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Original Paper

Geochemical Evaluation of Enrichment of Rare-Earth and Critical Elements in Coal Wastes from Jurassic and Permo-Carboniferous Coals in Ordos Basin, China

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Coal waste is a potential source of rare-earth elements (REEs) and some economically critical elements recovery. The present study reports the abundance and enrichment of REEs and critical elements in the Hancheng Permo-Carboniferous (Weibei coalfield) and Binxian Jurassic coals (Huanglong coalfield) of Shaanxi, China. The Binxian coal is distinctly enriched in all REEs. The Hancheng coal is enriched in Y, Ce, Sc, La, Yb, Nd, Pr, Gd, Er, Sm and Dy and depleted in Lu, Eu, Ho, Tb and Tm, compared with that of the average earth's crust abundance (ECA), world coal and the US coal. In the Binxian raw coal, the REEs contents, namely Sc 13.8, Y 13.1, La 27.8, Ce 48.49, Sm 4.1, Nd 22, Eu 0.8, Gd 3.8, Pr 5.43, Dy 2.5, Er 1.4 and Yb 1.3 in mg kg^{-1}. The contents (mg kg^{-1}) of REEs in the Hancheng raw coal were Sc 8.8, Y 18.6, La 34.8, Ce 60.2, Nd 26, Yb 1.8, Eu 01, Pr 6.71, Sm 5.3, Dy 3.4, Tb 0.66, Er 1.9 and Gd 5.16. The contents (mg kg^{-1}) of critical elements in the Binxian raw coal were Cr 30.8, Pb 41.5, Ni 49.7, Cu 35.7, Ba 257.9, V 51.7, Zn 63.1, Li 135, Ga 20.6, U 2.9, Th 10.2 As 12.7, Al 98,887, Fe 23,916 and Ti 4289. The contents (mg kg^{-1}) of critical elements in the Hancheng coal were Cr 384, Pb 56.1, Ni 93.9, Cu 49.5, Ba 371, V 90.7, Zn 7653, Li 183, Ga 35.9, U 4.9, Th 17.7, As 10.1, Al 108,344, Fe 20,433 and Ti 2873. The contents of REEs in the Binxian and Hancheng coals were not in a promising range, whereas some of the critical elements were highly abundant. The Al_2O_3/TiO_2 ratio indicated that the Ordos Basin sediment was derived from intermediate-felsic rocks with a slight variation ($r = 0.98$). The Eu and Gd show positive anomalies with negative Ce anomalies almost in all the samples. The positive anomalies of Gd represent the intrusion of hydrothermal fluid with possibly Ba interference in the Binxian coal. The high volatile matter in the Binxian coal reflects bituminous to anthracite coal, whereas the low volatility of the Hancheng coal reflects peat to lignite coal. The recovery of the REEs and critical elements as a by-product from these coals may not only increase the revenue but will also lead to an improvement in the environmental quality.

KEY WORDS: China, Coal ash, Jurassic coal, Permo-Carboniferous coal, Rare-earth recovery, Critical elements.

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INTRODUCTION

China has been playing a dominant role in the mining and production of rare-earth elements (REEs), more than the USA, Japan and all other countries combined (USGS 2017). The local consumption of REEs in China, as well as the exports of REEs from China to the rest of the world, has increased significantly over the past two decades (90%) (Alonso et al. 2012; Kynicky et al. 2012). In 2018, China extracted 100.2 million tons (Mt) of REEs, whereas the rest of the world extracted only 74.5 Mt.

China is currently the major world supplier of REEs, exporting more than 90% of REE consumption to the global markets (Franus et al. 2015). However, in 2010–2012, China imposed restrictions on its exports of REEs, reducing its output by 40% as compared with 2008 (Massari and Ruberti 2013). Haque et al. (2014) reported that China has almost all of the REE mines with greater than 55% reserves and > 90% exporting quantity. However, continuous mining in China holds approximately 85% (REEs) of the total world production (Du and Graedel 2011; USGS 2017). All these REE mines are land-based deposits, and some of the REEs are available from coal waste and coal combustion products, which have not been extracted until now (Lai Quang et al. 2019).

North China, especially in the Ordos Basin, is a major coal resource hub producing huge amounts of coal wastes, which are also potential sources of REEs (Chen 2007; Dai et al. 2012b; Feng et al. 2017; Hussain et al. 2018). In north China, most of the coal hubs, e.g., Ordos Basin belong to the Permian and Carboniferous age, are exemplified by the Junger, Dongcheng and Daqingshan coalfields, which are major potential sources of REEs and other strategically important critical elements (Zhao et al. 2012). However, the economic development of these resources has not been sustainable but the demand and price of these critical trace elements are increasing day by day (Franus et al. 2015).

The exploration for metal resources, particularly economic trace elements (such as Pb, Fe, Cu, Ag, Y, platinum group elements and REEs), requires extensive investment and stringent regulatory oversight (Lin et al. 2013). The study of trace elements in coal has attracted much attention because of the availability of critical elements in coal wastes and coal combustion products (Seredin and Finkelman 2008; Seredin and Dai 2012; Hower et al. 2016; Dai and Finkelman 2018; Stuckman et al. 2018). Coal's depositional environment, physical and biochemical processes generally influence the concentration and origin of trace elements. Additionally, during coal exploration, cleaning and disposing of coal combustion products, significant amounts of critical elements are wasted without being utilized (Mastalerz and Drobniak 2012; Equeenuddin et al. 2016). If coal mining and the handling of mining wastes and coal combustion by-products are not handled properly, it could have significant environmental consequences because of the release of toxic trace elements. However, the coal wastes and coal combustion by-products offer a potential source of economically beneficial elements, which might reduce the expenses and environmental hazards related to industrial activities (Norgate et al. 2007; Yang et al. 2008; Dai and Finkelman 2018).

Rare-earth and other trace elements can be used to identify the coal-forming environment and the coal-forming periods, which provide essential information about the nature of rocks, sediments, REE fractions and distribution (Zheng et al. 2007; Dai et al. 2008; Kang et al. 2014). However, REEs can be recovered as by-products from coal and coal-waste products globally (Pires and Querol 2004; Park et al. 2014). Among them, coal deposits in the southwest and some other areas of China and east Russia are of typical significance for REEs extraction (Zhou et al. 2000; Seredin and Dai 2012).

The availability of REEs is at great risk, especially those that have high economic value, low resources and significant uses. There is always a chance of losing precious resources such as REEs and critical elements (e.g., U, Bi, Al, Fe, Ti, Ga, L, and V) into mining wastes (e.g., coal ash, coal gangue and coal slime). Therefore, in this study, we evaluated the abundance and enrichment of REEs and critical elements in the Permo-Carboniferous and Jurassic coals of the mid-Shaanxi Province, China. The present study also investigated the modes of occurrence, geo-accumulation and mass abundance of the rare-earth and critical elements in the different coalfields in Shaanxi Province. This study can be of importance for the identification of the abundance and enrichment of REEs and other economically critical elements, which can help in the identification and exploration of REEs and trace elements in northern Shaanxi Province.

MATERIALS AND METHODS

Regional Geology

Geologically, the Ordos Basin has many major coalfields. However, in the present study, we selected the Huanglong coalfield and Weibei coalfield, which comprise several major and minor coalmines. Huanglong coalfield is situated within 35°2′35″ to 35°5′20″N latitudes and 107°52′43″ to 107°60′44″E longitudes (Fig. 1). The Binxian coalmines are located on the Weibei uplift north of the Ordos Basin, where the coal belt belongs to the Middle Jurassic (Hussain and Luo 2018). In the Huanglong coalfield, the most common and visible strata from bottom to top are Fuping, Yan'an, Jurassic-Zhiluo, Yijun, Luohe, Chihuahua, Cretaceous, Neogene and Quaternary Formations (Ren et al. 2014).

The Weibei coalfield is located within 35°34′ to 35°38′N latitudes and 110°25′30″ to 110°31′28″E longitudes (Fig. 1). The Weibei coalfield, in particular, the Hancheng district is situated southeast of the Ordos Basin, where the geological strata are separated into east and west belts. The eastern belt extends to the Chenghe and Hancheng districts, whereas the western belt extends from Chenghe to Tongchuan and Pubai regions (Yao et al. 2009; Hussain and Luo 2018). The regional stratigraphy is made up of Cambrian (Є1), Ordovician (O2-O3), Jurassic, Carboniferous, Permian, Triassic (T1, T2, and T3), Pliocene and Pleistocene. The Hancheng coal district is comprised of Carboniferous and Permian beds beneath the Quaternary Formation (Hussain et al. 2018; Hussain and Luo 2019).

Sample Collection

Initially, a background survey was conducted on the coal mining and coal-waste dumping places at the Jurassic Binxian coalmines (especially, Anhuagou, Chenjiahe, Lijiahe, Xujiagou, Xiahe, Zhaojin, Dafosi and Jin coalmines) and the Hancheng coalmines (Xiangshan, Xinyukou and Liaoyuan coalmines). Raw coal samples were collected from the mines/collecting places, coal-gangue samples were collected from waste debris, coal slime was collected from the washing and cleaning places, coal ash samples were collected from the power plants, and some coal ashes were generated in the laboratory. Altogether, 111 typical coal and coal-waste samples were collected from the Weibei and Huanglong coalfields (Fig. 1). The representative samples collected from the Weibei coalfield included 18 coal gangue, 7 raw coal, 5 coal ash and 4 coal slime samples (Fig. 1, Supplementary Tables S1 and S2). The samples collected from Binxian coalmines included 39 coal ash, 23 coal gangue, 10 raw coal and 5 coal slime samples (Supplementary Tables S3 and S4). All these samples were placed in geological grade bags and transferred to the Physical and Chemical laboratory of "Institute of Geographic Sciences and Natural Resources Research, UCAS" China for further processing.

Experimental Procedures

All the samples were dried in open air and were pulverized through a vibrating cup mill up to 200 mesh. For the chemical digestion of rare-earth and trace elements, 0.05 g coal/coal-waste samples as well as blank samples and reference geological grade standards (for maintaining quality control) of GBW 07401, GBW 07403 and GBW 07406 were digested with 1:5:5 ml of $HClO_4$, HF and HNO_3. Lids were then placed on the Teflon beakers, and the beakers were kept at 220°C on an electric hot plate until all the samples were digested. The digested samples were then transferred to 25-ml plastic bottles (Hussain et al. 2018). All the elemental contents were determined through ICP-MS and ICP-OES (NSPRC-China 2007; Luo 2011). The reproducibility and precision of the ICP-MS and OES determinations were greater than 98%. The ICP-MS and ICP-OES instruments were operated with detection limits of 0.001 μg l^{-1} and 0.001 mg l^{-1}, respectively.

