi coals indicates relatively oxidized peat-forming conditions, which facilitates the abundant generation of humic acid [10,77]. Volcanism-related acidic rain and the oxidation of local peatlands may have jointly caused the highly acidic conditions [10].

High-field-strength elements (e.g., REY, Zr, Hf, Nb, and Ta) are generally considered immobile elements in aqueous solutions at low temperatures but can be mobilized by strongly acidic solutions [78]. The twin pairs Zr-Hf and Nb-Ta were modified by acidic aqueous solutions, with Zr and Nb having a higher mobility capacity than Hf and Ta [79]. The ratios of Nb/Ta and Zr/Hf in the parting and roof were generally lower than those in the underlying coal seams (Figure 10a,b), indicating that Nb, Ta, Hf, and Zr were released from the parting and roof and leached into the underlying coal seams under acidic conditions. These elements were deposited as authigenic minerals or adsorbed ions on organic matter with water–rock interactions [3,10,80].

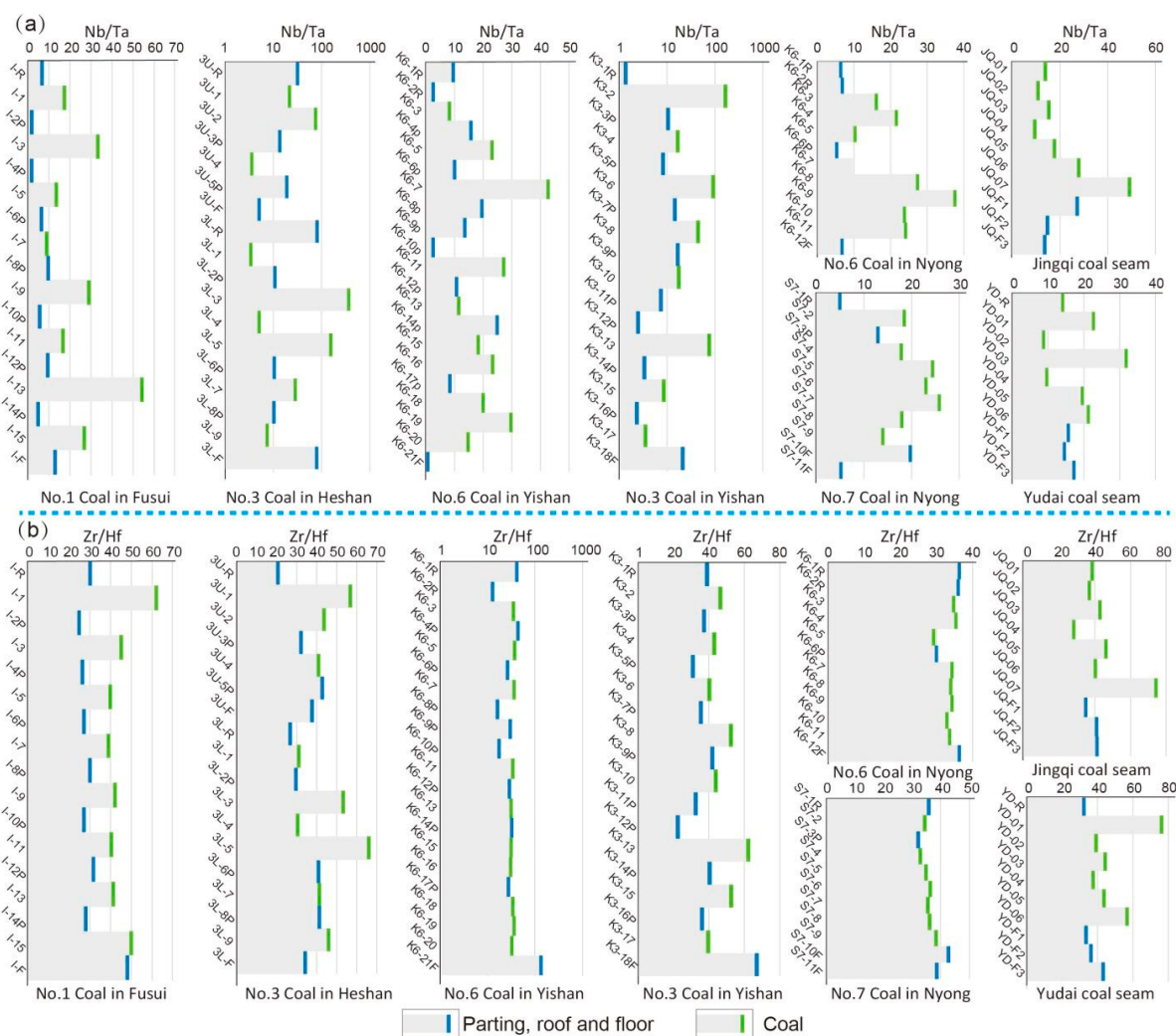


Figure 10. Nb/Ta (a) and Zr/Hf (b) ratios of coal, parting, roof, and floor.

The adsorption experiments show that REE can combine with $-\text{COOH}$ and $-\text{OH}$ to form a stable compound after replacing the Na^+ , K^+ , Ca^{2+} , and Mg^{2+} ions in coal through cation exchange under acidic conditions [81]. Meanwhile, compared to LREY, HREY are more likely to combine with organic compounds and form more stable organic compounds [71]. The ratios of REY/Ta in the parting and roof were generally lower than those in underlying coal seams (Figure 11a). However, the LREY/HREY ratios in the parting and roof were generally higher than those in the underlying coal seams (Figure 11b), indicating that REY, especially HREY, tended to combine with organic matter in acidic solution during coalification.

