

Geochemistry of rare earth elements in Permian coals from the Huaibei Coalfield, China

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Abstract

The rare earth elements (REEs) in coals are important because of: (a) REE patterns can be an indicator of the nature of source rocks of the mineral matter as well as sedimentary environments; (b) REEs abundance in coal may have industrial-significance. In this study, a total of thirty-four samples of Permian coal, partings, roof, and floor were collected from the Huaibei Coalfield, Anhui Province, China. Abundances of rare earth elements (REEs) and other elements in the samples were determined by inductively coupled-plasma mass spectrometry (ICP-MS) and inductively coupled-plasma atomic emission spectrometry (ICP-AES). The results show that the REEs are enriched in coals in the Huaibei Coalfield as compared with Chinese and U.S. coals and the world coal average. Coals in the Lower Shihezi Formation (No. 7, 5, and 4 Coals) and Upper Shihezi Formation (No. 3) have higher REE abundances than the coals in Shanxi Formation (No. 10). Magmatic intrusion resulted in high enrichment of REEs concentrations in No. 5 and 7 Coals. The REE abundances are positively correlated with the ash content. The mineral matter in these coals is mainly made up of clay minerals and carbonates. The REEs are positively correlated with lithophile elements including Si, Al, Ti, Fe, and Na, which are mainly distributed in clay minerals, indicating that REEs are contained mainly in clay minerals. The REE abundances in coals normalized by the ash are higher than that in partings. REEs abundances of coals cannot be accounted for by the REE content in the mineral matter, and some REEs associated with organic matter in coals.

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1. Introduction

The rare earth elements (REEs) in coals are important mainly because REEs are a coherent group of elements which are relatively immobile, and the REE patterns can be an indicator of the nature of source rocks of the mineral matter in coal as well as their sedimentary environments (Fleet, 1984; Huang et al., 2000; Qi et al., 2002; Zhao

et al., 1998). Generally, abundances of REEs in coal are not high, but they may be enriched in some coals and may have economical utilization (Finkelman, 1993; Seredin, 1996).

There have been many studies on the distribution and geochemistry of REEs in coal (Birk and White, 1991; Chen et al., 1985, 1996; Dai et al., 2002, 2003a,b; Eskenazy, 1987, 1996; Huang et al., 2000; Kortenski and Bakardjiev, 1993; Li et al., 2002; Liu et al., 2006; Seredin, 1996; Wang et al., 1989, 1999; Zhao et al., 1998, 2000a,b; Zhao, 2002). These studies indicate that $\sum$ REE content in most coals varies from several $\mu\text{g/g}$ to several hundred $\mu\text{g/g}$, and the REEs are distributed in minerals although some are associated with organic material in coal.

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The Huaibei Coalfield, located in Northern Anhui Province, is one of the major coalfields in China. Coal in the coalfield has been, and continues to be, a valuable energy resource, especially for the electric utility industry. Zhao et al. (2000a) studied REE abundances in coals from No. 3 and 6 coals and concluded that the REE patterns of the coals are mainly terrigenous and the REEs are distributed in clay minerals. Recently, Liu et al. (2005) reported mineral and trace element compositions in 14 samples from No. 3, 5, and 6 coals in the Huaibei Coalfield, but REEs were not included. The systematically geochemical studies of REEs from this basin are scarce, and the purpose of this study is to determine the abundances and geochemical significance of REEs in the Permian coals from the Huaibei Coalfield, Anhui Province, China.

2. Geological setting

The Huaibei Coalfield is in the southeastern part of the North China Craton, and located in the northern Anhui province (E115°58'–E117°12', N33°20'–N34°28'), China (Fig. 1). The coalfield covers approximately 9600 km² in total area, in which 4100 km² are covered by Pennsylvanian and Permian coal-bearing strata. The coal reserves in the Huaibei Coalfield are abundant and coals are mostly bituminous. Except several faults control the conformation, the geological condition of the coal seams in the Huaibei

Coalfields is comparatively simple. Currently there are 23 operating underground coal mines in the Huaibei Coalfield (Fig. 2), and the annual production is over 30 million metric tons which is mainly used by power plants and for industrial fuel.

The total thickness of the coal-bearing sequence of the Pennsylvanian and Permian age in the Huaibei Coalfield is more than 1300 m. There are 13–46 coal seams, but only three to 12 seams are economically minable. The cumulative thickness of minable coal seams varies from 1.5 to 15 m. Coal seams in the Benxi Formation and the Taiyuan Formation (Pennsylvanian) are thin and rarely mined. The economically minable seams are mainly in the Shanxi Formation and the Lower Shihezi Formation (Permian). The coal seams in the Upper Shihezi Formation are only partially minable, and no coal occurs in the overlying Shiqianfeng Formation (Upper Permian). The stratigraphic column and lithological characteristics of coal-bearing sequence in the Huaibei Coalfield are briefly described as Fig. 3.

3. Analytical methods and results

3.1. Sample description and sample preparation

Thirty-four samples of coal, partings, roof, and floor were collected from two underground mines in the Huaibei