Quantification Analysis

The quantification of critical elements was performed by using the enrichment factor (EF) model (Eq. 1). The EF model is an economical approach to assess elemental enrichment in the surrounding environment as compared with the specific protocol/required standard level (Du et al. 2018). The quantification of elements as compared with other areas (where the critical elements are enriched) was also determined through the concentration coefficient (CC) method (Eq. 2) (Dai et al. 2017b).

$$EF = \frac{\left(\frac{Ei}{TiO_2}\right)\text{current study}}{\left(\frac{Ei}{TiO_2}\right)ECA} \quad (1)$$

$$CC = Cn/Rc \quad (2)$$

In the above equations, Ei and TiO_2 (mg kg^{-1}) are elemental quantity in samples of the current study and reference value, respectively. ECA is earth crust

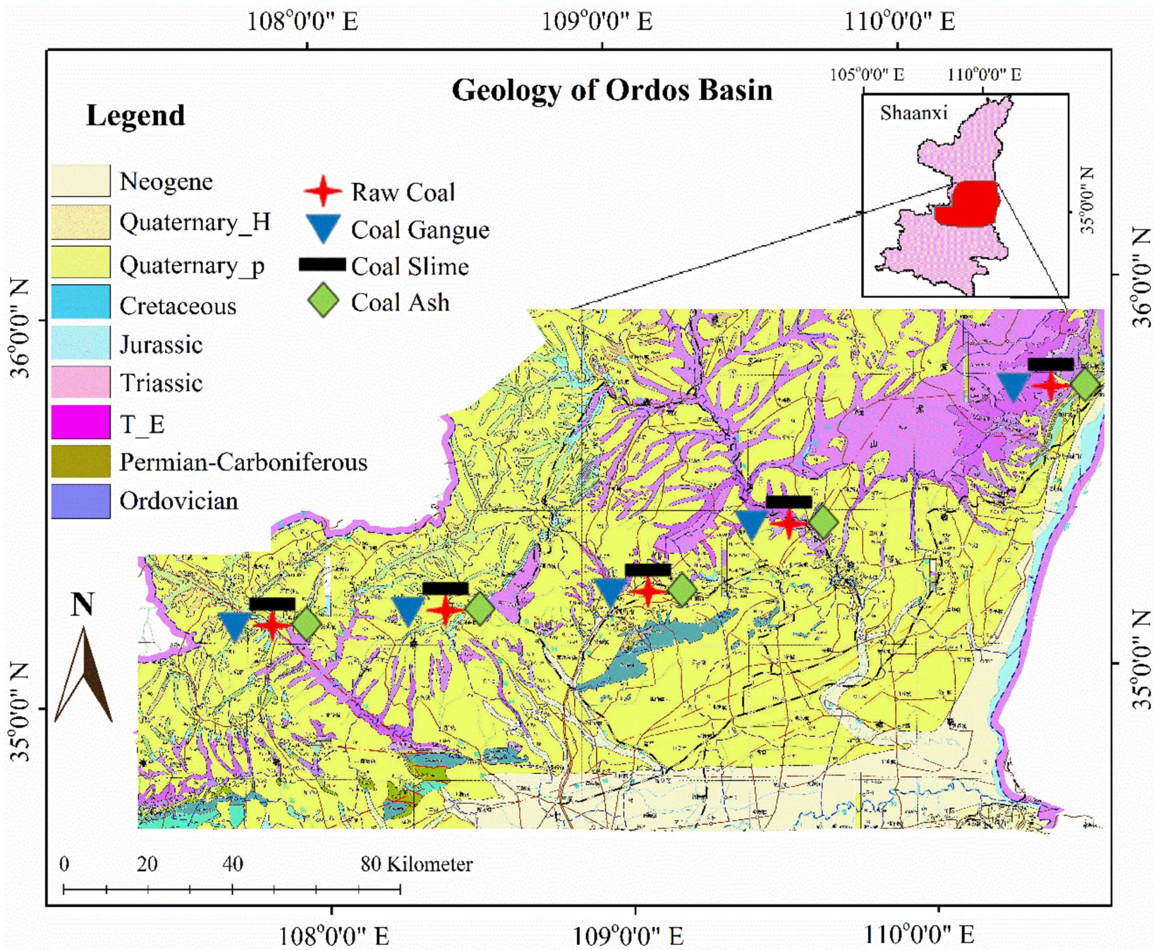

Figure 1. Geological map of the study areas [modified from Bureau of Geology (2018)] showing the locations of samples.

abundance value, as reported by Kennish (2000a), JeffersonLab (2007), Qi et al. (2007) and Hussain et al. (2015). In Eq. 2, Cn represents the analyzed data, and Rc is reference concentration from Ketris and Yudovich (2009) and Dai et al. (2017b). For the elemental estimation in kg/tons, mg kg^{-1} was converted to kg/tons; and, for the EF models, SPSS and Origin-Lab applications were used (Table 1).

Anomalies of redox-sensitive elements such as Eu and Ce and non-redox-sensitive elements such as Gd, La and Y in the coal were normalized with Post Archean Australian Shale (PAAS) using Eqs. 3–5 and normalized values are denoted with "n" (Dai et al. 2017c). Some of the samples were analyzed for mineral identification using a scanning electron microscope (SEM). Before SEM imaging, the powdered coal samples were coated with carbon tape and attached to aluminum stubs to charge the samples during imaging (Bassim et al. 2012). After sample preparation, an SEM image was taken under the required energy, as given in Figure 2.

$$\frac{\mathrm{Ce}_n}{\mathrm{Ce}_n^*} = \mathrm{Ce}_n/(0.5\mathrm{La}_n + 0.5\mathrm{Pr}_n) \qquad (3)$$

$$\frac{\mathrm{Eu}_n}{\mathrm{Eu}_n^*} = \mathrm{Eu}_n/[(\mathrm{Sm}_n + 0.67) + (\mathrm{Tb}_n + 0.33)] \qquad (4)$$

$$\frac{\mathrm{Gd}_n}{\mathrm{Gd}_n^*} = \mathrm{Gd}_n/[(\mathrm{Sm}_n + 0.33) + (\mathrm{Tb}_n + 0.67)] \qquad (5)$$

RESULTS AND DISCUSSION

Geochemistry of Rare-Earth Elements

The coal and coal-waste samples collected from the Jurassic Binxian and Permo-Carboniferous

Table 1. Average abundance (mg kg^{-1}) of REEs and selected trace elements in the studied coals

Elements	Jurassic Binxian coal (C1)				Permo-Carboniferous Hancheng coal (C2)				China-1 (2006)	China-2 (2017)	USA	World	ECA
	Coal	Coal gangue	Coal slime	Coal ash	Coal	Coal gangue	Coal slime	Coal ash	Coal	Coal	Coal	Coal	Coal
Sc	13.8	19.8	15.1	21.2	8.78	8.68	11.9	11.1		3.18	4.2	3.9	22
Y	13.1	15.4	12.6	18.9	18.6	21.6	22.6	26.7		46.1	8.5	8.4	33
La	27.7	36.4	28.7	48.6	34.8	46.5	44.3	48.4	26.9	52.1	12	11	39
Ce	48.5	64.3	49.8	84.3	60.2	79.6	75.9	81.1	50.1	95.1	21	23	66.5
Pr	5.43	7.31	5.68	9.64	6.71	9.07	8.56	9.46		10.7	2.4	3.5	9.2
Nd	21.8	28.9	21.9	37.9	26.1	35.1	33.1	36.9	26.14	40.9	9.5	12	41.5
Sm	4.11	5.29	4.24	7.09	5.31	6.56	6.34	7.20	4.56	6.96	1.7	2	7.05
Eu	0.76	1.02	0.96	1.41	1.01	1.32	1.25	1.42	0.73	0.87	0.4	0.47	2
Gd	3.76	4.74	3.78	6.24	5.16	6.02	5.91	6.72		9.01	1.8	2.7	6.2
Tb	0.51	0.62	0.49	0.79	0.667	0.73	0.75	0.87	0.59	1.34	0.3	0.32	1.2
Dy	2.53	3.09	2.42	3.93	3.43	3.69	3.94	4.69		8.26	1.9	2.1	5.2
Ho	0.52	0.64	0.505	0.78	0.672	0.73	0.77	0.94		1.68	0.35	0.54	1.3
Er	1.43	1.76	1.38	2.12	1.92	2.17	2.25	2.76		5.13	1	0.93	3.5
Tm	0.22	0.28	0.21	0.33	0.27	0.301	0.31	0.39		0.72	0.15	0.31	0.52
Yb	1.34	1.69	1.27	1.96	1.77	2.02	2.08	2.57	1.78	4.83	0.95	1	3.2
Lu	0.19	0.25	0.19	0.27	0.262	0.30	0.30	0.38	0.53	0.69	0.14	0.2	0.5
Cr	30.8	75.9	62.8	71.4	384	326	244	145	16.12	18.3	15	16	102
Pb	41.5	58.6	36.4	59.3	56.1	60.9	56.8	42.9	15.55	4.49	11	7.8	14
Cd	0.25	0.34	0.226	0.38	0.613	1.03	0.84	0.82	0.25	0.47	0.47	0.22	0.15
Co	5.51	10.8	9.89	14.3	11.9	20.1	13.7	13.3	6.88	4.01	6.1	5.1	25
Ni	49.7	81.4	85.2	49.7	93.9	102	96.1	85.7	14.04	9.4	14	13	84
Cu	35.7	61.9	61.0	55.7	49.5	41.8	77.5	51.4	18.39	19	16	16	60
Mo	3.03	2.56	1.93	4.44	7.37	3.27	17.9	7.19	3.72	3	3.3	2.2	1.2
Be	2.79	3.69	2.90	5.63	3.41	3.95	4.39	5.42	2.13	5.89	2.2	1.6	2.8
Ba	257	411	1030	848	371	524	437	703		4.68	170	150	425
Sr	228	195	371	633	147	162	152	453		50	130	110	370
V	51.7	101	93.2	98.6	90.7	96.1	127	122	35.05	52.9	22	25	120
Zn	63.1	107	91.1	104	7652	8484	5419	3824	42.16	14.3	53	23	70
Li	134	105	64.2	179	182	143	263	260		35.3	16	12	20
Tl	1.26	1.01	0.614	1.03	0.40	0.83	0.45	0.919	0.49	1	1.2	0.63	0.85
Cs	2.62	6.30	7.45	7.66	4.20	8.53	6.28	6.28		0.36	1.1	1	3
Ga	20.6	33.9	39.7	49.7	35.9	46.2	44.5	56.2	6.52	10.6	5.7	5.8	19
In	0.06	0.067	0.05	0.073	0.18	0.135	0.57	0.184		0.06	0.3	0.031	0.25
Rb	30.3	75.6	75.3	83.5	57.9	149	97.1	102		1.7	21	14	90
U	2.95	4.40	3.97	5.83	4.95	3.57	5.48	5.74	2.41	4.71	2.1	2.4	2.7
Bi	0.35	0.59	0.53	0.279	0.730	0.87	0.80	1.08		0.19	1	0.97	0.0085
Th	10.2	15.3	11.9	18.6	17.7	14.6	17.2	19.3	5.8	7.72	3.2	3.3	9.6
As	12.7	11.4	6.96	31.8	10.1	10.3	12.9	14.6	3.8	1	24	8.3	1.8
Al	98,886	59,083	75,395	113,731	108,344	110,910	78,486	160,677		21,380	14,818.7		82,300
Fe	23,916	21,857	17,253	40,593	20,433	24,230	23,319	26,202		9232	10,330		56,300
Ti	4289	2653	3606	5154	2873	41.5	25.3	36.45		1319	779	800	5600
SiO2%	64	44.3	46		26.5	37	29.7	43.5					
Volatile%	77	28.3	31.7		44.5	26	38	22					

China-1 Tang and Huang (2004) and Ren et al. (2006), *China-2* Dai et al. (2017b), *USA* Finkelman (1993), *ECA* Kennish (2000b) and JeffersonLab (2007), *World coal* Ketris and Yudovich (2009), *C1* Binxian Jurassic coal samples, *C2* Hancheng Permo-Carboniferous raw coal samples

Hancheng coalmines have almost similar significance and concentration of REEs. In the Binxian coal ash, the average concentrations (mg kg^{-1}) of light-REEs (RECe) were Ce 84, Sc 21.2, La 48.6, Pr 9.6, Nd 37.9, Sm 7.1 and Eu 1.41. The average concentrations (mg kg^{-1}) of RE-Yttrium (REY) were Y 18.9, Gd 6.1, Tb 0.79, Dy 3.9, Ho 0.78, Yb 02, Lu 0.3, Er 2.1 and Tm 0.331. The mode of occurrence of