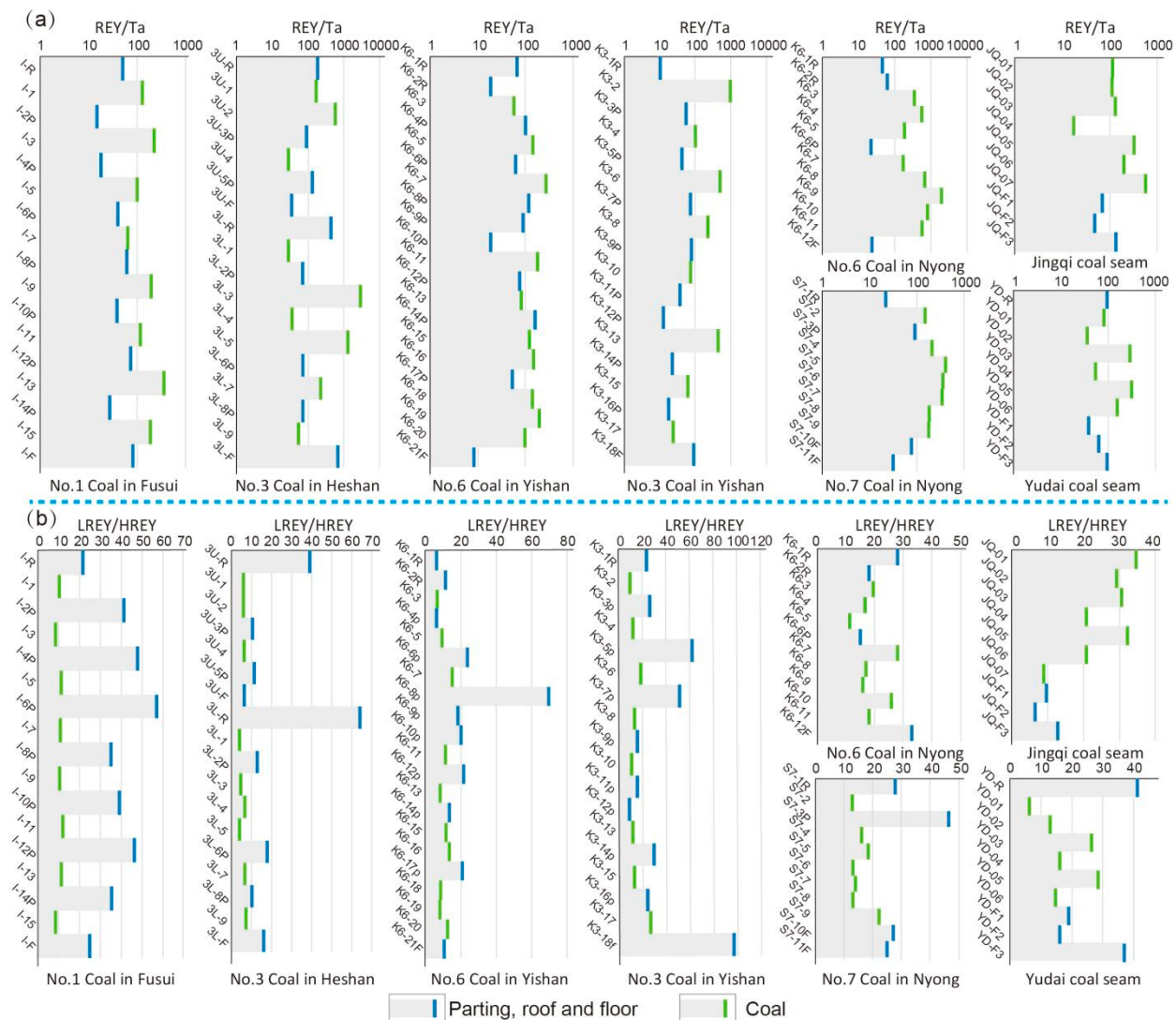


Figure 11. REY/Ta (a) and LREY/HREY (b) ratios of coal, parting, roof, and floor.

4.3. Metallogenic Model

According to paleomagnetic and paleoclimatic reconstruction, the South China Block straddles the equator, and the study area was probably located near the equator [82]. In addition, previous studies have shown that the South China Block underwent significant clockwise rotation during the Middle–Late Paleozoic and the ELIP was located to the west of the study area during the Late Permian [83]. The southern margin of the South China Block was a passive continental margin that merged with the Paleo-Tethys oceanic crust, which in turn subducted beneath the Indochina block, formed the Permian Island arc,

and finally coalesced into the Truong Son orogenic belt at the end of the Triassic [20,22] (Figure 12).

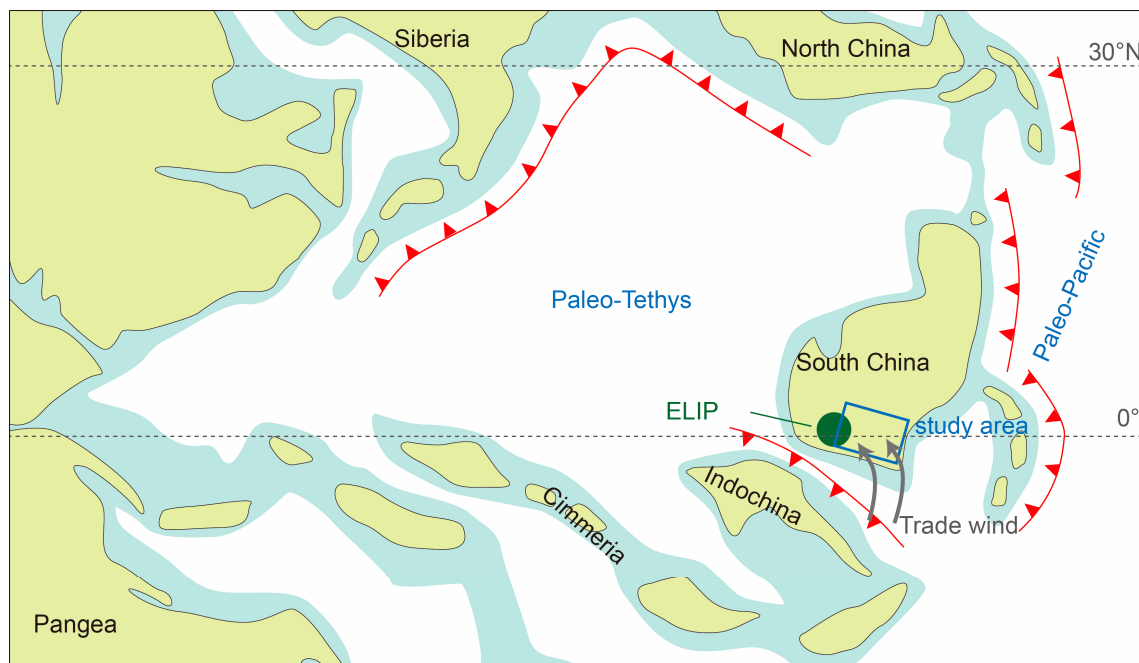


Figure 12. Study area paleogeographic map of the Late Permian (modified from Yang et al. [20]).

