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ORIGINAL ARTICLE

The abundance, distribution, and enrichment mechanism of harmful trace elements in coals from Guizhou, Southwestern China

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Abstract Coal seams can enrich a variety of harmful trace elements under specific geological conditions. The spatial distribution of harmful trace elements in coal is extremely uneven, and the distribution characteristics of each element content are different. The harmful elements released in the process of coal mining and utilization will cause serious harm to the environment and the human body. It is of great resource significance to study the geochemistry of coal that affects the enrichment and distribution characteristics of harmful trace elements. Based on the domestic and foreign literature on coal geochemistry in Guizhou published by previous investigators, this study counted 1097 sample data from 23 major coal-producing counties in Guizhou Province, systematically summarized the relevant research results of harmful trace elements in the coal of Guizhou, and revealed the overall distribution and enrichment characteristics of harmful trace elements in the coal of Guizhou. The results show that the average contents of Cd, Pb, Se, Cu, Mo, U, V, As, Hg, and Cr in coal of Guizhou are higher than those in Chinese coal and world coal. A variety of harmful trace elements in the coal of Guizhou have high background values, especially in Liupanshui, Xingyi and Qianbei coalfield. The enrichment of various harmful trace elements in the Late Permian coal in Guizhou is mainly related to the combined action of various geological and geochemical factors. The supply of terrigenous debris and sedimentary environment may be the basic background of the enrichment of harmful elements in western Guizhou, while low-temperature hydrothermal activity and volcanic ash deposition may be the main reasons for the enrichment of harmful elements in southwestern Guizhou.

Keywords Harmful trace elements · Distribution characteristics · Enrichment law · Geological and geochemical features · Guizhou

1 Introduction

Coal is a combustible organic rock with complex components, which can enrich various harmful trace elements under specific geological conditions (Li et al. 2018; Vejahati et al. 2010; Wei et al. 2020; Liu et al. 2001a, b). These harmful trace elements will be released into the surrounding environment of the mining area during the development and utilization of coal resources, causing environmental pollution and posing a certain threat to human health (Dai et al. 2012a, b; Tian et al. 2013; Chou 2006). The average abundance of harmful trace elements in coal is relatively low, but due to the huge production and consumption of coal and the cumulative effect of harmful trace elements in the environment (Bai 2004; Cao et al. 2022), the research on the content and enrichment characteristics of harmful trace elements in coal is of great significance.

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At present, direct combustion of coal is the most important form of its utilization, and the harmful substances emitted by coal in the process of combustion and utilization cause serious air pollution. Hazardous substances emitted into the atmosphere by coal combustion include sulfides, nitrides, fly ash, carbon monoxide, carbon dioxide, radioactive particles, various trace metal elements and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) (Tong et al. 2018; Li et al. 2023; Zhou 2006). In recent years, people have gradually realized the importance of sustainable development of resources and environment. While using coal resources, the relevant departments have increased the investment in coal-fired environmental pollution control and strengthened the research on the harm of coal-fired environmental pollution (Wang et al. 2020a, b; Wu et al. 2021). A large number of studies have been carried out on the production status and hazards of harmful inorganic substances such as S, Cl, F, Cr, Be, As, Sb, Se, Pb, and Hg in soot and residues of coal and its combustion products. In recent years, more and more people have realized the serious consequences of the accumulation of coal-fired emissions in the environment and the potential carcinogenic and mutagenic hazards to human health (Chen et al. 2018; Tian et al. 2013; da Silva Júnior et al. 2019; Hussainet al. 2018; Liu et al. 2001a, b). At the same time, harmful trace elements in coal will also be absorbed by plants, or accumulated in the soil, by entering the human food chain, endangering human health (Kiss et al. 1998; Dennis et al. 1997).

Guizhou Province in southern China is rich in coal resources and is famous for "The Jiangnan Coal Sea" (Zhang et al. 2023). However, previous studies have shown that coal in Guizhou Province is rich in various harmful trace elements, such as Cd, Pb, Se, Cu, Mo, U, V, etc. (Dai et al. 2005a; Xie et al. 2017; Liu et al. 2019, 2020; Yang et al. 2006; Yang, 2020). Specifically, environmental pollution and physical health problems in the province (such as coal-fired endemic fluorosis and arsenic poisoning) caused by harmful trace elements such as fluorine and arsenic in coal are frequently reported (Liu et al. 2005; Nie et al. 2004; Leite et al. 2011; Yang et al. 2023; Luo et al. 2011; Wang et al. 2006, 2020; Guo et al. 2021; Ng et al. 2003; Li et al. 2006; Zhang et al. 2007, 2018; Gao et al. 2013; Zheng et al. 2006). For example, Li (2009) conducted a statistical analysis of the prevalence of dental fluorosis and urinary fluoride content in 26 primary school students in urban and rural areas of Liupanshui City, Guizhou Province (Table 1). The results showed that the prevalence of dental fluorosis and urinary fluoride content in the fluorosis area were generally high, mainly affected by the proportion of household staple food coal-dried corn, economy, urban and rural mining areas, urban areas and other living environment changes.

Table 1 The prevalence of dental fluorosis and the mean range of urinary chlorine content in 26 primary school students in urban and rural areas of Liupanshui City, Guizhou Province

Regions (townships)	Number of samples	Prevalence of dental fluorosis ($\times 10^{-2}$)	Urinary fluoride G (mg/L)
Severe fluorosis	188	91.4–100	2.00–7.01
Moderate fluorosis	156	75.2–87.7	1.35–2.94
Mild fluorosis	722	30.7–88.9	0.48–1.75
No fluorosis	385	9.6–28.3	0.40–0.87

Table 2 Arsenic content in some tissues and organs of the human body in the arsenic poisoning area of southwest Guizhou

Organ	Unit	Arsenic content of patients in high disease incidence village	Arsenic content in normal human
Urine	mg/L	0.06–2.47	0.01–0.14
Hair	mg/kg	5.00–14.00	0.01–1.20
Blood	mg/L	0.03–0.41	0.03–0.16
Nails	mg/kg	2.41–63.50	0.12–2.83
Nails	mg/kg	11.30–53.50	0.06–1.20

Nie (1996) statistically analyzed the arsenic content in some tissues and organs of the human body in the arsenic poisoning area of southwestern Guizhou (Table 2). The results showed that the arsenic content of the human body in the ward was higher than that of the normal person, far exceeding the arsenic concentration that can be discharged from the body, and there was serious chronic arsenic poisoning.

The harmful elements in coal from Guizhou are relatively enriched and have the characteristics of great harm, but the overall distribution and enrichment rules are still unclear. Based on the relevant literature published since 1998 and a large number of data statistics, this paper analyzes the content and distribution characteristics of 21 harmful trace elements in Coal from Guizhou. This paper focuses on the analysis of nine relatively enriched harmful trace elements Cd, Pb, Se, Cu, Mo, U, V, As, Hg, and Cr in the coal. The characteristics and laws of the distribution and enrichment of harmful trace elements in the coal are revealed. The research results can provide a reference for the research of coal geochemistry, coalfield geology, ecological environment protection, and other related fields.