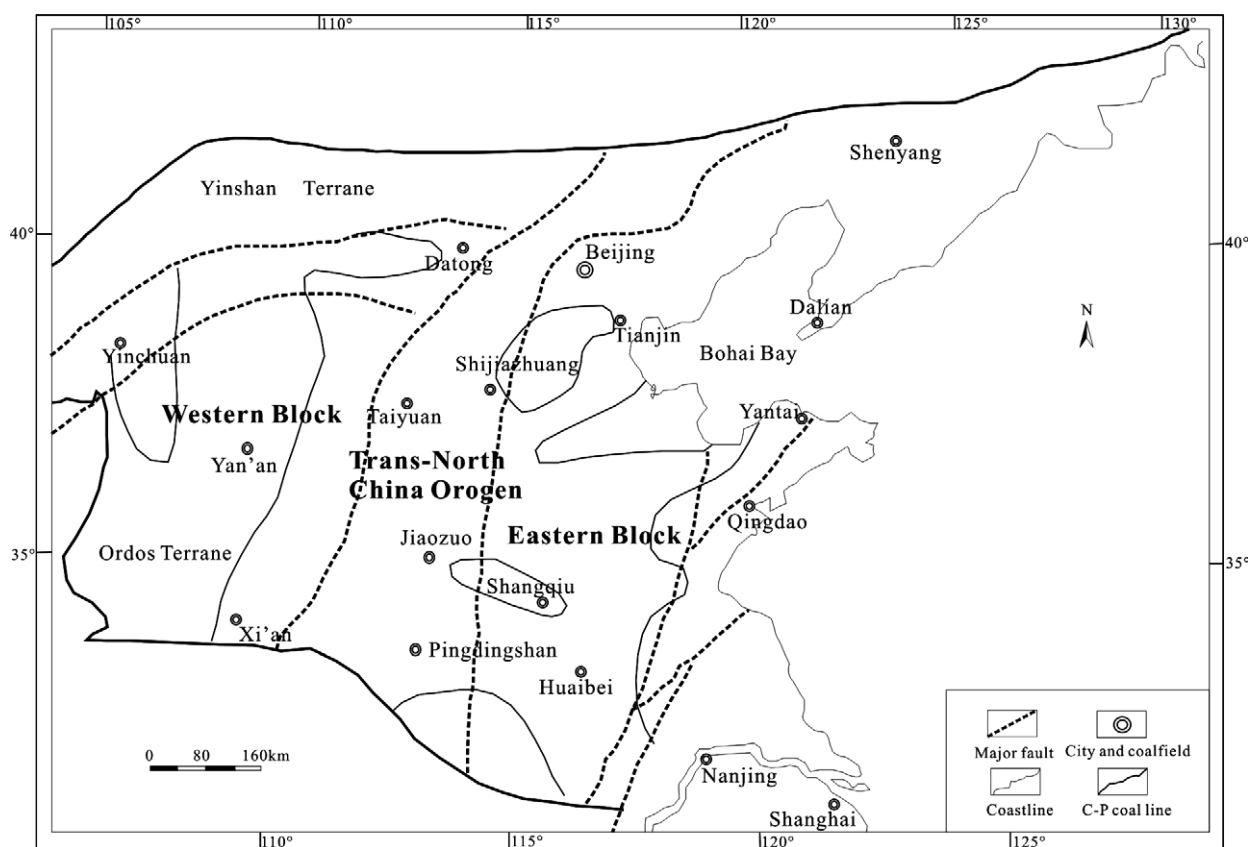


Fig. 1. Location of the Huaibei mining district in North China.

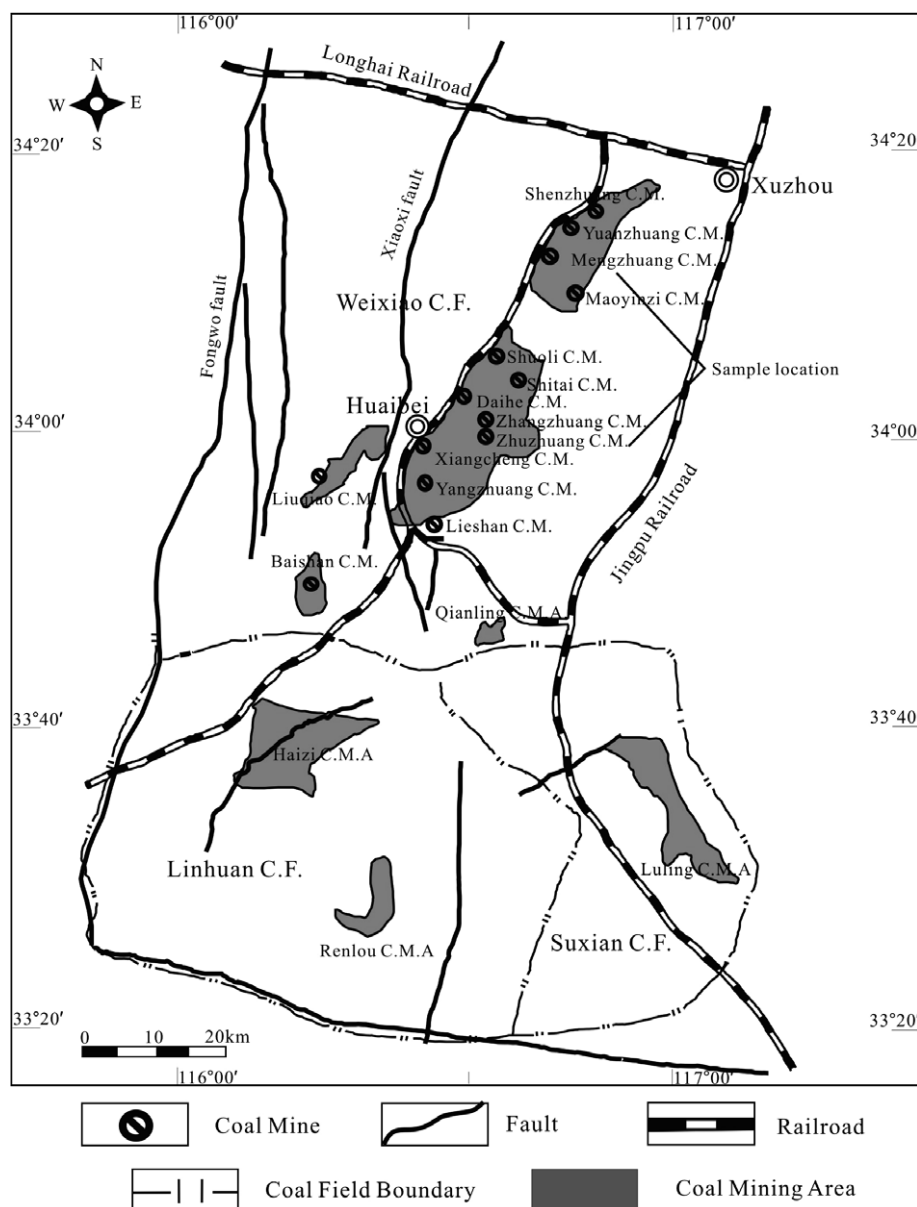


Fig. 2. Location of the coal mines in Huaibei mining district.

