



Geochemistry of Palaeogene coals from the Fuqiang Mine, Hunchun Coalfield, northeastern China: Composition, provenance, and relation to the adjacent polymetallic deposits



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ABSTRACT

This paper describes the geochemistry of the two Palaeogene coal seams (FQ-23 and FQ-26) from the Fuqiang mine, Hunchun Coalfield, Jilin Province, northeastern China. The samples investigated consist of coal, parting, and roof and floor strata. The two Fuqiang coals are lignite/subbituminous rank and have low sulfur contents (0.13% and 0.16% on average, respectively). In comparison with the average values for common global low-rank coals, the Fuqiang coals are richer in W, Cs, Sb, Pb, Li, V, Ga, and Zr.

The terrigenous components in the Fuqiang coals were derived from the Mesozoic (mostly Lower Cretaceous) and Paleozoic igneous and metamorphic rocks, which are abundant in areas surrounding the Hunchun coal basin. The elevated concentrations of trace elements are attributed to two processes: (1) Contribution of clastic materials derived from mineralized Paleozoic rocks, which also host economical ore deposits of these elements; and (2) Mobilisation and redeposition of these elements by acidic waters, which circulated within the coal basin. The latter is evidenced by enrichment in medium rare earth elements, distinct positive Gd anomalies, and high concentrations of boron in the coals. The overall similarity of the geochemical signatures of the Fuqiang coals and the adjacent Au, Cu and W deposits hosted by the Paleozoic igneous and metamorphic rocks underlying and bordering the Hunchun Basin, indicate that they are genetically linked.

1. Introduction

The eastern Hunchun area is located at the junction between the western Pacific continental margin and the eastern Xing'an-Mongolian Orogenic Belt (Cao et al., 2011; Sun et al., 2013; Chen et al., 2017; Yang et al., 2018), and the latter is situated between the North China and Siberian cratons. During the Phanerozoic, a series of intensive and extensive tectonic and magmatic activities associated with mineralization events occurred in this area. For example, numerous ore deposits were discovered in the Hunchun area, including the Late Permian Wudaogou orogenic gold and the Yangjingou hydrothermal vein scheelite deposits; the Cretaceous Xiaoxi'nancha porphyry gold-copper deposit and many

medium or small-sized tungsten and gold deposits (Fig. 1; Wu et al., 2000, 2002, 2007, 2011; Zhang et al., 2004; Zhang et al., 2010; Donskaya et al., 2012; Xu et al., 2013; Chen et al., 2014; Chai et al., 2015; Ren et al., 2016; Li, 2017). Nearly one hundred tons of gold and hundreds of thousands tons of tungsten resources have been proven in this mineralized zone (Wang et al., 2009). The Hunchun Coal Basin is also close to South Primorye, Far Eastern Russia (Fig. 1b), an area rich in coal resources and coal-hosted Ge–W deposits (Seredin and Danilcheva, 2001).

The Hunchun Basin is a Paleogene fault bounded graben structure (Wang and Wang, 2004). Its basement consists of a large Hercynian granite intrusion, which invaded the Permian and Jurassic-Early

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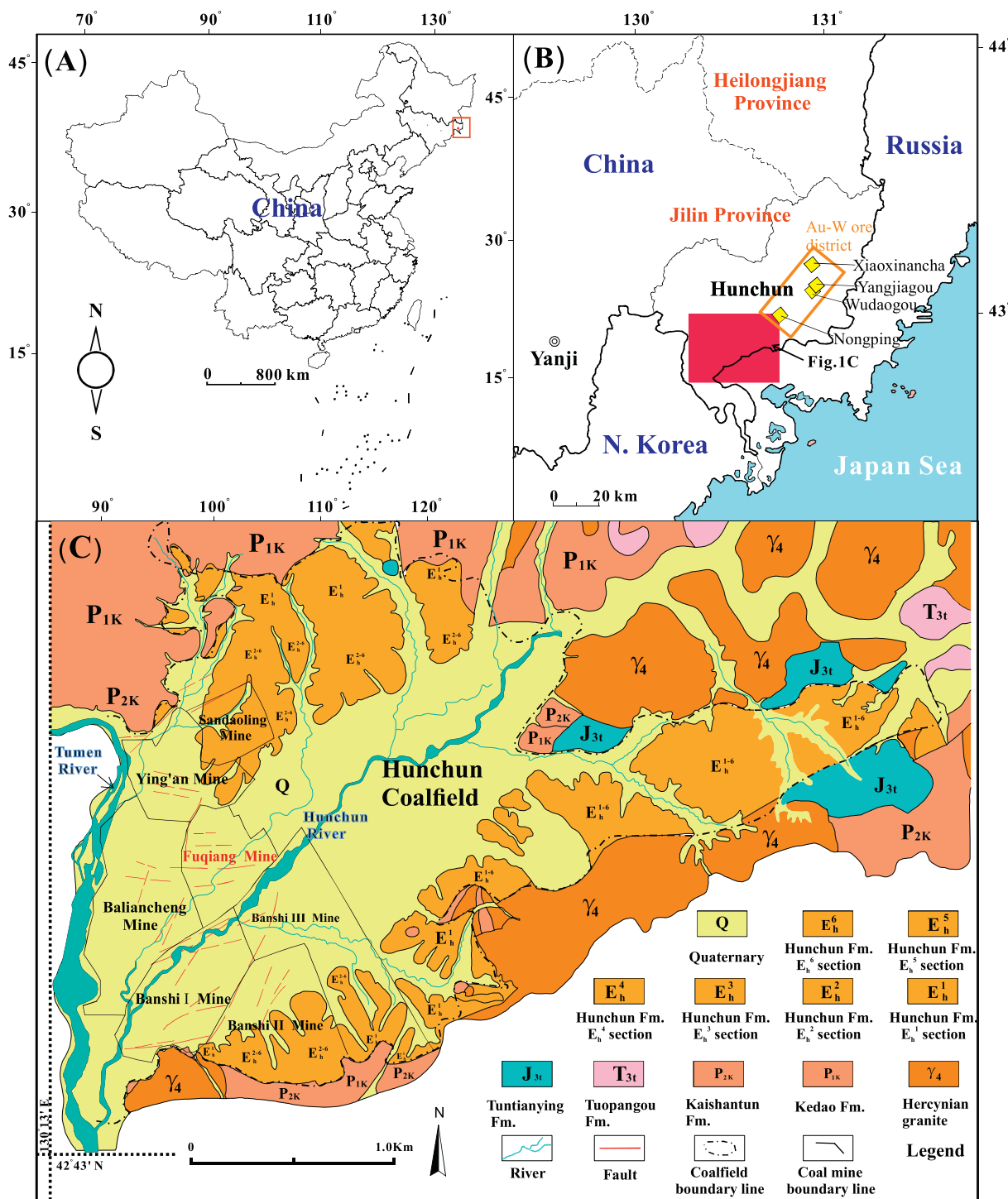


Fig. 1. Location of the Hunchun Coalfield and adjacent ore deposits (A, B), coal mines and geological map of the coalfield (C). (A) and (B) are modified after Dai et al. (2018); the locations of ore deposits are from Chen et al. (2017).

Cretaceous volcanic and sedimentary rocks (Xu et al., 2013; Chen et al., 2017; Wang and Wang, 2004). Some Middle Paleozoic metamorphic rocks also occur in the area (Chen et al., 2015). Previous studies focused on metallogenesis, petrology and geochronology of metal ore deposits hosted by rocks in the area (e.g., Zhang et al., 2006; Sun et al., 2008; Zhao et al., 2010; Ren et al., 2012, 2016; Zhao et al., 2013; Chai et al., 2015; Chen et al., 2015, 2017). A total of 25 mineable and non-mineable coal seams were identified in the Hunchun Coalfield (Wang and Wang, 2004). However, to date, there have been only a few reports on coal-bearing sequences in the Hunchun Basin (e.g., Sun, 2015; Wang,

2015) and environmental issues caused by coal combustion (Moon et al., 2000). A recent study by Dai et al. (2018) investigated the modes of occurrence and the source of mineral matter contained in the Palaeogene coal seam and its enclosed intra-seam tonstein in the Baliancheng Mine, near the Fuquian mine of the Hunchun Coalfield (Fig. 1C). There are still two unanswered questions related to geochemical compositions of the coals in this coalfield: 1) Are the sediment source regions of the terrigenous matter of the Fuqiang coals the same as for the coals in the nearby Baliancheng Mine described by Dai et al. (2018)? 2) Are the elevated concentrations of trace elements in the Hunchun coals

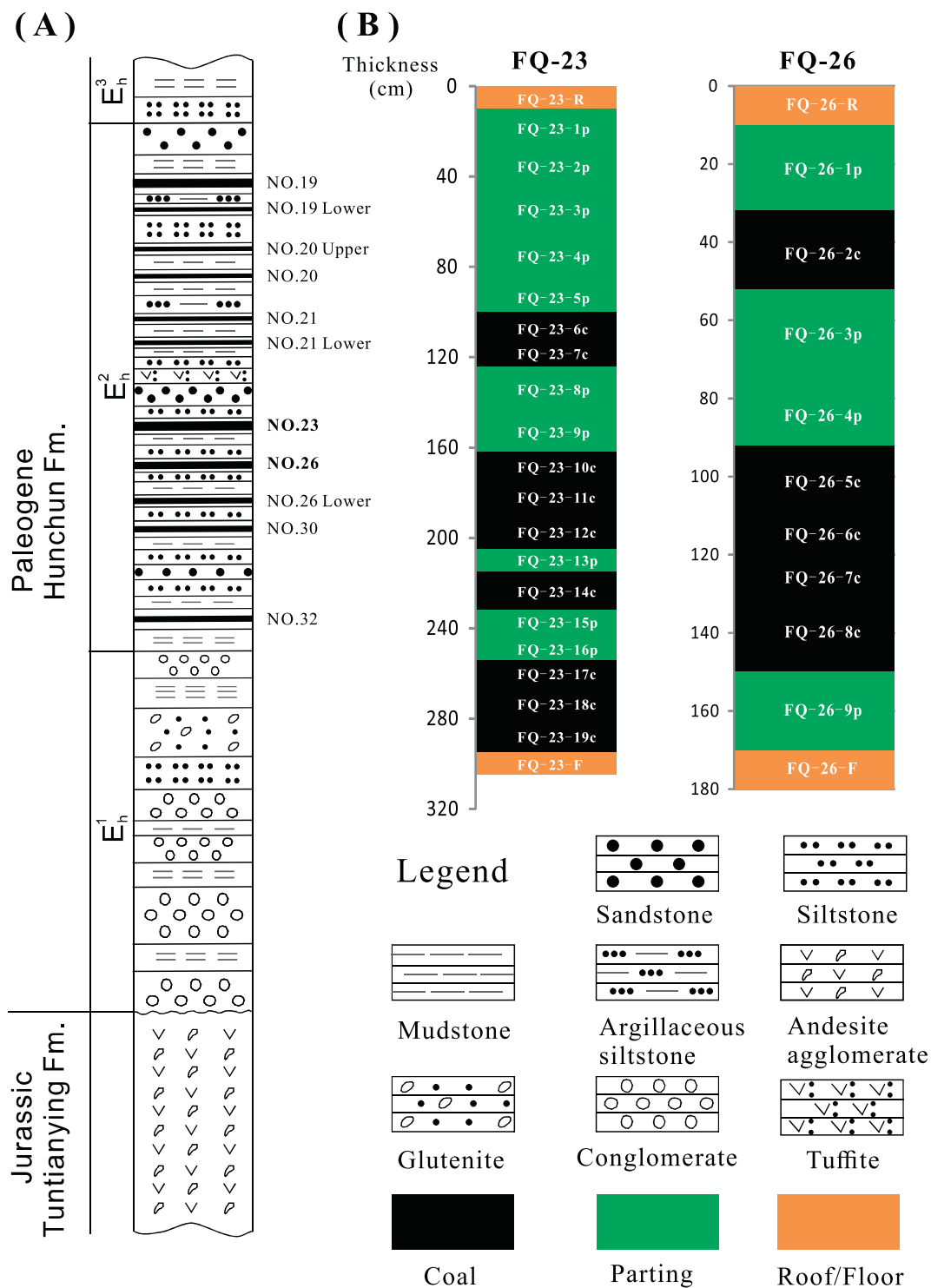


Fig. 2. Sedimentary sequences in the Fuqiang mine (A) and the sections of the Nos. 23 and 26 coal seams.

genetically related to polymetallic deposits in the areas surrounding the Hunchun Basin?