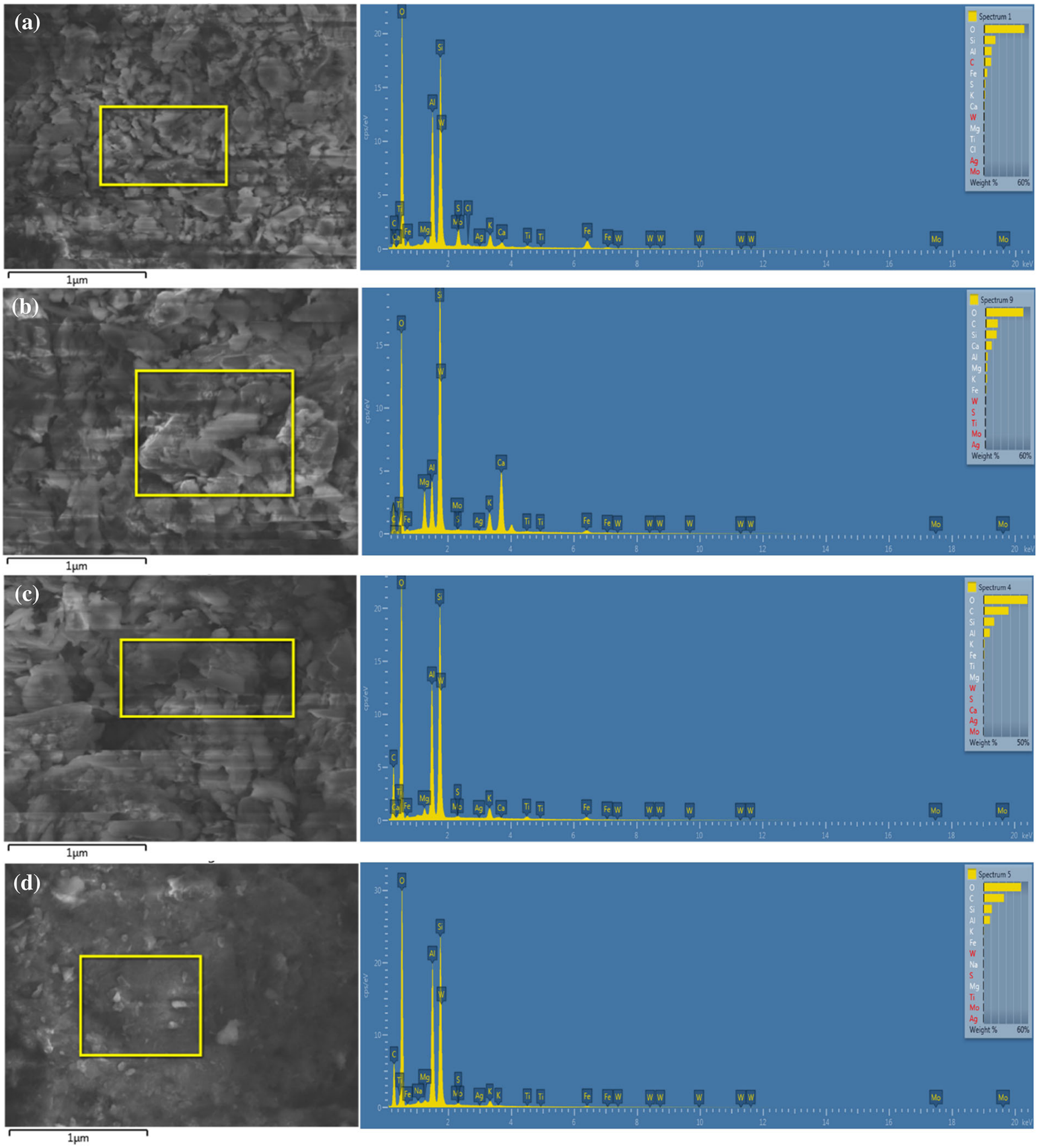

Figure 2. SEM backscattered images of Binxian coal [(a) CG16, (b) C4] and Hancheng coal and coal wastes [(c) HC23, (d) XS9] along with element concentrations.

REEs in the Binxian coalmine is chondrite and some other RE-bearing minerals (Wang 2010). The average concentrations (mg kg^{-1}) of RECe in the Hancheng coal ash were Ce 81.1, Sc 11.1, La 48.4, Pr 9.41, Nd 36.9, Sm 7.2 and Eu 1.42, whereas the average concentrations (mg kg^{-1}) of the REY were Y 26.7, Tb 0.8, Gd 6.7, Dy 4.7, Tm 0.4, Ho 0.94, Er 2.8, Lu 0.4 and Yb 2.57. REEs are mostly associated with rhabdophane, bastnaesite, xenotime as well as rare-earth associated minerals (Dai et al. 2017b), whereas some of the REEs commonly occur as carbonate (parisite, florencite), phosphate minerals (i.e., silico-rhabdophane, xenotime) and some are partially associated with organic matter (Dai et al. 2017a). The concentrations of REEs in the coal ash in the Hancheng and Binxian coals were almost similar but higher than in US coal, world hard coal, the Chinese reference coal and equivalent to the ECA (Table 1).

The distribution of Ce (Cerium) was higher among all REEs and as well as from the US coal, China coal and ECA. The average concentration (mg kg^{-1}) of Ce in the Binxian coal ash was 84.3, raw coal 48.5, gangue 64.3 and coal slime 48.9, whereas the average concentration (mg kg^{-1}) of Ce in the Hancheng raw coal was 60.2, coal ash 81.1, coal gangue 79.6 and coal slime 75.9, which were considerably higher than those reported in previous studies (Finkelman 1993; Ren et al. 2006; JeffersonLab 2007; Finkelman et al. 2018). The mode of occurrence of Ce together with La and Nd is monazite (Smolka-Danielowska 2010; Hower et al. 2013). The high concentration of Ce in Chinese coal is due to rhabdophane, xenotime and other Ce-bearing minerals (Dai et al. 2017b). In the Binxian raw coal, the average concentrations (mg kg^{-1}) of REEs, namely Sc 13.8, La 27.7, Ce 48.5, Pr 5.4, Nd 21.7, Eu 0.7, Y 13, Gd 3.8, Dy 2.5 and Er 1.4, were higher than in US coal (Finkelman 1993) and world coal (Ketris and Yudovich 2009), but lower than those reported by Dai et al. (2017b) (Table 1). In the Hancheng raw coal, the average concentrations (mg kg^{-1}) of REEs, namely Sc 8.8, La 34.8, Ce 60, Pr 6.7, Nd 26, Eu 0.1, Y 18.6, Gd 5.2, Dy 3.4 and Er 2, were higher than in US coal and world coal (Table 1 and Supplementary Table S2). Therefore, the REEs, especially REY, in coal wastes from these coals are important sources for REE extraction. Most researchers have reported that REEs in the Chinese coal are mostly associated with apatite, allanite, alunite, xenotime, florencite, zircon, rhabdophane-cherchite, oxide, phosphate and carbonates (Finkelman 1981; Dill 2001; Dai et al. 2017b), whereas REEs in the Hancheng coal are mostly associated with boehmite minerals (rutile, goyazite, zircon) and Pb-bearing minerals (clausthalite and Se-galena) (Dai et al. 2006).

Mayfield and Lewis (2013) reported that the total quantity of REEs in fly ash collected from the Kentucky power plant was in the range of 1214–1668 mg kg^{-1}, whereas the average quantity of REEs in bottom ash was 1202 mg kg^{-1}. However, the total quantity of REEs in the coal ash of Hancheng coal (243 mg kg^{-1}) and Binxian coal (246 mg kg^{-1}) was equivalent to the ECA (242 mg kg^{-1}) but lower than the fly ash from the Kentucky power plant (Mardon and Hower 2004). Similarly, the quantities of REEs in the coal ash of the Binxian and Hancheng coals were significantly lower than those in the Guizhou coal (Luizhi County) (2491 mg kg^{-1}) (Zhuang et al. 2000) and Poland coal ash (4006 mg kg^{-1}) (Franus et al. 2015). The REEs in the coal ash of the Binxian and Hancheng coals were significantly higher than those reported in the majority of national and international studies (Ren et al. 2006; Zhao et al. 2012; Dai et al. 2018a; Munir et al. 2018).

Compared with the relative abundances of REEs in the US coal, the relative abundances of REEs in the Hancheng and Binxian coals are higher (Fig. 3a). The relative abundances of REEs in the extensively studied ECA are slightly higher than the relative abundances of REEs in the Hancheng and Binxian coals in the current study (Fig. 3b). Compared with the relative abundances of REEs in the study of Ren et al. (2006) and in this current study, there is a close match of Yb and Nd, the depletion of Lu, Tm and Ho and enrichment of REEs (Tb, Eu, Er, Dy, Gd, Pr, Sc, Y, Sm, La, Ce) (Fig. 3c). It is assumed that the REE abundances in the current study (coal and coal waste) represent economically valuable elements. This reasonable assumption suggests that coal and coal wastes are potential sources of critical elements (e.g., Al, Fe, Ga, V, Cu, U, as well as REEs), as has also been proven by many scientists (Meawad et al. 2010; Yao et al. 2014; Joshi et al. 2015; Sahoo et al. 2016; Munir et al. 2018). The amount of REEs (in coal gangue) in the Hancheng coal is slightly higher than in the Binxian coal but higher than in US coal (Finkelman 1993), Chinese reference coal (Ren et al. 2006) and lower than those reported by Dai et al. (2017b).

Geochemistry of Trace Elements

In the proximate analysis, the average sulfur content in the Binxian coal was 2.8% with ash content of 35%, whereas the sulfur content in the Hancheng coal was 2.4% with ash content of 55% (Hussain and Luo 2019). Additionally, the volatile matter of Binxian coal (77%) was higher than that of Hancheng coal (44%). However, the SEM image indicated higher carbon/organics in the Hancheng

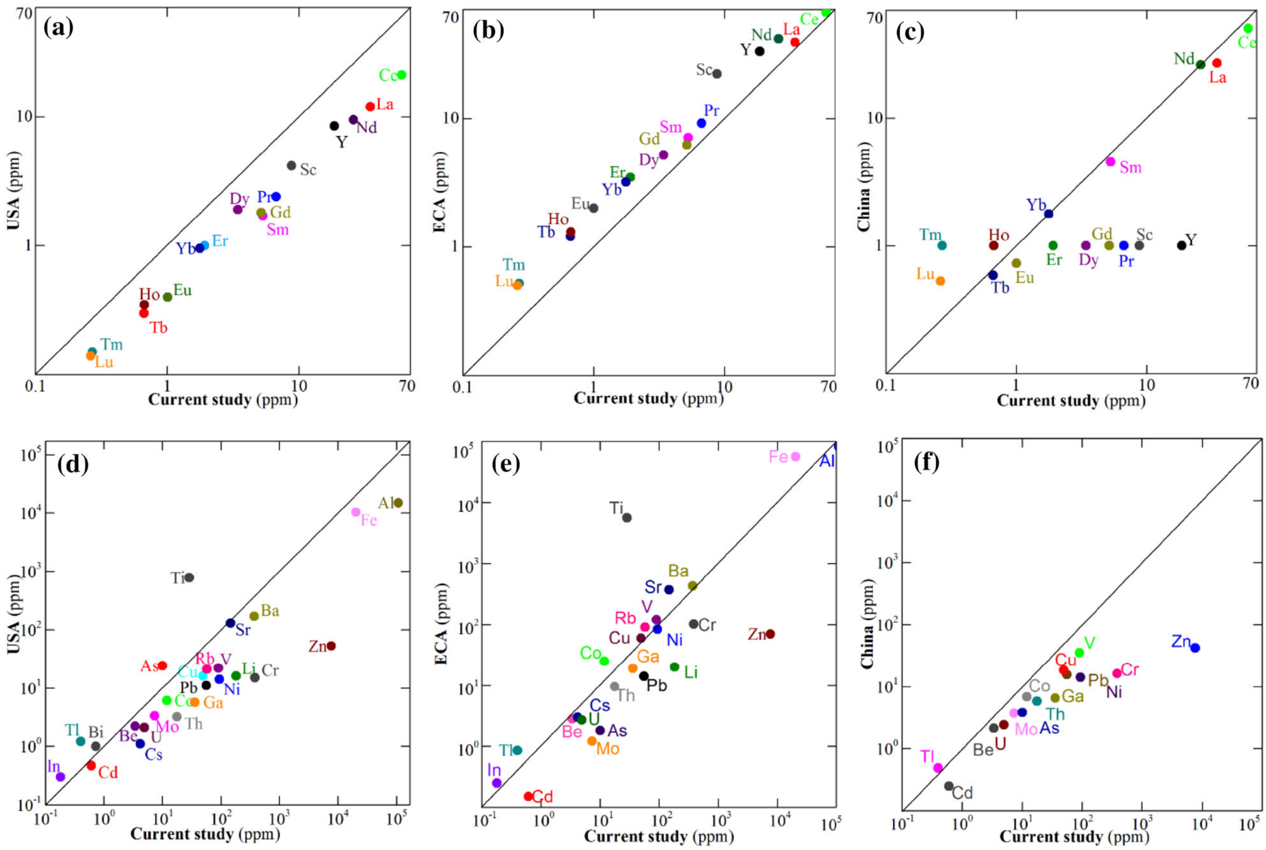

Figure 3. Comparison of abundance of rare-earth and trace elements in the current study with those in other national and international studies (USA: Finkelman (1993); ECA: JeffersonLab (2007); China: Ren et al. (2006)).

coal as compared with the Binxian coal (Fig. 2). The high concentration of volatile matter in the Binxian coal reflects bituminous to anthracite coal (Fig. 2a, b), whereas the low volatile matter in the Hancheng coal reflects lignite coal/peat with clay (Fig. 2c, d).

