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ORIGINAL ARTICLE

Trace elements of Carboniferous–Permian coal from the Adaohai Mine, Daqingshan Coalfield, Inner Mongolia, China

Piaopiao Duan[1] · Yanheng Li[1] · Teng Guan[1]

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Abstract A total of 48 samples of Carboniferous–Permian coal was taken from the Adaohai Mine, Daqingshan Coalfield, Inner Mongolia, China. Cu2 coal is the major coalseam of the Daqingshan Coalfield. The samples were analyzed by the ınductively coupled plasma–mass spectrometer method. The results indicate the content of V, Cr, Cu, Zn, Ga, Se, Ag, Cd, In, Ba, Pb and U of the Cu2 coals from Adaohai Mine is higher than that of the common Chinese coals. Compared to the world hard coals, the content of V, Cu, Zn, Ga, Se, Sr, Ag, Cd, In, Ba and U is relatively high. Compared to the clark values of the crust, only elements Se, Ag, Pb and Bi are enriched in the coal. Most of the elements in coal benches are lower than in those in roofs and partings. The statistical analysis and clustering analysis showed that the modes of trace elements occurrence for the Cu2 coal correlated positively with the minerals. The values of Sr/Ba show that the coal forming environment was influenced both by sea water and fresh water.

Keywords Adaohai Mine · Carboniferous–Permian coal · Trace element

1 Introduction

Coal is the richest fossil energy resource on Earth (Wu 2000). China is and will continue to be one of the largest coal producers and consumers in the world (BP Report 2012). Coal is not only China's main source of energy, but it is also the foundation of China's national economic and social development (Liang 2006; Sun et al. 2012a). The study of trace elements in coal is of great significance (Sun et al. 2010, 2012b, 2013a; Dai et al. 2014; Zhao et al. 2009). Using the theory of trace element geochemistry, geologists have discussed many geological problems in coal forming activities. Trace elements can be used as a sign of coal seam correlation (Tang and Huang 2002). The study of trace elements in coal can offer a theoretical basis for resource utilization and the prevention of environmental pollution (Xu et al. 2011; Dai et al. 2012a; Fan et al. 2013; Sun et al. 2013b; Zhao et al. 2014).

The Daqingshan Coalfield is one of the most important coalfields of Inner Mongolia. Many researchers have studied the trace elements of coal in the Adaohai Mine. Dai et al. (2012b) studied the mineralogical and geochemical composition of the Pennsylvanian coal in the Adaohai Mine. Zou et al. (2012) studied the trace elements and rare earth elements of coal in the Adaohai Mine. The study area is situated slighly north of the Jungur Coalfield. Taking the Carboniferous–Permian Cu2 coal of the Adaohai Mine in the Daqingshan Coalfield as the research object, this article discusses the contents and characteristics of trace element occurrences in the coal in order to compare it with the content of trace elements in Jungar Coalfield.

2 Geological setting

The Daqingshan Coalfield is located in Inner Mongolia of northern China, covering the area of north latitude 40°35′–40°44′ and east longitude 110°07′–110°31′, northwest of the Adaohai Mine (Dai et al. 2012a, b). The Adaohai Mine

✉ Yanheng Li
liyh1982@gmail.com

[1] Key Laboratory of Resource Exploration Research of Hebei Province, Hebei University of Engineering, Handan 056038, Hebei, China

Table 1 Maceral contents determined under optical microscope for Cu2 coals (vol%; on mineral-free basis)