In this paper, we report the results of our investigation of the geochemistry of the currently mined Nos. 23 and 26 coal seams (including their roof, partings, and floor horizons) in the Fuqiang Mine in the Hunchun Coalfield. We also discuss genetic relationships between the coals and the adjacent ore deposits with the aim of testing the idea that these coals have the characteristics of ‘coal-hosted rare-metal deposits’ (Dai et al., 2016a) or ‘metalliferous coal’ (Seredin and Finkelman, 2008; Dai and Finkelman, 2018), which represents coals with concentrations

of critical elements generally over 10-times higher than the averages of corresponding elements in the world coals (Seredin and Finkelman, 2008).

2. Geological setting

The geological setting of the Hunchun Coalfield was previously described by Dai et al. (2018). The coalfield is situated in the eastern part of Jilin Province, Northeast China (Fig. 1), covering the area of ~460 km² between longitudes 130°13′–130°46′E and latitudes

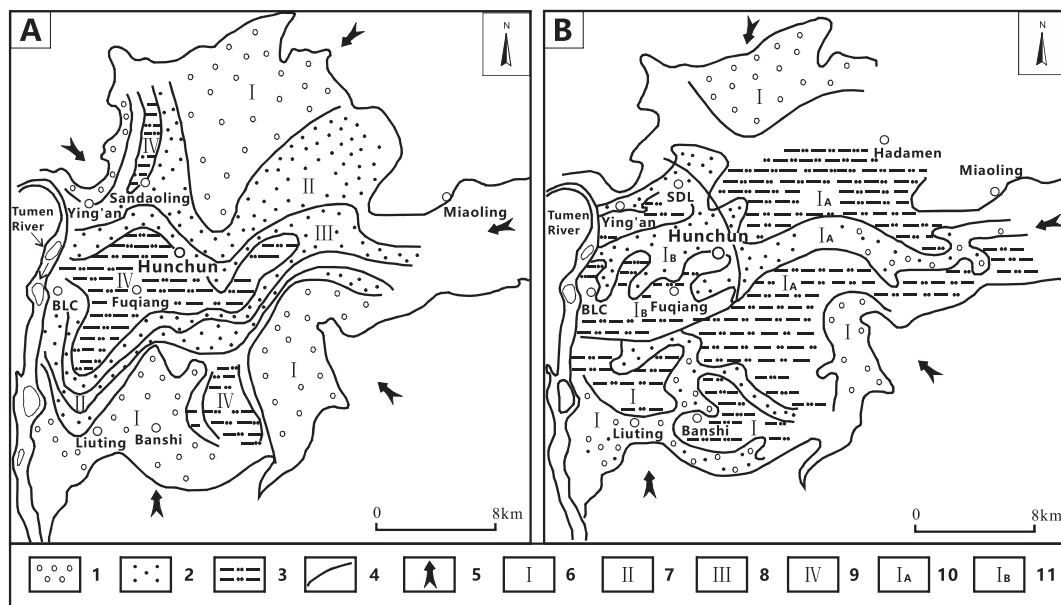


Fig. 3. Diagram of sedimentary environment of lower coal-bearing member (A and B, modified from Wang and Wang, 2004). 1. Conglomerate; 2. Sandstone; 3. Siltstone and mudstone; 4. Environment boundary; 5. Terrigenous direction; 6. Alluvial fan; 7. Transitional environment; 8. Fluvial; 9. Lacustrine, swamp; 10. Channel and floodplain; 11. Delta plain.

Table 1

Bench thickness (cm), proximate and ultimate analyses (%), total sulfur (%), gross calorific values (MJ/Kg), random huminite reflectance (%), and aluminosilicate mineral content in LTAs (wt%) of the Nos. 23 and 26 coal bench samples.

Sample	Thickness	M _{ad}	A _d	V _{daf}	C _{daf}	H _{daf}	N _{daf}	S _{t,d}	Q _{gr,d} (MJ/kg)	R _r	LTA	Quartz	Kaolinite	Illite	Chlorite	Plagioclase	K-feldspar
FQ-23-6c	14	14.38	43.58	53.29	77.84	5.87	1.45	0.14	16.61	0.38	51.51	26.7	28.1	27.9	2.3	5.8	5.3
FQ-23-7c	10	18.73	20.04	43.96	80.01	4.86	1.36	0.20	23.20	0.43	25.78	27.2	39.5	21			
FQ-23-10c	12	17.78	21.39	50.36	80.08	5.55	1.51	0.10	23.83	0.35	32.72	29.6	31.9	24.7			
FQ-23-11c	16	16.07	26.18	50.69	80.07	5.54	1.45	0.12	21.92	0.33	48.32	24.6	46.5	21.3			
FQ-23-12c	15	14.81	39.64	51.40	78.54	5.56	1.55	0.14	17.72	0.31	52.80	27.5	38.6	24.6			
FQ-23-14c	17	15.85	47.07	46.45	77.46	4.85	1.29	0.12	14.41	0.36	24.63	23.5	40.7	31.6		2.2	
FQ-23-17c	12	17.86	28.26	50.05	80.41	5.29	1.65	0.17	20.92	0.35	35.97	26	40.3	26.1			
FQ-23-18c	15	17.64	20.86	49.26	81.08	5.36	1.46	0.16	23.47	0.34	24.64	21.4	51.7	15			
FQ-23-19c	14	17.18	41.63	55.95	83.84	4.54	1.42	0.07	18.03	0.34	45.40	30.5	38.9	22.7	3	2.9	
WA-FQ-23	125*	16.56	32.93	50.27	79.85	5.27	1.46	0.13	19.74	0.35	38.34	26.1	39.9	24.0	0.59	1.27	0.59
FQ-26-2c	20	12.05	46.84	51.09	74.91	5.35	1.37	0.12	16.19	0.48	61.18	24.1	45.4	23.3		6.2	1.0
FQ-26-5c	18	12.39	43.07	51.91	76.59	5.56	1.55	0.17	18.18	0.46	56.54	26.3	35.3	30.3	6.1	1.5	
FQ-26-6c	10	15.64	18.56	47.96	80.48	5.49	1.38	0.22	27.13	0.44	26.89	23.1	51.8	23.8			
FQ-26-7c	10	13.00	43.62	50.57	73.89	5.49	1.22	0.11	16.42	0.45	52.61	6.1	83.0	10.7			
FQ-26-8c	20	16.48	19.23	46.59	81.51	5.38	1.45	0.17	26.99	0.49	22.40	24.0	52.9	21.7			
WA-FQ-26	78*	13.85	34.85	49.89	77.57	5.44	1.41	0.16	20.85	0.47	44.67	22.2	50.6	23.0	1.41	1.94	0.26

M, moisture; A, ash yield; V, volatile matter; C, carbon; H, hydrogen; N, nitrogen; S_t, total sulfur; Q_{gr,d}, gross calorific value; ad, as-received basis; d, dry basis; daf, dry and ash-free basis; R_r, random reflectance of huminite; WA, weighted average (weighted by thickness of sample interval); LTA, low-temperature ash yield. * Total thickness of coal benches (cm). The rows in bold are the weighted averages for each coal seam.

42°43′–42°59′N. The Hunchun Coalfield includes several major mines as shown in Fig. 1C. The Fuqiang underground mine (formerly known as the Chengxi Mine) is located in the northwestern part of the coalfield (Fig. 1C).

The Paleogene Hunchun Formation, which consists of typical continental sediments (Fig. 2) and is the coal-bearing sequence in the coalfield, was divided into three parts (Xu and Han, 1990). However, more recently, Wang and Wang (2004) and Wen (2014) divided the Hunchun Formation into six parts, from bottom to top as follows: E_h¹, conglomerate member; E_h², lower coal-bearing member; E_h³, member characterized by brown color and mainly composed of mudstone, siltstone, and sandstone; E_h⁴, middle coal-bearing member; E_h⁵, member containing similar lithological compositions with E_h³ member; and, E_h⁶, upper coal-bearing member.

The lower coal-bearing member (E_h²) (Fig. 2A), with a thickness of 145 m, is a major coal-bearing unit in the Fuqiang mine. It is composed of dark gray mudstone, siltstone, argillaceous siltstone, coal, and white

medium/coarse-grained sandstone. This unit includes a marker interval identified as K₂ (tuffite), which is located between the Nos. 21 and 23 coal seams and is used to determine the position of coal seams throughout the basin (Wang and Wang, 2004). In some locations, the K₂ layer is the roof of the No. 23 coal seam. The E_h² member consists of one or a few layers of green or grass-green tuffite.

The lower coal-bearing member (E_h²) in the Fuqiang mine contains ~16 coal seams, of which Nos. 19, 23, 26, 26 L, 30, and 32 are minable and the Nos. 19 L, 20, 21 and 31 are locally minable seams (Fig. 2A). The 1.5–2 m thick No. 23 and 26 coal seams (Fig. 2A, B) are currently being mined at the Fuqiang mine. Its roof and floor strata of the No. 23 seam are composed of siltstone and mudstone, respectively. The No. 26 coal seam (Fig. 2A, B) has a thickness of 1.0–1.5 m, and both its roof and floor horizons consist dominantly of siltstone.

The Upper Paleozoic and Mesozoic volcanic and clastic rocks are widely distributed in and around the coalfield. They form the basement of the coal basin and have an unconformable contact with the overlying

Table 2 Percentages of major-element oxides (%), concentrations of trace elements (ppm; Hg in ppb), and loss on ignition (LOI, %) for the coals from the Fuqiang mine (on a whole coal basis).