Coalfield, Anhui Province. They were bench samples taken by cutting channels downwards so that vertical variation of geochemical characteristics within a coal bed can be studied. Bench samples in each coal seam have equal thickness, and the samples were stored immediately in plastic bags to prevent contamination and weathering. The types of samples of stratigraphic position are shown in Fig. 4.

The bulk samples were air-dried, milled and split until a representative split of 0.5 kg was obtained. The sample for mineralogical, proximate, ultimate and chemical analyses was pulverized to less than 200-mesh and dried for 12 h in a desiccator. All samples were analyzed for REEs.

3.2. Results

The proximate and ultimate analyses were performed following ASTM (American Society for Testing and Mate-

rials, 1992) standard procedures at Laboratory for Coal Chemical Analysis at the Anhui University of Science and Technology, Huainan, Anhui Province (Table 1). Samples were digested with $\text{HNO}_3\text{:HCl:HF}(3\text{:}1\text{:}1)$ in a microwave oven, and the REEs and other elements were determined using the inductively coupled-plasma mass spectrometry instrument (ICP-MS, PE Elan 6000, America) and inductively coupled-plasma atomic-emission spectrometry instrument (ICP-AES, VISTA-PRO, America Varian) at the Guangzhou Institute of Geochemistry, Chinese Academy of Science. The analysis accuracy (RSD) was estimated to be $<5\%$, and the analytical data are given in Table 2.

The minerals of selected coal samples from No. 4 and 5 coals were determined in high-temperature ashes by X-ray diffraction method (XRD) using the XRD instrument D/max-1200 (Japan). The minerals were identified on the

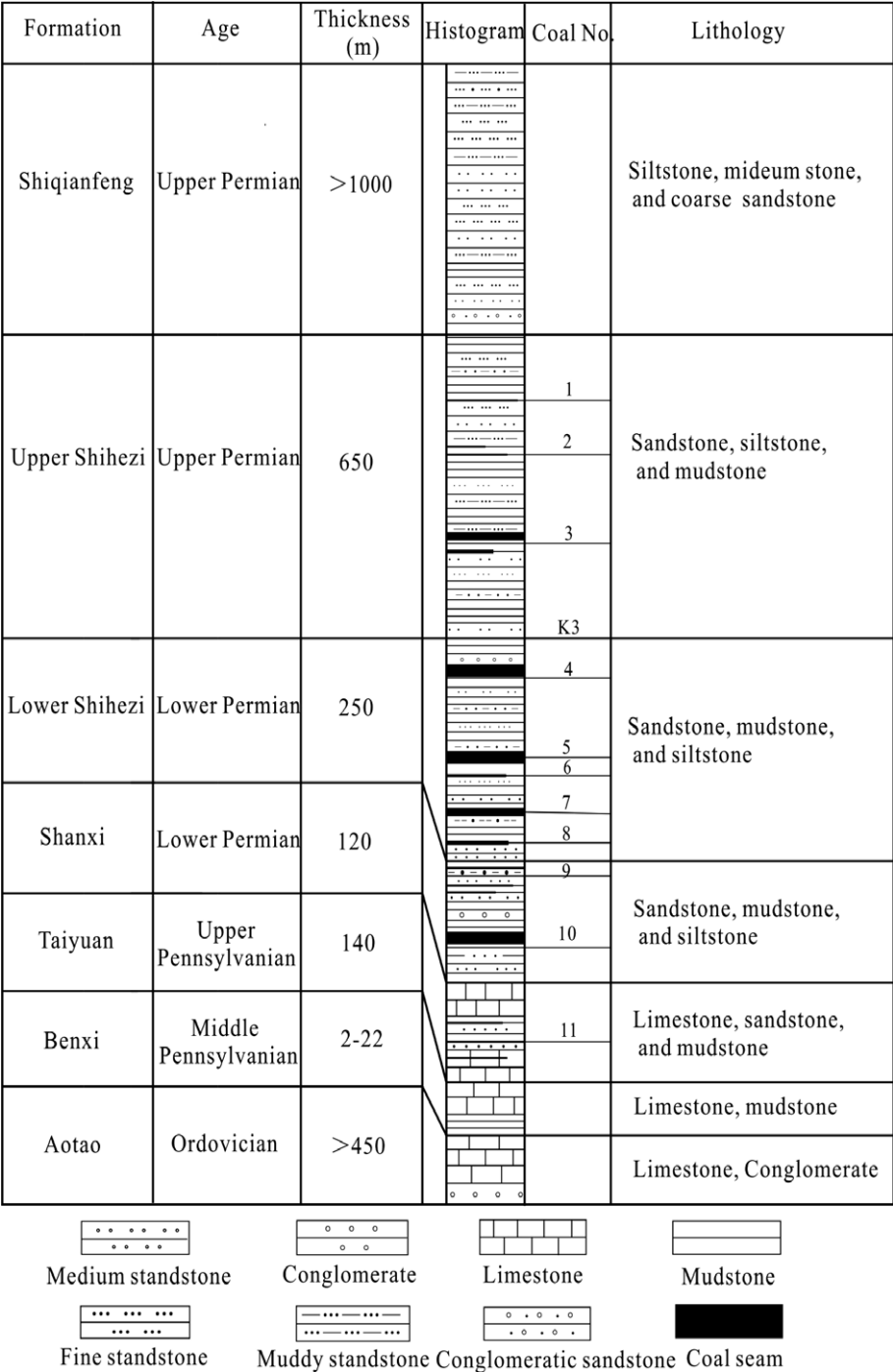


Fig. 3. Stratigraphic column and lithological characteristics of coal-bearing sequence in the Huaibei Coalfield.