2 The overall abundance of harmful trace elements in the coal

According to the average content of corresponding elements in Chinese coal (Dai et al. 2012a) and world coal (Ketris et al. 2009), the enrichment coefficients of the above elements in Guizhou coal were calculated (CC=the ratio of element content in coal to low-rank coal in China or the world) (Dai et al. 2015). Compared with Chinese coal, the CC of F, Hg, Ni, Be, Co, Sb, Sn, Th, TI, and Zn in Guizhou coal is 0.5–2, indicating that the above elements are slightly enriched. The element CC of Cr, As, Pb, Se, Cu, Mo, U and V is 2–5, indicating that the above elements are enriched. Cd element CC > 5, indicating that the element is significantly enriched (Fig. 1). Compared with the world coal, the CC of As, Cr, Hg, Ni, Be, Co, Sb, Sn, and TI elements in Guizhou coal is 0.5–2, indicating that the above elements are slightly enriched. The CC of Pb, Se, Cu, Mo, Th, U, V, and Zn is 2–5, indicating that the above elements are enriched. Cd element CC > 5, indicating that the element is significantly enriched (Fig. 2).

3 The abundance and distribution characteristics of several harmful elements

According to the data of relevant literature, we calculated the arithmetic mean of harmful elements in coal in various regions. The results are shown in Table 3. We calculated the arithmetic mean of the content of harmful elements in coal in each mining area, so as to reveal the distribution characteristics of several metal elements in Guizhou coal in each mining area of the province. The data of the study covers 23 major coal-producing counties or cities in the province. The data show that the most samples are Qianxi (259), Panzhou (238), Zhijin (136), followed by Shuicheng, Liuzhi, Bijie, Xingren, and other regions. These mining areas are rich in coal resources and have a high degree of research. According to the enrichment coefficient of coal in Guizhou and Chinese coal and world coal, we selected Cd, Pb, Se, Cu, Mo, U, V, As, Hg, and Cr to analyze the distribution and enrichment characteristics of elements.

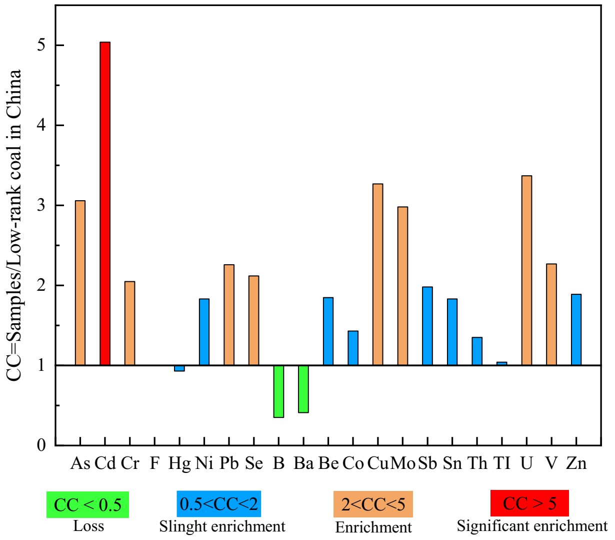

Fig. 1 Enrichment ratio of main harmful elements in Guizhou coal (based on the Chinese average)

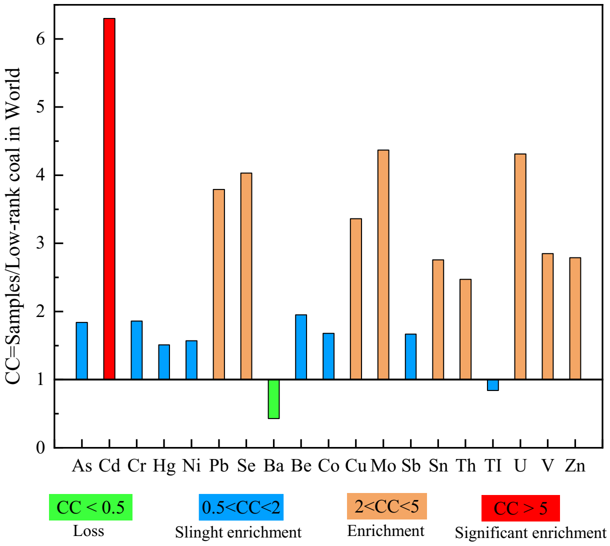

Fig. 2 Enrichment ratio of main harmful elements in Guizhou coal (based on the World average)

3.1 The distribution characteristics of Cd

The content of Cd was significantly enriched in the Late Permian coal in Guizhou. In the 774 samples counted in this paper, the Cd content ranged from 0.10 to 18 μg/g, with an average content of 1.26 μg/g, which was 5 times higher than the average content of 0.25 μg/g in Chinese coal (Dai et al. 2012a), and 6 times higher than the average content of 0.2 μg/g in world coal (Ketris et al. 2009). Cd element is widely distributed in Late Permian coal in Guizhou, and it is the most abundant in Zheng'an mining area of Qianbei coalfield, which is 18 μg/g. The second is Liupanshui coalfield Shuicheng mining area, Xingyi coalfield Pu 'an mining area and Qiandongnan Longli mining area, which are 0.58, 0.73 and 0.52 μg/g, respectively. The content of Cd in the above mining areas is significantly enriched (Fig. 3). Mainly due to the high content of Cd in Zheng'an mining area, the average value of Cd content is large, and the content of Cd in other mining areas except Zheng 'an mining area is generally high. Except for the above mining areas, the Cd content in other mining areas was relatively low, ranging from 0.10 to 0.40 μg/g, with an average of 0.21 μg/g.

Table 3 Average contents of some harmful elements in Late Permian coal from various mining areas of Guizhou (the unit of A_d, $S_{t,d}$ is %, others are μg/g)