Sample	LOI	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Li	Be	B	F	Sc	V	Cr	Co	Ni	Cu	Zn	Ga
FQ-23-R	21.55	49.36	0.62	18.27	4.64	0.030	1.08	1.12	0.84	2.46	0.028	28.7	3.05	42.3	468	7.61	58.4	38.8	7.9	18.7	25.6	77.9	20.4
FQ-23-1p	29.06	44.89	0.57	15.72	4.42	0.028	0.92	0.98	0.83	2.57	0.016	35.9	4.46	51.8	398	11.2	73.1	42.6	8.1	17.9	40.4	72.8	20.8
FQ-23-2p	10.04	58.34	0.82	18.06	5.80	0.052	1.53	0.69	1.20	3.44	0.039	33.0	1.80	49.3	442	14.9	97.7	55.3	9.1	20.1	41.7	116	21.1
FQ-23-3p	13.79	54.81	0.89	18.56	5.26	0.043	1.26	0.75	0.97	3.61	0.060	31.4	1.99	42.6	429	9.36	98.5	56.9	8.0	19.4	36.7	119	20.5
FQ-23-4p	16.64	53.17	0.78	17.12	5.18	0.042	1.27	0.82	0.97	3.88	0.122	31.4	2.11	44.6	505	11.7	93.1	51.3	7.8	19.6	36.0	118	20.1
FQ-23-5p	55.42	29.19	0.44	9.71	1.67	0.017	0.43	0.83	0.51	1.77	0.012	23.6	3.85	73.4	190	9.19	75.7	33.4	6.4	10.4	40.8	22.9	14.4
FQ-23-6c	62.69	23.11	0.37	8.76	2.01	0.022	0.48	0.93	0.38	1.23	0.011	20.0	2.89	72.2	184	8.13	70.0	49.7	9.9	28.6	38.8	38.9	12.6
FQ-23-7c	83.72	9.64	0.18	4.25	0.73	0.012	0.10	0.88	0.17	0.33	0.006	10.5	1.32	118.4	90.8	4.73	39.5	15.4	5.2	8.7	16.7	8.1	10.1
FQ-23-8p	31.69	41.89	0.54	18.11	3.10	0.022	0.78	0.74	0.59	2.50	0.036	64.4	1.44	62.9	383	10.8	55.8	40.9	5.4	15.6	20.5	65.4	20.8
FQ-23-9p	42.39	35.38	0.65	15.04	2.57	0.020	0.53	0.82	0.50	2.07	0.033	58.8	1.52	71.6	310	10.7	87.8	36.7	4.7	14.4	40.1	75.3	18.2
FQ-23-10c	82.42	10.75	0.18	4.34	0.64	0.014	0.12	0.94	0.17	0.41	0.008	11.5	1.30	93.0	107	4.62	45.2	17.0	11.1	10.9	26.2	7.3	7.3
FQ-23-11c	78.02	13.23	0.21	6.11	0.69	0.014	0.13	0.95	0.18	0.47	0.010	15.7	1.36	91.7	116	5.42	38.3	16.7	7.9	9.7	24.7	10.0	8.8
FQ-23-14c	66.23	21.27	0.39	9.00	0.95	0.014	0.22	0.95	0.20	0.76	0.012	21.9	1.66	81.3	195	4.75	63.9	26.6	7.5	12.3	33.6	13.1	13.9
FQ-23-13p	38.14	37.68	0.57	17.42	2.61	0.016	0.51	0.85	0.37	1.79	0.035	75.5	1.44	67.6	372	11.5	80.7	41.4	4.8	15.6	52.8	37.9	20.3
FQ-23-14c	60.39	23.68	0.37	10.76	1.94	0.016	0.37	0.84	0.31	1.28	0.037	33.8	1.42	88.1	258	5.88	85.8	31.4	4.5	14.4	35.3	34.6	18.4
FQ-23-15p	39.05	37.58	0.57	15.08	3.53	0.027	0.77	0.69	0.55	2.11	0.035	56.2	1.64	61.4	325	13.0	104	42.0	7.1	17.5	45.5	96.9	18.3
FQ-23-16p	30.63	43.30	0.64	16.83	3.99	0.028	0.80	0.75	0.62	2.37	0.043	91.0	1.56	55.6	374	12.6	100	44.8	6.7	20.9	46.2	92.1	19.9
FQ-23-17c	76.78	13.77	0.23	6.34	1.02	0.016	0.20	0.86	0.21	0.56	0.010	25.1	1.67	81.5	135	7.60	72.6	25.7	17.6	17.8	41.7	16.4	9.7
FQ-23-18c	82.82	9.96	0.19	4.93	0.62	0.015	0.10	0.94	0.16	0.26	0.007	12.9	2.21	89.7	91.9	6.21	36.8	15.1	7.8	8.9	24.7	7.2	8.0
FQ-23-19c	65.52	21.44	0.37	8.79	1.46	0.017	0.30	1.00	0.32	0.76	0.020	24.4	3.93	91.5	183	5.79	51.6	27.1	6.7	11.7	24.7	18.9	16.6
FQ-23-F	10.91	54.89	0.99	21.77	5.74	0.046	1.41	0.69	0.83	2.65	0.082	42.0	1.65	35.3	458	12.1	105	68.4	11.4	29.3	42.4	132	22.6
WA-23	72.43	16.78	0.28	7.25	1.15	0.016	0.23	0.92	0.24	0.70	0.014	20.1	1.99	88.8	156	5.92	56.7	25.3	8.5	13.7	29.9	17.8	22.0
FQ-26-R	24.50	44.46	0.71	17.96	6.67	0.054	1.48	0.84	0.69	2.47	0.166	41.9	2.36	56.1	717	16.2	138	65.7	17.9	33.3	60.0	155	22.8
FQ-26-1p	51.48	29.96	0.47	12.32	2.46	0.022	0.55	0.78	0.45	1.49	0.014	52.7	2.03	74.2	356	12.2	86.9	39.9	6.04	12.5	52.3	43.4	16.3
FQ-26-2c	58.81	24.88	0.39	11.34	2.05	0.018	0.39	0.85	0.33	0.92	0.016	56.3	1.51	68.9	315	6.62	68.4	28.8	5.72	12.6	35.0	34.2	14.7
FQ-26-3p	45.67	33.76	0.55	14.31	2.56	0.019	0.49	0.86	0.39	1.37	0.017	96.1	1.64	74.6	423	11.2	81.6	36.1	5.16	15.2	32.1	28.2	19.1
FQ-26-4p	21.79	47.76	0.68	18.46	5.98	0.047	1.34	0.64	0.57	2.70	0.038	49.2	1.49	77.6	585	15.1	106	56.0	7.99	21.5	45.6	134	21.4
FQ-26-5c	62.26	22.54	0.37	10.19	1.99	0.021	0.45	0.85	0.26	1.05	0.014	33.3	1.66	75.2	295	7.97	92.7	32.3	11.9	15.8	72.0	60.2	13.6
FQ-26-6c	84.35	8.93	0.18	4.37	0.65	0.016	0.11	0.93	0.15	0.30	0.006	10.5	1.23	102	136	5.93	41.8	14.4	7.19	7.32	34.7	7.91	7.74
FQ-26-7c	62.05	21.00	0.31	13.66	1.47	0.018	0.21	0.77	0.16	0.33	0.029	0.53	0.97	76.5	371	0.82	28.0	8.71	5.24	8.36	16.5	12.3	
FQ-26-8p	83.94	9.42	0.18	4.23	0.67	0.016	0.11	0.99	0.16	0.26	0.006	6.80	1.27	102	149	0.82	31.4	12.5	7.67	6.42	25.6	4.99	6.83
FQ-26-9p	49.14	30.56	0.55	14.17	2.54	0.024	0.56	0.86	0.36	1.22	0.015	77.0	3.33	77.1	348	13.2	102	46.3	11.1	17.3	40.0	34.9	18.9
FQ-26-F	10.53	55.12	0.87	20.00	6.96	0.065	1.81	0.86	0.78	2.75	0.248	38.1	1.63	64.8	723	16.4	122	66.8	11.8	27.2	46.9	162.9	23.9
WA-26*	69.74	17.84	0.30	8.66	1.43	0.018	0.27	0.89	0.23	0.63	0.013	25.3	1.38	84.1	252	5.64	55.9	21.0	7.76	10.5	38.9	27.1	11.2
Average*	8.47	8.47	0.33	5.98	4.85	0.015	0.22	1.23	0.16	0.19	0.092	10	1.2	56	90	4.1	22	15	4.2	9	15	18	5.5

(continued on next page)

Table 2 (continued)

Sample	Ge	As	Se	Rb	Sr	Zr	Nb	Mo	Cd	In	Sn	Sb	Cs	Ba	Hf	Ta	W	Hg	Tl	Pb	Bi	Th	U
FQ-23-15p	1.19	2.99	0.30	62.7	126	142	7.33	0.98	0.51	0.066	2.69	1.72	8.42	307	3.84	0.58	4.43	105	0.63	25.9	0.73	11.3	2.86
FQ-23-16p	1.14	4.77	0.32	61.7	139	157	8.16	0.68	0.59	0.078	3.16	1.15	12.0	326	4.32	0.69	5.01	68	0.63	38.1	0.99	12.2	3.54
FQ-23-17c	1.23	4.31	0.96	25.6	128	57.1	3.88	2.86	0.29	0.030	1.21	3.13	5.27	156	1.62	0.35	7.43	24	0.39	18.6	0.58	7.66	2.10
FQ-23-18c	0.84	2.50	0.50	16.2	141	72.1	4.43	2.23	0.17	0.028	1.12	1.57	3.82	134	1.95	0.38	13.0	12	0.38	14.2	0.56	6.95	2.17
FQ-23-19c	3.31	3.90	0.76	31.1	143	92.7	5.17	1.01	0.18	0.038	1.61	4.53	5.88	192	2.54	0.46	17.0	47	0.51	16.2	0.42	6.89	2.18
FQ-23-F	1.24	14.6	0.07	53.6	114	197	12.7	0.21	0.50	0.086	3.50	0.68	6.90	336	5.52	1.15	7.77	42	0.39	27.9	0.67	11.6	3.40
WA-23	1.70	3.01	0.50	31.5	140	74.8	4.64	3.00	0.23	0.031	1.47	2.99	7.45	178	2.07	0.46	10.6	23	0.44	14.6	0.49	6.92	2.30
FQ-26-R	1.33	10.8	0.54	79.8	123	155	9.13	1.00	0.86	0.092	3.64	2.19	11.1	405	4.36	0.68	5.82	64	0.61	38.7	1.12	12.5	3.45
FQ-26-1p	1.66	3.35	0.23	70.1	129	118	5.75	0.49	0.52	0.064	2.55	2.45	12.9	305	3.39	0.45	7.07	108	0.75	35.6	0.90	10.3	3.04
FQ-26-2c	1.43	4.16	0.06	44.9	116	94.3	7.94	1.37	0.31	0.048	2.42	2.47	8.8	214	2.82	1.82	9.38	103	0.67	23.0	0.65	9.02	3.26
FQ-26-3p	1.57	2.54	0.00	74.9	143	136	7.50	0.49	0.33	0.066	3.02	1.97	14.2	296	3.93	0.60	6.14	45	0.69	28.1	0.76	9.82	3.21
FQ-26-4p	1.29	6.24	0.11	86.0	104	136	7.29	0.20	0.53	0.087	3.52	1.39	11.7	395	3.90	0.55	5.61	101	0.57	32.1	1.03	11.1	3.05
FQ-26-5c	1.75	4.13	0.39	46.1	113	85.5	4.69	2.13	0.88	0.058	2.16	4.40	9.16	210	2.45	0.62	6.38	70	0.59	25.2	1.44	8.05	3.20
FQ-26-6c	1.30	2.73	1.04	23.8	110	40.4	2.83	2.35	0.19	0.026	1.08	2.70	4.71	118	1.21	0.26	7.80	23	0.52	17.8	0.68	5.56	1.98
FQ-26-7c	1.36	3.50	0.31	13.6	79	130	9.03	1.48	0.30	0.060	3.19	1.48	2.38	92.7	4.43	0.91	5.63	30	0.35	25.9	0.68	3.32	3.08
FQ-26-8c	0.85	1.98	0.71	13.2	114	43.9	2.45	2.39	0.16	0.018	0.91	1.56	4.00	113	1.30	0.23	8.09	11	0.44	11.0	0.40	4.61	1.64
FQ-26-9p	5.43	4.82	0.00	46.7	122	136	7.77	1.05	0.34	0.056	2.60	7.41	9.63	253	3.75	0.57	5.60	89	0.50	25.2	0.55	9.99	2.89
FQ-26-F	1.34	10.9	0.41	76.9	103	183	9.60	0.97	0.63	0.092	3.73	0.94	7.59	434	5.12	0.75	7.63	50	0.44	31.0	0.65	9.90	3.15
WA-26	1.33	3.33	0.46	30.3	109	77.0	5.27	1.95	0.39	0.041	1.90	2.59	6.30	159	2.34	0.82	7.67	52	0.53	20.1	0.78	6.49	2.64
Average*	2	7.6	1	10	120	35	3.3	2.2	0.24	0.02	0.79	0.84	0.98	150	1.2	0.26	1.2	100	0.68	6.6	0.84	3.3	2.6