XRD patterns, and crystal TiO₂ as interior label material was used for semi-quantitative analysis. The relative abundances of the minerals in samples were calculated using the ratio of relative intensity I_s/I_i (where I_s is the intensity of specific spectrum of examined minerals, and I_i is the intensity of the specific spectrum of interior label material). The results of relative abundances of the minerals are listed in Table 3.

4. Discussions

4.1. REE abundances in Huaibei coals as compared with other coals

The total $\sum$ REE in Permian coals of the Huaibei Coalfield range from 56.0 to 262 $\mu\text{g/g}$, with an average of 141 $\mu\text{g/g}$. They are about 20–100 times than chondritic

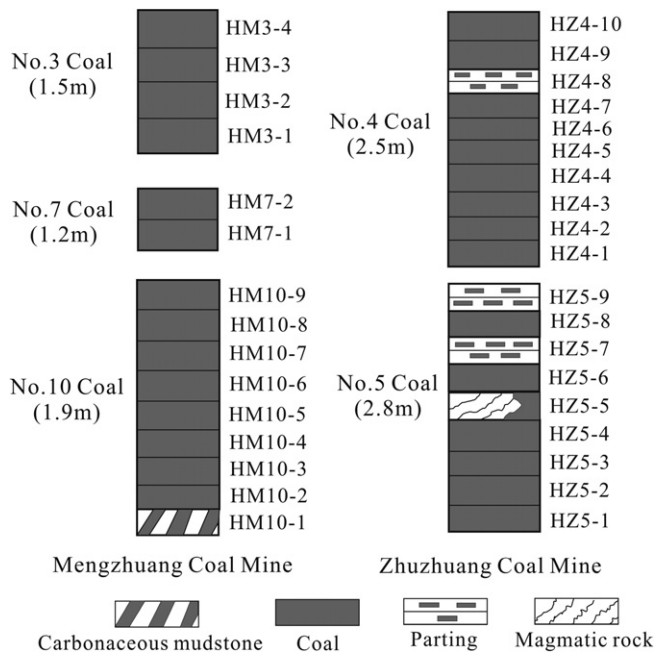


Fig. 4. Samples collected from the No. 10, 7, 5, 4 and 3 Coals of Permian age in the Huaibei Coalfield.

abundances which reported by Evensen et al. (1978). The range of $\sum$ REE abundances in coals of the Huaibei Coalfield are within that Permo-Pennsylvanian coals of northern China and Chinese coals, however, the average $\sum$ REE abundances in the Huaibei coals are 1.0–1.6 times that in Permo-Pennsylvanian coals of northern China (Wang et al., 1997), and 1.0–1.8 times that in Chinese coals (Zhao, 2002). Compared with the world average $\sum$ REE value of 46.3 $\mu\text{g/g}$ (Valkovic, 1983) and the average $\sum$ REE value of 62.1 $\mu\text{g/g}$ in U.S. coals (Finkelman, 1993), the average $\sum$ REE value of Huaibei coals are 3.0 times and 2.3 times, respectively. Thus, the Huaibei coals are enriched in REEs as compared with coals from many other coalfields.

4.2. Variation of REEs in coals from the Huaibei coalfield

The REE abundances are variable in samples from different mines, between different coal seams and within individual coal seams in the Huaibei Coalfield. As noted by many workers (Liu and Yang, 1999a; Liu et al., 1999b, 2001, 2004, 2007; Ren et al., 1999), variation of REE abun-

Table 1
The proximate and ultimate analyses and total Hg concentrations of the Huaibei coals