The critical elements in the different types of samples (i.e., raw coal, coal ash, gangue and slime) collected from the Hancheng and Binxian coalmines are given in Table 1 and Supplementary Tables 3 and 4. In the Binxian raw coal, the average concentrations (mg kg^{-1}) per element were Al 98,887, Fe 23,916, Ti 4289, Li 135, Th 10.2, Ba 258 and Pb 41.5, whereas the average concentrations (mg kg^{-1}) of some critical elements in the Hancheng raw coal were Al 108,244, Fe 20,433, Ti 2873, Li 183, Th 17.7, Ba 371 and Pb 56 (Table 1). The mode of occurrence of Al as illite, gibbsite, zeolite, feldspars, kaolinite, diaspore, phosphate, boehmite, sulfate and crandallite group is common in Chinese coals (Fig. 2) as also reported by Hussain et al. (2018). The total alkali concentration ($Na_2O + K_2O$) in the Binxian coal was 0.9–4.5%, whereas in the Hancheng coal it was 1.6–27%. The lithologies in the Binxian and Hancheng coalmines included sub-alkalis enriched in intermediate to ultrabasic rocks (Fig. 4), which indicated felsic basalt, diorite and other basic rocks. However, the sediments in Permian coal of Sichuan were derived from mafic basalt and other basic rocks (Dai et al. 2016). High alkalis along with siliceous and peraluminous rocks are the sources of REEs (Li et al. 2017). This also proved that in both the Binxian and Hancheng coals, SiO_2 is higher as compared with the total alkalis (Fig. 4). Similarly, the silica composition in the Binxian coal (raw coal 64%, coal gangue 44% and coal slime 46%) was higher than in the Hancheng coal (raw coal 26%, coal gangue 37%, coal slime 29% and coal ash 43%) (Table 1). However, the volatile matter in Carboniferous coalmines (i.e., raw coal 44%, coal gangue 26% and coal slime 38%) was higher than in the Binxian coalmine (i.e., raw coal 77%, coal gangue 28% and coal slime 31%).

Dai et al. (2015a) reported that Fe is commonly associated with eskebornite and ferroselite, whereas Finkelman et al. (2018) reported Fe in carbonate, sulfate, silicate, sulfide, mica and phosphate. Barium (Ba) is commonly associated with gorceixite, barite, carboxylic compounds and baryto-celestine (Bytnar and Makowska 2017; Hussain et al. 2018). The observed raw coal and coal-waste quantities (mg kg^{-1}) in the US coal (Finkelman 1993), namely Al 4818, Fe 10,330, Ti 779, Li 16, Th 3.2, Ba 170 and Pb 11, were extremely lower than in the present work. Moreover, concentrations of Al, Fe, Ti, Th, Ba, Pb, and some other elements in the present study were mostly equivalent to those in ECA (Kennish 2000a; JeffersonLab 2007) (Table 1). Lu et al. (2004) reported that Pb occurred as a carbonate mineral, sulfate, silicate and galena (PbS), whereas Li was associated with tourmalines, mica and clay minerals (Finkelman et al. 2018). Titanium (Ti) mostly occurs with titanium-oxide especially rutile, brookite, anatase and clay (Ward 2002).

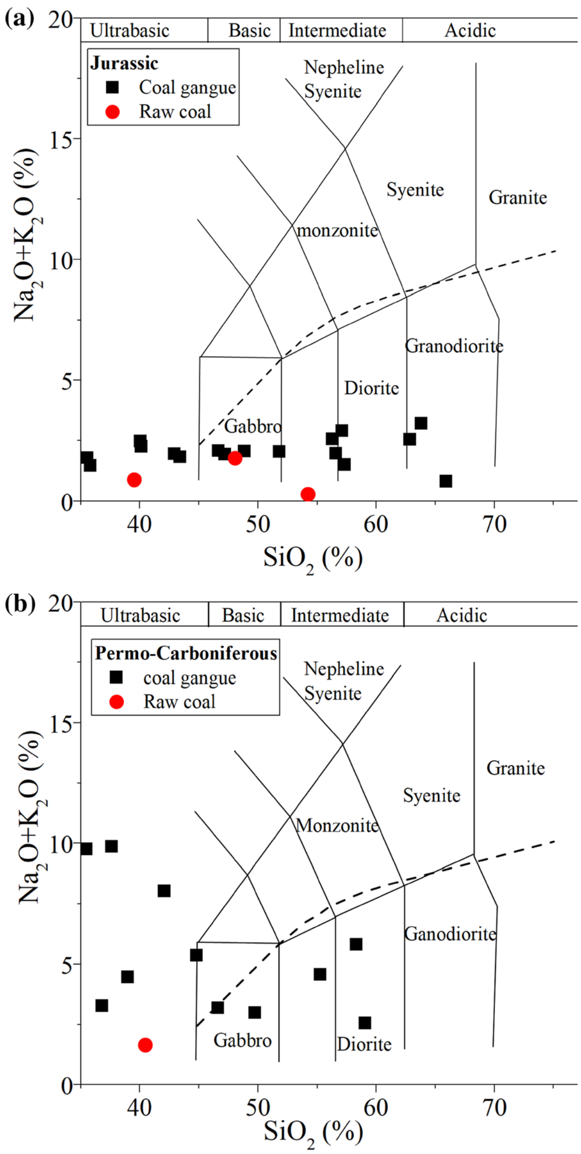

Figure 4. Nature of coal and coal gangue in the Binxian and Hancheng coalfield. The dashed line represents the boundary between alkalic rocks (above) and sub-alkalic rocks (below).

The concentrations (mg kg^{-1}) of Cr in the Binxian and Hancheng coals were 30.8 and 382, respectively (Table 1), which are mostly associated with spinel group and clay minerals (Finkelman et al. 2018), while also exhibiting association with Cr oxy-hydroxide and organics (Huggins et al. 2000). All Cr in coals is trivalent except in coal ash, which is hexavalent (i.e., converted to carcinogenic hexavalent during combustion) (Evans et al. 2011). The concentrations (mg kg^{-1}) of Ni in the Binxian and Hancheng coals were 49.7 and 93.9, respectively, which were commonly associated with organics especially sulfides and clay minerals (Finkelman et al. 2018). The concentrations (mg kg^{-1}) of Cu and Ba in the Binxian coal were 35.7 and 258, respectively, whereas concentrations (mg kg^{-1}) of Cu and Ba in the Hancheng coal were 49.5 and 371, respectively. In coal, Cu commonly occurs with sulfide and chalcopyrite, whereas Ba is mostly bounded in barite, silicate, carbonate, phosphate and organics (Finkelman et al. 2018); in Chinese coal, Cu commonly occurs in gorceixite, barite (Dai et al. 2012b), calcite, goyazite and gorceixite series minerals (Wang 2010). The concentrations (mg kg^{-1}) of Sr in the Binxian and Hancheng coals were 229 and 147, respectively, which are associated with crandallite mineral group, phosphate, barite, celestite, carbonate and clays (Finkelman 1981; Swaine 1990; Finkelman et al. 2018).

In the Binxian coal, the average concentrations (mg kg^{-1}) of critical elements were V 51.7, Zn 63, Li 134, Ga 20.6, Rb 30.3, Th 10 and As 12.7, whereas in the Hancheng coal, they were V 90.68, Zn 7652, Li 182.6, Ga 35.9, Rb 57.9, Th 17.7 and As 10.1. Vanadium and some other trace elements are associated with organic matter and to a lesser extent to illite or mixed illite–smectite (Liu et al. 2015). Zinc is associated with pyrite, mostly bounded with sulfide, and organic compounds (Finkelman et al. 2018) and calcite/dolomite (Wang 2010). Swaine (1990) reported that the mode of occurrence of Zn is sphalerite with organics. However, the current study also observed some important minerals in the Binxian coal (Fig. 2). Uranium is associated with silicate, zircon and phosphate, whereas a small portion may be bound in carbonates (Finkelman et al. 2018). Uranium is mostly bounded with U-minerals, whereas Rb in Rb-minerals, clay, feldspar and illite minerals (Dai et al. 2015b). The mode of occurrence of Mo is chalcophile but commonly associated with organics and slightly inorganic (Wang et al. 2008). Arsenic is mostly associated with arsenopyrite, organic, clay, phosphate (Kang et al. 2011), organically bounded pyrite (Kolker et al. 2000) and getchellite ($AsSbS_3$) (Dai et al. 2016). The mode of occurrence of Ga is boehmite, kaolinite and organic matter (Dai et al. 2018b). The content of these critical elements in the Binxian coal was comparably higher than in the US coal, world coal and some Chinese coals (Finkelman 1993; Tang and Huang 2004; Ketris and Yudovich 2009; Dai et al. 2017b). In the Binxian raw coal, few elements were too low as 0.02–10 mg kg^{-1} (Table 1). The average concentrations of majority of the critical elements in the Hancheng raw coal were, namely Cr 26-fold, Pb 5-fold, Ni 7-fold, Cu 3-fold, V 4-fold, Zn 144-fold, Li 11-fold, Ga 6-fold, Th 6-fold, Al 7-fold, Fe 2-fold and Ti 4-fold, higher than those in the US coal (Table 1).

Comparison between the relative abundance of critical elements in the US coal and the current study raw coals shows that Bi, As, In, Ti and Tl were in the depleted range while all the other critical elements were enriched in the Binxian and Hancheng coals (Fig. 3d). Comparison between the abundance of critical elements in the ECA and the current study raw coals shows that In, Tl Co, Cu, Rb, V, Sr, Ba and Fe were depleted while the other elements were enriched in the current study coals (Fig. 3e). Comparison between the extensively studied critical elements in the current study raw coals and in the Chinese reference coal shows that only Tl is depleted while all other selected trace elements are enriched in the current study coals (Fig. 3f). These observations prove that majority of the critical elements in the currently studied coals have high recoverable ratios. This reasonable dominance of rare-earth and selected critical elements in the Binxian and Hancheng coalmines represent the economic source of China. The relative abundances of the REEs and critical elements in the current study coals are potentially higher than in other regions but also enriched in coal-waste debris in some other regions (Zhuang et al. 2000; Chen 2007; Fan et al. 2014; Haque et al. 2014; Hussain et al. 2018).

REE Enrichment

By keeping sustainable and reliable sources of REE production and consumption, the vast majority of which are currently found in China is a fundamental need of rest of the world. However, new sources need to be identified and quantified to ensure an adequate supply of REEs for today and the future. The current study quantified REEs and trace elements that are more significant than in other regions (Ketris and Yudovich 2009; Medina et al. 2010; Zhao et al. 2012; Kruger 2017). The contents of REEs along with critical elements (and their minimum, maximum and average values) are significantly enriched in the Binxian coal (Fig. 5c1), whereas a few REEs and trace elements, namely Eu, Tb, Ho, Tm, Lu, Cd, Th, In and Bi are deficient in the Hancheng coal (Fig. 5c2). The average concentrations of REEs in the Binxian coal were expressively higher than those in the USA coal (Finkelman 1993), equivalent concentrations to the Chinese reference coals (Ren et al. 2006), but lower than in the ECA (Kennish 2000a; JeffersonLab 2007) (Table 2 and Figure 6).

Similarly, the average enrichment of REEs in the coal ash of Binxian was observed to be dominant for raw coal followed by coal gangue and coal slime. The trend of element enrichment in raw coal was Ce > La > Pr > Gd > Sm > Sc > Nd > Dy > Eu > Tb > Tm > Yb > Er > Ho > Lu (Fig. 7c1). Comparing the relative abundances of RECe (Sm, Sc, Pr) and REY (Gd, Yb, Tb, Lu, Ho, Tm, Er, Dy), the Binxian coal is enriched than the Hancheng coal (Fig. 7c2). Compared with relative abundances of REEs reported in Dai et al. (2017b), all REEs in the Binxian coal were high except Y, La, Ce and Nd (Fig. 7c1), whereas REEs in the Hancheng coal were of lower concentrations (Fig. 7c2). Among all the REEs, Ce was dominantly observed in the Binxian coalmines, i.e., raw coal was 48.5, coal slime 49.8, coal gangue 64.3 and coal ash 84.2 in mg kg^{-1}, respectively (Table 1). However, the enrichment indices for coal slime (10.9), coal gangue (10.1) and coal ash (11.8) were higher than the normal range (Fig. 7c1). In the Binxian coal, Ce enrichment was 2.3-fold higher than in the USA coal (C1/USA), 0.9-fold higher than in the reference Chinese coal (C1/China) and 0.7-fold higher than the ECA (C1/ECA).