Sample	T	CT	CD	VD	TV	SF	F	Mac	Mic	ID	TI	TE
A44	0.00	0.28	0.53	0.00	0.81	0.04	0.05	0.00	0.00	0.08	0.18	0.01
A43	0.00	0.02	0.49	0.13	0.65	0.06	0.20	0.00	0.00	0.06	0.33	0.02
A42	0.00	0.46	0.19	0.06	0.71	0.06	0.00	0.00	0.01	0.17	0.24	0.05
A41	0.01	0.40	0.33	0.04	0.78	0.01	0.01	0.00	0.00	0.20	0.22	0.00
A40	0.02	0.11	0.60	0.03	0.76	0.01	0.12	0.00	0.01	0.05	0.19	0.05
A35	0.08	0.24	0.43	0.01	0.76	0.00	0.16	0.00	0.00	0.08	0.24	0.01
A32	0.01	0.13	0.46	0.00	0.60	0.00	0.23	0.00	0.00	0.11	0.34	0.06
A31	0.04	0.28	0.35	0.03	0.70	0.06	0.12	0.00	0.05	0.08	0.30	0.00
A29	0.00	0.42	0.36	0.05	0.82	0.01	0.02	0.02	0.02	0.10	0.16	0.02
A28	0.00	0.28	0.39	0.03	0.71	0.09	0.01	0.03	0.01	0.13	0.28	0.01
A25	0.00	0.50	0.22	0.03	0.75	0.05	0.01	0.00	0.02	0.16	0.24	0.00
A24	0.02	0.39	0.27	0.05	0.73	0.07	0.01	0.02	0.01	0.14	0.26	0.01
A23	0.03	0.33	0.40	0.02	0.78	0.00	0.14	0.00	0.00	0.08	0.22	0.00
A22	0.00	0.39	0.31	0.06	0.76	0.08	0.03	0.04	0.00	0.06	0.21	0.03
A21	0.00	0.35	0.35	0.01	0.71	0.07	0.08	0.04	0.00	0.09	0.28	0.01
A19	0.03	0.45	0.26	0.02	0.76	0.00	0.15	0.00	0.00	0.08	0.23	0.00
A18	0.00	0.37	0.33	0.02	0.72	0.00	0.18	0.00	0.00	0.10	0.28	0.00
A17	0.00	0.33	0.43	0.02	0.78	0.04	0.03	0.01	0.03	0.09	0.20	0.01
A16	0.03	0.18	0.54	0.01	0.77	0.00	0.16	0.00	0.00	0.07	0.23	0.00
A13	0.00	0.41	0.35	0.03	0.79	0.08	0.04	0.02	0.01	0.04	0.19	0.02
A12	0.00	0.38	0.32	0.02	0.73	0.13	0.07	0.03	0.01	0.03	0.27	0.01
A11	0.02	0.14	0.35	0.01	0.51	0.26	0.07	0.05	0.03	0.06	0.47	0.02
A10	0.00	0.46	0.22	0.02	0.70	0.17	0.05	0.02	0.00	0.06	0.29	0.01
A9	0.02	0.27	0.34	0.00	0.63	0.21	0.09	0.02	0.01	0.03	0.36	0.01
A8	0.02	0.07	0.43	0.01	0.53	0.23	0.13	0.04	0.02	0.03	0.45	0.02
A7	0.13	0.05	0.43	0.01	0.62	0.16	0.13	0.05	0.02	0.02	0.38	0.00
A6	0.01	0.48	0.21	0.01	0.70	0.10	0.11	0.02	0.03	0.02	0.29	0.01
A5	0.02	0.32	0.39	0.00	0.74	0.07	0.10	0.05	0.01	0.00	0.24	0.02
A4	0.01	0.51	0.24	0.00	0.77	0.10	0.04	0.04	0.00	0.03	0.21	0.02
A3	0.03	0.23	0.37	0.02	0.65	0.14	0.08	0.08	0.01	0.03	0.34	0.00
A2	0.18	0.39	0.19	0.03	0.78	0.06	0.10	0.02	0.00	0.03	0.21	0.01
A1	0.03	0.45	0.33	0.03	0.84	0.00	0.12	0.01	0.00	0.01	0.13	0.03
av.	0.02	0.32	0.36	0.03	0.72	0.08	0.09	0.02	0.01	0.07	0.26	0.02

T telinite, *CT* collotelinite, *CD* collodetrinite, *CG* corpogelinite, *VD* vitrodetrinite, *TV* total vitrinites, *SF* semifusinite, *F* fusinite, *Mac* macrinite, *Mic* micrinite, *Fg* funginite, *ID* inertodetrinite, *TI* total inertinites, *Tl* total exinite, *av.* average

is 2 km long (N–S) and 7.5 km wide (W–E), with a total area of 15 km^2.

The coal-bearing strata is the Carboniferous–Permian Shuangmazhuang Formation. From top to bottom, the coal has been divided into four groups: Cu1, Cu2, Cu3 and Cu4. The Cu2 coal is the major coal-bearing strata in the Daqingshan Coalfield and has a thickness varying from 4.72 to 42.79 m (22.58 m on average). The coal seam structure is very complex. The coal in this area contains 3–42 parting layers with thicknesses ranging from 0.02 to 3.4 m. The roof of the coalseam is mainly made up of kaolinite, siltstones, carbonaceous mudstone and some local sandy mudstone. The Cu2 coal is in direct contact with its overlying clay rock, which has a thickness of 30 m. The floor of the coal is conglomerate and has a thickness of 15 m.

3 Samples and methods

Following the Chinese Standard Method GB482-1985, a total of 48 bench samples were taken from the workface of the mined coal at the Adaohai Mine; these include 33 coal benches, 4 roof samples and 11 partings. Every coal bench

Table 2 Concentrations of trace elements in coal benches, partings, roof samples from Adaohai Mine (elements in μg/g)