Areas	Samples	A_d	S	As	Cd	Cr	F	Hg	Ni	Pb	Se	B	Ba	Be	Co	Cu	Mo	Sb	Sn	Th	TI	U	V	Zn
Panzhou	238	16.82	3.31	35.78	0.26	29.49	109.75	0.07	27.00	18.66	2.93	7.59	103.67	2.01	30.77	63.62	3.21	0.51	5.89	8.91	0.29	2.80	92.46	59.93
Shuicheng	97	21.66	1.50	8.40	0.58	31.20	144.30	0.13	25.80	17.49	6.61	16.42	76.36	3.16	13.39	50.81	2.47	0.66	3.70	18.94	0.29	3.83	113.04	43.93
Liuzhi	65	21.91	2.76	9.93	0.29	21.40	nd	0.19	25.95	10.63	1.06	18.75	145.04	3.16	13.39	50.81	2.47	0.66	3.70	18.94	0.29	3.83	113.04	43.93
Zhenning	2	7.93	4.19	11.29	0.10	7.76	nd	nd	8.02	1.84	nd	nd	18.76	1.67	9.86	34.99	4.64	0.50	1.36	5.20	0.26	3.39	85.20	42.92
Zhijin	136	20.77	1.84	5.44	0.23	18.60	173.18	0.15	17.62	17.08	5.54	30.74	91.77	0.93	7.82	82.11	3.36	0.63	3.67	4.53	0.18	5.71	74.06	31.79
Nayong	11	nd	1.11	2.38	0.18	32.20	179.00	0.09	17.57	11.84	1.19	5.18	90.39	1.00	8.71	85.88	3.51	0.54	2.80	4.81	0.22	6.26	80.31	30.34
Weining	11	10.40	1.77	12.84	0.16	13.68	nd	nd	24.25	12.30	nd	nd	16.94	0.50	1.60	52.00	2.30	0.80	8.90	2.50	0.01	0.80	24.00	42.00
Hezhang	2	nd	nd	nd	nd	nd	nd	nd	2.52	4.11	nd	nd	15.46	1.65	17.25	21.29	2.71	0.94	0.56	1.88	0.45	1.07	37.48	45.35
Bijie	85	23.59	1.98	4.53	0.10	23.47	86.45	0.05	18.63	70.78	1.35	nd	24.62	nd	0.76	nd	nd	nd	0.58	1.80	nd	0.81	12.31	nd
Dafang	16	23.72	1.61	5.22	0.40	40.50	179.58	0.11	20.10	119.84	2.65	8.87	93.48	0.58	8.13	84.76	3.38	1.35	3.90	3.62	0.03	8.24	91.47	55.91
Jinsha	7	23.93	2.31	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.45	12.45	125.25	3.05	0.41	7.10	5.75	0.33	4.89	77.63	152.62
Tongzi	16	15.70	6.99	8.64	nd	26.56	nd	nd	17.49	7.53	10.68	17.08	16.31	nd	nd	nd	nd	nd	nd	3.71	nd	7.71	nd	nd
Zheng’an	4	nd	nd	13.0	18.0	23.0	nd	nd	25.0	42.0	15.0	3.0	6.0	nd	7.66	78.71	16.27	3.31	0.31	6.79	0.51	3.95	50.46	62.64
Pu’an	51	21.96	3.27	13.46	0.73	56.89	63.54	0.42	23.89	17.21	5.82	63.62	124.51	11.00	4.00	24.00	7.00	3.00	5.00	9.00	nd	7.00	36.00	368.00
Qingnong	6	17.17	2.67	10.03	0.20	58.88	85.50	0.12	25.50	5.93	1.15	nd	88.00	1.65	11.14	57.47	17.63	1.00	3.10	6.08	0.17	13.93	137.26	45.00
Xingren	69	18.93	8.06	37.16	0.34	31.49	97.30	0.24	28.36	13.59	1.44	40.44	182.16	0.90	7.68	48.38	34.85	2.00	5.40	3.74	0.15	25.33	155.88	44.50
Zhenfeng	5	nd	nd	61.10	0.27	11.42	nd	nd	21.48	6.28	nd	nd	40.20	1.78	7.40	84.98	18.93	8.56	6.34	8.46	0.22	13.71	101.53	37.31
Xingyi	1	30.67	6.70	17.10	0.10	16.00	nd	nd	54.00	nd	1.90	nd	nd	3.43	3.58	11.84	4.40	3.61	nd	1.87	2.33	12.10	42.75	48.23
Wuchuan	21	21.34	2.47	11.00	1.00	75.87	nd	nd	39.39	46.00	15.71	2.00	16.75	nd	1.70	nd	nd	1.30	nd	4.13	nd	3.50	nd	170.00
Kaili	7	39.48	6.97	nd	nd	nd	nd	nd	47.90	238.00	nd	nd	48.20	8.65	7.56	27.89	9.08	0.00	6.57	13.00	nd	10.47	109.90	108.27
Tianzhu	2	nd	nd	6.61	0.38	nd	nd	nd	31.85	7.76	nd	nd	11.04	19.70	17.50	88.90	19.40	nd	13.80	42.90	1.52	31.90	nd	nd
Longli	2	nd	nd	8.88	0.52	nd	nd	nd	29.10	19.35	nd	nd	19.22	nd	6.02	nd	nd	2.58	1.19	8.52	0.57	11.63	132.75	nd
Qianxi	259	26.28	2.97	23.41	0.10	50.38	182.22	0.09	21.02	27.74	5.48	10.94	133.18	nd	10.82	83.37	8.78	3.31	0.31	7.73	0.30	3.64	106.72	54.46

Note: A_d—ash yield (dry basis); $S_{t,d}$—total sulfur(dry basis); nd—Missing data (See supplementary material for details)

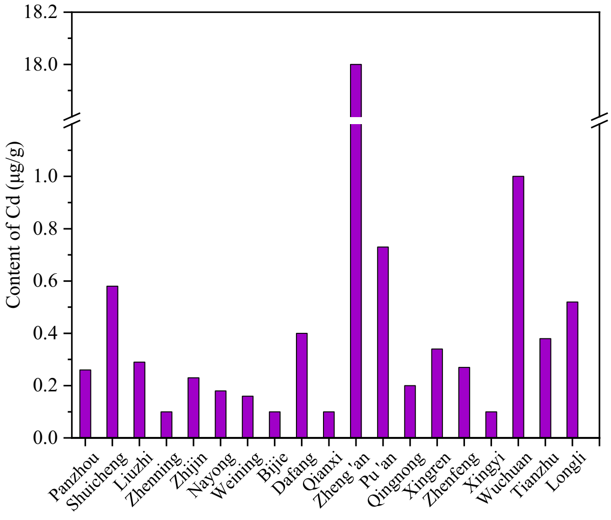

Fig. 3 Average content of Cd element

3.2 The distribution characteristics of Pb

The content of Pb element is enriched. Among the 809 samples counted in this paper, the Pb content ranged from 1.84 to 238 μg/g, with an average content of 34.09 μg/g, which was significantly higher than the average content of 15 μg/g in Chinese coal (Dai et al. 2012a), and higher than the average content of 9 μg/g in world coal (Ketris et al. 2009). The Pb element is widely and unevenly distributed in the Late Permian coal in Guizhou. It is enriched in the Dafang mining area of the northern Guizhou coalfield and the Kaili mining area of the southeastern Guizhou coalfield, which are 119.84 and 238 μg/g, respectively. The second is Bijie, Qianxi, Zheng'an mining area and Xingyi mining area of Qianbei coalfield, which are 70.78, 27.74, 42.00 and 46.00 μg/g, respectively. The content of Pb in the above mining areas is significantly enriched (Fig. 4). Except for the above mining areas, the Pb content in other mining areas ranged from 1.84 to 19.35 μg/g, with an average of 11.29 μg/g, which was slightly lower than the average content of coal in China of 15 μg/g.