In the Late Permian, Emeishan basaltic magma erupted over a relatively short time span, generating massive mantle-derived flood basalts [32]. At the same time, the Paleo-Tethys oceanic crust subducted to the Indosinian Block, resulting in the eruption of a large amount of intermediate-felsic volcanic ash that was dispersed by easterly trade winds and deposited on the Maokou Formation limestone in the east of the study area (Figure 13a). The study area was situated close to the equator, characterized by a warm and humid climate, which resulted in intense chemical weathering of the Emeishan flood basalts and intermediate-felsic volcanoclastic rocks. This process led to the loss of Si, the accumulation of Al in situ (Figure 13b), and the formation of bauxite and Al-claystone over the limestone [35]. With the formation of bauxite, Nb, Ta, and Zr in basalt and intermediate-felsic volcanic ash remained in the form of heavy minerals in situ (e.g., rutile, zircon, and anatase), which led to enrichment of Nb, Ta, and Zr in bauxite and Al-claystone. Because a large amount of REY was lost with flow transportation in the form of dissolved, suspended, or detrital material, REY is relatively enriched only in Al-claystone, with a weak weathering degree.

In the late stage of the Emeishan volcanism, the warm, humid climate in the study area was conducive to plant growth, resulting in the accumulation of peat and the formation of peatlands (Figure 13c). The intermediate-felsic volcanic ash of ELIP and the Truong Son orogenic belt was ejected into the atmosphere, and then fell into peatlands, providing Nb, Ta, Zr, and REY for the Upper Permian coal-bearing strata (Figure 13d), which was evidenced by the existence of tuffaceous claystone, tuff, tonsteins, and K-bentonites in the coal measures in eastern Yunnan and western Guizhou [84]. The intermediate-felsic volcanic ash from ELIP deposited mainly in the intermediate–outer zone of ELIP, while the Truong Son orogenic belt deposited mainly on the area outside of ELIP, and the deposition decreased with the increase in the distance from the eruption center. At the same time, volatiles (e.g., SO₂ and H₂S) were absorbed by rain, resulting in acid rain and strongly acidic conditions. Nb, Ta, Zr, and REY in the claystone and volcanic ash interlayer were leached by acidic aqueous solution and migrated into the underlying peat layers (Figure 13e), leading to enrichment and ore formation in coal.

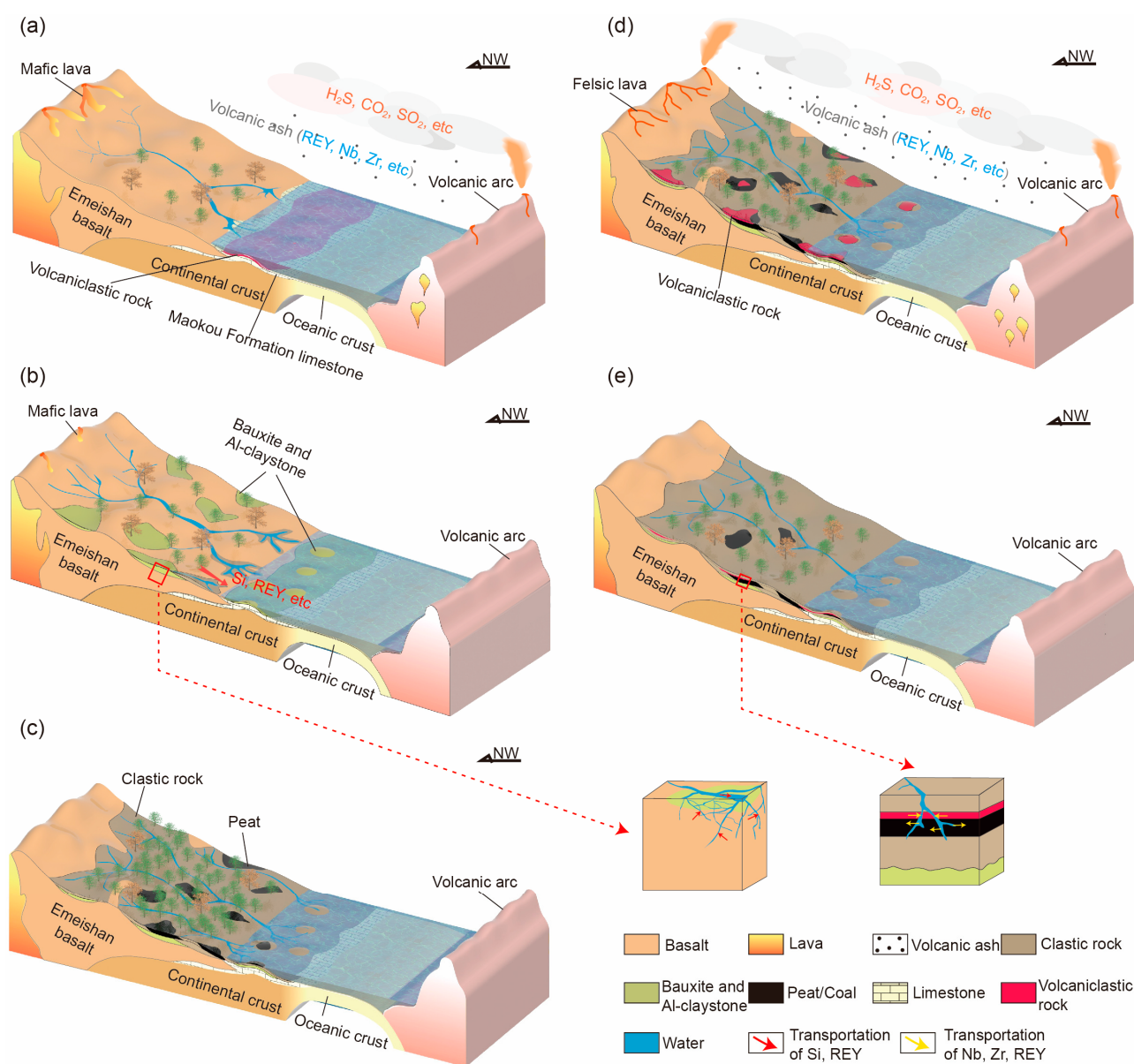


Figure 13. (a) The formation of Emeishan basalt and the deposition of intermediate-felsic volcanic ash on Maokou Formation limestone. (b) The transportation of Si and REY during the formation of bauxite and Al-claystone. (c) The accumulation of peat and the formation of coal and clastic rock. (d) The intermediate-felsic volcanic ash of ELIP and the Truong Son orogenic belt fell into peatlands. (e) The leaching of Nb, Zr, and REY in acidic solution.