Sample	Li	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Se	Rb
A48-R	221.4	3.0	46.9	32.8	4.6	11.9	18.3	147.0	32.6	1.1	19.2
A47-R	15.6	2.5	209.0	97.5	50.7	67.3	62.6	114.0	32.5	1.6	8.8
A46-R	6.2	3.3	60.8	22.9	1.5	8.9	28.5	14.0	26.3	7.2	1.2
A45-R	12.9	3.1	58.6	21.6	1.3	6.9	26.8	10.0	31.4	7.2	0.6
A44	1.2	1.2	21.3	3.6	5.4	3.8	7.4	8.0	13.8	2.3	0.0
A43	4.7	1.6	55.4	7.7	5.1	6.1	12.8	14.0	19.5	4.6	1.3
A42	8.4	2.6	44.1	8.0	3.0	18.0	14.8	22.0	14.3	12.3	0.0
A41	3.7	2.8	72.0	13.4	5.5	26.1	27.9	36.0	14.8	5.1	0.0
A40	5.5	1.6	57.6	14.4	8.2	7.8	63.1	30.0	15.2	3.8	0.5
A39-P	13.8	2.4	136.0	65.8	18.2	32.4	60.7	182.0	20.0	2.2	8.9
A38-P	1.9	1.7	227.0	76.8	25.5	34.3	56.1	139.0	27.0	2.8	11.5
A37-P	13.8	2.0	109.0	50.0	19.0	38.7	44.9	164.0	18.8	6.9	10.4
A36-P	7.2	2.3	175.0	79.5	25.7	40.8	70.8	269.0	26.7	3.5	8.0
A35-P	1.5	1.5	287.0	75.3	8.1	12.7	35.6	448.0	16.8	5.1	2.7
A34	1.7	2.9	91.8	21.3	2.6	4.4	44.9	8.0	32.0	10.4	0.3
A33	0.0	3.2	75.5	15.0	3.4	6.5	28.5	61.6	27.7	3.2	0.4
A32-P	11.4	4.8	60.8	11.0	1.1	5.0	39.3	17.3	29.0	8.8	2.5
A31	7.8	4.0	50.4	11.6	2.1	6.5	18.2	7.6	20.2	19.2	0.0
A30	1.1	2.3	90.0	9.1	6.6	8.9	33.6	12.3	22.2	13.6	0.0
A29	4.5	2.0	53.5	15.6	6.0	14.8	16.0	6.2	19.3	11.8	0.0
A28	0.7	1.7	45.9	7.0	6.5	12.6	15.7	40.2	26.9	10.9	0.0
A27-P	6.9	1.1	11.1	12.0	3.1	20.8	6.5	22.6	17.5	0.2	0.0
A26-P	19.4	1.6	23.4	3.1	1.0	7.0	5.2	7.7	10.9	2.8	2.6
A25	10.9	2.0	33.7	4.4	2.5	11.2	16.7	10.7	14.1	9.0	1.0
A24	0.6	1.3	47.8	5.4	6.0	7.2	14.2	8.0	38.9	2.0	1.6
A23	0.0	1.1	49.0	3.9	7.1	6.1	10.9	6.2	21.7	2.4	0.0
A22	5.7	1.4	60.0	6.3	7.5	1.8	20.5	8.1	17.1	4.7	0.0
A21	4.1	1.3	25.4	4.5	4.3	2.6	9.4	11.0	22.5	2.8	0.0
A20-P	4.2	1.2	18.6	3.5	3.1	2.1	6.2	12.2	13.9	3.1	0.0
A19	8.7	0.9	17.6	1.7	2.5	2.0	8.5	27.5	9.9	4.0	0.0
A18	0.4	0.7	14.3	7.0	3.0	11.0	6.4	4.8	8.4	1.7	0.0
A17	3.7	1.3	18.1	5.9	2.1	1.2	8.3	6.9	12.8	2.7	0.0
A16-P	10.9	1.9	15.1	6.4	0.9	2.7	6.4	13.8	26.8	2.0	3.9
A15	0.0	1.8	13.7	1.7	1.2	1.1	10.6	15.8	8.9	2.7	0.0
A14	0.0	0.9	10.7	1.6	1.2	2.2	8.2	6.7	8.8	3.2	0.0
A13	0.8	1.4	16.0	2.8	1.5	2.2	17.9	6.5	9.2	3.0	0.0
A12-P	1.2	2.8	21.6	5.1	1.0	1.5	9.7	8.1	8.7	2.8	0.0
A11	0.7	1.9	22.5	2.2	2.6	2.7	12.4	17.7	9.2	2.9	0.0
A10	2.3	2.5	41.6	4.2	1.8	1.9	10.3	4.4	13.8	1.4	0.0
A9	16.9	2.4	16.6	4.3	0.8	1.5	7.2	26.4	17.2	5.2	1.9
A8	4.5	2.3	19.4	1.6	1.8	1.8	7.8	6.1	11.3	2.3	0.1
A7	6.8	2.0	36.2	6.0	1.4	1.7	10.3	8.0	14.5	2.8	0.8
A6	1.8	2.0	32.7	14.9	3.4	20.4	15.8	10.1	10.8	3.3	0.2
A5	4.8	1.7	33.6	4.5	1.6	1.6	8.2	10.0	12.4	3.9	0.1
A4	1.7	1.5	27.7	4.3	3.3	3.3	10.8	3.6	12.6	3.5	0.2
A3	2.5	1.8	37.8	3.2	2.6	2.3	12.0	14.5	14.1	5.1	0.0
A2	17.2	2.0	41.8	5.7	1.1	2.1	10.2	8.8	12.4	2.9	0.4
A1	9.0	0.9	73.9	6.5	2.9	3.5	18.7	65.8	15.8	4.5	0.0