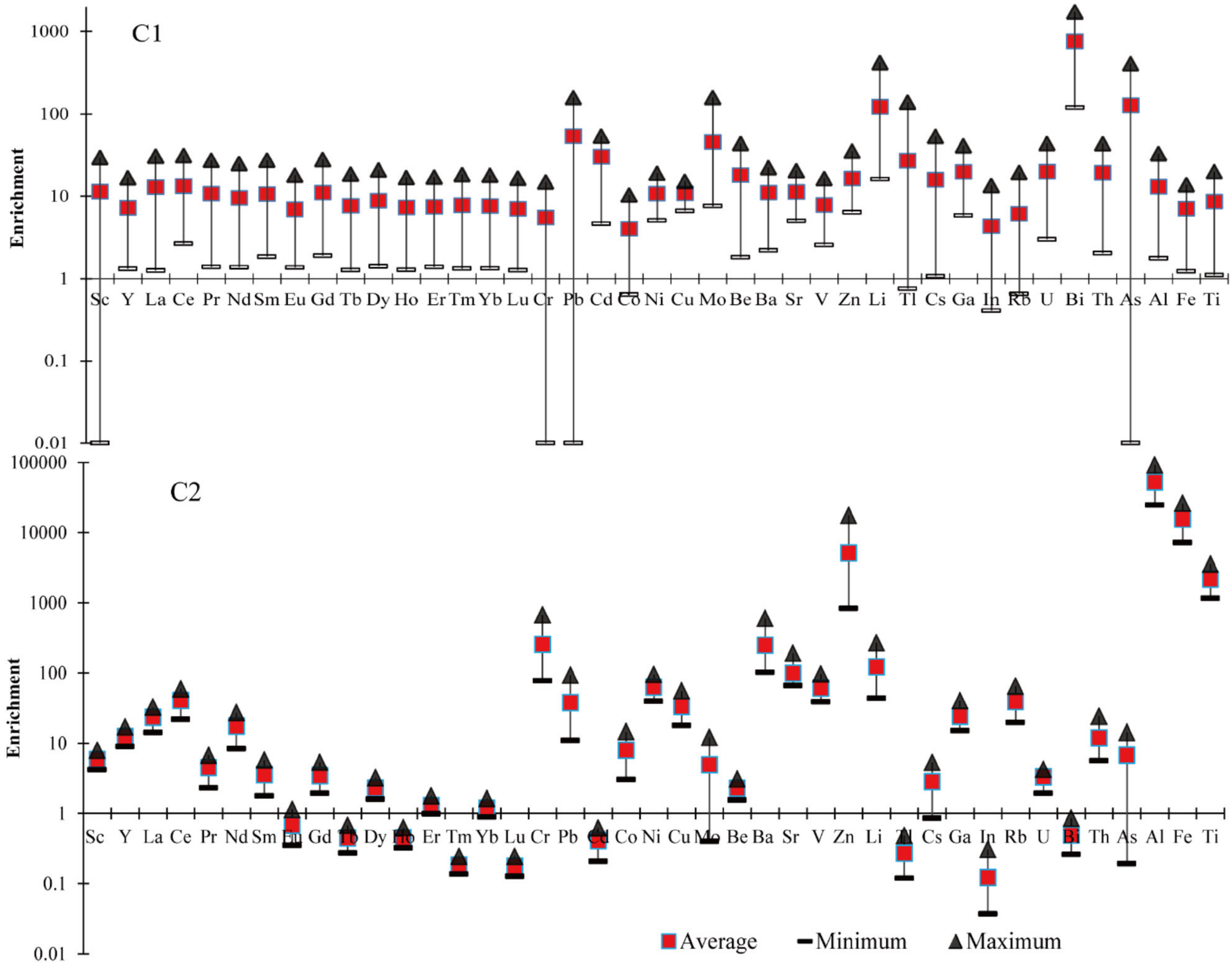

Figure 5. Enrichment of REEs and trace elements in the Binxian (c1) and Hancheng (c2) coalmines.

Cerium enrichment in the Hancheng raw coal was 2.8-fold higher than in the USA coal (C2/USA), 1.2-fold higher than in the Chinese reference coals (C2/China) and 0.9-fold higher than in the ECA (C2/ECA) (Table 2). Cerium is mostly associated with monazite (Smolka-Danielowska 2010).

Europium and Ce are redox-sensitive elements that show anomalies of depletion and enrichment in distribution pattern (when normalized to PAAS). The anomalous behavior of Ce and Eu reveals tectonic evolution, sediment deposition, lithological composition and post-depositional history of coals/rocks (Dai et al. 2017c). The negative anomalies of Ce may be because of Fe and Mn (oxide/hydroxide) redox reaction. However, their anomalies may also be disrupted due to deep-sea and running water. Oxidized Ce^{4+} is commonly retained in the oxidation process and inherited as secondary minerals with high-temperature fluid, indicating negative Ce anomalies (Loges et al. 2012; Tostevin et al. 2016). Positive anomalies of Eu in the Binxian and Hancheng coals (Fig. 8) prove the domination of hydrothermal fluid/high-temperature fluid, which led to the enrichment of REEs, V, Bi, Th, Ba and some other elements. Additionally, Al_2O_3/TiO_2 ratios (8–70) indicated that the sediment source of Jurassic and Permo-Carboniferous coals is intermediate to felsic composition (Fig. 9b). The REEs distribution along with the positive anomalies of Eu is similar to that in Kangdian upland Emeishan, a large Igneous Province of tholeiitic basalt (95% by volume) (Shao et al. 2007) and mafic basalt (Dai et al. 2016).

The Ba/Eu high ratios (> 1000) reflect the interference of Ba-oxide or Ba-hydroxide (Dai et al.

Table 2. Enrichment of REEs and trace elements in the Binxian Jurassic and Hancheng Permo-Carboniferous coalmines and adjacent areas

Elements	Jurassic Binxian coalmines				Permo-Carboniferous Hancheng coal				Jurassic Binxian coalmine			Permo-Carboniferous Hancheng coalmines			Resource estimation (kg/tons)	
	Coal	CG	CM	CA	Coal	CG	CM	CA	C1/USA	C1/China	C1/ECA	C2/UCA	C2/China	C2/ECA	C1	C2
Sc	11.4	10.1	9.18	9.98	5.91	4.25	5.83	5.12	3.28		0.627	2.092		0.399	0.014	0.009
Y	7.22	5.26	5.09	5.33	12.5	10.6	11.1	12.3	1.50		0.397	2.192		0.565	0.013	0.019
La	12.9	10.5	9.86	11.6	23.5	22.8	21.6	22.3	2.31	1.031	0.711	2.898	1.293	0.892	0.028	0.035
Ce	13.3	10.9	10.0	11.8	40.5	39.1	37.0	37.5	2.30	0.968	0.729	2.866	1.201	0.905	0.049	0.060
Pr	10.7	8.94	8.26	9.73	4.51	4.44	4.17	4.37	2.26		0.591	2.796		0.729	0.005	0.007
Nd	9.54	7.83	7.09	8.47	17.5	17.2	16.1	17.0	2.29	0.833	0.525	2.739	0.995	0.627	0.022	0.026
Sm	10.6	8.45	8.05	9.19	3.57	3.22	3.09	3.33	2.41	0.901	0.583	3.122	1.164	0.753	0.004	0.005
Eu	6.93	5.75	6.41	6.23	0.68	0.647	0.609	0.65	1.90	1.044	0.381	2.515	1.378	0.503	0.001	0.001
Gd	11.0	8.59	8.16	9.32	3.47	2.95	2.88	3.10	2.09		0.607	2.867		0.832	0.004	0.005
Tb	7.66	5.84	5.53	6.16	0.45	0.356	0.368	0.40	1.68	0.856	0.421	2.223	1.131	0.556	0.001	0.001
Dy	8.89	6.69	6.23	6.98	2.31	1.81	1.923	2.16	1.33		0.486	1.807		0.660	0.003	0.003
Ho	7.29	5.51	5.19	5.63	0.45	0.356	0.378	0.43	1.48		0.401	1.920		0.517	0.001	0.001
Er	7.41	5.64	5.27	5.65	1.29	1.06	1.100	1.27	1.42		0.407	1.919		0.548	0.001	0.002
Tm	7.79	5.99	5.47	5.92	0.18	0.148	0.151	0.18	1.48		0.429	1.800		0.519	0.000	0.000
Yb	7.61	5.95	5.30	5.69	1.19	0.987	1.016	1.18	1.40	0.752	0.418	1.864	0.995	0.553	0.001	0.002
Lu	6.99	5.60	4.96	5.13	0.18	0.149	0.146	0.17	1.37	0.362	0.384	1.871	0.494	0.524	0.000	0.000
Cr	5.49	8.37	8.24	6.11	258	160	119.1	67.4	2.05	1.911	0.302	25.62	23.8	3.768	0.031	0.384
Pb	53.9	47.1	34.8	41.4	37.7	29.8	27.69	19.8	3.77	2.669	2.965	5.099	3.61	4.006	0.042	0.056
Cd	30.3	25.4	20.2	23.2	0.41	0.49	0.410	0.37	0.53	1.000	1.667	1.304	2.45	4.087	0.000	0.001
Co	4.01	4.88	5.29	5.08	8.04	9.81	6.690	6.16	0.90	0.801	0.220	1.959	1.73	0.478	0.006	0.012
Ni	10.8	10.9	13.6	5.55	63.2	50.2	46.85	39.6	3.55	3.541	0.592	6.706	6.68	1.118	0.050	0.094
Cu	10.8	11.6	13.6	8.61	33.3	20.5	37.78	23.7	2.23	1.941	0.595	3.091	2.69	0.824	0.036	0.050
Mo	45.8	23.9	21.5	33.4	4.96	1.60	8.774	3.32	0.91	0.813	2.521	2.233	1.98	6.141	0.003	0.007
Be	18.1	14.9	13.9	18.6	2.29	1.94	2.142	2.51	1.26	1.305	0.993	1.548	1.59	1.216	0.003	0.003
Ba	11.1	10.9	32.4	12.5	249	257	213.5	325	1.51		0.607	2.183		0.873	0.258	0.371
Sr	11.2	5.94	13.4	12.9	98.9	79.5	74.23	209	1.75		0.618	1.132		0.398	0.229	0.147
V	7.83	9.48	10.4	7.54	61.0	47.1	61.96	56.6	2.34	1.474	0.431	4.122	2.58	0.756	0.052	0.091
Zn	16.4	17.2	17.4	14.1	5148	4155	2642	1767	1.19	1.498	0.902	144.4	181	109.3	0.063	7.653
Li	122	58.9	42.9	82.1	123	70.5	127	120.5	8.41		6.730	11.41		9.130	0.135	0.183
Tl	27.1	13.3	9.67	11.3	0.27	0.40	0.221	0.424	1.05	2.582	1.488	0.333	0.816	0.471	0.001	0.000
Cs	15.9	23.6	33.2	21.8	2.83	4.19	3.064	2.90	2.38		0.873	3.820		1.401	0.003	0.004
Ga	19.7	20.1	27.9	21.7	24.1	22.6	21.69	25.9	3.61	3.158	1.084	6.291	5.500	1.887	0.021	0.036
In	4.33	3.04	2.79	2.93	0.12	0.066	0.276	0.085	0.20		0.240	0.603		0.724	0.0001	0.0002
Rb	6.12	9.45	11.2	8.34	38.9	73.4	47.4	47.1	1.44		0.336	2.757		0.643	0.030	0.057
U	19.8	18.3	19.6	19.7	3.33	1.75	2.67	2.65	1.41	1.225	1.094	2.359	2.056	1.835	0.003	0.005
Bi	758	788	839	416	0.49	0.425	0.391	0.499	0.35		41.6	0.730		85.88	0.0004	0.001
Th	19.3	17.9	16.7	18.0	11.9	7.154	8.39	8.91	3.18	1.755	1.060	5.544	3.059	1.848	0.01	0.018
As	128	71.1	51.7	142	6.79	5.05	6.29	6.74	0.53	3.337	7.044	0.421	2.658	5.611	0.013	0.010
Al	13.1	13.5	12.3	13.2	52,806	51,209	52,830	51,268	6.67		1.202	7.311		1.316	9.89	10.83
Fe	7.06	4.79	4.10	6.47	2.35	1.92	1.49	1.676	2.31		0.425	1.978		0.363	2.91	2.43
Ti	8.62	8.62	8.62	8.553	2193	2193	2193	2193	5.51		0.766	0.037		0.005	4.28	0.029