5. Conclusions

The Late Permian coal measures in Yunnan, Guizhou, and Guangxi were abnormally enriched in Nb (Ta), Zr, and REY, and the contents of these elements exceeded the cut-off grade with high economic value in some areas. The bauxite and Al-claystone in the bottom of the Upper Permian in the intermediate zone of ELIP were mainly derived from Emeishan mafic magmatic rocks, while the detrital mineral matter within coal measures in the middle and upper parts of the Upper Permian in the intermediate zone, outer zone, and outside zone of ELIP were derived from intermediate-felsic volcanic rocks from the ELIP, the mixture from ELIP and the Truong Son orogenic belt, and the Truong Son orogenic belts, respectively. Nb (Ta) and Zr were enriched in bauxite and Al-claystone in the form of heavy minerals (e.g., rutile, zircon, and anatase) during the weathering of Emeishan flood basalt. Acidic solutions, including acid rain and humic acid, led to the leaching of Nb (Ta),

Zr (Hf), and REY from the parting and roof to underlying coal seams during coalification, which generated enrichment and ore formation in coal in the form of organic compounds.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14020206/s1>, Table S1: Major and trace elements data of the coal measures in study area; Table S2: U-Pb age and Lu-Hf isotope data for the coal measures in study area; Table S3: The average content of Zr, Nb and REY in bauxite and Al-claystone.

Author Contributions: B.C., P.T. and H.X. collected previous data; B.C. and P.T. wrote the original draft; X.F. and J.K. revised and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Project of Xuzhou (No. KC22345), Jiangsu Collaborative Innovation Center for Building Energy Saving and Construction Technology (No. SJXTBS2115), and the Major Scientific and Technological Innovation Projects in Jiangsu Province (No. BM2022037).

Data Availability Statement: Data are contained within the article and supplementary materials.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Dai, S.; Finkelman, R.B. Coal as a promising source of critical elements: Progress and future prospects. *Int. J. Coal Geol.* **2018**, *186*, 155–164. [CrossRef]
2. Ning, S.Z.; Huang, S.Q.; Zhu, S.F.; Zhang, W.; Deng, X.L.; Li, C.C.; Qiao, J.W.; Zhang, J.Q.; Zhang, N. Mineralization zoning of coal-metal deposits in China. *Chin. Sci. Bull.* **2019**, *64*, 2501–2513. (In Chinese with English Abstract)
3. Dai, S.; Finkelman, R.B.; French, D.; Hower, J.C.; Graham, I.T.; Zhao, F. Modes of occurrence of elements in coal: A critical evaluation. *Earth-Sci. Rev.* **2021**, *222*, 103815. [CrossRef]
4. Liu, J.J.; Han, Q.C.; Zhao, S.M.; Jia, R.K. The sources of abnormally enriched critical metals in the Late Permian coals of Western Guizhou Province. *J. China Coal Soc.* **2022**, *47*, 1782–1794. (In Chinese with English Abstract)
5. Cao, B.; Qin, Y.H.; Zhu, S.F.; Fu, X.H.; Xu, H.; Zong, S. Origin and enrichment mechanism of lithium and rare earth elements in carbonaceous mudstone of Heshan Formation, Shanglin, Guangxi. *J. China Coal Soc.* **2022**, *47*, 1851–1864. (In Chinese with English Abstract)
6. Zhang, J.; Wang, Q.; Liu, X.; Zhou, G.; Xu, H.; Zhu, Y. Provenance and ore-forming process of Permian lithium-rich bauxite in central Yunnan, SW China. *Ore Geol. Rev.* **2022**, *145*, 104862. [CrossRef]
7. Wang, N.; Dai, S.; Wang, X.; Nechaev, V.P.; French, D.; Graham, I.T.; Zhao, L.; Song, X. New insights into the origin of Middle to Late Permian volcanoclastics (Nb–Zr–REE–Ga-rich horizons) from eastern Yunnan, SW China. *Lithos* **2022**, *420–421*, 106702. [CrossRef]
8. Dai, S.; Zhou, Y.; Zhang, M.; Wang, X.; Wang, J.; Song, X.; Jiang, Y.; Luo, Y.; Song, Z.; Yang, Z.; et al. A new type of Nb (Ta)–Zr(Hf)–REE–Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: Possible economic significance and genetic implications. *Int. J. Coal Geol.* **2010**, *83*, 55–63. [CrossRef]
9. Dai, S.; Nechaev, V.P.; Chekryzhov, I.Y.; Zhao, L.; Vysotskiy, S.V.; Graham, I.; Ward, C.R.; Ignatiev, A.V.; Velivetskaya, T.A.; Zhao, L.; et al. A model for Nb–Zr–REE–Ga enrichment in Lopingian altered alkaline volcanic ashes: Key evidence of H–O isotopes. *Lithos* **2018**, *302–303*, 359–369. [CrossRef]
10. Li, B.; Zhuang, X.; Querol, X.; Moreno, N.; Córdoba, P.; Shangguan, Y.; Yang, L.; Li, J.; Zhang, F. Geological controls on the distribution of REY–Zr (Hf)–Nb (Ta) enrichment horizons in late Permian coals from the Qiangdongbei Coalfield, Guizhou Province, SW China. *Int. J. Coal Geol.* **2020**, *231*, 103604. [CrossRef]
11. Ling, K.; Wen, H.; Zhang, Q.; Luo, C.; Gu, H.; Du, S.; Yu, W. Super-enrichment of lithium and niobium in the upper Permian Heshan Formation in Pingguo, Guangxi, China. *Sci. China Earth Sci.* **2021**, *64*, 753–772. [CrossRef]
12. Wen, J.; Liu, Z.C.; Zhao, J.X.; Zhu, H.L.; Zhang, H.F.; Zhang, J.Y.; Chen, D.F.; Zhong, H.R.; Guo, W.Y.; You, X.J.; et al. Enrichment regularity, sedimentary environment and metallogenic model of niobium-rare earth polymetallic enrichment layer in bottom of Xuanwei Formation in Muchuan area, South Sichuan. *Acta Geol. Sin.* **2021**, *96*, 592–617. (In Chinese with English Abstract)
13. Deng, W.; Wen, H.; Du, S.; Ling, K.; Fan, H.; Zhu, C.; Luo, C.; Yang, Y. Provenance of Late Permian Nb–Zr–REE–Ga enrichment in western Guizhou: Implications for the waning volcanism of Emeishan large igneous province. *Ore Geol. Rev.* **2022**, *150*, 105160. [CrossRef]
14. Zhang, F.Q.; Li, B.Q.; Zhuang, X.G.; Querol, X.; Moreno, N.; Shangguan, Y.; Zhou, J.M.; Liao, J.L. 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. *Minerals* **2021**, *11*, 301. [CrossRef]
15. Liu, X.; Wang, Q.; Zhang, Q.; Zhang, Y.; Li, Y. Genesis of REE minerals in the karstic bauxite in western Guangxi, China, and its constraints on the deposit formation conditions. *Ore Geol. Rev.* **2016**, *75*, 100–115. [CrossRef]