Table 2 continued

Sample	Sr	Ag	Cd	In	Cs	Ba	Tl	Pb	Bi	U	Sr/Ba
A48-R	9.3	2.5	0.4	0.1	1.1	336.0	0.2	39.9	0.1	5.0	0.03
A47-R	17.7	1.6	0.5	0.1	0.4	134.0	0.5	28.2	0.4	2.9	0.13
A46-R	9.9	3.5	0.4	0.2	0.1	96.0	0.0	64.6	2.7	7.8	0.10
A45-R	9.2	3.3	0.3	0.2	0.1	89.0	0.1	70.7	2.1	6.8	0.10
A44	15.1	1.6	0.2	0.1	0.0	95.0	0.3	16.6	0.4	2.5	0.16
A43	9.8	3.4	0.3	0.1	0.1	91.0	0.4	35.4	0.3	3.0	0.11
A42	15.8	2.0	0.2	0.1	0.0	65.0	0.1	69.6	0.5	4.5	0.24
A41	10.0	1.3	0.3	0.1	0.0	80.0	0.2	23.6	0.6	2.3	0.13
A40	60.0	1.2	0.8	0.1	0.1	82.0	0.2	16.7	0.4	1.9	0.73
A39-P	40.2	2.0	0.7	0.1	0.4	127.0	0.3	24.9	0.3	2.4	0.32
A38-P	51.4	1.6	0.5	0.1	0.5	136.0	0.7	34.8	0.4	2.5	0.38
A37-P	45.0	2.1	0.4	0.1	0.4	130.0	0.7	36.4	0.2	2.4	0.35
A36-P	33.4	1.8	0.6	0.1	0.4	128.0	0.4	30.1	0.4	3.2	0.26
A35-P	51.6	3.3	1.0	0.1	0.2	107.0	0.6	52.8	0.6	6.2	0.48
A34	47.5	6.1	0.5	0.2	0.0	84.0	0.2	47.3	1.9	6.6	0.57
A33	61.1	3.2	0.4	0.1	0.2	128.0	0.3	43.0	1.1	5.8	0.48
A32-P	31.7	2.6	0.3	0.2	0.3	116.0	0.2	54.3	1.7	10.7	0.27
A31	80.1	2.8	0.2	0.1	0.0	103.0	0.0	74.6	0.4	8.0	0.78
A30	21.6	4.6	0.3	0.2	0.0	90.0	0.1	44.9	1.9	8.4	0.24
A29	31.2	2.6	0.2	0.1	0.0	73.0	0.2	37.9	0.7	5.9	0.43
A28	211.6	2.2	0.2	0.1	0.0	700.0	0.2	31.4	0.2	4.1	0.30
A27-P	251.9	0.8	0.2	0.0	0.0	578.0	1.2	15.7	0.1	1.2	0.44
A26-P	11.7	1.3	0.1	0.1	0.3	84.0	0.5	14.4	0.3	1.9	0.14
A25	31.6	1.6	0.2	0.1	0.1	86.0	0.3	33.7	0.9	4.3	0.37
A24	890.0	2.3	0.2	0.1	0.1	1696.0	0.4	15.6	0.3	2.9	0.52
A23	984.0	0.8	0.1	0.0	0.0	762.0	0.2	9.6	0.2	2.1	1.29
A22	5.0	1.9	0.2	0.1	0.0	32.0	0.1	16.9	0.7	3.1	0.16
A21	125.0	1.3	0.1	0.1	0.0	451.0	0.4	14.5	0.5	2.6	0.28
A20-P	28.0	0.9	0.2	0.0	0.0	309.0	0.2	15.4	0.2	2.0	0.09
A19	43.3	1.3	0.1	0.1	0.0	98.0	0.2	16.4	0.4	2.1	0.44
A18	268.0	0.6	0.1	0.0	0.0	197.0	0.1	10.6	0.2	1.1	1.36
A17	25.1	0.9	0.1	0.1	0.0	78.0	0.1	17.6	0.3	3.3	0.32
A16-P	205.0	0.7	0.1	0.0	0.3	898.0	0.4	16.1	0.3	2.5	0.23
A15	136.7	0.4	0.1	0.0	0.0	175.0	0.2	8.8	0.2	1.3	0.78
A14	44.2	0.6	0.0	0.0	0.0	172.0	0.2	11.1	0.2	1.4	0.26
A13	26.0	0.8	0.1	0.0	0.0	85.0	0.3	12.8	0.2	1.9	0.31
A12-P	18.4	0.9	0.1	0.1	0.0	35.0	0.2	13.8	0.3	2.4	0.53
A11	164.0	1.0	0.1	0.0	0.0	77.0	0.2	13.2	0.3	1.8	2.13
A10	52.8	4.9	0.3	0.1	0.0	52.0	0.1	18.8	0.4	11.3	1.02
A9	44.4	1.3	0.2	0.1	0.3	54.0	0.3	41.1	0.3	3.5	0.82
A8	0.0	1.4	0.1	0.0	0.0	4.0	0.3	7.0	0.2	4.4	0.00
A7	0.0	1.6	0.1	0.1	0.1	30.0	0.1	19.1	0.3	5.1	0.00
A6	0.0	1.4	0.1	0.1	0.1	11.0	0.1	14.8	0.2	2.2	0.00
A5	0.0	1.8	0.2	0.0	0.0	18.0	0.1	22.7	0.2	2.7	0.00
A4	3.2	1.5	0.1	0.0	0.0	15.0	0.1	13.6	0.2	1.3	0.21
A3	0.0	1.3	0.2	0.0	0.0	22.0	0.1	20.7	0.1	2.3	0.00
A2	0.0	1.5	0.2	0.1	0.1	20.0	0.1	16.2	0.3	2.3	0.00
A1	0.0	2.2	0.6	0.1	0.0	14.0	0.1	24.2	0.3	2.5	0.00

sample was cut over an area 10 cm wide, 10 cm deep and 50 cm thick. All collected samples were immediately stored in plastic bags, to minimize contamination and oxidation. From bottom to top, the 33 bench samples and the 11 partings (with a suffix -P) were identified as A1–A44. The roof samples, from bottom to top, were Roof-45 to -48.

The mean random reflectance of vitrinite was determined using a Leica DM-4500P microscope. Maceral constituents were identified using white-light reflectance microscopy under oil immersion, and more than 500 counts were measured for each polished pellet. Inductively coupled plasma mass spectrometry (X series II ICP-MS) was used to determine the trace elements in the coal samples. All the samples were crushed and ground to pass 200 mesh (75 μm) for elemental analysis.