Sample	A _d %	M _{ad} %	V _{daf} %	S _{t,d} %	P _d %	Q _{ad} (MJ/Kg)	C _{daf} %	H _{daf} %	N _{daf} %	Hg(mg/kg)
HM3-1	10.08	2.62	36.07	0.22	0.002	26.0	81.8	5.12	1.43	0.07
HM3-2	11.34	2.03	37.86	0.34	0.003	27.9	83.1	5.24	1.47	0.07
HM3-3	14.33	3.17	40.76	0.81	0.053	30.1	83.9	6.11	1.63	0.21
HM3-4	14.63	2.42	38.57	0.55	0.016	27.6	83.1	5.47	1.54	0.14
HZ4-1	8.75	2.13	37.21	0.49	0.004	29.3	81.1	3.72	3.58	0.10
HZ4-2	11.68	2.01	36.89	0.85	0.012	28.1	79.4	3.19	2.92	0.24
HZ4-3	27.74	1.94	39.33	0.23	0.004	28.4	64.8	1.17	1.94	0.15
HZ4-4	18.33	1.97	38.57	0.50	0.021	29.1	72.2	2.25	3.19	0.06
HZ4-5	20.29	2.31	41.24	0.57	0.009	30.2	70.8	2.68	3.52	0.14
HZ4-6	20.18	2.02	39.13	0.54	0.011	29.4	71.2	3.00	3.37	0.27
HZ4-7	24.98	1.89	40.22	0.49	0.008	28.7	65.5	3.08	2.26	0.25
HZ4-8	67.01	nd	nd	nd	nd	nd	nd	nd	nd	0.33
HZ4-9	12.87	2.44	39.27	0.46	0.016	26.4	79.5	3.18	2.25	0.15
HZ4-10	14.78	2.05	38.98	0.43	0.008	28.9	76.1	3.21	2.96	0.27
HZ5-1	15.01	1.77	43.67	0.88	0.022	32.2	76.0	3.35	3.3	0.33
HZ5-2	15.78	2.06	42.58	0.50	0.014	30.8	73.8	3.60	3.05	0.79
HZ5-3	18.35	2.26	44.43	0.83	0.009	33.7	72.0	3.22	3.64	0.43
HZ5-4	16.16	1.68	40.32	0.67	0.032	32.1	74.1	3.39	2.66	0.41
HZ5-5	96.59	nd	nd	nd	nd	nd	nd	nd	nd	8.02
HZ5-6	16.18	2.03	44.26	0.49	0.018	34.2	73.0	3.65	3.10	0.64
HZ5-7	64.70	nd	nd	nd	nd	nd	nd	nd	nd	4.95
HZ5-8	17.14	1.74	43.18	0.46	0.027	29.8	72.4	3.83	2.90	0.64
HZ5-9	87.02	nd	nd	nd	nd	nd	nd	nd	nd	1.82
HM7-1	13.53	1.91	38.28	0.44	0.004	28	81.5	5.22	1.53	0.31
HM7-2	13.88	1.94	41.93	0.74	0.002	29.4	83.8	5.72	1.76	0.37
HM10-1	65.01	nd	nd	nd	nd	nd	nd	nd	nd	0.39
HM10-2	13.60	1.93	39.72	0.64	0.009	26.7	82.7	5.45	1.60	0.16
HM10-3	1.51	1.62	40.97	0.46	0.003	26.3	81.2	5.29	1.43	0.11
HM10-4	22.52	2.98	47.20	0.50	0.036	31.2	83.7	7.40	1.73	0.15
HM10-5	13.82	2.22	43.29	0.92	0.014	29.5	82.3	5.80	1.58	0.27
HM10-6	13.21	2.32	41.24	0.32	0.008	29.2	82.9	6.01	1.53	0.12
HM10-7	10.93	1.53	45.32	0.87	0.013	29.3	82.3	5.78	1.62	0.19
HM10-8	13.65	1.86	42.17	1.24	0.007	27.9	83.1	4.78	1.55	0.29
HM10-9	23.14	2.01	39.83	0.74	0.120	24.3	79.0	5.83	1.71	0.21

nd, not detected; A, ash yield; d, dry; M, moisture; ad, air dried; V, volatile content; daf, dry ash free; S_t, total sulfur; P, phosphorus; Q, calorific value; %, wt.%.