3.3 The distribution characteristics of Se

The content of Se element is enriched. Among the 683 samples, the Se content ranged from 0.11 to 19.26 μg/g, with an average content of 5.23 μg/g, which was significantly higher than the average content of 2.47 μg/g in Chinese coal (Dai et al. 2012a) and 4 times higher than the average content of 1.3 μg/g in world coal (Ketris et al. 2009). The distribution of Se element in Late Permian coal in Guizhou is not uniform. Among them, it is more abundant in Zheng'an mining area of Qianbei coalfield and Wuchuan mining area of Zunyi coalfield, which are 15.00 and 15.71 μg/g respectively. The second is Shuicheng mining area of Liupanshui coalfield, Zhijin mining area of Zhina coalfield, Qianxi mining area of Qianbei coalfield and Pu'an mining area of Xingyi coalfield, which are 6.61, 6.65, 5.48 and 5.82 μg/g, respectively. The content of Se in the above mining areas is significantly enriched (Fig. 5). In addition to the above mining areas, the content of Se in other mining areas is relatively low, ranging from 1.06 to 2.93 μg/g, with an average of 1.64 μg/g.

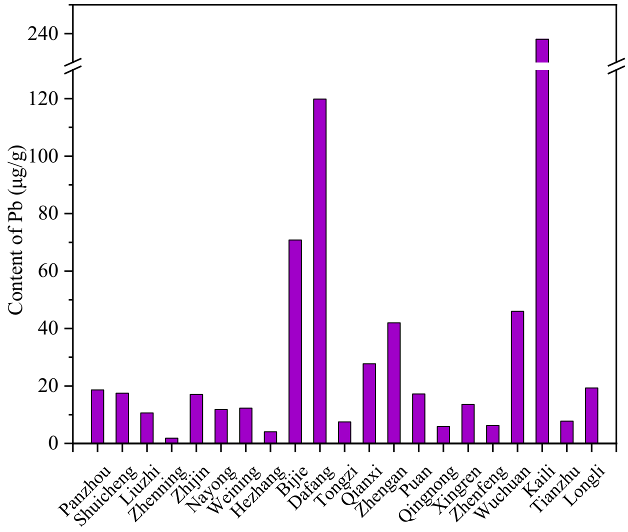

Fig. 4 Average content of Pb element

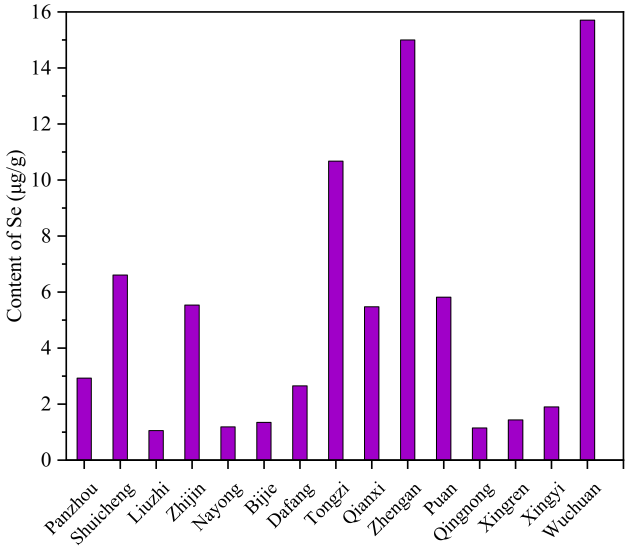

Fig. 5 Average content of Se element

3.4 The distribution characteristics of Cu

The content of Cu element is enriched. Among the 988 samples counted in this paper, the content of Cu varies from 0.03 to 356.00 μg/g, with an average content of 57.17 μg/g, which is significantly higher than the average content of 17.5 μg/g in Chinese coal (Dai et al. 2012a), and higher than the average content of 17 μg/g in world coal (Ketris et al. 2009). The distribution of Cu element in Late Permian coal in Guizhou is uneven, and it is the most abundant in Dafang mining area of Qianbei coalfield, which is 125.25 μg/g. The second is Zhijin and Nayong mining area of Zhina coalfield, Bijie and Qianxi mining area of Qianbei coalfield, Xingren mining area of Xingyi coalfield, Kaili mining area of Qiandongnan coalfield, which are 85.88, 73.00, 83.37, 78.71, 84.98 and 88.90 μg/g, respectively. The content of Cu in the above mining areas is abnormally enriched (Fig. 6). In addition to the above mining areas, the Cu content in other mining areas ranged from 9.22 to 63.62 μg/g, with an average of 36.50 μg/g, which was significantly higher than the average content of Cu in Chinese coal and world coal. This shows that the overall background value of Cu in Guizhou coal is higher.

3.5 The distribution characteristics of Mo

The content of Mo element is enriched. Among the 898 samples counted in this paper, the content of Mo ranges from 0.09 to 59.00 μg/g, with an average content of 9.18 μg/g. The average content is significantly higher than the average content of 3.08 μg/g of Chinese coal (Dai et al. 2012a) and 2.1 μg/g of world coal (Ketris et al. 2009). The distribution of Mo element in Late Permian coal in Guizhou is not uniform. It is the most enriched in Qinglong mining area of Xingyi coalfield, which is 34.85 μg/g. The second is Tongzi mining area of Qianbei coalfield, Pu'an and Xingren mining areas of Xingyi coalfield, Kaili mining area of Qiandongnan coalfield, which are 17.38, 16.27, 17.63, 18.93 and 19.40 μg/g, respectively. Qianxi and Zheng'an mining areas in Qianbei coalfield and Wuchuan mining area in Zunyi coalfield were 8.78, 7.00 and 9.08 μg/g, respectively. The content of Mo element in the above mining areas is abnormally enriched (Fig. 7). In addition to the above mining areas, the Mo content in other mining areas ranges from 0.76 to 4.64 μg/g, with an average of 3.14 μg/g, which is slightly higher than the average content of Mo in Chinese coal and world coal. The overall background value of Mo in Guizhou coal is higher.

3.6 The distribution characteristics of U

The content of U element is enriched. Among the 1073 samples counted in this paper, the content of Mo ranges from 0.03 to 45.00 μg/g, with an average content of 8.19 μg/g. The average content of is 3 times higher than the average content of 3.43 μg/g of Chinese coal (Dai et al. 2012a), and 4 times higher than the average content of 1.9 μg/g of world coal (Ketris al. 2009). U element is widely and unevenly distributed in Late Permian coal in Guizhou. It is enriched in Kaili mining area of Qiandongnan coalfield and Qinglong mining area of Xingyi coalfield, which are 31.90 and 25.33 μg/g, respectively. The second is Pu'an, Xingren and Zhenfeng mining areas in Xingyi coalfield, Wuchuan mining area in Zunyi coalfield, Tianzhu mining area in Qiandongnan coalfield, which are 13.93, 13.71, 12.10, 10.47 and 11.63 μg/g, respectively. Bijie, Jinsha and Zheng'an mining areas in Qianbei coalfield and Longli mining area in Qiandongnan