16. Li, B.; Zhuang, X.; Querol, X.; Moreno, N.; Yang, L.; Shangguan, Y.; Li, J. Mineralogy and Geochemistry of Late Permian Coals within the Tongzi Coalfield in Guizhou Province, Southwest China. *Minerals* **2020**, *10*, 44. [\[CrossRef\]](#)
17. Hou, Y.; Zhong, Y.; Xu, Y.; He, B. The provenance of late Permian karstic bauxite deposits in SW China, constrained by the geochemistry of interbedded clastic rocks, and U–Pb–Hf–O isotopes of detrital zircons. *Lithos* **2017**, *278–281*, 240–254. [\[CrossRef\]](#)
18. Dai, S.; Chekryzhov, I.Y.; Seredin, V.V.; Nechaev, V.P.; Graham, I.T.; Hower, J.C.; Ward, C.R.; Ren, D.; Wang, X. Metalliferous coal deposits in East Asia (Primorye of Russia and South China): A review of geodynamic controls and styles of mineralization. *Gondwana Res.* **2016**, *29*, 60–82. [\[CrossRef\]](#)
19. Dai, S.; Xie, P.; Ward, C.R.; Yan, X.; Guo, W.; French, D.; Graham, I.T. Anomalies of rare metals in Lopingian super-high-organic-sulfur coals from the Yishan Coalfield, Guangxi, China. *Ore Geol. Rev.* **2017**, *88*, 235–250. [\[CrossRef\]](#)
20. Yang, S.; Wang, Q.; Lai, X.; Qiao, L.; Wang, R.; Huang, Y.; Wang, Y. Genesis of end-Guadalupian bauxite and pyrite deposits in the Youjiang Basin (South China): Insights into the causative link between magmatic events and mass extinction. *J. Asian Earth Sci.* **2021**, *215*, 104801. [\[CrossRef\]](#)
21. Yu, W.; Algeo, T.J.; Du, Y.; Zhang, Q.; Liang, Y. Mixed volcanogenic–lithogenic sources for Permian bauxite deposits in southwestern Youjiang Basin, South China, and their metallogenic significance. *Sediment. Geol.* **2016**, *341*, 276–288. [\[CrossRef\]](#)
22. Hou, Z.; Fan, J.; Henderson, C.M.; Yuan, D.; Shen, B.; Wu, J.; Wang, Y.; Zheng, Q.; Zhang, Y.; Wu, Q.; et al. Dynamic palaeogeographic reconstructions of the Wuchiapingian Stage (Lopingian, Late Permian) for the South China Block. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2020**, *546*, 109667. [\[CrossRef\]](#)
23. Hou, L.; Xiong, F.; Wang, W.; Guo, L.; Zhang, Q. Carboniferous–Triassic felsic igneous rocks and typical mineral deposits in the Truong Son orogenic belt, SE Asia: Implications for Paleo-Tethyan tectonic evolution and metallogeny. *Ore Geol. Rev.* **2019**, *112*, 103036. [\[CrossRef\]](#)
24. Shi, M.; Lin, F.; Fan, W.; Deng, Q.; Cong, F.; Tran, M.; Zhu, H.; Wang, H. Zircon U–Pb ages and geochemistry of granitoids in the Truong Son terrane, Vietnam: Tectonic and metallogenic implications. *J. Asian Earth Sci.* **2015**, *101*, 101–120. [\[CrossRef\]](#)
25. Qian, X.; Wang, Y.; Zhang, Y.; Zhang, Y.; Senebottalath, V.; Zhang, A.; He, H. Petrogenesis of Permian–Triassic felsic igneous rocks along the Truong Son zone in northern Laos and their Paleotethyan assembly. *Lithos* **2019**, *328–329*, 101–114. [\[CrossRef\]](#)
26. Shellnutt, J.; Denysyn, S.; Mundil, R. Precise age determination of mafic and felsic intrusive rocks from the Permian Emeishan large igneous province (SW China). *Gondwana Res.* **2012**, *22*, 118–126. [\[CrossRef\]](#)