* Average content of major-element oxides for common Chinese coals are from Dai et al. (2012b); average concentrations of trace elements are from Kettis and Yudovich (2009). WA, weighted average (weighted by thickness of sample interval). The rows in bold are the weighted averages for each coal seam.

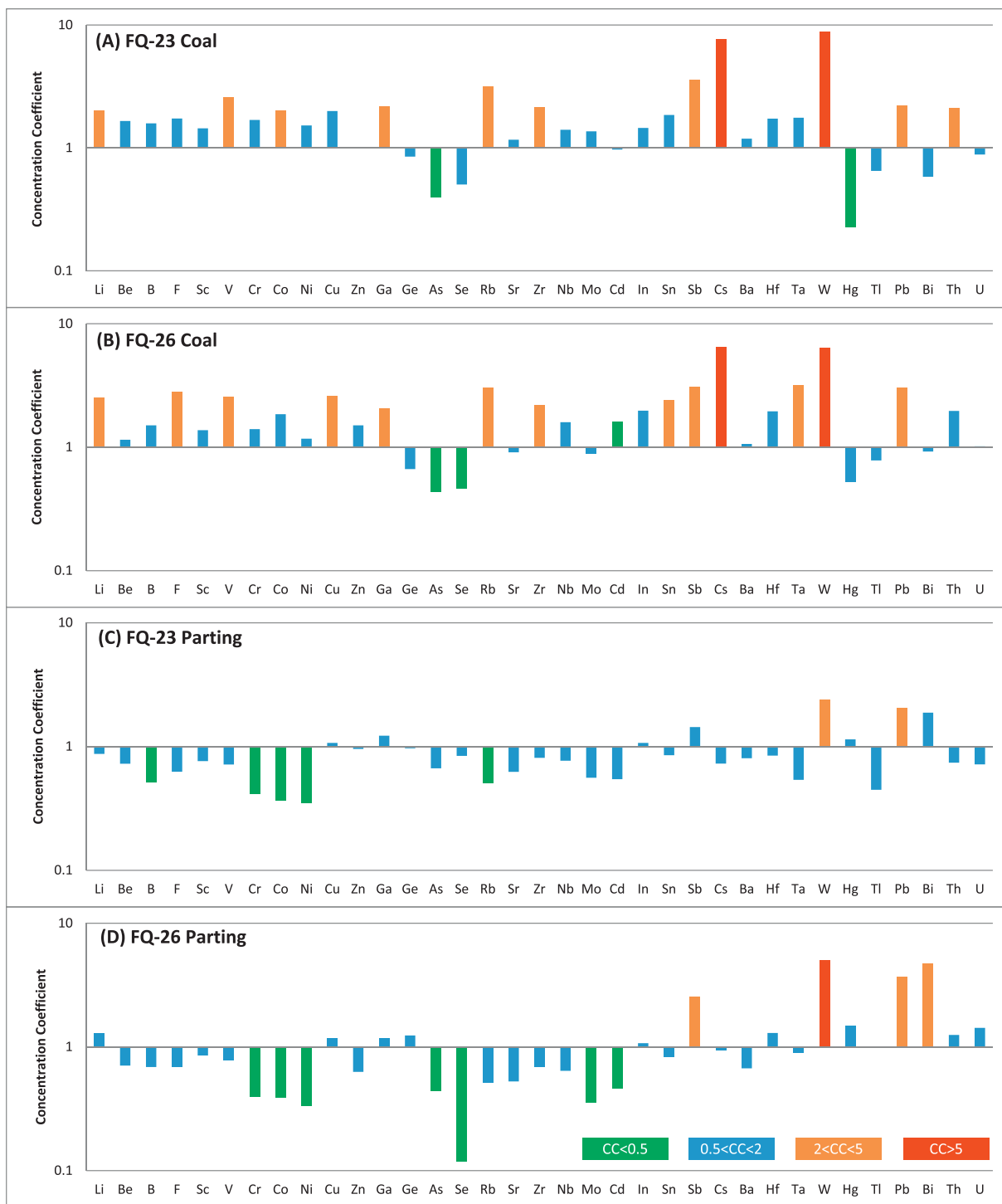


Fig. 4. Concentration coefficients (CC) of trace elements in the Fuqiang coals and partings, normalized by average trace element concentrations in the world low-rank coals (Ketris and Yudovich, 2009) and world clays Grigoriev (2009) respectively.

coal-bearing Hunchun Formation. Faults trending NNE, NEE and W-E are well developed within the coal basin (Fig. 1C).

According to Wang and Wang (2004), there were two different sedimentary environments in the Hunchun Basin in the lower coal-bearing member (E_h^2), based on the characteristics of lithological compositions of the sediments. Coal seams from Nos. 30 to 23 were formed in alluvial fan, fluvial, and lacustrine environments in stage I (Fig. 3A), and coal seams above No. 23 (from Nos. 21 lower to 19) were deposited in alluvial fan, fluvial, and delta plain environments in stage II (Fig. 3B). The basin was relatively low in the middle and western

parts, but the surrounding areas to the north, east and south of the basin are high during deposition of the coal-bearing sequences and thus these areas could have provided terrigenous materials for the sediments in the basin (Fig. 3).

3. Samples and methods

3.1. Sample collection

A total of 32 bench samples (including 14 coal benches and 18 non-

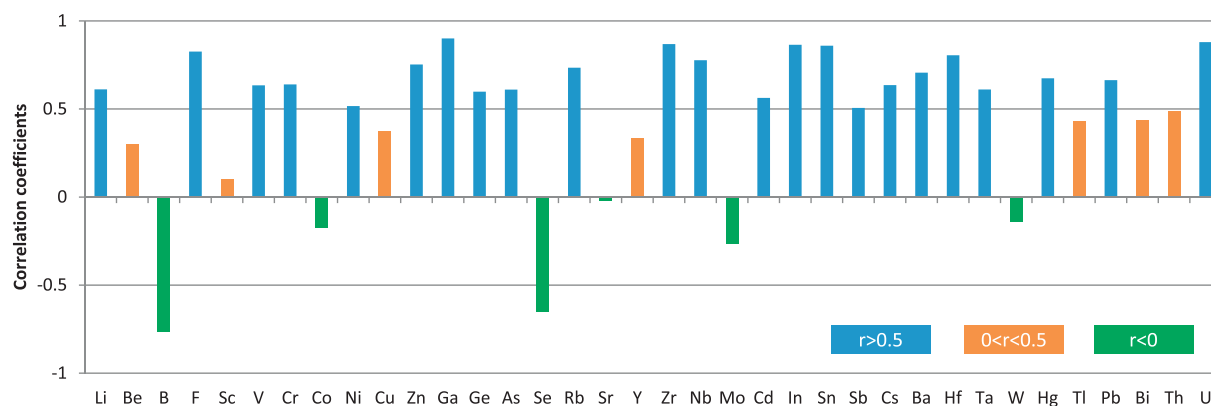


Fig. 5. Correlation coefficients (r) between ash yield and trace elements.

coal roof, parting and floor strata) of the Nos. 23 and 26 coals were collected from the underground working faces at the Fuqiang mine of the Hunchun Coalfield. From top to bottom, the samples (except the roof and floor ones) are numbered in an increasing order as indicated in Fig. 2B. The cumulative thickness of the Nos. 23 and 26 coals are respectively 2.85 m and 1.60 m, including partings, which account for 56.1% and 51.3% of the total thickness of the seams, respectively.

3.2. Analytical methods

The proximate analysis including the determination of moisture, ash yield, volatile matter, and total sulfur, as well as gross calorific values, were conducted according to ASTM Standards D3174-12 (2012), D3173M-17a (2017), D3175-17 (2017), D3177-02 (2011), and D5865-13 (2013), respectively. A Vario Macro Elemental Analyzer was used to determine the C, H, and N contents in the coal bench samples. Mean random reflectance values of huminite were measured using a Leica DM-4500P microscope equipped with a Craic QDI 302™ spectrophotometer based on ASTM Standard D2798-11a (2011).

The concentrations of trace elements (except F and Hg) in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) following the methods described in detail by Dai et al. (2014a) and Li et al. (2014). X-ray fluorescence spectrometry (XRF) was used to determine the concentrations of major-element oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , MnO , Na_2O , K_2O , and P_2O_5) for each sample after ashing at 815 °C. A Milestone DMA-80 Hg analyzer was used to determine the Hg concentration in all samples. The concentration of fluorine in each sample was determined by pyrohydrolysis, with an ion-selective electrode, according to ASTM Standard D5987-96 (2015).

Aliquots of all the coal bench samples were subjected to low temperature ashing (LTA, < 150 °C), and subsequent determination of mineral phases by X-ray powder diffraction (XRD). Quantitative analysis of minerals was conducted using the Siroquant technique, described in detail by Ward et al. (2001) and Liu et al. (2018).