4 Results and discussion

4.1 Vitrinite reflectance and maceral content of the Cu2 coal

The average vitrnite reflectance was 1.58 %, indicating a low volatile bituminous rank range. The maceral contents of the Cu2 coal are listed in Table 1. The maceral content in the Cu2 coal is dominated by vitrinite (60 %～84 %, 72 % on average), followed by inertinite (16 %～47 %, 26 % on average). The liptinite content is very low. The vitrinite is mainly composed of collodetrinite and collotelinite, followed by vitrodetrinite. The inertinite is dominated by inertodetrinite, semifusinite and fusinite.

4.2 The trace element content of the Cu2 coal

4.2.1 General distribution of trace elements in the Cu2 coal

The contents of trace elements in the coal samples are listed in Table 2. The comparison between the abundance of trace elements in the coal samples and the average values for other Chinese coals and world hard coals, are listed in Table 3.

1. Compared to Chinese coals (Dai et al. 2011), the Cu2 coals from the Adaohai Mine are higher in V, Cr, Cu, Zn, Ga, Se, Ag, Cd, In, Ba, Pb and U. Compared to world hard coals (Ketris and Yudovich 2009), V, Cu, Zn, Ga, Se, Sr, Ag, Cd, In, Ba and U are enriched.

Table 3 The characteristics of trace elements content (elements in μg/g) in Adaohai Cu2 coal

Sample	The Clark value of crust[a]	Number of samples	Max	Min	AM	EF	China[b]	World[c]
Li	20.0	48	221.35	0	10.21	0.5	31.8	14
Be	2.8	48	4.75	0.72	2.00	0.7	2.11	2
V	135.0	48	286.95	10.72	58.48	0.4	35.1	28
Cr	100.0	48	97.46	1.56	16.51	0.2	15.4	17
Co	25.0	48	50.65	0.76	5.85	0.2	7.08	6
Ni	75.0	48	67.34	1.08	10.41	0.1	13.7	13
Cu	55.0	48	70.78	5.21	21.16	0.4	17.5	16
Zn	70.0	48	447.79	3.57	43.76	0.6	41.4	23
Ga	15.0	48	38.88	8.44	18.35	1.2	6.55	5.8
Se	0.1	48	19.17	0.21	4.80	96.1	2.47	1.3
Rb	90.0	48	19.23	0	1.85	0.02	9.25	14
Sr	375.0	48	983.98	0	87.92	0.2	140	110
Ag	0.1	48	6.06	0.36	1.92	27.5	0.037	0.5
Cd	0.2	48	0.95	0.04	0.27	1.3	0.3	0.22
In	0.1	48	0.23	0.02	0.08	0.8	0.047	0.031
Cs	3.0	48	1.12	0	0.11	0.0	1.13	1
Ba	430.0	48	1696.5	3.92	188.43	0.4	159	150
Tl	0.4	48	1.16	0.03	0.26	0.6	0.47	0.63
Pb	12.5	48	74.57	6.99	27.74	2.2	15.1	7.8
Bi	0.2	48	2.67	0.09	0.53	3.1	0.79	0.97
U	2.7	48	11.29	1.05	3.71	1.4	2.43	1.9

[a] Taylor (1964), *AM* Arithmetic mean, *EF* arithmetic mean/clark value

[b] Dai et al. (2011)

[c] Ketris and Yudovich (2009)

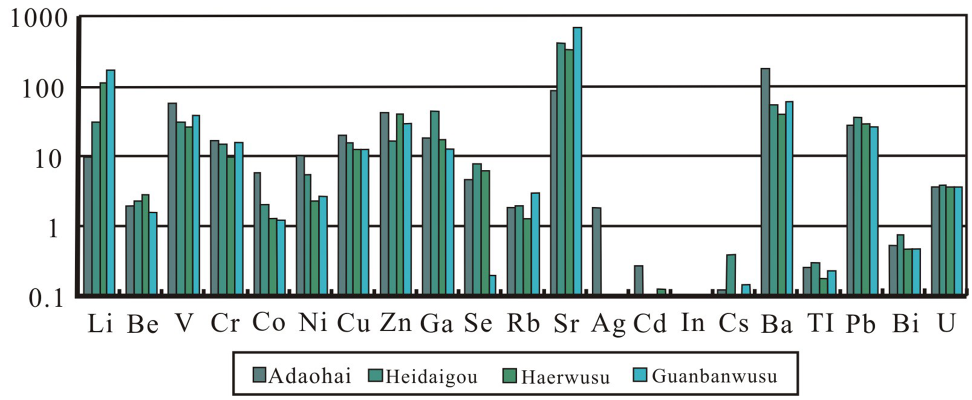

Fig. 1 The mean contents (elements in μg/g) of elements in Adaohai, Heidaigou, Haerwusu and Guanbanwusu coals

2. The Haerwusu Mine, Heidaigou Mine and Guanbanwusu Mine are close to the Adaohai Mine. The contents of V, Cr, Co, Ni, Cu, Zn, Cd and Ba in Adaohai Cu2 coals are higher in comparsion with those in the Haerwusu coals, Heidaigou coals and Guanbanwusu coals (Fig. 1).

4.2.2 The distribution of trace elements in coal, roof and partings

The distribution and enrichment of trace elements in coal were controlled by multiple factors and multiperiodic activity (Liu et al. 2003). The mean content of trace elements in the coal benches, partings and roof have the following characteristics.