27. Xu, Y.G.; Luo, Z.Y.; Huang, X.L.; He, B.; Xiao, L.; Xie, L.W.; Shi, Y.R. Zircon U–Pb and Hf isotope constraints on crustal melting associated with the Emeishan mantle plume. *Geochim. Cosmochim. Ac.* **2008**, *72*, 3084–3104. [\[CrossRef\]](#)
28. Hei, H.Y.; Su, S.G.; Wang, Y.; Mo, X.X.; Luo, Z.H.; Liu, W.G. Rhyolites in the Emeishan large igneous province (SW China) with implications for plume-related felsic magmatism. *J. Asian Earth Sci.* **2018**, *164*, 344–365. [\[CrossRef\]](#)
29. Huang, H.; Cawood, P.A.; Hou, M.C.; Xiong, F.H.; Ni, S.J.; Deng, M.; Zhong, H.T.; Yang, C.C. Zircon U–Pb age, trace element, and Hf isotopic constrains on the origin and evolution of the Emeishan Large Igneous Province. *Gondwana Res.* **2022**, *105*, 535–550. [\[CrossRef\]](#)
30. Hieu, P.T.; Li, S.Q.; Yu, Y.; Thanh, N.X.; Dung, L.T.; Tu, V.L.; Siebel, W.; Chen, F. Stages of late Paleozoic to early Mesozoic magmatism in the Song Ma belt, NW Vietnam: Evidence from zircon U–Pb geochronology and Hf isotope composition. *Int. J. Earth Sci.* **2016**, *106*, 855–874. [\[CrossRef\]](#)
31. Usuki, T.; Lan, C.Y.; Tran, T.H.; Pham, T.D.; Wang, K.L.; Shellnutt, G.J.; Chung, S.L. Zircon U–Pb ages and Hf isotopic compositions of alkaline silicic magmatic rocks in the Phan Si Pan-Tu Le region, northern Vietnam: Identification of a displaced western extension of the Emeishan Large Igneous Province. *J. Asian Earth Sci.* **2015**, *97*, 102–124. [\[CrossRef\]](#)
32. Xu, Y.G.; Chung, S.L.; Hui, S.; He, B. Silicic magmas from the Emeishan large igneous province, Southwest China: Petrogenesis and their link with the end-Guadalupian biological crisis. *Lithos* **2010**, *119*, 47–60. [\[CrossRef\]](#)
33. Shellnutt, J.; Pham, T.; Denysyn, S.; Yeh, M.; Anh, T. Magmatic duration of the Emeishan large igneous province: Insight from northern Vietnam. *Geology* **2020**, *48*, 457–461. [\[CrossRef\]](#)
34. Hou, Z.S. High-Resolution Quantitative Paleogeographic Study of the Permian in South China. Master’s Thesis, University of Science and Technology of China, Beijing, China, 2020. (In Chinese with English Abstract)
35. Zhou, J.; Yu, W.; Du, Y.; Liu, X.; Wang, Y.; Xiong, G.; Zhao, Z.; Pang, D.; Shen, D.; Weng, S.; et al. Provenance change and continental weathering of Late Permian bauxitic claystone in Guizhou Province, Southwest China. *J. Geochem. Explor.* **2022**, *236*, 106962. [\[CrossRef\]](#)
36. Hou, Y.L. Tracing Source Rocks of the Late Permian Karstic Bauxite in the Western Guangxi by Geochemistry of the Sedimentary Rocks from the Heshan Formation. Ph.D. Thesis, University of Chinese Academy of Sciences, Guangzhou, China, 2017. (In Chinese with English Abstract)
37. Zhang, S.Y. Enrichment and Differentiation Mechanism of Elements and Minerals in the Late Permian Super-High-Organic Sulfur Coal in the Central Area of Guangxi Province. Ph.D. Thesis, China University of Mining & Technology-Beijing, Beijing, China, 2021. (In Chinese with English Abstract)
38. Xie, P.P. Occurrence and Enrichment Mechanism of Mineral Matters in the Late Permian Coals from Western Guizhou and Middle Guangxi Provinces, China. Ph.D. Thesis, China University of Mining & Technology-Beijing, Beijing, China, 2019. (In Chinese with English Abstract)