4. Results

4.1. Coal chemistry and huminite reflectance

Table 1 displays the proximate analyses (moisture content, ash yield, and volatile matter content) and ultimate analyses (content of C, H, N), total-S content, gross calorific values, random huminite reflectance values, and aluminosilicate mineral compositions in LTAs of all samples of the Nos. 23 and 26 coal benches. The two coals are classified as a medium-high ash coal according to the ash-yield-based Chinese standard classification (GB/T 15224.1-2010, 2010; coals with ash yields 30.01–40.0% are classified as medium-high ash coal). The

Nos. 23 and 26 coals have very low total S content (0.13% and 0.16% on average, respectively) and are, therefore, classified as low-sulfur coals, based on the classification by Chou (2012). The two coals have high moisture contents (average values of 16.56% and 13.85%, respectively).

The volatile matter yields, gross calorific values, and random huminite reflectance values (Table 1) indicate a lignite-subbituminous coal rank based on the ASTM classification D388-12 (2012). The huminite reflectance increases from the No. 23 seam (0.35%) to the No. 26 seam (0.47%). It is noteworthy that these characteristics of the low rank and low calorific values for the Fuqiang coals are similar to those in the three coal-hosted Ge deposits that are currently being mined at the Wulantuga, Lincang (both in China), and Spetzugli (Far Eastern Russia) (Dai et al., 2012a, 2015a; Medvedev et al., 1997). The Spetzugli Ge deposit is located in a few hundred kilometers to NE of the study area.

4.2. Geochemistry

4.2.1. Abundances of major oxides and trace elements

Table 2 presents the percentages of major-element oxides (wt%) and concentrations of trace elements (ppm) in the Nos. 23 and 26 coals (on a whole coal basis), as well as their comparisons with the average values for Chinese coals (Dai et al., 2012b) and world low-rank coals (Ketris and Yudovich, 2009).

The percentages of major-element oxides in the Fuqiang coals are generally similar to the average values for Chinese coals (Table 2; Dai et al., 2012b). However, percentages of K_2O and SiO_2 are higher and Na_2O and Al_2O_3 are slightly higher in the Fuqiang coals, probably due to the relatively high amounts of illite and feldspar (plagioclase and K-feldspar). Percentages of TiO_2 , MgO , CaO , and MnO are either lower than or close to the average values for Chinese coals, while those of Fe_2O_3 and P_2O_5 are distinctly lower.

Coal bench sample FQ-26-7c, has the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio value (1.54), whilst this ratio in other coal bench samples are > 2 (2.30 and 2.10 on average for Nos. 23 and 26 coals, respectively). These are much higher than that of the average value for Chinese coals (1.42; Dai et al., 2012b) and the theoretical value for kaolinite (1.18). The higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ values in these coals are probably due to the high content of quartz and the occurrence of feldspar. The lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ value of sample FQ-26-7c is due to the lower proportion of quartz (Table 1).

The two coals present similar trace-element abundances (Table 2; Fig. 4). Compared with averages for the common world low-rank coals by Ketris and Yudovich (2009), W and Cs are enriched in the Fuqiang coals ($5 < \text{CC} < 10$) (CC, the ratio of an element concentration in the Fuqiang coals vs. the corresponding average value in the world common low-rank coals). The elements Li, V, Ga, Rb, Zr, Sb, and Pb are slightly enriched in the two coals. In addition, F, Cu, Sn and Ta are slightly enriched in the No. 26 seam ($2 < \text{CC} < 5$). The two coals are

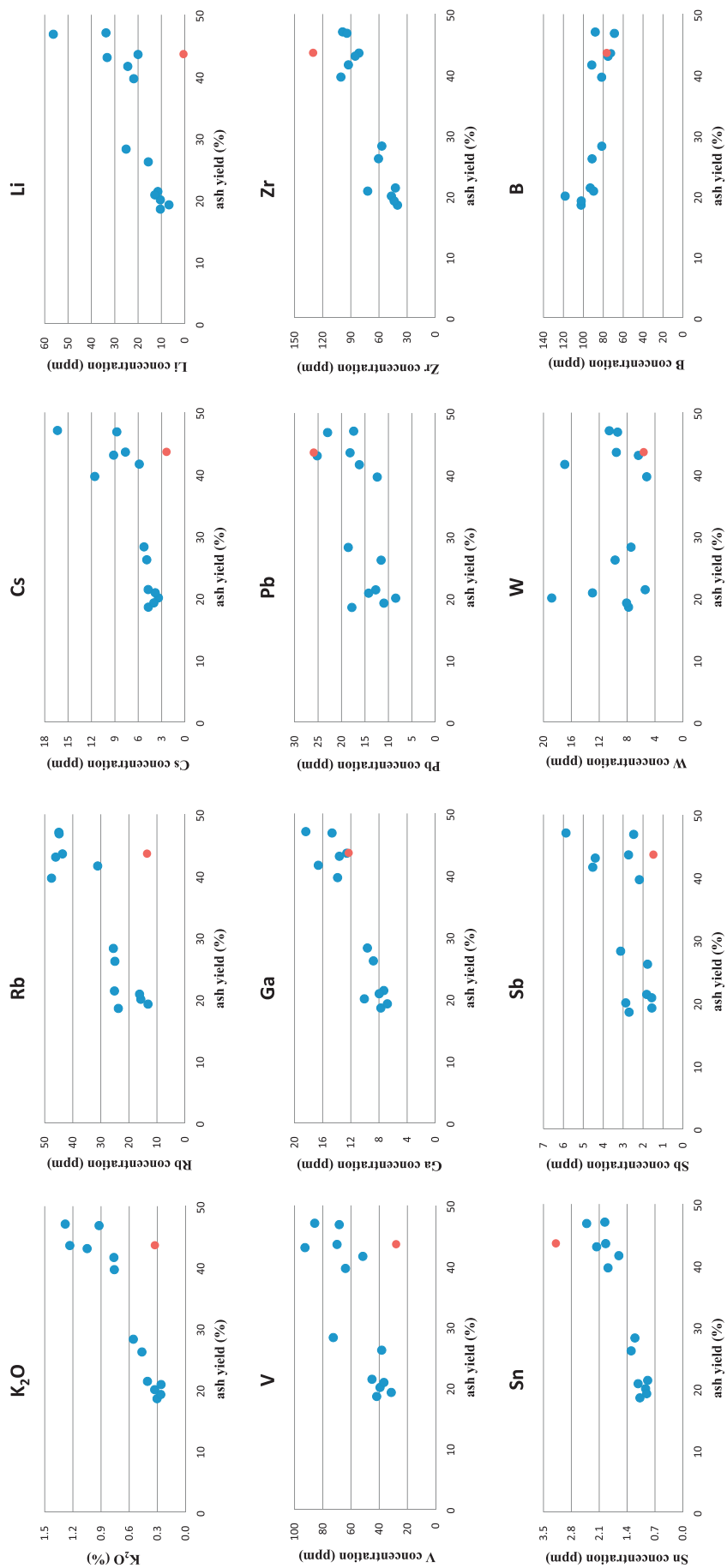


Fig. 6. Relation between ash yield and concentrations of selected elements in samples.

Table 3

Correlation coefficients between ash yield and selected elements, between selected trace elements and major elements, and between selected trace elements and ash yield of the Fuqiang coals.

Li-ash = 0.61	Rb-ash = 0.73	Cs-ash = 0.64	Ga-ash = 0.90	Zr-ash = 0.87
V-ash = 0.63	Pb-ash = 0.66	Sb-ash = 0.51	W-ash = -0.14	
Li-Al ₂ O ₃ = 0.45	Li-SiO ₂ = 0.65	Li-K ₂ O = 0.71	Li-Na ₂ O = 0.71	
Rb-Al ₂ O ₃ = 0.52	Rb-SiO ₂ = 0.78	Rb-K ₂ O = 0.90	Rb-Na ₂ O = 0.75	
Cs-Al ₂ O ₃ = 0.46	Cs-SiO ₂ = 0.66	Cs-K ₂ O = 0.80	Cs-Na ₂ O = 0.58	Cs-Rb = 0.85
Ga-Al ₂ O ₃ = 0.79	Ga-SiO ₂ = 0.89	Ga-K ₂ O = 0.80	Ga-Na ₂ O = 0.75	
Zr-Al ₂ O ₃ = 0.94	Zr-SiO ₂ = 0.84	Zr-K ₂ O = 0.48	Zr-Na ₂ O = 0.43	
V-Al ₂ O ₃ = 0.43	V-SiO ₂ = 0.66	V-K ₂ O = 0.87	V-Na ₂ O = 0.69	
Pb-S _{1,d} = -0.07	Sb-S _{1,d} = -0.06	Pb-Zn = 0.68	Sb-Zn = 0.60	

depleted in As, Se and Hg ($CC < 0.5$) and have similar concentrations ($0.5 < CC < 2$) of the remaining elements to the averages for the world low-rank coals (Table 2; Fig. 4).

Compared with the average values for world clays (Grigoriev, 2009), the partings of No. 23 coal are only slightly enriched in W, Pb, and Bi ($CC = 1.88$); and the partings in No. 26 coal are enriched in W ($5 < CC < 10$) and slightly enriched in Sb, Pb, and Bi. The remaining elements are either depleted or close to the average values for world clays (Table 2; Fig. 4).

The roof and floor of the Nos. 23 and 26 coal seams show similar enrichment patterns and are similar to those of the partings, in comparison with the worldwide clays (Grigoriev (2009)). With the exception of sample FQ-23-F, which is depleted in W, other non-coal rocks are all slightly enriched in W, Pb and Bi.

4.2.2. Modes of occurrence of some elements in the coals

Concentrations of most trace elements in the Fuqiang coals are positively correlated with ash-yield (correlation coefficient $r > 0.5$; Figs. 4, 5), indicating an inorganic affinity. However for some trace elements, correlation coefficients values are low (Be, Sc, Cu, Y, Tl, and Bi) or negative (B, Co, Se, Mo, and W) indicating organic affinity or both organic/inorganic affinities. (Fig. 6.)

According to the correlation coefficients between their concentrations and ash yields, the elements with distinctly elevated concentrations in the Fuqiang coals can be classified into three groups:

- 1) Group 1 including F, Ga, Zr, and Sn, with relatively high correlation coefficients ($r > 0.75$), indicating a high inorganic affinity. Gallium and Zr are more positively correlated to SiO₂ and Al₂O₃ than to K₂O and Na₂O (Table 3), indicating that Ga and Zr in the coals occur mainly in kaolinite.
- 2) Group 2 consisting of Li, V, Cu, Rb, Sb, Cs, Ta, Pb and Th, with correlation coefficients with ash yields ranging from 0.36 to 0.75, indicating a moderate inorganic affinity.

Positive correlations have been observed between Li and K₂O ($r = 0.71$), Li and Na₂O ($r = 0.71$), Li and SiO₂ ($r = 0.65$), and Li and Al₂O₃ ($r = 0.45$), indicating that clay minerals are the major carriers for Li in the coals. Vanadium, like Li, is highly correlated to K₂O, indicating that V mainly occurs in K-bearing minerals.