Table 2

Abundances and geochemical parameters of REEs in coal and rock samples on whole-coal basis from the Huaibei Coalfield (in $\mu\text{g/g}$)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(La/Yb) _N	δEu	δCe
HM3-1	23.5	48.1	5.32	19.3	4.27	0.854	3.29	0.654	3.99	0.847	2.34	0.346	2.08	0.582	7.61	0.7	1.03
HM3-2	35.7	56.6	6.17	22.1	4.37	0.78	3.1	0.636	4.13	0.834	2.19	0.308	1.76	0.437	13.66	0.65	0.92
HM3-3	31.5	62.2	6.88	25	5.17	0.844	3.35	0.686	3.89	0.839	2.35	0.354	2.16	0.385	9.82	0.62	1.02
HM3-4	25.7	54	6.65	26.9	4.69	0.903	3.33	0.633	3.77	0.792	2.16	0.316	1.88	0.405	9.21	0.7	0.99
HZ4-1	8.6	26	2.26	9.1	2.05	0.427	2.02	0.339	2.13	0.422	1.14	0.173	1.07	0.187	5.41	0.64	1.42
HZ4-2	15.4	38.6	3.21	12.3	2.65	0.598	2.68	0.443	2.92	0.634	1.85	0.284	1.79	0.328	5.79	0.69	1.32
HZ4-3	24.7	75.6	6.08	22.5	3.98	0.689	3.02	0.487	2.96	0.601	1.69	0.264	1.73	0.299	9.62	0.62	1.48
HZ4-4	35.3	69.4	5.45	20.9	3.85	0.671	3.12	0.524	3.17	0.655	1.86	0.275	1.86	0.31	12.78	0.59	1.2
HZ4-5	29.7	63.1	5.27	21	4.09	0.741	3.42	0.582	3.72	0.758	2.08	0.323	2.06	0.358	9.71	0.61	1.21
HZ4-6	32.2	62.7	5.14	21.2	4.27	0.918	4.55	0.799	4.92	1.07	2.97	0.468	3.04	0.532	7.13	0.64	1.17
HZ4-7	42.7	86.9	6.66	26.4	4.98	0.994	4.68	0.764	4.51	0.968	2.76	0.42	2.84	0.474	10.13	0.63	1.24
HZ4-8	47.3	143	11.3	40.5	6.15	1.04	4.18	0.822	5.05	1.06	3.06	0.477	3.35	0.554	9.53	0.63	1.49
HZ4-9	23.1	47.5	3.86	15.2	3.04	0.796	3.22	0.52	3.35	0.747	2.07	0.322	2.38	0.367	6.54	0.78	1.21
HZ4-10	62.6	122	9.51	36.6	7.24	1.59	6.47	1.011	5.89	1.21	3.55	0.504	3.31	0.574	12.74	0.71	1.2
HZ5-1	32.6	63.1	4.97	19.7	3.67	0.741	3.17	0.566	3.29	0.685	1.81	0.277	1.77	0.294	12.4	0.66	1.19
HZ5-2	34.8	66.9	5.2	19.5	3.8	0.72	3.38	0.582	3.46	0.701	1.94	0.286	1.87	0.306	12.53	0.61	1.2
HZ5-3	40.5	80	6.06	23.8	4.38	0.785	3.83	0.646	3.89	0.816	2.26	0.343	2.24	0.373	12.18	0.59	1.23
HZ5-4	33.4	63.6	5.05	19.7	3.84	0.794	3.54	0.631	3.79	0.806	2.22	0.356	2.39	0.399	9.41	0.66	1.18
HZ5-5	378	690.1	45.6	157	22.3	4.21	12.22	1.77	8.27	1.38	3.36	0.435	2.46	0.387	103.72	0.78	1.27
HZ5-6	35.9	74.7	5.78	22.2	4.23	0.796	3.52	0.631	3.76	0.76	2.09	0.329	2.12	0.354	11.41	0.63	1.25
HZ5-7	61.9	182.1	12.7	46.5	7.62	1.41	5.44	0.867	5.07	1.05	2.96	0.452	3.15	0.53	13.26	0.67	1.56
HZ5-8	44.9	83.4	6.53	23.6	4.38	0.847	3.38	0.576	3.49	0.672	1.83	0.281	1.8	0.309	16.8	0.67	1.17
HZ5-9	64.6	210	15.7	59.6	10.93	2.09	8.87	1.352	7.53	1.4	3.69	0.529	3.23	0.573	13.5	0.65	1.59
HM7-1	32.3	63.6	7.42	28.4	5.32	0.917	3.38	0.643	4.43	0.946	2.62	0.391	2.36	0.514	9.22	0.66	0.99
HM7-2	43.5	81.8	9.1	33.2	6.46	1.22	4.25	0.766	4.78	1.04	2.96	0.452	2.79	0.655	10.5	0.71	0.99
HM10-1	42	83	9.07	32.5	5.23	0.99	3.55	0.656	4.73	1.01	2.79	0.415	2.5	0.622	11.34	0.7	1.02
HM10-2	29.6	57.1	6.19	22	3.73	0.651	2.49	0.49	3.24	0.694	1.93	0.289	1.75	0.325	11.39	0.65	1.01
HM10-3	14.8	28.1	2.73	8.7	1.89	0.337	1.29	0.255	1.46	0.318	0.9	0.136	0.84	0.142	11.87	0.66	1.06
HM10-4	19.2	40.8	4.19	14.1	2.48	0.424	1.58	0.305	1.81	0.407	1.19	0.186	1.18	0.172	10.96	0.65	1.09
HM10-5	16.5	36.2	4.11	15.3	2.7	0.498	1.84	0.349	2.2	0.459	1.24	0.181	1.07	0.182	10.39	0.68	1.06
HM10-6	42.3	79	7.9	25.9	4.29	0.701	2.68	0.527	3.34	0.744	2.15	0.335	2.11	0.549	13.5	0.63	1.04
HM10-7	41.1	75.2	7.54	24.8	4.03	0.613	2.44	0.501	3.45	0.755	2.15	0.328	2.03	0.532	13.64	0.6	1.03
HM10-8	26.8	49.2	5.53	20.4	3.31	0.61	2.18	0.402	2.69	0.526	1.34	0.183	1.01	0.234	17.87	0.69	0.97
HM10-9	39.8	86.6	9.13	31.6	5.51	1.023	4.62	1.08	9.09	2.18	6.76	1.13	7.65	1.52	3.5	0.62	1.09

Table 3

Correlation coefficients between $\sum\text{REE}$ and other trace elements in the Huaibei coals

Elements	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	Rb	Sr	Zr	Nb	Ba	Hf
r	0.55	0.41	0.59	−0.36	0.53	0.41	0.13	0.84	0.49	0.6	0.44	0.81	0.77	0.73	0.83
Elements	Ta	Pb	Th	U	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	TiO ₂	SiO ₂	
r	0.77	0.43	0.83	0.54	0.79	−0.3	0.53	0.64	0.43	−0.23	0.52	0.91	0.74	0.80	

dances of coals from different mines and different seams may be influenced by many factors.

From Table 2, there is significant vertical variation of REE contents among benches of individual coal seam, and high REEs contents occur in magmatic intrusion rock sample (HZ5-5) and parting samples (HZ4-8, HZ5-7, HZ5-9, and HM10-1). Especially in No. 5 and No. 7 Coals, igneous intrusion resulted in higher average $\sum\text{REE}$ content, 154 and 173 $\mu\text{g/g}$, respectively, than other seams in the two mines.

Fig. 5 shows the chondrite-normalized REE patterns of the Huaibei coals, and the REE abundances of chondrites were taken from Evensen et al. (1978). As it can be seen from Fig. 5, all the REE patterns look rather similar despite of their large difference in total REE concentrations. The REE patterns are characterized by LREE

enrichment with (La/Yb)_N ratios of 3.70 (HM3-5) to 103.7 (HZ5-5), and relatively flat HREE distributions. All patterns show negative Eu anomalies, with δEu values ranging from 0.59 (HZ4-4 and HZ5-3) to 0.78 (HZ4-9 and HZ5-5). In fact, these patterns are quite similar to those of the most abundant rock type in the continental crust – granitic rocks.