39. Dai, S.; Zhang, W.; Ward, C.R.; Seredin, V.V.; Hower, J.C.; Li, X.; Song, W.; Wang, X.; Kang, H.; Zheng, L. Mineralogical and geochemical anomalies of late Permian coals from the Fusui Coalfield, Guangxi Province, southern China: Influences of terrigenous materials and hydrothermal fluids. *Int. J. Coal Geol.* **2013**, *105*, 60–84. [\[CrossRef\]](#)
40. Yu, W.; Wang, R.; Zhang, Q.; Du, Y.; Chen, Y.; Liang, Y. Mineralogical and geochemical evolution of the Fusui bauxite deposit in Guangxi, South China: From the original Permian orebody to a Quaternary Salento-type deposit. *J. Geochem. Explor.* **2014**, *146*, 75–88. [\[CrossRef\]](#)
41. Yang, J.; Cawood, P.A.; Du, Y.; Huang, H.; Huang, H.; Tao, P. Large Igneous Province and magmatic arc sourced Permian–Triassic volcanogenic sediments in China. *Sediment. Geol.* **2012**, *261–262*, 120–131. [\[CrossRef\]](#)
42. Liu, X.; Wang, Q.; Zhang, Q.; Yang, S.; Zhang, Y.; Liang, Y.; Qing, C. Transformation from Permian to Quaternary bauxite in southwestern South China Block driven by superimposed orogeny: A case study from Sanhe ore deposit. *Ore Geol. Rev.* **2017**, *90*, 998–1017. [\[CrossRef\]](#)
43. He, Q.; Dong, T.; He, S.; Zhai, G.; Guo, X.; Hou, Y.; Yang, R.; Han, Y. Sedimentological and geochemical characterization of the Upper Permian transitional facies of the Longtan Formation, northern Guizhou Province, southwest China: Insights into paleo-environmental conditions and organic matter accumulation mechanisms. *Mar. Pet. Geol.* **2020**, *118*, 104446. [\[CrossRef\]](#)
44. Yang, T.; Shen, Y.; Qin, Y.; Jin, J.; Zhang, Y.; Tong, G.; Liu, J. Distribution of radioactive elements (Th, U) and formation mechanism of the bottom of the Lopingian (Late Permian) coal-bearing series in western Guizhou, SW China. *J. Pet. Sci. Eng.* **2021**, *205*, 108779. [\[CrossRef\]](#)
45. Yang, J.; Cawood, P.A.; Du, Y. Voluminous silicic eruptions during late Permian Emeishan igneous province and link to climate cooling. *Earth Planet. Sci. Lett.* **2015**, *432*, 166–175. [\[CrossRef\]](#)
46. Shao, L.; Jones, T.; Gayer, R.; Dai, S.; Zhang, P. Petrology and geochemistry of the high-sulphur coals from the Upper Permian carbonate coal measures in the Heshan Coalfield, southern China. *Int. J. Coal Geol.* **2003**, *55*, 1–26. [\[CrossRef\]](#)
47. Dai, S.; Zhang, W.; Seredin, V.V.; Ward, C.R.; Hower, J.C.; Song, W.; Wang, X.; Li, X.; Zhao, L.; Kang, H. Factors controlling geochemical and mineralogical compositions of coals preserved within marine carbonate successions: A case study from the Heshan Coalfield, southern China. *Int. J. Coal Geol.* **2013**, *109*, 77–100. [\[CrossRef\]](#)
48. Du, F.; Qiao, J.; Zhao, X.; Tan, F.; Li, C.; Luo, Z. Enrichment of V in Late Permian coals in Gemudi Mine, Western Guizhou, SW China. *J. Geochem. Explor.* **2021**, *221*, 106701. [\[CrossRef\]](#)
49. Liu, J.; Dai, S.; Song, H.; Nechaev, V.P.; French, D.; Spiro, B.F.; Graham, I.T.; Hower, J.C.; Shao, L.; Zhao, J. Geological factors controlling variations in the mineralogical and elemental compositions of Late Permian coals from the Zhijin-Nayong Coalfield, western Guizhou, China. *Int. J. Coal Geol.* **2021**, *247*, 103855. [\[CrossRef\]](#)
50. Huang, H.; Cawood, P.A.; Hou, M.; Yang, J.; Ni, S.; Du, Y.; Yan, Z.; Wang, J. Silicic ash beds bracket Emeishan Large Igneous province to <1m.y. at ~260 Ma. *Lithos* **2016**, *264*, 17–27.
51. Dai, S.; Li, T.; Seredin, V.V.; Ward, C.R.; Hower, J.C.; Zhou, Y.; Zhang, M.; Song, X.; Song, W.; Zhao, C. Origin of minerals and elements in the Late Permian coals, tonsteins, and host rocks of the Xinde Mine, Xuanwei, eastern Yunnan, China. *Int. J. Coal Geol.* **2014**, *121*, 53–78. [\[CrossRef\]](#)
52. Deng, X.; Yang, J.; Cawood, P.A.; Wang, X.; Du, Y.; Huang, Y.; Lu, S.; He, B. Detrital record of late-stage silicic volcanism in the Emeishan large igneous province. *Gondwana Res.* **2020**, *79*, 197–208. [\[CrossRef\]](#)
53. Dai, S.; Graham, I.T.; Ward, C.R. A review of anomalous rare earth elements and yttrium in coal. *Int. J. Coal Geol.* **2016**, *159*, 82–95. [\[CrossRef\]](#)
54. Seredin Vladimir, V.; Shifeng, D. Coal deposits as potential alternative sources for lanthanides and yttrium. *Int. J. Coal Geol.* **2012**, *94*, 67–93. [\[CrossRef\]](#)
55. DZ/T 0203-2020; Geology Mineral Industry Standard of P.R. China: Specifications for Rare Metal Mineral Exploration. Geological Press: Beijing, China, 2020.
56. DZ/T 0204-2002; Geology Mineral Industry Standard of P.R. China: Specifications for Rare Earth Mineral Exploration. Geological Press: Beijing, China, 2002.
57. Zhao, H.; Ling, K.; Du, S.; Wen, H. Provenance of the Nb-rich bauxite and Li-rich claystone at the base of the Heshan Formation in Pingguo, Guangxi, SW China: Constrained by U–Pb ages and trace element contents of detrital zircon. *Ore Geol. Rev.* **2023**, *161*, 105633. [\[CrossRef\]](#)
58. Wang, H.; Gu, J.; Huang, Z.; Zhao, L. The migration and enrichment of REE in the formation process of the Xinmin bauxite deposit in the Wuchuan-Zhengan-Daozhen area, Northern Guizhou, China. *Acta Mineral. Sin.* **2021**, *41*, 439–453. (In Chinese with English Abstract)
59. Yu, W.; Du, Y.; Zhou, J.; Cheng, L.; Deng, X.; Dai, X.; Pang, D.; Wong, S.; Lei, Z.; Li, P.; et al. Provenance and deep-time environmental factors for bauxitization in China: Progress and discussion. *Acta Geol. Sin.* **2023**, *97*, 3056–3074. (In Chinese with English Abstract)
60. Dai, S.; Yan, X.; Ward, C.R.; Hower, J.C.; Zhao, L.; Wang, X.; Zhao, L.; Ren, D.; Finkelman, R.B. Valuable elements in Chinese coals: A review. *Int. Geol. Rev.* **2018**, *60*, 1–31. [\[CrossRef\]](#)
61. Wen, H.J.; Luo, C.G.; Du, S.J.; Yu, W.X.; Gu, H.N.; Ling, K.Y.; Cui, Y.; Li, Y.; Yang, J.H. Carbonate-hosted clay-type lithium deposit and its prospecting significance. *Chin. Sci. Bull.* **2020**, *65*, 53–59. (In Chinese with English Abstract) [\[CrossRef\]](#)