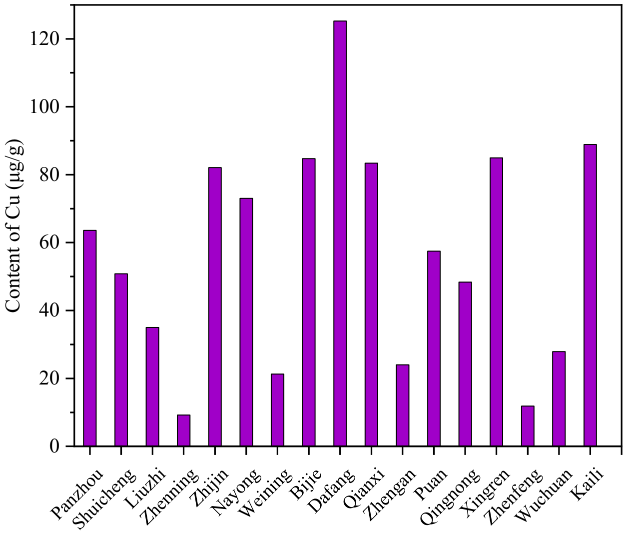

Fig. 6 Average content of Cu element

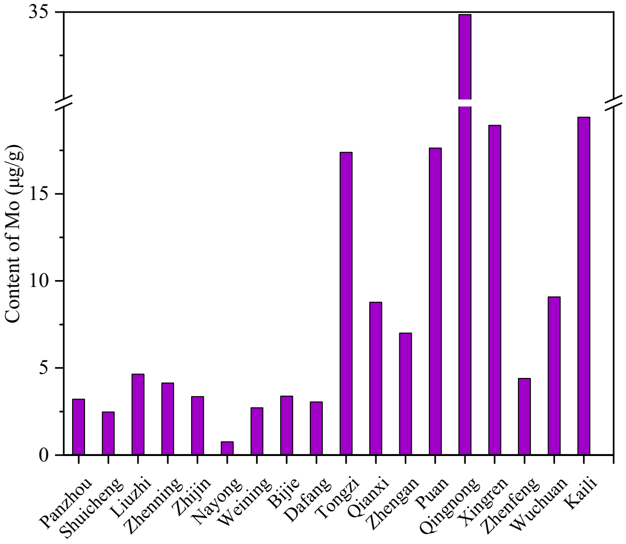

Fig. 7 Average content of Mo element

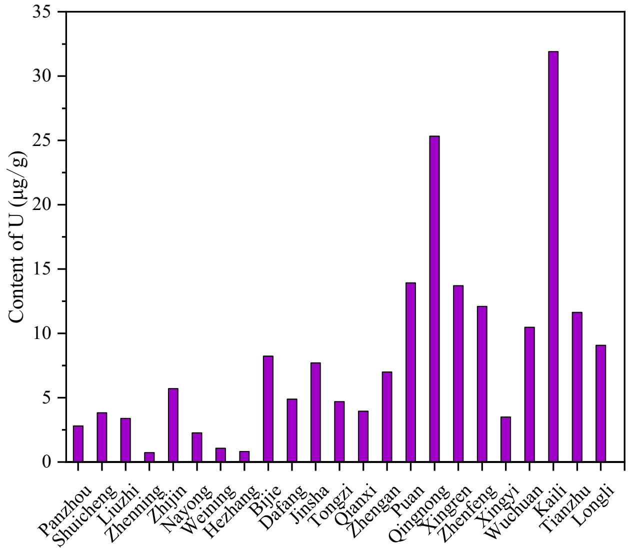

Fig. 8 Average content of U element

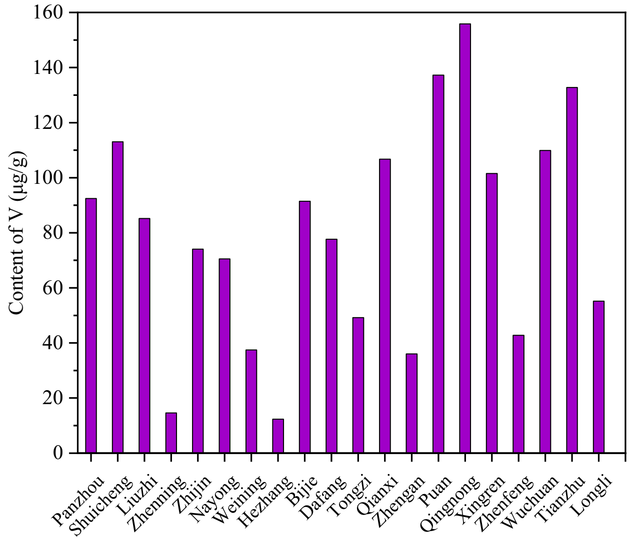

Fig. 9 Average content of V element

coalfield were 8.24, 7.71, 7.00 and 9.08 μg/g, respectively. The content of U element in the above mining areas is significantly enriched (Fig. 8). Except for the above mining areas, the U content in other mining areas ranges from 0.73 to 5.17 μg/g, with an average of 2.87 μg/g, which is higher than the average content of U in Chinese coal and world coal. The overall background value of U in Guizhou coal is higher.

3.7 The distribution characteristics of V

The content of V element is enriched. Among the 1034 samples counted in this paper, the V content ranged from 0.03 to 396.67 μg/g, with an average content of 79.80 μg/g. The average content is significantly higher than the average content of Chinese coal 35.1 μg/g (Dai et al. 2012a), higher than the average content of the world coal 28 μg/g (Ketris et al. 2009). The distribution of V element in Late Permian coal in Guizhou is uneven. Among them, Qinglong mining area in Xingyi Coalfield is the most enriched, which is 155.88 μg/g. Followed by Panzhou, Shuicheng and Liuzhi mining areas of Liupanshui coalfield, Zhijin and Nayong mining areas of Zhina coalfield, Bijie, Dafang and Qianxi mining areas of Qianbei coalfield, Pu'an and Xingren mining areas of Xingyi coalfield, Wuchuan mining area of Zunyi coalfield, Tianzhu mining area of Qiandongnan coalfield. They were 92.46, 113.04, 85.20, 80.31, 70.52, 91.47, 106.72, 77.63, 137.26, 101.53, 109.90, 132.75 μg/g, respectively. Tongzi mining area in Qianbei coalfield and Longli mining area in Qiandongnan coalfield are 49.25 and 55.15 μg/g respectively. The content of element V in the above mining areas is abnormally enriched (Fig. 9). In addition to the above mining areas, the relative content of V in other mining areas is relatively low. The content range is 12.31–42.75 μg/g and the average value is 27.86 μg/g, which is lower than the average content of V in Chinese coal and world coal.

3.8 The distribution characteristics of As, Hg and Cr

The contents of the seven elements in the above statistics showed significant enrichment and enrichment. In addition, As, Hg and Cr are important harmful trace elements in coal, which are classified as Class I by the National Resources Committee of the United States. Therefore, it is necessary to analyze the enrichment and distribution characteristics of As, Hg and Cr.