1. Compared to world hard coals, a large number of the trace elements are enriched in the Adaohai Cu2 coals (Table 2; Fig. 2a), there are no trace elements with a Concentration Coefficient >5 (CC is the ratio of element concentration in Adaohai coals and world hard coals) in the coals. Trace elements Ga, Se, Ag, In and Pb have a weak enrichment ($2 < CC < 5$). Elements including Li, Cr, Ni, Rb, Cs, Tl and Bi are lower relative to world hard coals ($CC < 0.5$). The concentrations of remaining elements V, Co, Cu, Zn, Sr, Cd, Ba and U ($0.5 < CC < 2$), are close to those of average world hard coals.
2. The average abundance of trace elements in the partings and roof samples from the Adaohai Mine are compared with world hard coals (Fig. 2b and c). The partings are higher in V, Cr, Ga, Se, Ag, In, Pb($2 < CC < 5$) and Zn($CC = 5.07$). The roof is significantly enriched in Li, Ga, Ag, In and Pb ($CC > 5$). Elements V, Cr, Co, Cu, Zn, Se and U ($2 < CC < 5$) is relative high.
3. Most of the trace elements content, except Se and Sr, in the coal benches is lower than that in both the partings and the roof. Compared to the content in the partings and roof, the content of Ag, Bi and U are higher than those in the partings, but lower than those in the roof. The Ba content in the coal is lower than those in the partings but higher than those in the roof (Fig. 2d).

4.2.3 The vertical distribution of trace elements

The vertical variations of trace elements in the Adaohai coal are shown in Fig. 3. Some of the trace elements (e.g., V, Ni, Ga, Se, Pb) are enriched near the roof. This is mainly because trace elements input constantly at the end of the peat forming period. On the other hand, due to the change of environment, swamp environment is adverse to the growth of plants. The cycle of trace elements was controlled and then trace elements were settled down, so trace elements were accumulated in the upper part of swamp. This is the reason why the content of trace elements was high near the roof.

The majority of trace elements are also enriched near the partings. This is caused by the leaching of elements out of the partings and the strong hydrodynamic action during the prating forming process.

Most of the trace elements content in the upper part of the coal seam is higher. The Li in vertical distribution is uniform. The Be in the upper and lower half of coal seam is high, but the content in the midst of the coal seam is

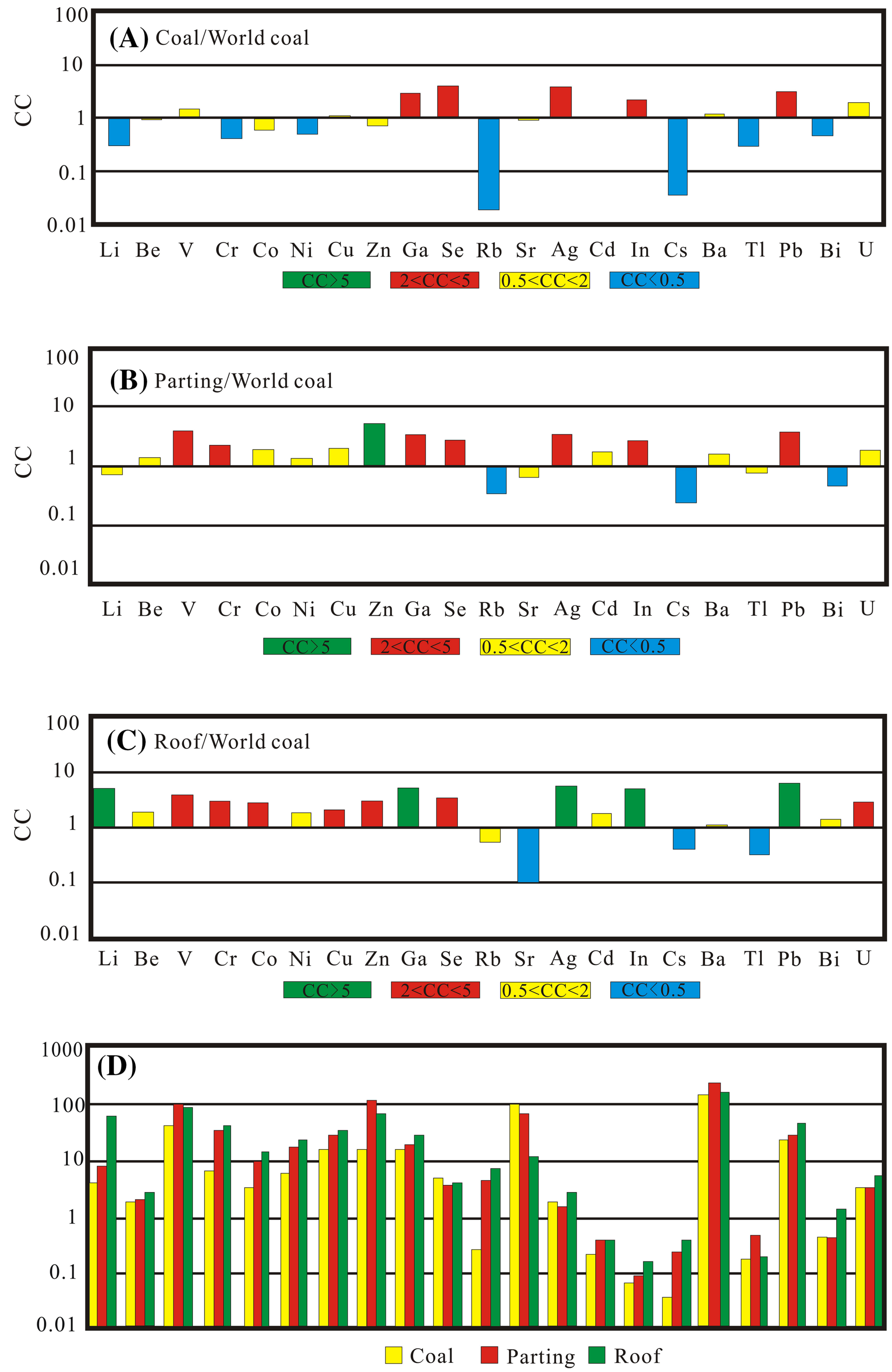

Fig. 2 The ratio of world hard coals to the Adaohai coals (**a**), partings (**b**) and roof (**c**). **d** The mean content of trace elements (elements in μg/g) in coal, partings and roof