CG coal gangue, *CM* coal slime, *CA* coal ash, *USA* United States of America, *ECA* earth crust abundance

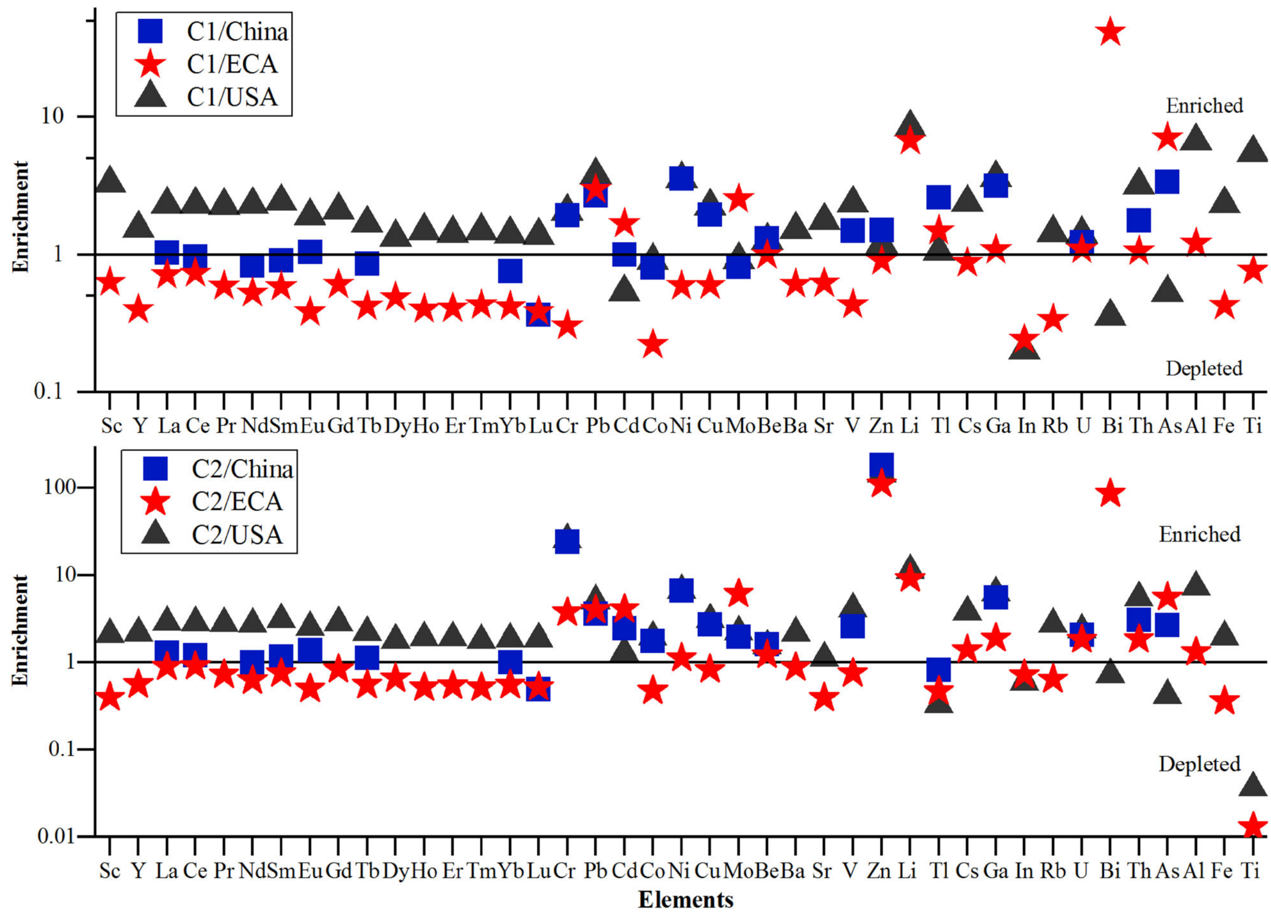

Figure 6. Relative enrichment of rare-earth and trace elements in the current study (c1, c2), China, ECA, and the USA.

2017c). If the Ba/Eu ratio is less than ~ 1000, Ba interference can be ignored and the measured values of Eu determined by ICP-MS are reliable (Yan et al. 2018). The Ba/Eu ratio of Binxian coal was 555 (average), and Hancheng coal was 3.7 (average) (Fig. 9a). The Hancheng coal and coal wastes do not show the Ba interference, whereas some samples of the Binxian coal show Ba interference. The lower Ba/Eu ratios suggest positive anomalies of Eu with no Ba interference (Fig. 8). In the Binxian coal, the lower Ba/Eu ratios of samples C4 (r = 125) and C5 (r = 191) suggest negative Eu anomalies, whereas that of sample C9 (r = 1836) shows the strongest positive anomalies of Eu (Fig. 8a). Figure 9a clearly shows the interfered Eu values with increasing Ba concentrations. The Ba interference may also occur due to improper handling of the samples to remove BaO/BaOH (Yan et al. 2018).

Similarly, majority of the samples show positive anomalies of Gd in all categories (i.e., coal, coal gangue, coal ash and coal slime). The weak positive anomalies of Gd and strong positive anomalies of Eu in the Binxian (average 1.18) and Hancheng (average 1.25) coals indicate the intrusion of hydrothermal fluid (Fig. 8), as also reported by Yan et al. (2018).

Trace Elements Enrichment

Various studies reported the abundance of critical elements in coal gangue and coal combustion products (e.g., Norgate et al. 2007; Meawad et al. 2010; Zhao et al. 2012; Du and Graedel 2013; Hussain et al. 2018). The compositions and enrichment levels of the studied raw coals and

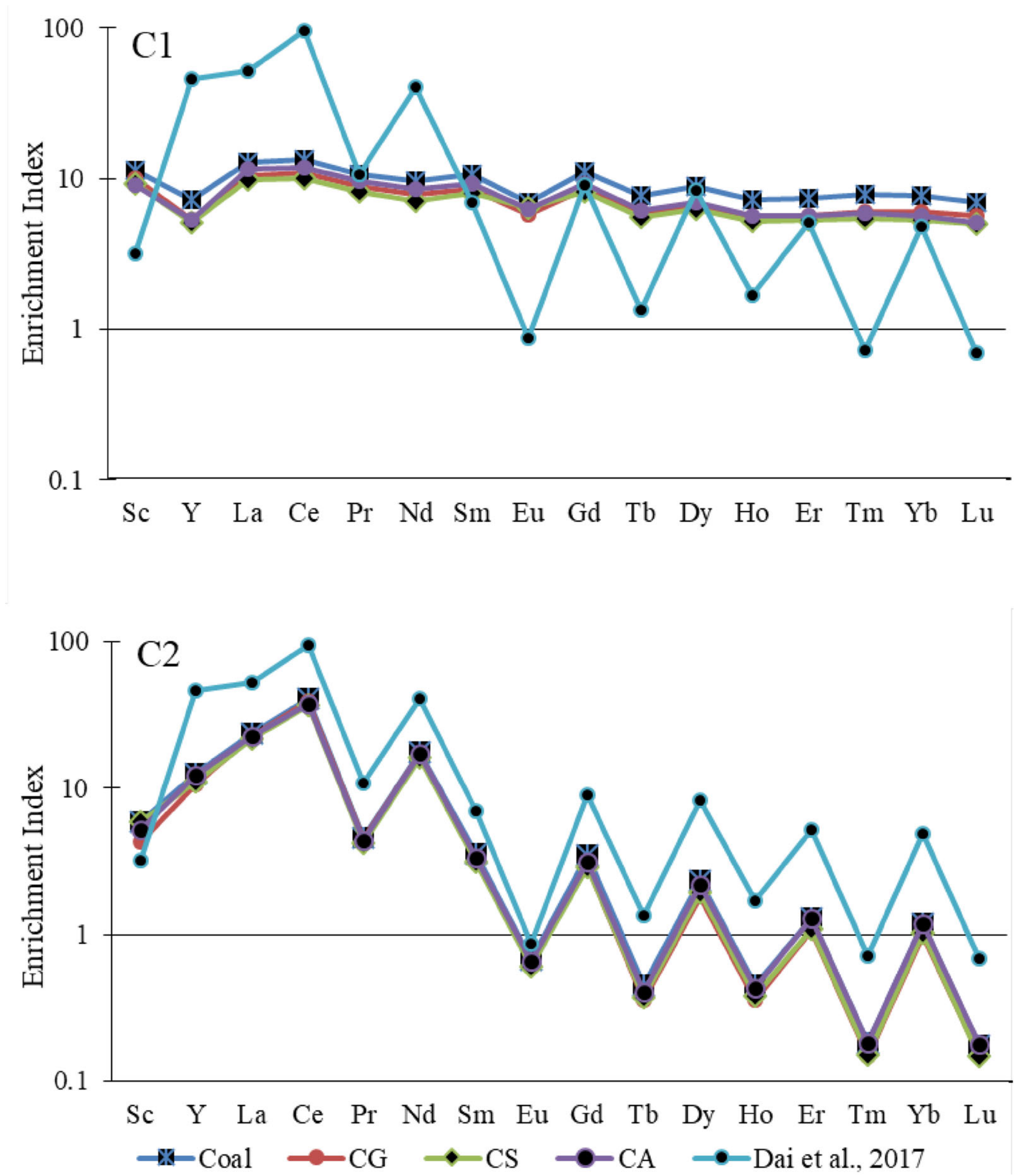

Figure 7. Enrichment of REEs in the Binxian (c1) and Hancheng (c2) coalmines. CG = coal gangue, CS = coal slime CA = coal ash.

unprocessed coal wastes are given in Table 2. Many scientists reported that some of the Chinese coal deposits are significantly enriched with REEs and critical elements (Chen 2007; Seredin and Dai 2012; Haque et al. 2014). Similarly, the Binxian and Hancheng raw coals and coal wastes have relatively high amounts of critical elements (Ba, Cr, Pb, Ni, Li, Rb, Cs and Zn). In addition, the final disposed coal wastes have almost similar enrichment levels of critical elements as the raw coal, especially in the Hancheng coalmines (Figs. 6, 7). The most common and plentiful critical elements in the Hancheng raw coal are Cr, Pb, Ni, Ba, Zn, Li, As, Cu, V, Sr, Al, Ti and Fe, whereas in the Binxian raw coal, the abundant critical elements are Cr, Pb, Ni, Cu, Ba, Sr, V, Zn, Li, Ga, Rb, Th, As, Al, Fe and Ti (Table 1). These elements along with other critical elements, namely Cd, Mo, Be Cs, U and Bi,