Compared with Chinese coal, the content of As element is enriched. Compared with the world coal, the content of As element is slightly enriched. Among the 980 samples counted in this paper, the As content ranged from 0.18 to 181.09 μg/g, with an average content of 15.31 μg/g. The average content is significantly higher than the average content of Chinese coal 5 μg/g (Dai et al. 2012a), higher than the average content of the world coal 8.3 μg/g (Ketris et al. 2009). The distribution of As element in Late Permian coal in Guizhou is not uniform. It is most enriched in Zhenfeng mining area of Xingyi coalfield, which is 61.10 μg/g. The second is Panzhou mining area of Liupanshui coalfield, Xingren mining area of Xingyi coalfield and Qianxi mining area of Qianbei coalfield, which are 35.78, 37.16 and 23.41 μg/g respectively. The content of V element in the above mining areas is abnormally enriched (Fig. 10). In addition to the above mining areas, the V content in other mining areas ranges from 2.38 to 17.10 μg/g, which is generally higher than the average content of As in Chinese coal and

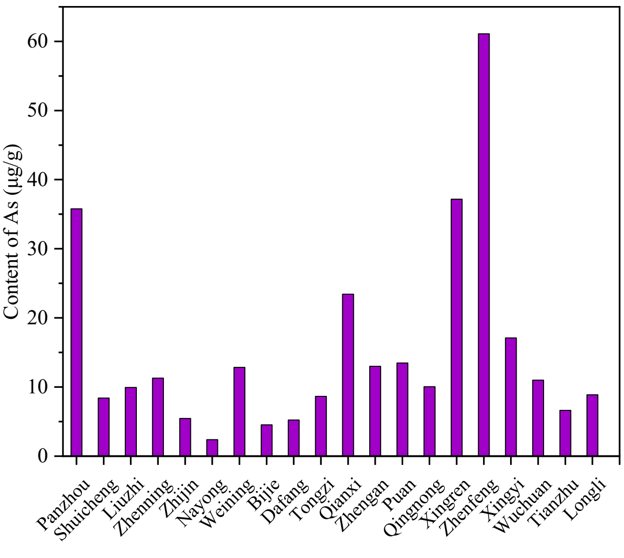

Fig. 10 Average content of As element

world coal. Therefore, the overall background value of As in Guizhou coal is higher.

The content of Hg element is slightly enriched and mainly enriched in Xingyi mining area. Among the 315 samples, the Hg content ranged from 0.03 to 0.75 μg/g, with an average content of 0.15 μg/g, which was slightly lower than the average content of 0.163 μg/g in Chinese coal (Dai et al. 2012a) and higher than the average content of 0.1 μg/g in world coal (Ketris et al. 2009). The distribution of Hg element in Late Permian coal in Guizhou is not uniform. Among them, Pu 'an mining area in Xingyi coalfield is the most enriched, which is 0.42 μg/g, the second is Xingren mining area in Xingyi coalfield and Liuzhi mining area in Liupanshui coalfield, which are 0.24 and 0.19 μg/g, respectively. The content of Hg in the above mining areas is abnormally enriched (Fig. 11). In addition to the above mining areas, the average content of Hg in other mining areas is relatively low. The range is 0.05–0.12 μg/g, which is lower than the average content of Hg in Chinese coal and world coal.

Compared with Chinese coal, the content of Cr element is enriched. Compared with the world coal, the content of Cr element is slightly enriched. Among the 722 samples in this paper, the Cr content ranged from 0.01 to 154.67 μg/g, with an average content of 30.49 μg/g, which was significantly higher than the average content of 15.4 μg/g in Chinese coal (Dai et al. 2012a), and higher than the average content of 17 μg/g in world coal (Ketris et al. 2009). The distribution of Cr element in the Late Permian coal in Guizhou is not uniform. Among them, the Wuchuan mining area in Zunyi coalfield is the most enriched, which is 75.87 μg/g, followed by Pu 'an and Qinglong mining areas in Xingyi coalfield and Dafang mining area in Qianbei coalfield, which were 56.89, 58.88 and 40.50 μg/g, respectively. Panzhou and Shuicheng mining areas in Liupanshui coalfield, Nayong mining area in Zhina coalfield and Xingren mining area in Xingyi coalfield are 29.49, 31.20, 32.20 and 31.49 μg/g, respectively. The Cr element content in the above mining areas is abnormally enriched (Fig. 12). In addition to the above mining areas, the content of Cr in other mining areas is 7.76–23.47 μg/g, which is generally higher than the average content of Cr in Chinese coal and world coal. It shows that the overall background value of Cr in Guizhou coal is higher.

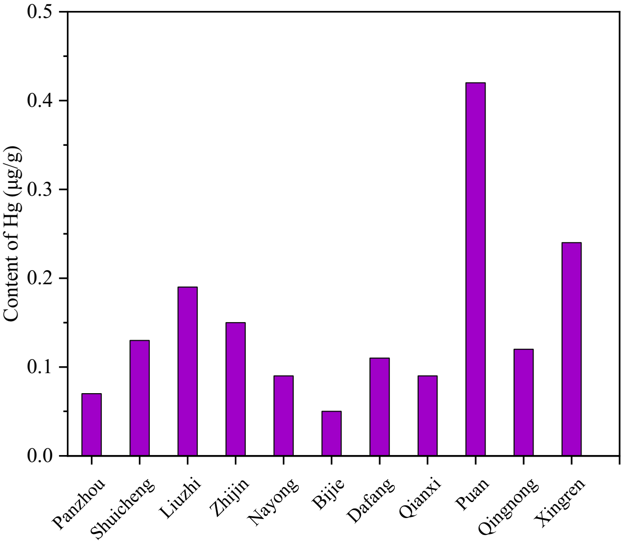

Fig. 11 Average content of Hg element

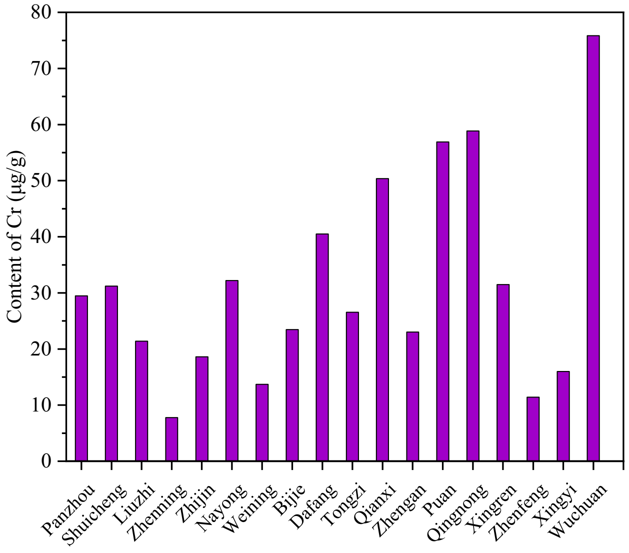

Fig. 12 Average content of Cr element

4 Enrichment mechanism discussion

The enrichment of trace elements in coal is the result of a variety of geological and geochemical factors (Dai et al. 2004, 2008, 2012a; Ren et al. 2006; Nechaev et al. 2020). Cheng (2015) studied the enrichment characteristics of trace elements in Late Permian coal in Liupanshui coalfield, Guizhou Province. It was found that the abundance of trace elements in coal was affected by many factors, such as terrigenous clastic supply, sedimentary environment, volcanic ash deposition, low-temperature hydrothermal action and so on.