relatively low. The V content is higher in the midst of the coal seam. The different vertical distribution of trace elements was caused by their different sedimentary environments, and the content of trace elements vary in different parts of the coal seam. Therefore, the distribution and content of trace elements change regularly.

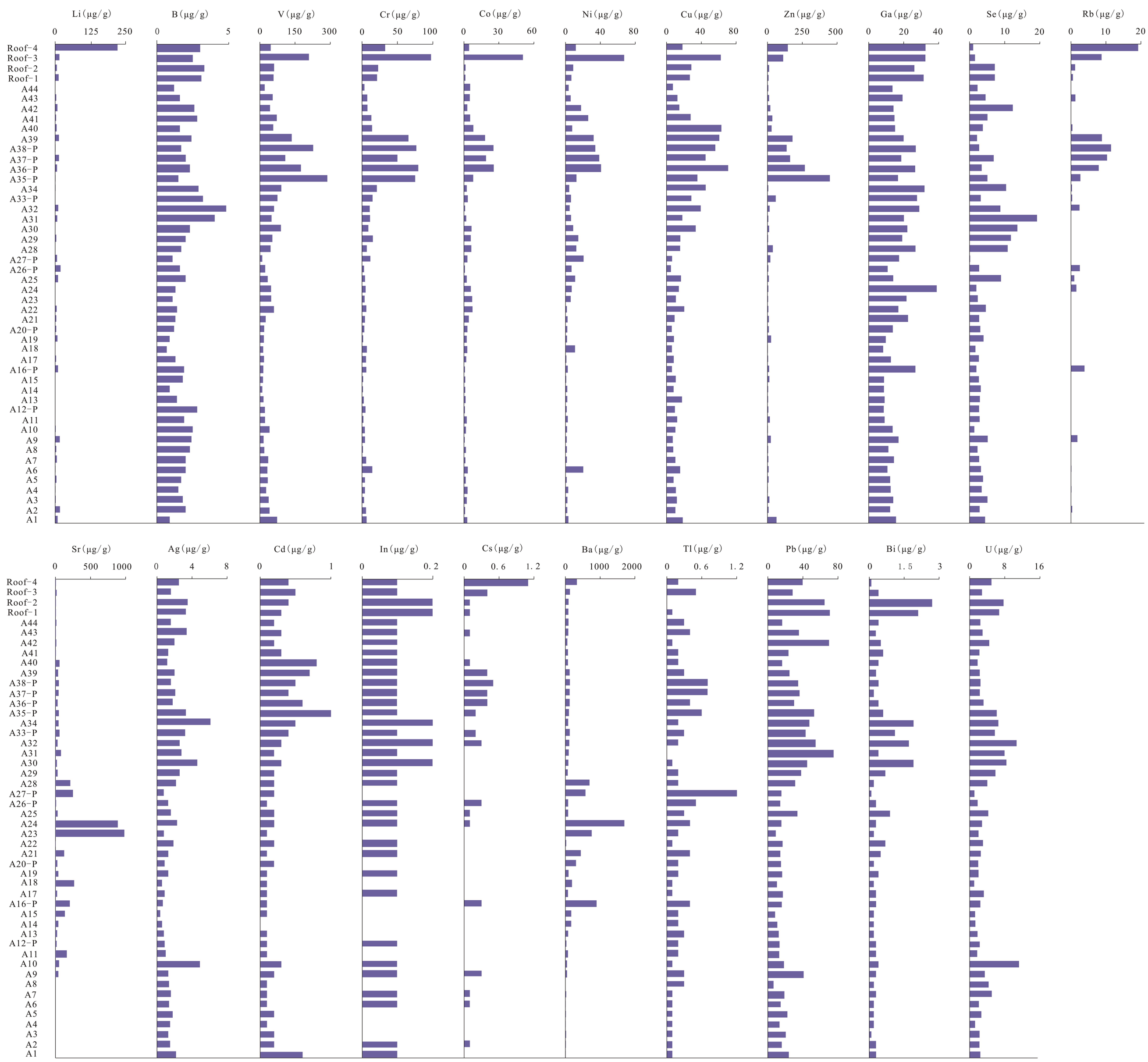

Fig. 3 Vertical variations of trace elements in the coal

4.3 The enrichment of trace elements in the Cu2 coal

The concentration factor (EF) is used to evaluate the dispersal or enrichment in coal. The EF value is the ratio of the content of trace elements in the coal to the clark value of the crust.

Filippidis et al. (1996) argued that if the EF value is higher than 2, the element in coal is enriched. The EF values of Se, Ag, Pb and Bi in the Adaohai coals are higher than 2, and the values are 96.1, 27.5, 2.2 and 3.1, respectively.