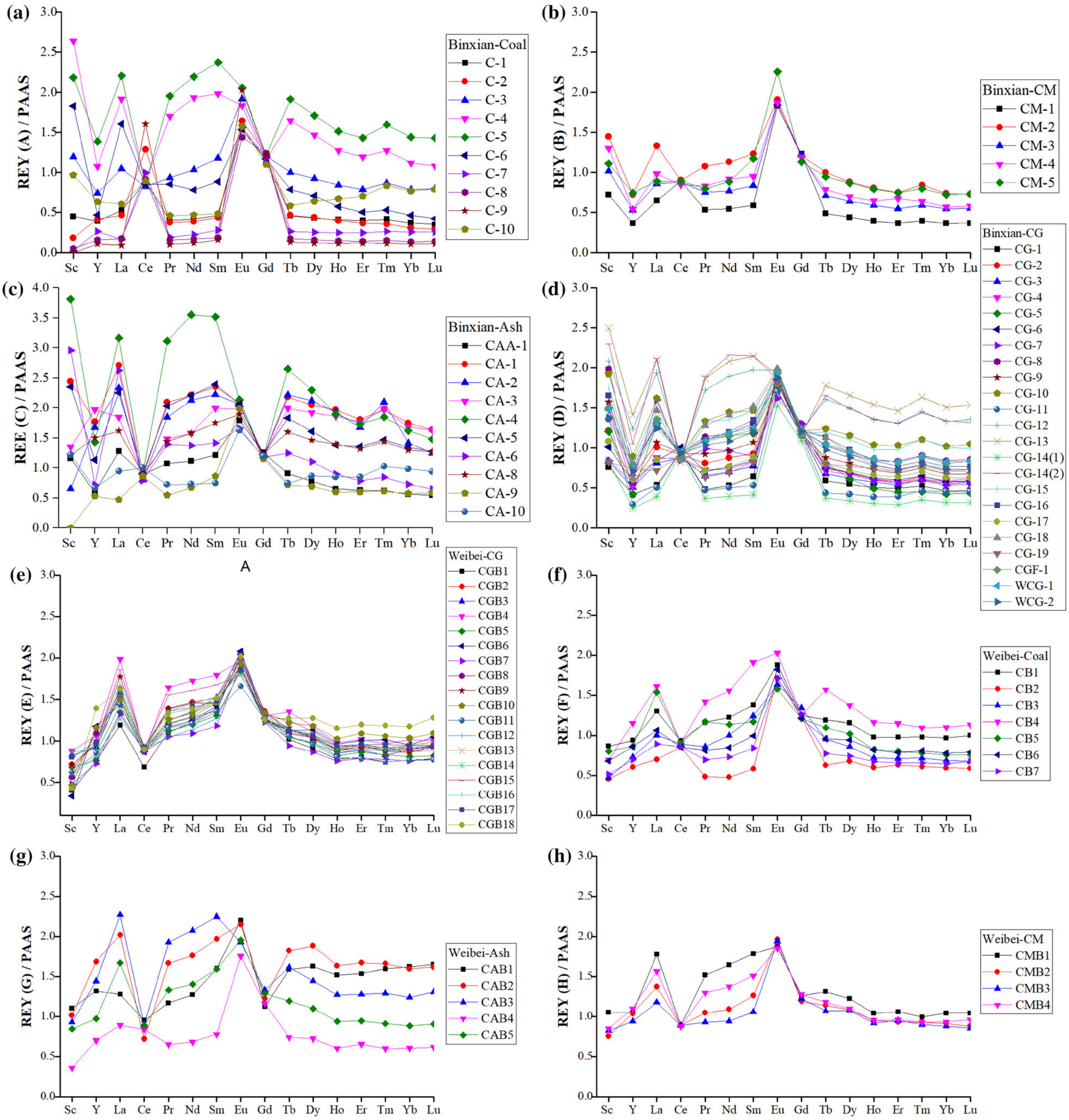

Figure 8. REY distribution pattern in the Jurassic and Permo-Carboniferous coal and coal wastes samples normalized to PAAS (Taylor and McLennan 1985). (a) Jurassic coal. (b) Jurassic coal slime. (c) Jurassic coal ash. (d) Jurassic coal gangue. (e, f, g, h) Permo-Carboniferous coal gangue, coal, coal ash and coal slime, respectively.

in the presently studied coals were higher than in the USA coal (Finkelman 1993), world coal (Ketris and Yudovich 2009), ECA (Kennish 2000a; JeffersonLab 2007) and Chinese coals (Ren et al. 2006; Dai et al. 2017b). The study also observed that most of the critical elements in ash residues, especially in the Hancheng coalmines, were enriched in the raw coal, while their concentrations are similar to their host ores. This condition, where the residues (coal slime, coal gangue or coal ash) have similar concentrations of trace and REEs as the host ores, suggests the possible sources for ele-

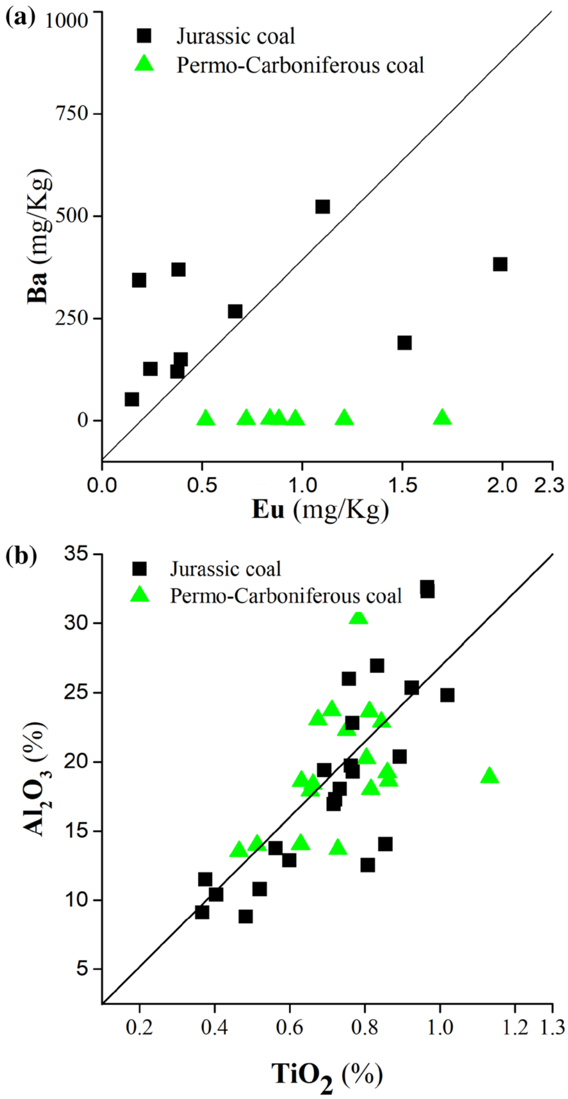

Figure 9. Relationship between (a) Ba and Eu, (b) Al_2O_3 and Tio_2, for the coal and coal wastes sample from typical coals in Shaanxi, China.

ments extraction (Long et al. 2010; Hussain and Luo 2018).

Critical elements in the Binxian coal were enriched from significant to extremely high, whereas in the Hancheng coal, the critical elements were enriched from moderate to extremely high (Table 3). However, enrichment of critical elements in both studied coals was dominantly higher than those in international studies (e.g., Huang et al. 2004; Meij and Winkel 2007) (Table 4). The elements included in significant enrichment to extremely high enrichment should have high economic value (Fig. 10). Their recovery will limit environmental consequences and disposal expenditure (Norgate et al. 2007; Sahoo et al. 2016).

CRITICAL ANALYSIS

According to on-site observation in the Weibei and Huanglong coalfields, huge amounts of coal gangue consist of gray-black, brownish-black and black mudstone-like material. Coal ash and coal slime debris were observed at specific places in the power plants and washing plants. In the Weibei coalfield, the Hancheng coal entered into the gas generation stage during the Early Cretaceous (Xiao et al. 2005). Currently, all the Permo-Carboniferous coals in the entire basin have reached thermal maturation stage. The coal rank was increased from flame coal (vitrinite reflectance R_0 0.58%) to anthracite coal (R_0 3%) (Tang et al. 2012). The mode of occurrence of critical elements in coals (Fig. 10) are mostly associated with carbonate, sulfide and clay hosted minerals (i.e., allophane, halloysite, hydroxide, pyrite, siderite, feldspar, mica, illite, zeolite and rock salt) (Dai et al. 2005), which were mostly evolved from felsic volcanic materials (Zhou et al. 2000). This indicates that felsic volcanic inputs exist in the Carboniferous coal. The Al_2O_3/TiO_2 ratio is an efficient and potential indicator to evaluate the sediments source of coal deposit as well as the magmatic contents of volcanic ash (Zhou et al. 2000; He et al. 2010; Dai et al. 2014). Al_2O_3/TiO_2 ratios are categorized as 3–8, 8–21 and 21–70 for sediments derived from mafic, intermediate and felsic rocks, respectively (Hayashi et al. 1997; Dai et al. 2016). The range of Al_2O_3/TiO_2 ratios in the Binxian coal was 15.5–34 (average 25.5), while in the Hancheng coal it was 16.6–38 (average 26.9) (Fig. 9b), which indicates that the entire basin sediments were derived from intermediate to felsic rocks. This suggests that there is a great variation in the concentrations of elements in various areas in the entire basin, but the source has no variation. All the REEs in the Binxian and Hancheng coals showed the strongest positive correlations (> 95%) (Supplementary Fig. S1; Table S5 and Table S6). Their similar properties are due to their controlling factors, disposal and evolution of elements in coals in the basin (Zhou and Ren 1992; Dai et al. 2012a). The observed ratios of Al_2O_3/TiO_2 (Fig. 9b) and REEs anomalies (Fig. 8) are similar to those reported in Dai et al. (2017b) and Zhou et al. (2000), indicating felsic to intermediate composition of

Table 3. Classification of elemental enrichment in raw coal of the Binxian Jurassic and Hancheng Permo-Carboniferous coalmines

Grading	EF indices	Enrichment degrees	REEs Binxian Jurassic	REEs Hancheng Permo-Carboniferous	Trace elements Binxian Jurassic	Trace elements Hancheng Permo-Carboniferous
1	EF ≤ 1	Background level		Eu, Tb, Ho, Tm, Lu		Cd, Tl, In,
2	EF 1–2	Depletion to minimal enrichment		Er, Yb		
3	EF 2–5	Moderate enrichment		Pr, Sm, Gd, Dy	Co, In	Mo, Be, Cs, U, Fe
4	EF 5–20	Significant enrichment	Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Sc, Y, La, Ce, Nd	Cr, Ni, Cu, Be, Ba, Sr, V, Zn, Cs, Ga, Rb, U, Th, Al, Fe, Ti	Co, Ga, Th, As,
5	EF 20–40	Very high enrichment			Cd, Tl	Pb, Cu, Rb,
6	EF > 40	Extremely high enrichment			Pb, Mo, Li, Bi, As	Cr, Ni, Ba, Sr, V, Zn, Li, Bi, Al, Ti

sources of sediments in the Ordos Basin. Wang et al. (2011) reported that the Hancheng coal has abundant compositions of kaolinite and tonsteins, which decrease from northwest to southeast. However, tonsteins are mostly composed of sanidine, quartz and zircon, which may evolve in felsic volcanic minerals (Liang et al. 1995). The Hancheng coal is abundantly composed of kaolinite, sulfide, carbonate and clay minerals, which evolved from felsic volcanic materials (Wang et al. 2011) and are the major sources of REEs and critical elements.

The world hard coal (Ketris and Yudovich 2009) and Chinese coals (Dai et al. 2017b) have been categorized into six classes of enrichment, i.e., unusual enrichment $CC < 100$, significant enrichment $10 < CC < 100$, enriched $5 < CC < 10$, slight enrichment $2 < CC < 5$, normal $0.5 < CC < 2$ and depleted $CC < 0.5$ as suggested by Dai et al. (2017b). The Binxian vs. word coal-based classifications revealed that Li, Ho, Eu, Tb, Tm and Lu were significantly enriched, Sm, Pb, Ti, Yb and Er were enriched, and Tl, V, Sr, Rb, Cu, Cs, Zn, Sc, Pr, Th, Ga, Ni, Gd and Dy were slightly enriched, Ce, Nd, Y, Co, Cd, La, U, Mo, As, Ba, In, Cr, and Be were in normal range, while Bi was depleted (Fig. 10a). Similarly, the Hancheng vs. world coal-based classification revealed that Zn was unusually enriched, Li and Cr significantly enriched, Th, In, Ga, Pb and Ni were enriched, U, Be, La, Co, Ba, Cd, Cu, Mo, Ti, V, Rb and Cs were slightly enriched, while Tm, Tl, Bi, Ho, Lu, Dy, Yb, As, Gd, Er, Sr, Er, Tb, Eu, Nd, Y, Sc, Ce and Sm were in normal range (Fig. 10b).