4.3. Origin and occurrence of REEs in coals

The REEs in coals were mainly derived from the source regions and were transported into the coal-forming swamp, and a little amount of REEs in coals may be originated from coal-forming plants (Birk and White, 1991; Eskenazy, 1987, 1996; Finkelman, 1993, 1994; Steven and Brian, 2003; Wang et al., 1989). In REE-rich coals, the REEs

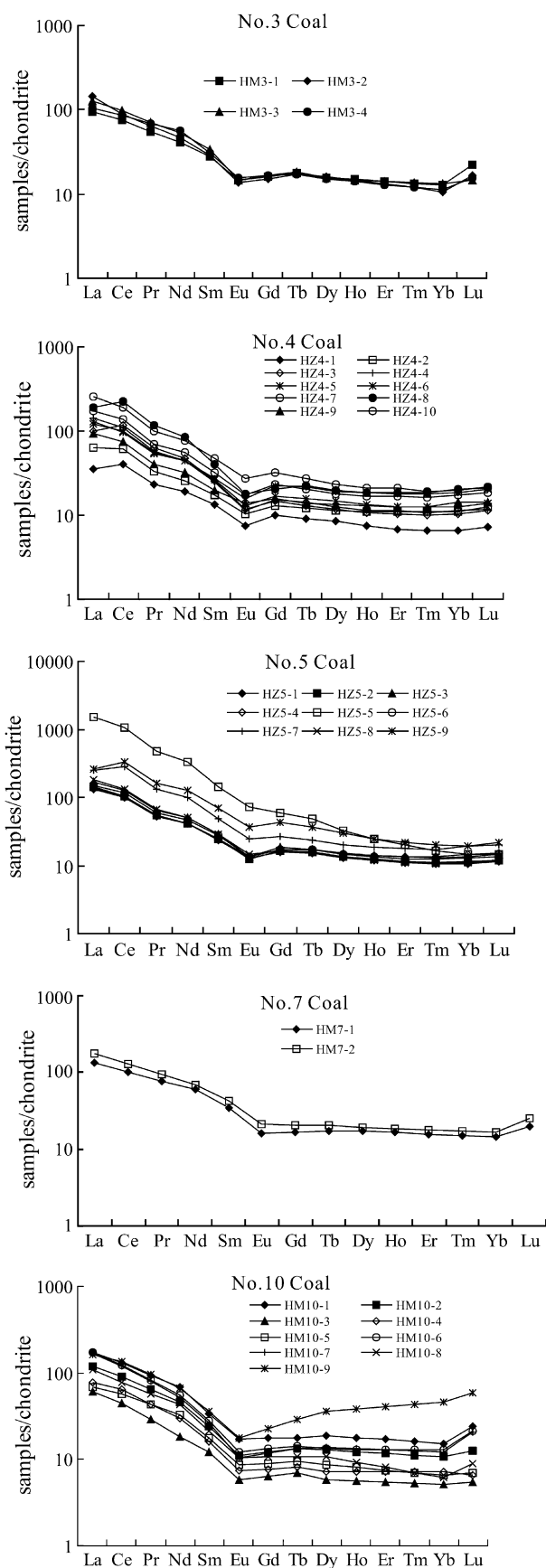
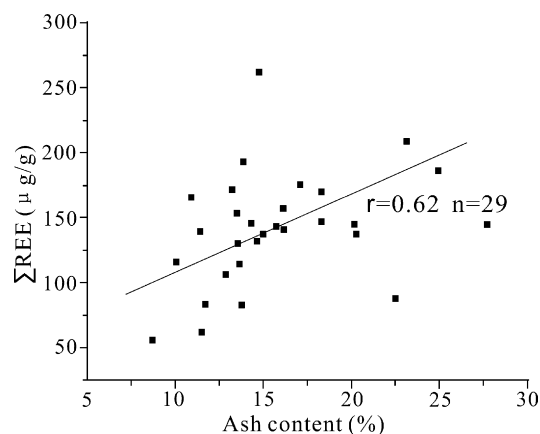


Fig. 5. REE patterns of coal samples in the Huaibei Coalfield.

Fig. 6. Correlation between Σ REE and ash content.

may be partly associated with organic matter (Dai et al., 2002; Eskenazy, 1996; Finkelman, 1993, 1994; Seredin, 1996; Steven and Brian, 2003; Wang et al., 1989). This is particularly true for the coals that are slightly enriched in heavy rare earth elements (HREE) relative to light rare earth elements (LREE) on their REE patterns (Querol et al., 1995). Experiment conducted by Eskenazy (1999) shows that ions, including Na^+ , K^+ , Ca^{2+} and Mg^{2+} , bound to COOH and OH^- groups may be replaced by REE ions by ion exchange.

Our results of REE abundances of the Huaibei coals have following characteristics.

(1) The negative Eu anomaly in coal is well established, with an average δEu of 0.653 (Table 2). Similar to studies on Bulgarian coals reported by Eskenazy (1987) and on Nova Scotia coals by Birk and White, 1991, the negative Eu anomaly in the Huaibei coals is inherited from the source regions.

(2) There is a positive correlation between ΣREE and ash contents of coals ($r = 0.62$, $n = 29$) (Fig. 6). The No. 10 Coal of the Shanxi Formation is lower in ash content than the coals of other formations; and so is the ΣREE content in coals. The correlation coefficients between ΣREE and associated trace elements are calculated in Table 3. It is shown that the ΣREE content correlates positively not only with major elements of the minerals, including P, Si, Al, Ti, K, Fe and Na, but also with trace elements, including Cr, Th, Ta, Sc, Hf, Zr and Nb, which are lithophile elements likely being associated with clay minerals and transported to the coal swamp during peat deposition (Chou, 1997). The association of ΣREE content and P_2O_5 is interesting. It indicates that either a significant amount of rare earth elements is contained in a phosphate mineral (such as aluminophosphate mineral, apatite, etc.) or phosphate and rare earth elements were closely associated when they were transported to the coal swamp during peat formation. However, the ΣREE content correlate negatively with Ca ($r = -0.3$), and MnO ($r = -0.23$) because Ca and Mn are associated with calcite which was deposited from groundwater (Kolker and Chou, 1994).