The supply of terrigenous debris will affect the content of trace elements in coal. This effect will inherit the element content characteristics of the original rocks or weathering products in the terrigenous area, and is related to the transport distance of clastic materials. The terrigenous clastic material source area of the coal-accumulating basin in western Guizhou is the Kangdian ancient land covered with thick Emeishan basalt (Xu et al. 2003; Liu et al. 2022; Xu et al. 2007; Nie et al. 2004). The contents of Cr, V, Cu, Zn, Co, U and Th are high in Emeishan basalt and weathering products (Xiao et al. 2004). It may be a factor that leads to the enrichment of these harmful elements in coal in western Guizhou. Cheng (2013) showed that Cu, Zn, V and other elements were enriched in the Late Permian coal in Bijie area. The enrichment reason may be directly related to the supply of weathering products of Emeishan basalt in the continental source area (Kangdian ancient land). And the content of these elements in coal in Bijie area has the characteristics of high northwest and low southeast. It may be due to the fact that the northwest region is close to the source area.

The effect of sedimentary environment on the enrichment of trace elements in coal is mainly manifested by seawater. The seawater will not only change the physical and chemical properties of the coal-accumulating environment and lead to element enrichment, but also enter the coal-forming site and directly input inorganic matter. The advance and retreat of seawater and the strength of seawater dynamics will also affect the supply of terrigenous clastic materials (Ren et al. 2006; Yang et al. 2011). The Late Permian sedimentary environment in western Guizhou is dominated by continental, marine-terrigenous and marine sediments from west to east (Xu et al. 2003). The delta plain is dominated by sedimentary environment. However, Zhijin, Nayong, Qianxi, Liuzhi and other places in the southeast are close to the ocean, and the sedimentary environment is dominated by interdistributary bay, lower delta plain and tidal flat (Yang 1989; Shao 1998; Wang 2011a, b). Ren et al. (1999) compared and studied the trace element characteristics of the late Permian Longtan Formation coal, Liuzhi Longtan Formation coal and the late Permian Changxing Formation coal in Sanjiaoshu, Panxian, Guizhou. The above three sedimentary environments are the upper delta plain environment, the lower delta plain environment and the limited carbonate platform tidal flat environment. With the increase of the influence of seawater on the coal-forming environment, the trace elements such as U, V and Mo in coal increase significantly. Cheng (2015) found that the enrichment of Cr, Mo, V, Li, Rb, Ba, Sc, Cd and Sb in coal seams in Liupanshui coalfield was significantly affected by seawater. When the seawater effect is strong, its concentration increases, and when the seawater effect is weak, it decreases. In addition, according to the calculation of Table 1 data, the Th/U of coal seams in the northwest mining area of Guizhou is 1.76–4.95 (average 3.05), and the Th/U of coal seams in the southeast mining area is 0.44–4.95 (average 1.68). There are great differences in the characteristics of element content in coal seams in different sedimentary environments. It shows that the sedimentary environment may be the influencing factor of the enrichment of some harmful trace elements in coal in western Guizhou.

The low-temperature hydrothermal action caused by magmatic activity may have an impact on the abnormal enrichment of trace elements in coal. Previous studies have reported that the coal seams affected by low-temperature hydrothermal activity in western Guizhou are mainly concentrated in the triangular fault depression area controlled by the Shuicheng-Ziyun fault, the Shizong-Guiyang fault and the Nanpanjiang fault in southwestern Guizhou (Ren et al. 1999; Zhang et al. 2002, 2004; Dai et al. 2005b; Yang et al. 2006) and the Zhina coalfield in Bijie (Dai et al. 2004, 2006). The average values of As, Hg, Sb and Sn in coal seams of Pu'an, Qinglong, Xingren, Zhenfeng and Xingyi in southwestern Guizhou are as high as 27.77, 0.26, 3.63 and 4.96 μg/g, respectively. The average value is significantly higher than that of other mining areas in the province and the average value of Chinese coal and world coal. The southwestern Guizhou area is the concentrated distribution area of typical low-temperature hydrothermal deposits such as Au, Sb, Hg and TI, and the strata (Dachang layer) mainly developed by these minerals are close to the coal-bearing rock series. It shows that the enrichment of harmful elements in coal in southwestern Guizhou may be related to low-temperature hydrothermal action. In addition, the volcanic activities in western Guizhou were frequent during the Late Permian, and the Emeishan basalt erupted many times, resulting in a large area of volcanic ash subsidence. Volcanic eruption and late Permian coal-forming are overlapped in time, so a large amount of volcanic ash has been deposited into the coal-forming environment many times. Volcanic ash-altered clay rock, tuff and its influence on trace element anomalies in Late Permian coal in South China are also frequently reported (Liu et al. 2022; Dai et al. 2010). For example, ' carbonaceous volcanic gel ' was identified in the Late Permian coal seams in Zhijin and Qinglong in western Guizhou (Dai et al. 2003; Li et al. 2005).

Coal can be classified into four categories based on its degree of metamorphism, in descending order: anthracite, bituminous, sub bituminous, and lignite. In Guizhou Province, the Liupanshui region is mainly rich in bituminous coal (mainly coking coal), while regions such as Bijie, Xingyi and Zunyi mainly produce anthracite coal (Xu et al. 2003). As shown in Table 3, coal from Liupanshui is mainly rich in As、Cd、Cr、Ni、Pb、Co、Cu、Sn、Th、U、V, coal from Bijie is rich in Cr、Ni、Pb、Co、Cu、Mo、Sb、Sn、Th、U、V, while coal from Zunyi is rich in As、Cd、Cr、Ni、Pb、Se、Co 、Cu、Mo、Sn、Th、U、V. It seems that different types of coal have different element enrichment characteristics. However, even the same type of coal has different element enrichment characteristics, for example, coal in various mining areas from Xingyi and Bijie are all of anthracite, but their differences in element enrichment characteristics are significant. This implies that the relation between coal type and trace element enrichment is complex and needs more investigation.

In summary, there are many factors affecting the enrichment of harmful trace elements in coal. As shown in Fig. 13, the supply of clastic materials in the terrigenous area and the change of sedimentary environment (seawater action) and groundwater action have great influence on the enrichment of trace elements in coal. This is the basic background factor for the enrichment of most harmful trace elements. The low-temperature hydrothermal action and volcanic ash deposition mixing mainly affect local areas (such as southwestern Guizhou) or a few coal seams. This is the controlling factor for the abnormal enrichment of some harmful elements such as As, Hg, Sb, Sn and so on.