In contrast to world coal, the Chinese coal enrichment-based classification (Dai et al. 2017b) is given in Figure 10 (Fig. 10c, d). The Binxian coal vs. Dai et al. (2017b) revealed that elements, namely Lu, Tm, As, Rb and Ba, were significantly enriched, Ni, Tb, Cs, Eu, Pb and Cr were enriched, Ti, Sc, Li, Ho, Zn and Sr were slightly enriched, Cd, U, V, Pr, Mo, Dy, Gd, Tl, Th, Co, Er, Sm, Yb, Bi, Cu and Ga were in normal range, whereas In, Ce, Y, Nd, La and Be were depleted (Fig. 10c). Similarly, the Hancheng coal vs. Dai et al. (2017b) revealed that Zn was unusually enriched, As, Cs, Pb, Cr, Rb and Ba were significantly enriched, Li and Ni were enriched, Ti, Th, Mo, Cu, Sr, Co, In, Ga and Bi were slightly enriched, Sm, Be, Eu, U, Cd, Sc and V were in normal range, whereas Yb, Er, Tm, Lu, Ho, Y, Dy, Tb, Gd, Tl, Pr, Ce, Nd, and La were depleted (Fig. 10d). The world coal (Ketris and Yudovich 2009) enrichment-based classification revealed that 2% of elements were depleted in the Binxian coal,

Table 4. Comparison of REEs in coal (mg kg^{-1}) in the current study and in other national and international studies

Countries	Region	Deposit	Age	Y	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Russia-1	Kuzbass	Kuzbass	P1	144		250	384	45	158	32	3	30	5	26	5	15	2	14	2
Russia-2	Kizelovsk		C1	330		81	163	20	91	24	6	28	5	33	9	23	3	22	3
Belorussia-3	Lel'chitsk		C1	590		839	1784	239	967	170	19	154	21	111	19	54	8	51	9
China-4	SW China	Songzao	P2	183.2		227	434	53.8	205	39.1	5.8	34.3	5.2	31.3	6.4	20.1	2.7	17.8	2.7
China-5	Inner Mongolia	Jungar	C5	102.7		229	385	43.3	153	29.7	5.0	26.3	4.3	22.0	4.3	12.0	2.0	11.3	2.0
China-6	Yunnan	Enhong	P3	143.4		213	453	50.4	193	33.6	6.6	30.6	5.2	27	4.8	14.8	2	12.2	1.8
China-7	Guangxi	Heshan	P3	226.3		143	292.2	36	145	32.3	4.7	33.3	6	38.7	7.75	24.3	3.7	25.3	3.75
China-8	Guizhou	Luizhi	P2	233		441	955	117	436	79	8	73	11	55	11	31	5	30	5
USA-9	Kentucky	Appalachian	C2	173		261	534	63	231	48	5	36	6	42	8	23	6	21	3
USA-10	North Dakota			17.4		12.9	26.8	3.4	13.6	3.1	0.8	3.2	0.5	3.2	0.7	2	0.3	1.9	0.3
Poland-11		Ash		48.4	23.8	58.5	117.3	13.5	52.4	10.7	2.4	9.0	1.5	8.1	1.6	4.6	0.7	4.4	0.7
China-12	Shaanxi	Coal				10.9	23.3	2.75	11.6	2.23	1.95	2.08	0.29	1.55	0.3	0.96	0.13	0.94	0.14
China-13	Chongqing (SW China)	Coal		46.1	3.18	52.1	95.1	10.7	40.9	6.96	0.87	9.01	1.34	8.26	1.68	5.13	0.72	4.83	0.69
World-14	Earth crust abundance	Coal		22		30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	0.33	2.2	0.32
Current study China	Binxian Jurassic Coalmine	Raw coal		13.1	13.8	27.7	48.5	5.4	21.8	4.1	0.8	3.8	0.5	2.5	0.5	1.4	0.22	1.4	0.19
		Coal gangue		15.4	19.8	36.4	64.3	7.3	28.9	5.3	1.0	4.7	0.6	3.09	0.6	1.8	0.3	1.7	0.3
		Coal slime		12.6	15.1	28.7	49.9	5.7	21.9	4.2	0.96	3.8	0.5	2.4	0.5	1.4	0.21	1.3	0.2
		Coal ash		18.9	21.2	48.6	84.3	9.6	37.9	7.1	1.5	6.2	0.8	3.9	0.8	2.1	0.33	1.9	0.3
Current study	Hancheng Permo-Carboniferous Coalmine	Raw coal		18.6	8.8	34.8	60.2	6.7	26.0	5.3	1.0	5.2	0.7	3.4	0.7	1.9	0.27	1.8	0.26
		Coal gangue		21.6	8.7	46.5	79.6	9.1	35.1	6.6	1.3	6.0	0.7	3.7	0.7	2.2	0.30	2.0	0.3
		Coal slime		22.6	11.9	44.3	75.9	8.6	33.1	6.4	1.3	5.9	0.8	3.9	0.8	2.3	0.31	2.08	0.3
		Coal ash		26.7	11.1	48.4	81.1	9.5	36.9	7.2	1.4	6.7	0.9	4.7	0.9	2.8	0.39	2.6	0.38

1–7 Seredin and Dai (2012), *8* Zhuang et al. (2009), *9* Mardon and Hower (2004), *10* Kruger (2017), *11* Franus et al. (2015), *12* Zhao et al. (2012), *13* Dai et al. (2017b), *14* Castor and Hedrick (2006)


(a)
(b)
(c)
(d)
Concentration coefficient
1000
100
10
1
0.1
0.01
Sc Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Cr Pb Cd Co Ni Cu Mo Be Ba Sr V Zn Li Tl Cs Ga In Rb U Bi Th As Ti
CC<0.5 Depleted
0.5<CC<2 Normal
2<CC<5 Slightly enriched
5<CC<10 Enriched
10<CC<100 Significantly enriched
100<CC Unusually enriched

◀**Figure 10.** Concentration coefficients (CC) of trace elements in coals from the Weibei and Huanglong coalfields, north Shaanxi. (a) Binxian vs Ketris and Yudovich (2009). (b) Hancheng vs Ketris and Yudovich (2009). (c) Binxian vs Dai et al. (2017b). (d) Hancheng vs Dai et al. (2017b).

whereas in the Hancheng, all the elements were enriched, i.e., from normal to unusual enrichment. Enrichment classification based on Dai et al. (2017b) revealed that 6% of elements in the Binxian coal were below the normal range, whereas in the Hancheng coal 34% of elements were below the normal range (Fig. 10).

Enrichment factor (Eq. 1)-based classification and correlation between raw coal and coal ash revealed that REEs and critical elements in both the Hancheng and Binxian coals do not show huge variations among the groups (i.e., raw coal, coal ash and coal gangue). The positive correlations revealed that the source rock is the same (belongs to the same age), while slight regular changes in the REEs and trace elements may be because of their ionic radius (which increased their organic affinity index) as also suggested by Jianye (2010) (Fig. 9). Based on EF model, the enrichment of elements in the Binxian coal is higher than in the Hancheng coal (Fig. 7). In the Binxian coal, the enrichment of elements, namely Pr, Sc, Ho, Eu, Gd, Lu, Yb, Tm, Tb, Dy and Er, was higher than in the other studies (Finkelman 1993; Kennish 2000a; Tang and Huang 2004; JeffersonLab 2007; Ketris and Yudovich 2009) and was included in a significant enrichment category. However, the critical elements enrichment shows variations, i.e., Co and In, were moderately enriched, Cr, Ni, Cu, Be, Ba, Sr, V, Zn, Cs, Ga, Rb, U, Th, Al, Fe and Ti were significantly enriched, Cd and Tl were highly enriched, whereas Pb, Mo, Li, Bi and As were extremely high enriched (Table 3). It was reported that the Chinese coals had almost all the critical and REEs in huge quantities (Dai et al. 2017b; USGS 2017; Hussain et al. 2018), which have the potential of extraction as a by-product.

The EF model revealed that REEs in the Hancheng raw coal exhibit variations in different grades, i.e., background levels to significant enrichment. The elements Eu, Tb, Ho, Tm and Lu (equivalent to the normal range of Dai et al. (2017b)) were in background level, Er and Yb were in depletion to minimal enrichment, Pr, Sm, Gd and Dy were moderate enriched, whereas Sc, Y, La, Ce and Nd were significantly enriched (Table 3). The anomalous behaviors of Eu, Tb, Ce and Ho in the Hancheng coalmines are typically inherited from detrital source rock (Tang and Huang 2004). This anomalous behaviors of low enriched elements, especially Eu and Ho in the Ordos Basin (both Weibei and Huanglong coalfield), indicate various inputs of source rocks. The Hancheng coal evolved from Proterozoic moyite associated with the old land of Yinshan, in which the Eu, may have reduced to Eu^{2+} in magmatic process. All the hydrothermal magmatic fluids were emitted at mid-oceanic ridges (Wang 2010). The Hancheng coal has lower Ba/Eu ratios (2.3–5.5) as compared to the standard level (1000) (Loges et al. 2012), which indicates no Ba–O/Ba–OH interference and ICP-MS measurement was reliable (Fig. 9a). In the Hancheng raw coal, the critical elements, namely Cd, In and Tl, were in background level, Mo, Be, Cs, U and Fe were moderately enriched, Co, Ga, Th and As were significantly enriched, Pb, Cu and Rb very highly enriched, whereas Cr, Ni, Ba, Sr, Zn, Li, Bi, Al and Ti were extremely high enriched (Table 3). The enrichment-based classification with some renowned studies (Finkelman 1993; Tang and Huang 2004; Ketris and Yudovich 2009; Wang 2010; Dai et al. 2017b) revealed that the current study trace elements in coal are enriched from normal to unusually enrichment (Table 1, Figs. 3, 10). Therefore, the study recommends the extraction of REEs especially critical elements as a by-product from the Hancheng and Binxian coalmines of Shaanxi Province.

From an economic perspective, the present study proved that the coal and coal wastes of the Hancheng and Binxian coalmines have high quantities of critical elements, as also reported by some researchers (Dai et al. 2006; Jianye 2010; Wang 2010). In Shaanxi Province, several studies have been conducted on REEs related to gold deposits (Liu et al. 2013), loess (Wen et al. 1985), molybdenum and granitoids deposits (Huanglongpu mine) (Nie 1994). These deposits have higher concentrations of REEs (than in the current study), but their deposits are smaller and not economical. However, the concentrations of REEs in the Hancheng and Binxian coals are average to high compared with those from Chongqing, Yunnan, Guizhou and Sichuan, but the waste deposits are huge in the Weibei and Huanglong coalfields, which are economically viable. In the future, the coal wastes will be important for the recovery of REEs and critical elements.

The possible consequences of disposal of REEs and critical elements enriched in coal wastes can lead to an increase in disposal cost and cause environmental and health problems. A possible solution could be (1) recovery of economically valuable REEs and critical elements, which can contribute to the national economy, (2) installation of advanced environment friendly technologies and to reduce the danger impoundment coal breaches and (3) recovery of REEs and critical elements from coal wastes/coal combustion products, which will limit the disposal expenditure as well as abate environmental and health problems.

CONCLUSION

The Binxian and Hancheng coals of the Shaanxi Province were evolved from sediments of intermediate to felsic composition. The REEs in both coalfields showed slight variation ($r = 0.98$) and unpromising abundance, whereas the critical elements are high in both coalfields. The Eu and Gd showed positive anomalies, whereas Ce showed negative anomalies almost in all samples. The positive anomalies of Gd indicate intrusion of hydrothermal fluid. Moreover, Al_2O_3/TiO_2 ratios in the Binxian coal (15.5–34.3) and Hancheng coal (16.6–38.7) showed that the sediments were derived from intermediate-felsic rocks. In both coalfields, the REEs are comparatively higher than in the USA coal, world hard coal and higher/equal to the Ex-study of China, whereas equal/lower than in the ECA and Chongqing coalfield of China. In the Binxian coal, the REEs are, namely Y 1.5-fold, La 2.3-fold, Ce 2.3-fold, Nd 2.2-fold, Sm 2.4-fold, Gd 2.1-fold and Er 1.4-fold, higher than in the US coal. However, the REEs in the Hancheng coal are, namely Sm 3.1-fold, Sc 2.1-fold, La 2.9-fold, Y 2.2-fold, Ce 2.8-fold, Nd 2.7-fold, Gd 2.9-fold and Er 1.9-fold, higher than in the US coal.

Moreover, the coal/coal wastes of Binxian were predominantly enriched in all the REEs compared with those in the US coal and Chinese reference coals. However, the Hancheng coal is enriched in Y, Ce, Sc, Er, Gd, Nd, La, Dy, Pr, Yb and Sm and depleted in Eu, Lu, Ho, Tm and Tb compared with world coal, ECA and US coal. Overall, the enrichment of critical elements in coal/coal wastes of Binxian is higher than the normal range and included mostly in significant enrichment category. In the Hancheng coal, REEs and few critical elements were in the normal range of enrichment, whereas all the remaining elements were significantly enriched. Additionally, the critical elements, namely Cr, Pb, Ni, Sr, V, Zn, Li, As, Al, Fe and Ti were predominantly enriched in both the Binxian and Hancheng coals.

Potential recovery of profitable REEs in these coalfields, especially critical elements as by-products of coal production, could be beneficial for industrial and commercial technology. The identification, exploration and utilization of these elements will limit disposal cost as well as associated health and environmental problems.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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