Table 4
Relative abundances of minerals in mineral matter of coals from the Huaibei Coalfield by X-ray diffraction (in %)

Sample	smectite	illite	kaolinite	chlorite	quartz	plagioclase	calcite	dolomite	goethite
HZ4-1	–	24	–	39	–	–	25	11	–
HZ4-2	–	54	–	16	8	–	15	7	–
HZ4-3	20	10	30	–	22	–	5	5	–
HZ4-4	18	46	–	10	–	–	11	4	–
HZ4-5	17	41	–	25	–	–	16	–	–
HZ4-6	–	40	–	21	–	–	28	4	–
HZ4-7	15	15	55	7	6	–	6	–	–
HZ4-8	20	5	70	–	4	–	–	–	–
HZ4-9	16	29	–	18	–	–	32	4	–
HZ4-10	–	57	–	30	–	–	7	5	–
HZ5-1	–	43	34	21	–	–	–	–	–
HZ5-2	–	37	30	15	–	–	5	6	–
HZ5-3	22	17	33	26	–	–	–	–	–
HZ5-4	–	47	26	12	14	–	–	–	–
HZ5-5	–	26	–	35	–	22	11	6	–
HZ5-6	10	–	60	–	6	–	–	–	23
HZ5-7	–	6	65	–	–	–	3	2	–
HZ5-8	–	22	56	–	–	–	–	–	19
HZ5-9	–	8	38	–	45	7	–	–	–

“–”, peak not detected on spectrum.

(3) Minerals identified in the Huaibei coals include illite, kaolinite, chlorite, smectite, quartz, calcite, dolomite, plagioclase and goethite, and the clay mineral content (smectite, illite, kaolinite, and chlorite) is more than 60% (Table 4). The rare earth elements appear to be distributed in clay minerals. Quartz is very low in REE because the composition of quartz is SiO_2 , and REEs generally substitute Al in minerals (Wang et al., 1989).

(4) There have been discussions about to what extent rare earth elements are associated with the organic matter (e.g., Eskenazy, 1999; Zhao, 2002). The REE patterns in coals and partings are similar (Fig. 5), indicate that REEs in coals and partings may be derived from similar sources. Partings are much higher in REEs than coals, first because partings have higher clay mineral content, if the REE abundances in the clay minerals of coal and partings are similar, REEs in the mineral matter of coals cannot account for REEs abundances in whole coal, so it appears that a significant amount of REEs may be associated with the mineral matter, on the other hand, it also indicate that there are differences in composition or relative abundance between the minerals in the coals and the parting materials.

Some studies reported that a portion of the REE may be associated with the organic fraction of coal based on selective leaching and particle segregation experiments (Dai et al., 2002; Palmer et al., 1990; Willett et al., 2000). In this study, we may consider that the average $\sum\text{REE}$ content in coals is 141 $\mu\text{g/g}$, coal contains an average of 15.8% ash, and if all the REEs are in the ash, the $\sum\text{REE}$ content in ash is calculated to be 892 $\mu\text{g/g}$. This value is much higher than the contents of $\sum\text{REE}$ in ash of the partings (carbonaceous mudstone) (290–448 $\mu\text{g/g}$, Table 1). It is likely that REEs are not all in the ash, and a part amount of REE may be in the organic matter of coal. (5) Effects of magmatic intrusion on REEs in coals.

The No. 5 and 7 Coals were intruded by magmatic rock, and sample HZ5-5 is the magmatic rock in the No. 5 Coal. Sample HZ5-5 has been weathered and the major minerals are clay minerals such as illite, chlorite, and part of plagioclase remains (22%) (Table 4). The rock sample has a high $\sum\text{REE}$ content of 1327 $\mu\text{g/g}$ and the chondrite-normalized La/Yb ratio is 103.5. The REE pattern of this igneous rock sample slightly differs from coals and shows a steeply sloped pattern especially for the light REEs, and the phenomena is consistent with No. 9 Coal influenced by volcanic ash from the Zhijin coalfield, Guizhou Province, China reported by Dai et al. (2003b) (Fig. 5). The range of REEs in the No. 5 and 7 Coals overlaps with the No. 3, 4 and 10 Coals, and $\sum\text{REE}$ in these two Coals are also higher than other coal seams, but the REE patterns are similar to other coals in the Huaibei Coalfield. Magmatic intrusion may result in the enrichment of REEs in coals (Dai et al., 2003a; Huang et al., 2000; Shao et al., 1997). Enrichment of REEs in No. 5 and 7 coals may be related to: (1) the magmatic intrusion resulting in the thermal decomposition of macerals and minerals and input of REEs from the dike into the coal or vice versa, or (2) after the magmatic intrusion, REEs could migrate with groundwater into the rest of the coals. We also found that the No. 5 and 7 Coals are several times higher in Hg concentrations than other coals in the Huaibei Coalfield (Zheng et al., 2007). Further work is needed to obtain more information on the mechanism of REE migration from igneous rock to coal.

5. Conclusions

The $\sum\text{REE}$ content in the Huaibei coals ranges from 56.0 to 262 $\mu\text{g/g}$, which is within the range of Permo-Pennsylvanian coals from northern China. The average $\sum\text{REE}$ in the Huaibei coals is 141 $\mu\text{g/g}$, which is higher than the

average of the northern China coals, Chinese coals and the world coals.

The REE abundances in coals vary in different coal seams and within the same coal seam. The partings are higher in REE because of higher clay minerals contents, and have similar REE pattern to the coals. The igneous intrusion resulted in enrichment of REEs in No. 5 and 7 Coals, but no obvious effect on the REE pattern of coal.

The coals and partings in the Huaibei Coalfield have a clear Eu anomaly, which is inherited from the source regions. The Σ REE content correlates positively with ash content and lithophile elements, including Si, Al, Ti, Fe, and Na, indicating REEs are distributed in clay minerals.

Some of REEs occurred in the organic matter. It appears that REEs were transported to the coal swamp during peat accumulation possibly by adsorption on clay minerals or in colloidal form in solution. The REEs were largely incorporated into clay minerals during diagenesis. Part of REEs in solution were adsorbed by organic matter and incorporated into the mineral matter.

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