There are also strong correlations between Rb and Cs ($r = 0.85$), as well as Rb-ash ($r = 0.73$), Rb-K₂O ($r = 0.90$), Rb-SiO₂ ($r = 0.78$), Cs-ash ($r = 0.64$), Cs-K₂O ($r = 0.83$) and Cs-SiO₂ ($r = 0.66$), but low correlation coefficients between Rb-Al₂O₃ ($r = 0.52$) and Cs-Al₂O₃ ($r = 0.46$). However, correlation coefficients of Li-Al₂O₃, Rb-Al₂O₃, and Cs-Al₂O₃ are high ($r = 0.88, 0.92, 0.81$, respectively) if sample FQ-26-7c is excluded in this calculation. Sample FQ-26-7c has unusual mineralogical and geochemical features (described more fully below). Therefore, K-bearing clay minerals (e.g., illite) are major carriers of Rb and Cs in the Fuqiang coals.

Antimony and Pb in coal are generally associated with sulfide minerals (e.g., Finkelman et al., 2017; Qin et al., 2018; Dai et al., 2015a). In this study, concentrations of Sb and Pb are weakly correlated with

total sulfur ($r = -0.06$ and $r = -0.07$, respectively), while sulfides are all below the detection limit of the XRD technique. However, correlation coefficients for Pb-Zn and Sb-Zn are 0.68 and 0.60, respectively, indicating that Pb and Sb may be associated with some Zn-bearing minerals.

- 3) Only W is weakly correlated to ash yield ($r = -0.14$), indicating an organic-inorganic mixed affinity. Tungsten is the most enriched element in the Fuqiang coals and has a unique behavior as indicated by its highest W content (18.8 ppm) in the lowest-ash-yield (~20%) coal bench sample FQ-23-7c, showing a sharp contrast with other enriched elements (e.g., Li, V, Ga, Zr, Rb and Cs) (Fig. 7). In addition, the W enrichment in these sections correlates with a distinct depletion in Ge relative to the world low-rank coals (Fig. 4; Ketris and Yudovich, 2009). This differs from the behaviour of Ge-W enrichment assemblage in the large coal-hosted Wulantuga, Lincang, Spetzugli coal deposits (Dai et al., 2012a, 2015a; Seredin et al., 2006), as well as from Ge-W relations in the low-Ge coal of the Shengli Coalfield (Dai et al., 2015b) and the BLC 19-2 coal in the Hunchun basin (Dai et al., 2018).

4.2.3. Distribution patterns of REY in coal and host rocks

For many years rare earth elements and yttrium (REY) have been widely used as geochemical indicators of the sediment-source area, sedimentary condition, and post-depositional history of coal deposits (Qi et al., 2007; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Hower et al., 2015a; Dai et al., 2015c, 2016b). In the present study, the concentrations of REY are normalized to UCC (upper continental crust; Taylor and McLennan, 1985) in order to identify characteristics of REY distribution patterns in the samples investigated. The geochemical classification by Seredin and Dai (2012) distinguishes three types of REY enrichment: L-type ($La_N/Lu_N > 1$), M-type ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type ($La_N/Lu_N < 1$; where N stands for the normalization of REY concentration in samples to UCC).

Based on Dai et al. (2016b), anomalies of Ce, Eu, and Gd (Ce_N/Ce_N^* , Eu_N/Eu_N^* and Gd_N/Gd_N^* , respectively) in coal and sedimentary rocks are calculated using the following formulae (where * stands for the theoretical normalized values of REY, calculated from its two neighboring elements in the periodic table):

$$Ce_N/Ce_N^* = Ce_N / (0.5La_N + 0.5Pr_N) \quad (1)$$

$$Eu_N/Eu_N^* = Eu_N / [(Sm_N \times 0.67) + (Tb_N \times 0.33)] \quad (2)$$

$$Gd_N/Gd_N^* = Gd_N / [(Sm_N \times 0.33) + (Tb_N \times 0.67)] \quad (3)$$

The total concentrations of REY in the Nos. 23 and 26 Coals are 95.1 and 87.1 $\mu\text{g/g}$, respectively (Table 4), slightly higher than the average value for the average world lignites and subbituminous coals (65.3 $\mu\text{g/g}$; Ketris and Yudovich, 2009). The REY in the Fuqiang samples, including coal plies, partings and host rocks are mainly represented by the M- and H-REY joint enrichment, and, to a lesser extent, H-REY enrichment types (Fig. 8), except for sample FQ-26-7c with a L- and M-REY joint enrichment type.

Coal samples from the No. 23 seam have distinct positive Gd

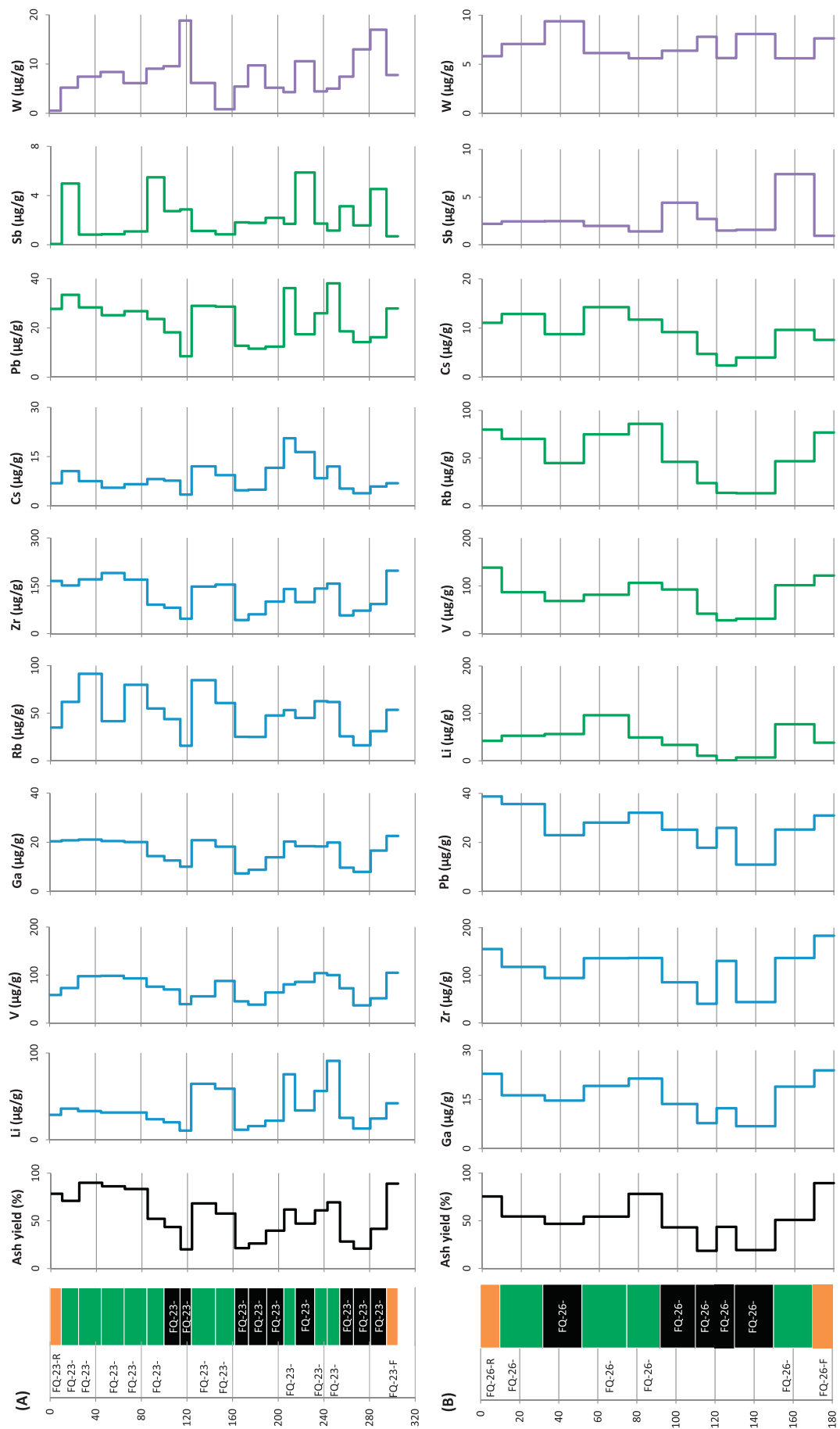


Fig. 7. Variations in concentration of selected rock components through the studied coal sections.