62. Wei, X.; Ji, H.; Li, D.; Zhang, F.; Wang, S. Material source analysis and element geochemical research about two types of representative bauxite deposits and terra rossa in western Guangxi, southern China. *J. Geochem. Explor.* **2013**, *133*, 68–87. [\[CrossRef\]](#)
63. Li, Q.; Xu, S.L.; Chen, H.D.; Ling, L.B.; Yang, S.; Yu, Y.; Sun, F.R.; Dong, Y.X.; Deng, X. Geochemical characteristics and palaeo-environmental implication of Middle Permian Maokou Formation in Wangcang region, Sichuan Basin, China. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* **2018**, *45*, 268–281. (In Chinese with English Abstract)
64. McLennan, S.M. Weathering and Global Denudation. *J. Geol.* **1993**, *101*, 295–303. [\[CrossRef\]](#)
65. Nesbitt, H.W.; Wilson, R.E. Recent chemical weathering of basalts. *Am. J. Sci.* **1992**, *292*, 740. [\[CrossRef\]](#)
66. McLennan, S.M.; Hemming, S.; Mcdaniel, D.K.; Hanson, G.N.; Johnsson, M.J.; Basu, A. Geochemical approaches to sedimentation, provenance, and tectonics. *Spec. Pap. (Geol. Soc. Am.)* **1993**, *284*, 21–40.
67. Murali, A.V.; Parthasarathy, R.; Mahadevan, T.M.; Das, M.S. Trace element characteristics, REE patterns and partition coefficients of zircons from different geological environments—A case study on Indian zircons. *Geochim. Cosmochim. Acta* **1983**, *47*, 2047–2052. [\[CrossRef\]](#)
68. Finkelman, R.B.; Dai, S.; French, D. The importance of minerals in coal as the hosts of chemical elements: A review. *Int. J. Coal Geol.* **2019**, *212*, 103251. [\[CrossRef\]](#)
69. Cao, B.; Zhu, S.F.; Qin, Y.H.; Wang, S.M. Research status and prospect of rare earth elements in coal. *Coal Sci. Technol.* **2022**, *50*, 181–194. (In Chinese with English Abstract)
70. Seredin, V.V.; Shpirt, M.; Vassyanovich, A. REE contents and distribution in humic matter of REE-rich coals. In *Mineral Deposits: Processes to Processing*; Stanley, C.J., Ed.; Aa Balkema: Rotterdam, The Netherlands, 1999; pp. 267–269.
71. Aide, M.T.; Aide, C. Rare Earth Elements: Their Importance in Understanding Soil Genesis. *Isrn Soil Sci.* **2012**, *2012*, 783876. [\[CrossRef\]](#)
72. Moldoveanu, G.A.; Papangelakis, V.G. Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism. *Hydrometallurgy*. **2012**, *117–118*, 71–78. [\[CrossRef\]](#)
73. Dill, H.G. Kaolin: Soil, rock and ore: From the mineral to the magmatic, sedimentary and metamorphic environments. *Earth-Sci. Rev.* **2016**, *161*, 16–129. [\[CrossRef\]](#)
74. Wang, P.; Ji, D.; Yang, Y.; Zhao, L. Mineralogical compositions of Late Permian coals from the Yueliangtian mine, western Guizhou, China: Comparison to coals from eastern Yunnan, with an emphasis on the origin of the minerals. *Fuel* **2016**, *181*, 859–869. [\[CrossRef\]](#)
75. Liu, J.; Nechaev, V.P.; Dai, S.; Song, H.; Nechaeva, E.V.; Jiang, Y.; Graham, I.T.; French, D.; Yang, P.; Hower, J.C. Evidence for multiple sources for inorganic components in the Tucheng coal deposit, western Guizhou, China and the lack of critical-elements. *Int. J. Coal Geol.* **2020**, *223*, 103468. [\[CrossRef\]](#)
76. Dai, S.; Li, T.; Jiang, Y.; Ward, C.R.; Hower, J.C.; Sun, J.; Liu, J.; Song, H.; Wei, J.; Li, Q.; et al. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Hailiushu Mine, Daqingshan Coalfield, Inner Mongolia, China: Implications of sediment-source region and acid hydrothermal solutions. *Int. J. Coal Geol.* **2015**, *137*, 92–110. [\[CrossRef\]](#)
77. Ward, C.R. Analysis, origin and significance of mineral matter in coal: An updated review. *Int. J. Coal Geol.* **2016**, *165*, 1–27. [\[CrossRef\]](#)
78. Dai, S.; Luo, Y.; Seredin, V.V.; Ward, C.R.; Hower, J.C.; Zhao, L.; Liu, S.; Zhao, C.; Tian, H.; Zou, J. Revisiting the late Permian coal from the Huayingshan, Sichuan, southwestern China: Enrichment and occurrence modes of minerals and trace elements. *Int. J. Coal Geol.* **2014**, *122*, 110–128. [\[CrossRef\]](#)
79. Arbuzov, S.I.; Spears, D.A.; Vergunov, A.V.; Ilenok, S.S.; Mezhibor, A.M.; Ivanov, V.P.; Zarubina, N.A. Geochemistry, mineralogy and genesis of rare metal (Nb-Ta-Zr-Hf-Y-REE-Ga) coals of the seam XI in the south of Kuznetsk Basin, Russia. *Ore Geol. Rev.* **2019**, *113*, 103073. [\[CrossRef\]](#)
80. Dai, S.; Seredin, V.V.; Ward, C.R.; Jiang, J.; Hower, J.C.; Song, X.; Jiang, Y.; Wang, X.; Gornostaeva, T.; Li, X.; et al. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int. J. Coal Geol.* **2014**, *121*, 79–97. [\[CrossRef\]](#)
81. Eskenazy, G.M. Aspects of the geochemistry of rare earth elements in coal: An experimental approach. *Int. J. Coal Geol.* **1999**, *38*, 285–295. [\[CrossRef\]](#)
82. Yu, W.; Algeo, T.J.; Yan, J.; Yang, J.; Du, Y.; Huang, X.; Weng, S. Climatic and hydrologic controls on upper Paleozoic bauxite deposits in South China. *Earth-Sci. Rev.* **2019**, *189*, 159–176. [\[CrossRef\]](#)
83. Huang, B.; Yan, Y.; Piper, J.D.A.; Zhang, D.; Yi, Z.; Yu, S.; Zhou, T. Paleomagnetic constraints on the paleogeography of the East Asian blocks during Late Paleozoic and Early Mesozoic times. *Earth-Sci. Rev.* **2018**, *186*, 8–36. [\[CrossRef\]](#)
84. Shen, M.; Dai, S.; Graham, I.T.; Nechaev, V.P.; French, D.; Zhao, F.; Shao, L.; Liu, S.; Zuo, J.; Zhao, J.; et al. Mineralogical and geochemical characteristics of altered volcanic ashes (tonsteins and K-bentonites) from the latest Permian coal-bearing strata of western Guizhou Province, southwestern China. *Int. J. Coal Geol.* **2021**, *237*, 103707. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.