5 Suggestions and measures for the control of harmful elements in coal

In the process of effective control of harmful trace elements in coal, the following control measures can be taken:

Removal of harmful elements by coal preparation technology. Although wet coal preparation is currently the most widely used method for removing trace elements from coal, it will also cause all or part of the harmful trace elements in coal to dissolve in the solution and precipitate from the coal together with the solution, endangering the environment and causing secondary pollution (Zhao et al. 2017; Ma et al. 2022). The dry high gradient magnetic separation technology of coal not only reduces the ash content of coal, but also reduces the secondary pollution problem of wet coal preparation (Mo et al. 2012; Zhang et al. 2020a, b; Liu et al. 2015). In addition, He (2023) introduced hot air flow and impeller in the gas–solid fluidized bed to realize the integration of lignite dry separation, and used dry physical separation technology to purify typical Chinese bituminous coal (He et al. 2017). Yang et al. (2024) used triboelectric separation to effectively remove harmful trace elements in low-rank coal with different particle sizes, providing another way for the removal of harmful trace elements

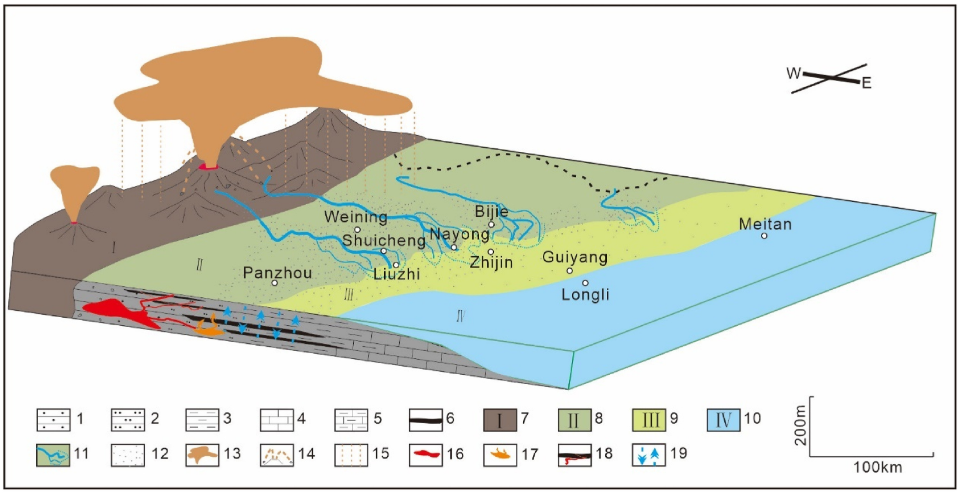

Fig. 13 A general model for trace elements enrichment in Late Permian coals in Guizhou, SW China. 1. sandstone; 2. siltstone; 3. mudstone; 4. limestone; 5. argillaceous limestone; 6. coal; 7. archicontinent; 8. alluvial plains and distributary channels; 9. delta-flat alternations; 10. restricted carbonate platform; 11. distributary channels and delta lobes; 12. terrigenous clastic material; 13. volcanic ash; 14. volcanic breccia; 15. ash deposition; 16. intrusive rock; 17. gas-liquid mass; 18. low-temperature hydrothermal veins; 19. groundwater circulation

in coal. Focusing on the combination of traditional coal preparation methods with new technologies and new means is an important development direction for coal removal of harmful trace elements.

Control the particulate matter in coal combustion. The emission of harmful trace elements in coal during combustion is mainly through ash or fly ash (Izquierdo et al. 2011). Therefore, it is possible to use an electrostatic precipitator device during the combustion of coal to remove this part of the ash or fly ash, improve the dust removal efficiency, and thus reduce the emission of harmful substances (Ohenoja et al. 2017; Qi et al. 2019). Li (2021) studied that the hydrophobic polytetrafluoroethylene (PTFE) membrane can efficiently remove coal fly ash when the relative humidity is 60%. Yuan (2021) reduced harmful heavy metals in fly ash from coal-fired power plants by dry grinding and wet grinding. At the same time, reasonable coal preparation process and the use of clean coal are also the key factors to effectively suppress the emission of fly ash and harmful elements during coal combustion (Park et al. 2021). Reducing the production of fly ash in coal combustion or removing the harmful elements in fly ash cannot only reduce the adverse environmental effect, but also facilitate the subsequent comprehensive utilization of fly ash.

Remove harmful elements from flue gas by using adsorbents. Wang (2022) prepared activated carbon suitable for adsorbing SO_2 and NO_x by activating zinc-containing dust with low-rank coal as raw material. The high-value production of activated carbon can improve the economic benefits of direct reduction of zinc-containing dust. Rodwihok (2023) combined zinc oxide (ZnO) and reduced graphene oxide on zeolite derived from fly ash to prepare a simple upgrading and recycling of FA waste to produce low-cost integrated photocatalytic adsorbents to remove harmful organic pollutants. Wang (2023) prepared a series of Mn-Cr mixed oxide adsorbents by co-precipitation method for the removal of elemental mercury from coal-fired flue gas. Zhang (2024) prepared a new Fe-Ni bimetallic composite adsorbent by hydrothermal calcination method, which can effectively adsorb arsenic in coal-fired flue gas. It is very important to find low-cost and efficient adsorbents for the emission and control of harmful trace elements in coal. At present, metal adsorbents have great potential for development.

6 Conclusion

Compared with harmful trace elements in Chinese coal and world coal, many harmful elements in coal of Guizhou are enriched. Among them, the average content of Cd is 1.26 μg/g, which is 5 times higher than the average content of Chinese coal and 6 times higher than the average content of world coal. It is the only harmful trace element that is significantly enriched in the 21 elements. The Cd-rich areas are Zheng'an, Shuicheng, Pu'an, Longli and other places. The content of Pb element is enriched, and the enrichment area is Dafang, Kaili and other places; the content of Se element is enriched, and the enrichment area is Zheng'an, Wuchuan and other places; the content of Cu element is enriched; the rich areas are Dafang, Zhijin and other places; the content of Mo element is enriched, and the enrichment area is Qinglong, Tongzi and other places; the U element content is enriched, and the enrichment area is Kaili, Qinglong and other places; the content of V element is enriched, and the enrichment area is Qinglong, Panzhou and other places; the content of As element is enriched, and the enrichment area is Zhenfeng, Panzhou and other places; the content of Hg element is slightly enriched, and the enrichment area is Pu'an, Xingren and other places; the content of Cr element is enriched, and the enrichment areas are Wuchuan, Pu'an and other places.

Cd, Pb, Se, Cu, Mo, U, V, As, Hg, Cr and other important harmful trace elements in coal of Guizhou are rich and unevenly distributed. Its enrichment areas are mainly three areas of Liupanshui coalfield, Qianbei coalfield and Xingyi coalfield. The overall research level of northwestern Guizhou coalfield, Zunyi coalfield and southeastern Guizhou coalfield is low, so the amount of data available is relatively small. The coal geochemical characteristics of these three coalfields can be further studied.

The supply of terrigenous debris, sedimentary environment, volcanic ash deposition, low temperature hydrothermal and other geological and geochemical factors are the main factors for the enrichment of trace elements such as As, Hg, Cr, Cd, Pb and Se in the Late Permian coal in Guizhou. The supply of terrigenous debris and sedimentary environment may be the basic background factors for the enrichment of the most harmful trace elements in coal in western Guizhou. The enrichment of harmful elements in coal in southwestern Guizhou may be related to low-temperature hydrothermal activity and volcanic ash deposition.

Some technologies can be used to effectively remove harmful trace elements in coal in coal preparation, combustion process control, flue gas purification and other processes. Correct understanding of harmful elements in coal, rational processing and utilization of coal, and environmental protection, should become a primary task of coal production and coal industry. This is not only of practical significance to the clean and efficient use of coal, but also an important guarantee for ensuring China

’s sustainable development and an effective measure to improve economic efficiency.

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Declarations

Conflict of interest We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, and there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript.

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