Table 4
Concentrations of rare earth elements and Y in the Nos. 23 and 26 coals from the Fuqiang mine.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	REY	Eu _N /Eu _N *	Gd _N /Gd _N *	Type
FQ-23-R	15.3	40.7	3.59	13.3	2.59	0.55	2.69	0.41	2.35	9.11	0.51	1.52	0.24	1.60	0.25	94.71	1.04	1.18	H
FQ-23-1p	24.9	52.6	5.49	21.0	4.13	0.90	4.25	0.63	3.86	19.9	0.79	2.45	0.35	2.34	0.36	143.93	1.09	1.19	H
FQ-23-2p	30.7	65.8	6.83	27.0	5.50	1.21	5.64	0.78	4.52	22.0	0.86	2.65	0.39	2.66	0.40	176.85	1.13	1.21	M-H
FQ-23-3p	15.7	52.1	4.23	17.1	3.51	0.84	3.79	0.54	3.27	12.0	0.65	1.95	0.28	1.95	0.30	118.18	1.19	1.25	M-H
FQ-23-4p	26.0	61.0	6.08	24.2	4.80	1.11	5.12	0.68	4.04	19.5	0.78	2.30	0.32	2.19	0.32	158.48	1.18	1.26	M-H
FQ-23-5p	18.5	39.6	4.27	17.4	3.60	0.85	4.09	0.60	3.50	19.8	0.70	2.14	0.30	2.08	0.30	117.73	1.14	1.28	M-H
FQ-23-6c	19.7	42.0	4.63	18.5	3.81	0.89	4.09	0.60	3.51	18.4	0.68	2.02	0.27	1.92	0.27	121.31	1.15	1.23	M-H
FQ-23-7c	8.45	17.1	1.91	7.64	1.63	0.39	1.95	0.30	1.80	10.2	0.37	1.09	0.15	1.07	0.15	54.22	1.13	1.29	M-H
FQ-23-8p	27.0	55.7	5.81	22.5	4.54	0.89	4.63	0.63	3.67	18.4	0.70	2.18	0.31	2.20	0.33	149.37	1.01	1.22	M-H
FQ-23-9p	26.6	60.2	6.05	23.7	4.63	1.00	4.75	0.67	3.78	17.5	0.72	2.15	0.30	2.10	0.31	154.55	1.10	1.21	M-H
FQ-23-10c	12.4	30.3	2.71	10.3	2.01	0.44	2.21	0.31	1.78	9.93	0.35	1.03	0.15	1.01	0.15	75.06	1.09	1.28	M-H
FQ-23-11c	14.1	33.2	3.21	12.5	2.55	0.52	2.74	0.38	2.28	11.6	0.44	1.31	0.19	1.31	0.19	86.52	1.03	1.25	M-H
FQ-23-12c	16.2	33.6	3.44	13.2	2.64	0.56	2.92	0.40	2.34	12.7	0.47	1.42	0.19	1.37	0.22	91.66	1.06	1.28	M-H
FQ-23-13p	21.0	52.7	5.24	21.1	4.52	0.93	4.69	0.68	4.02	19.3	0.78	2.37	0.34	2.37	0.35	140.48	1.03	1.21	M-H
FQ-23-14c	17.4	35.6	3.94	15.7	3.35	0.74	3.75	0.56	3.39	17.4	0.67	2.00	0.28	1.91	0.29	106.98	1.07	1.25	M-H
FQ-23-15p	31.0	69.4	7.03	27.7	5.40	1.17	5.55	0.76	4.35	21.0	0.82	2.45	0.35	2.39	0.34	179.69	1.11	1.22	M-H
FQ-23-16p	31.3	72.4	7.27	28.5	5.81	1.20	5.98	0.83	4.68	23.0	0.90	2.66	0.37	2.61	0.38	187.90	1.05	1.22	M-H
FQ-23-17c	19.8	47.9	4.79	19.3	3.95	0.87	4.30	0.60	3.55	17.5	0.67	1.97	0.27	1.81	0.27	127.55	1.10	1.26	M-H
FQ-23-18c	12.5	28.8	2.95	12.0	2.53	0.55	2.82	0.41	2.57	12.9	0.50	1.54	0.22	1.49	0.23	82.03	1.07	1.26	M-H
FQ-23-19c	14.0	30.1	3.30	13.4	2.78	0.68	3.49	0.55	3.64	23.2	0.76	2.29	0.31	2.13	0.33	100.91	1.11	1.32	H
FQ-23-F	30.4	69.9	6.89	27.3	5.55	1.22	5.89	0.82	4.71	23.8	0.92	2.78	0.41	2.77	0.41	183.71	1.11	1.24	M-H
WA-23	15.2	33.5	3.47	13.8	2.84	0.63	3.18	0.46	2.80	15.0	0.55	1.65	0.23	1.58	0.24	95.14	1.09	1.27	
FQ-26-R	31.0	66.1	7.19	28.8	5.80	1.28	6.17	0.89	5.42	29.4	1.06	3.44	0.47	3.25	0.48	190.72	1.10	1.23	M-H
FQ-26-1p	28.0	59.9	6.24	24.9	4.79	1.02	5.10	0.68	3.99	19.7	0.76	2.35	0.32	2.32	0.34	160.41	1.09	1.26	M-H
FQ-26-2c	17.4	36.0	3.75	14.4	2.96	0.62	3.20	0.46	2.72	13.5	0.52	1.61	0.23	1.62	0.24	99.13	1.04	1.25	M-H
FQ-26-3p	24.2	48.5	5.21	20.2	4.03	0.82	4.22	0.59	3.51	18.4	0.69	2.12	0.31	2.18	0.32	135.30	1.03	1.23	M-H
FQ-26-4p	31.9	69.9	7.49	30.4	6.25	1.29	6.25	0.87	4.87	23.1	0.91	2.82	0.40	2.79	0.40	189.66	1.06	1.19	M-H
FQ-26-5c	19.0	43.1	4.46	17.8	3.69	0.81	4.14	0.62	3.77	19.6	0.76	2.31	0.32	2.34	0.34	123.02	1.06	1.25	M-H
FQ-26-6c	11.7	25.3	2.70	10.8	2.31	0.47	2.62	0.41	2.52	13.6	0.50	1.55	0.23	1.49	0.22	76.45	0.97	1.24	H
FQ-26-7c	6.3	33.2	1.43	5.51	0.99	0.14	1.10	0.13	0.72	2.69	0.13	0.38	0.06	0.39	0.06	53.16	0.72	1.35	L-M
FQ-26-8c	10.5	22.2	2.40	9.51	2.03	0.39	2.15	0.33	1.95	10.6	0.39	1.20	0.17	1.16	0.17	65.14	0.94	1.20	M-H
FQ-26-9p	21.6	46.5	4.92	19.6	4.36	1.02	4.97	0.78	4.98	29.0	1.05	3.21	0.45	3.04	0.45	146.05	1.11	1.25	H
FQ-26-F	31.0	69.9	7.25	29.5	6.15	1.43	6.72	0.94	5.68	28.6	1.11	3.16	0.46	3.16	0.46	195.43	1.16	1.26	M-H
WA-26	13.8	32.4	3.14	12.3	2.56	0.52	2.80	0.41	2.48	12.8	0.49	1.50	0.21	1.49	0.22	87.13	0.97	1.25	

REY, sum of rare earth elements and yttrium; values normalized by the average REY content of Upper Continent Crust (Taylor and McLennan, 1985) WA, weighted average (weighted by thickness of sample interval). The rows in bold are the weighted averages for each coal seam.

anomalies, slightly positive Ce and Eu anomalies, and weak negative Y anomalies (Fig. 8). The associated partings and floor and roof horizons of the No. 23 coal seam exhibit similar REY distribution patterns with those in the coal, but show more negative Y anomalies (Fig. 8).

All coal samples from the No. 26 seam exhibit similar REY distribution patterns (Fig. 8C), with the exception of the unusual sample FQ-26-7c, which has the highest Ce_N/Ce_N* value (2.53) and lowest Eu_N/Eu_N* value (0.72). The No. 26 Coal also has a distinct positive Gd anomalies and weak negative Y anomalies (Fig. 8C). The partings and roof and floor horizon samples from the No. 26 coal have distinct positive Gd anomalies, slight positive Ce and Eu anomalies, and weak negative Y anomalies (Fig. 8D).

5. Discussion

5.1. Sediment-source region

The Al₂O₃/TiO₂ ratio may stay almost unchanged during surface weathering and alteration of sedimentary deposits (Hayashi et al., 1997; He et al., 2010) indicating, in particular, the sediment-source regions for coal deposits (Hower et al., 2015b; Dai et al., 2015d, 2017). Typical Al₂O₃/TiO₂ ratios are 3–8, 8–21, and 21–70 for sediments derived from mafic, intermediate, and felsic igneous rocks, respectively (Hayashi et al., 1997).

With the exception of parting sample FQ-23-3p (Al₂O₃/TiO₂ = 20.8), the Al₂O₃/TiO₂ ratios for almost all the samples are higher than 21 (Fig. 9), indicating felsic compositions of the sediment-source region. A previous study by Dai et al. (2018) of the Balianchen mine showed that terrigenous materials in the coal and its roof and floor horizons were dominantly derived from Mesozoic volcanic rocks.

However, the Fuqiang coals in the present study are relatively rich in lithophile elements including Li, Rb, Zr, Ga, Pb, Sb, and, especially W, indicating some different terrigenous sediment sources between the Baliancheng and Fuqiang coals.

A comparison of the Fuqiang samples (coals, roofs, partings and floors) with the metamorphic and igneous rocks from the possible provenances (Zhang et al., 2006; Li et al., 2007; Guo et al., 2009; Liu et al., 2010; Ren et al., 2012; Chai et al., 2015; Chen et al., 2015, 2017; Li, 2017; Wu et al., 2017) is presented in Fig. 10 in terms of the Sr/Y, La/Yb, and Al₂O₃/TiO₂ ratios. Fig. 10 shows that the terrigenous materials for the samples of the Hunchun Basin were derived mainly from the Mesozoic (mostly Lower Cretaceous) intermediate-felsic volcanic rocks in addition to the Paleozoic crystalline rocks as previously suggested by Dai et al. (2018). Some Fuqiang samples show lower Sr/Y ratios relative to those of the Baliancheng mine samples (Fig. 10), indicating that the role of Paleozoic metamorphics (the Wudaogou Group) was probably higher for the samples of the Fuqiang mine than those of the Baliancheng mine. Metamorphic rocks of the Wudaogou Group are enriched in W, Pb, Sb, Cu, Zn and As (Chen et al., 2015; Li, 2017) in comparison with the averages for the continental crust in eastern China (Yan and Chi, 2005), and these metamorphic rocks mainly occur within the eastern Hunchun area and also provide the metallic materials for the W and Au mineralization (Chen et al., 2015). Thus, the Wudaogou Group and the Fuqiang coals and partings have similar Sr/Y and La/Yb ratios and elevated concentrations of elemental assemblage (e.g., W, Pb, and Sb). The paleogeography during deposition of coal-bearing sequences in the Hunchun Basin (Fig. 3) agrees with the input of the terrigenous materials from the metamorphic rocks surrounding the Hunchun Basin (Figs. 1C, 3).

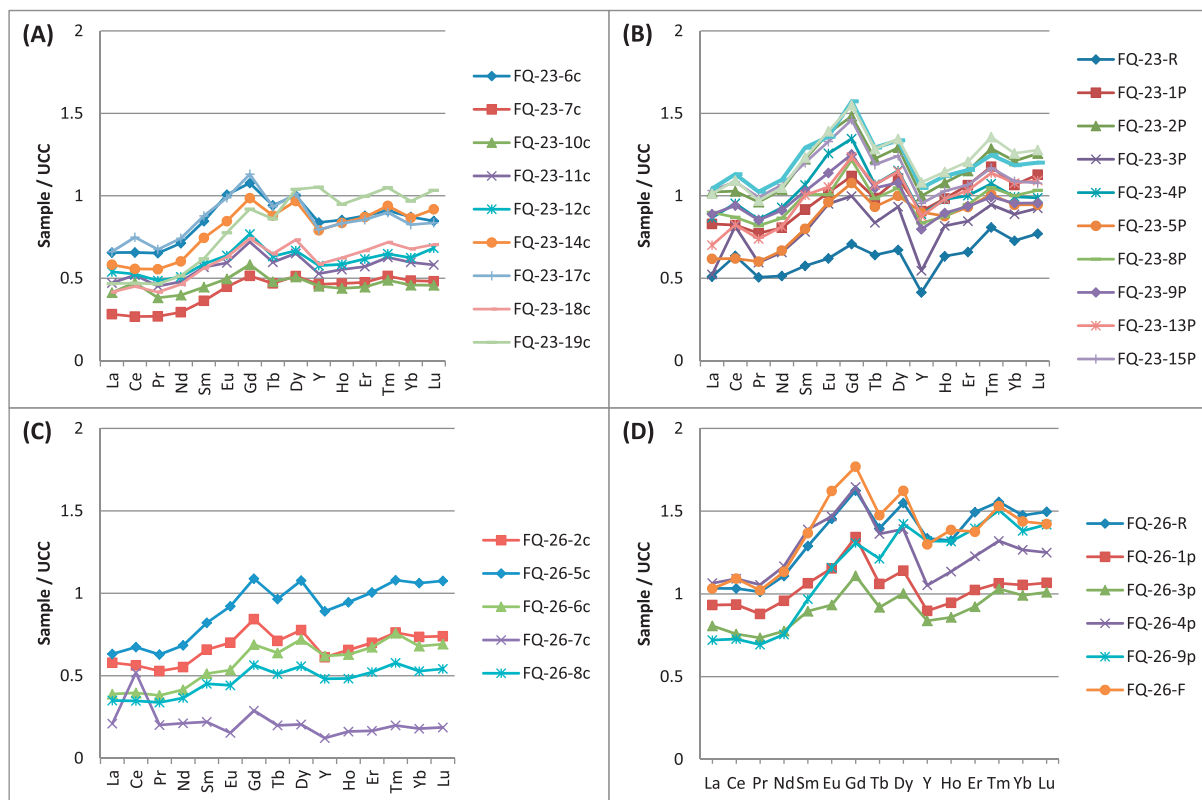


Fig. 8. Distribution patterns of rare earth elements and yttrium in the Nos. 23 and 26 Coals. (A) and (B), No. 23 Coal; (C) and (D), No. 26 Coal. REY are normalized by Upper Continental Crust (UCC; Taylor and McLennan, 1985).

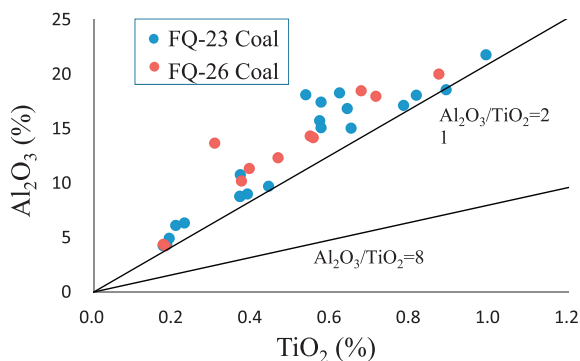


Fig. 9. Plot of TiO_2 vs. Al_2O_3 for the No. 23 and 26 Coals.

5.2. REY distribution

As described above, most samples of the Fuqiang coals are characterized by M- and H-type joint enrichment with a Gd-maximum. The study by Dai et al. (2018) shows that the Baliancheng coal has a similar Gd-maximum. This signature has not been found in any of the probable terrigenous rocks, but is well known for acidic natural waters, some of which circulated in coal basins (Johannesson and Zhou, 1997; Shand et al., 2005; Dai et al., 2014b, 2015b, 2015d, 2016c), as exemplified by the Late Permian coal of the Xinde Mine, Xuanwei, eastern Yunnan (Dai et al., 2014b) and the low-Ge coal of the Shengli Coalfield, northern China (Dai et al., 2015b). Although the M-type of REY enrichment in coal can also be caused by mafic volcanic ashes (Dai et al., 2015b, 2015d), no mafic contribution has been observed in the rocks of this study; instead, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio distinctly indicates a felsic source lithology.

Thus, in terms of REY distribution patterns of coals from the

Hunchun Coalfield, both presented in this study and reported from the nearby Baliancheng mine by Dai et al. (2018), these coals appear to have been strongly subjected to acidic waters. This conclusion is also supported by elevated concentrations of B in the Fuqiang and Baliancheng coals (86 and 92 $\mu\text{g/g}$ on average, respectively). The concentrations and correlation coefficients between B and ash yields in the Fuqiang coals (-0.75) and Baliancheng coal (-0.73 , Dai et al., 2018) indicate that B was derived from acidic waters. A similar source of B in lignite has been reported by Dai et al. (2015b) in the Shengli Coalfield, northern China. Although the elevated concentration of B in coal can be caused by marine influence (Goodarzi and Swaine, 1994), precipitated from hydrothermal solutions (Lyons et al., 1989), or derived from volcanic activity (Bouška and Pešek, 1983; Karayigit et al., 2000), no evidence for these factors has been identified in the Fuqiang and Baliancheng coals.

In addition to a mafic rocks in the terrigenous region, the highly positive Eu anomalies in coal could be caused by extremely reducing conditions coupled with high-temperatures (e.g., $> 250^\circ\text{C}$, Sverjensky, 1984), which do not appear within natural aquatic systems (Bau, 1991; Dai et al., 2016b). Dai et al. (2018) shows that the weak anomalies of positive Eu in the Baliancheng coal ($\text{Eu}_N/\text{Eu}_N^* = 1.19$ on average) were inherited from the source rocks. The weak positive Eu anomalies in the Fuqiang coals (except sample FQ-26-7c) were probably related to the Paleozoic metamorphic rocks, some of which also display positive Eu anomalies (Chen et al., 2015; Li, 2017).

In contrast to the other samples, sample FQ-26-7c has a distinct positive Ce anomaly (Fig. 8C). This indicates that the coal bench has been subjected to strong leaching under oxidizing conditions, which is supported by the highest clay concentration in the low temperature-ash of this sample ($\sim 93.7\%$), relatively high contents of resistant elements such as Zr and Ga (Fig. 7), and a high ash yield of this bench. It may be speculated that the coal or its parent peat was exposed to the Earth's surface oxidizing conditions for a relatively long time and consequently

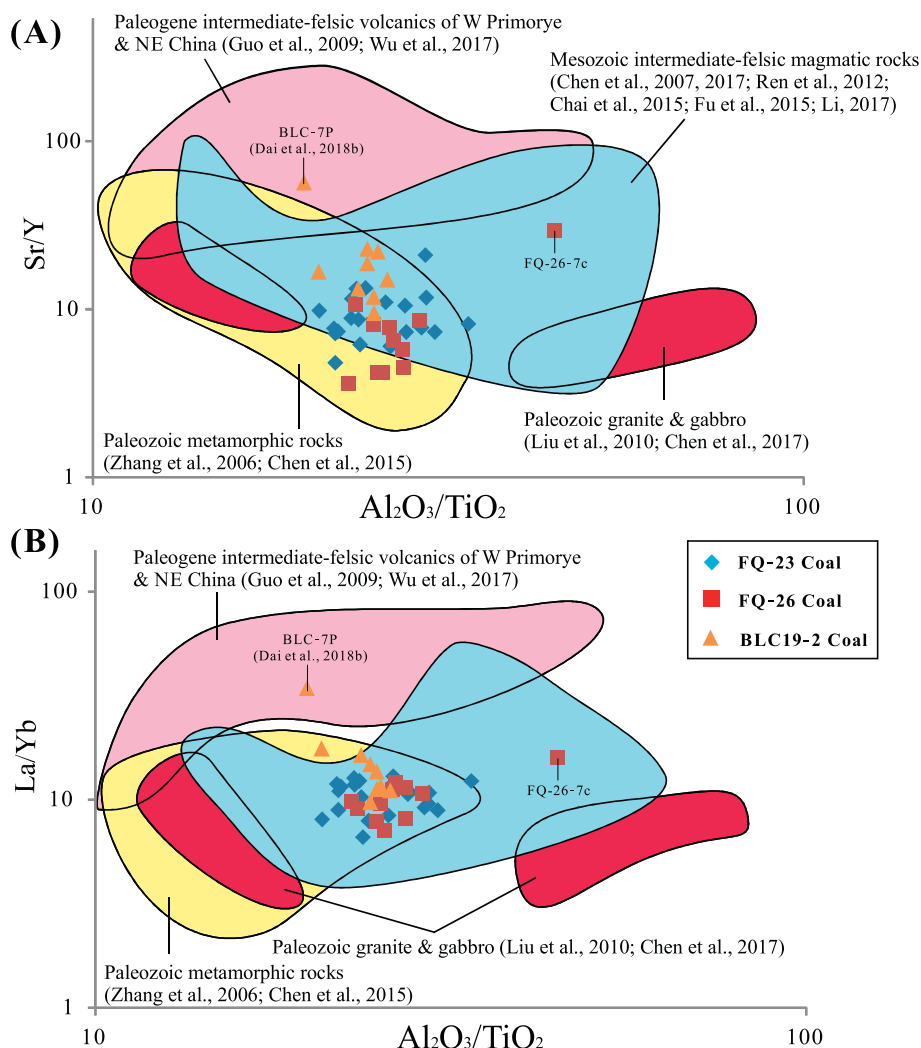


Fig. 10. Comparison between the studied samples (including Dai et al., 2018) and their possible magmatic and metamorphic source rocks with the Al_2O_3/TiO_2 vs. Sr/Y and La/Yb (modified after Dai et al., 2018).

resulted in strong leaching. During exposure of the ply of coal/peat to aerobic leaching process, Ce^{3+} was oxidized to Ce^{4+} , which is usually immobile and is preferentially precipitated in-situ (Braun et al., 1990; De Carlo et al., 1998; Taunton et al., 2000). This leaching process leads to the generation of Ce-poor REY-rich leachates from the coal/peat ply, and results in low total REY content, and consequently high Ce content and Ce_N/Ce_N^* values in the in-situ coal/peat ply.

The negative Y anomalies, which occur in almost all of the studied rocks, especially partings, roofs, and floors (Fig. 8), probably reflect significant leaching of this element from the lower coal-bearing unit of the Hunchun basin. Dai et al. (2018) also showed the similar negative Y anomalies in the Baliancheng coal. This might result in its redeposition at the artesian-water discharge zones along faults cutting and framing the basin. This phenomenon was observed in South Primorye (Nechaev et al., 2018).

5.3. Relationship between Hunchun coals and adjacent ore deposits

Mineralization is common in the eastern Jilin Province of NE China (Ren et al., 2016; Chen et al., 2017) and several Au–Cu and W deposits were discovered in this area. The Paleozoic low-grade metamorphic rocks (mainly the Wudaogou Group), Permian granitoids and Mesozoic (mainly Early Cretaceous) magmatic rocks are important host rocks for the ore mineralization in the eastern Hunchun area (Chen et al., 2015,

2017; Ren et al., 2016). These rocks also served as sediment-source rocks for the Paleogene coal-bearing sediments in the Hunchun Coalfield as shown in this study and the investigation by Dai et al. (2018). It is noteworthy that many of the ore deposits are situated nearer to the Fuqiang coal mine than to the Baliancheng coal mine (Fig. 1). Mineralization of Yangjingou and Wudaogou scheelite deposits (Zhang et al., 2006; Li, 2017) in the Paleozoic rocks in Eastern Jilin is a probable reason for the W enrichment in the Fuqiang samples.

The geological setting, which led to the trace element enrichment in coals in the Hunchun Coalfield, probably included the following processes:

- 1) W-mineralized igneous and metamorphic rocks surrounding the coal basin have been subjected to weathering and erosion after tectonic uplift, and subsequently provided scheelite and other ore components as solid particles and dissolved elements and compounds into the coal basin by stream and ground waters, particularly by those with $pH > 8$ (e.g., Grimes et al., 1995; Johannesson et al., 2013).
- 2) The ore detrital particles or the leached elements were deposited in the peat deposit layers and their adjacent non-peat host sediments in the coal basin, which served as geochemical barriers of the groundwater aquifer in the basin. The acidic environment during peat deposition as evidenced by the REY's distribution could facilitate the deposition of ore detrital particles and leached elements.

6. Conclusions

The Fuqinag coals (Nos. 23 and 26) from the Hunchun Coalfield have low random huminite reflectances (0.31–0.49%) and are rich in W, Cs, Rb, and some other lithophyte elements (Li, V, Ga, and Zr). The terrigenous regions for the coals are Mesozoic intermediate-felsic volcanic rocks and Paleozoic low-grade metamorphic (mainly the Wudaogou Group) and magmatic rocks.

The coals of the Hunchun Coalfield are rich in tungsten and may be classified as ‘coal-hosted rare-metal deposit’ or ‘metalliferous coal’ with related potential economic value. These characteristics are due to their proximity to the eastern Hunchun ore district, where gold and tungsten mineralizations are abundant.

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