4.4 Paragenetic association of trace elements in the Cu2 coal

There is a different degree of relationship between the various elements in coal. The mode of occurrence and enrichment regularity of 21 kinds of trace elements in Cu2 coal were analyzed with Excel and SPSS software.

4.4.1 Correlation analysis

Because some of the trace elements in coal have similar geochemical properties, the mode of occurrence in coal has

Table 4 Correlation matrix of trace elements

	Li	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Se	Rb	Sr	Ag	Cd	In	Cs	Ba	Tl	Pb	Bi	U
Li	1.00																				
Be	0.21	1.00																			
V	−0.01	0.16	1.00																		
Cr	0.14	0.18	0.91	1.00																	
Co	0.02	0.02	0.73	0.86	1.00																
Ni	0.07	0.14	0.67	0.84	0.90	1.00															
Cu	0.01	0.34	0.77	0.81	0.73	0.70	1.00														
Zn	0.20	0.03	0.84	0.81	0.50	0.52	0.58	1.00													
Ga	0.28	0.42	0.42	0.44	0.39	0.36	0.48	0.23	1.00												
Se	−0.13	0.48	0.07	−0.07	−0.12	−0.02	0.13	−0.09	0.18	1.00											
Rb	0.70	0.21	0.51	0.70	0.58	0.60	0.52	0.57	0.46	−0.20	1.00										
Sr	−0.10	−0.28	−0.09	−0.13	−0.01	−0.06	−0.15	−0.10	0.30	−0.17	−0.09	1.00									
Ag	0.07	0.48	0.33	0.17	−0.01	0.00	0.30	0.14	0.49	0.48	0.05	−0.15	1.00								
Cd	0.09	0.19	0.81	0.72	0.49	0.47	0.81	0.75	0.40	0.10	0.42	−0.17	0.42	1.00							
In	0.14	0.69	0.45	0.43	0.24	0.29	0.59	0.22	0.62	0.48	0.28	−0.24	0.73	0.50	1.00						
Cs	0.80	0.30	0.38	0.56	0.41	0.44	0.40	0.49	0.47	−0.19	0.96	−0.12	0.08	0.36	0.29	1.00					
Ba	0.04	−0.23	−0.10	−0.08	0.00	−0.01	−0.15	−0.06	0.50	−0.17	0.07	0.82	−0.12	−0.14	−0.18	0.05	1.00				
Tl	−0.02	−0.22	0.38	0.46	0.42	0.49	0.25	0.43	0.22	−0.32	0.37	0.17	−0.16	0.24	−0.08	0.32	0.30	1.00			
Pb	0.14	0.69	0.36	0.29	0.04	0.17	0.34	0.24	0.49	0.73	0.16	−0.23	0.62	0.40	0.76	0.22	−0.18	−0.11	1.00		
Bi	−0.09	0.56	0.16	0.06	−0.09	−0.05	0.31	−0.08	0.45	0.46	−0.11	−0.17	0.64	0.25	0.85	−0.06	−0.17	−0.23	0.65	1.00	
U	0.08	0.71	0.18	0.05	−0.13	−0.10	0.17	0.04	0.40	0.54	−0.02	−0.17	0.78	0.23	0.69	0.07	−0.15	−0.28	0.67	0.65	1.00

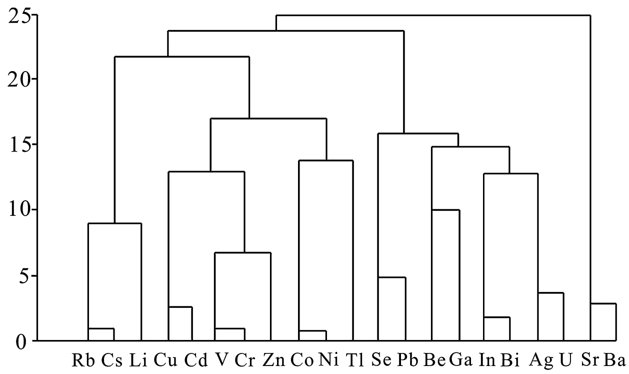

Fig. 4 Cluster analysis of analytical results on 48 samples

consistency. The occurrence pattern of trace elements in coal is substantially similar, due to being affected by same geological factors during the process of coal formation. In general, there is certain relevance between the distributions of trace elements in coal. Excel software was used to analyze the correlation of the trace elements above and the results were listed in Table 4.

V has a high positive correlation coefficient with Cr, Co, Ni, Cu, Zn, Rb and Cd, ranging from 0.70 to 0.91. Cr has a high positive correlation coefficient with Co, Ni, Zn, Rb, Cd and Cs, ranging from 0.70 to 0.86. The correlation coefficient between Cu and Cd (0.81), Zn and Cd (0.75), Rb and In (0.96), Sr and Ba (0.82), Ag and In (0.73), In and Bi (0.85), In and Pb (0.76) are all relatively high.

The high correlation coefficients of Co–Ni (0.9), Co–Cu (0.7) and Ni–Cu (0.7) suggest that Co, Ni, Cu have a similar source. In addition, the correlation coefficients of Li–Rb (0.7), Li–Cs (0.8) and Cs–Rb (0.96) indicate that the element association Li–Rb–Cs might have the same carrier.

4.4.2 *R cluster analysis*

The R cluster analysis, which is based on the relationship between various elements, can cluster and combine the elements. The different element combination reflects the different geochemical characteristics of the sedimentary environment and a variety of palaeostructure, ancient climate and hydrological conditions. Therefore, the paragenetic association of the sedimentary is close, because the environment has a similar physical chemistry and geological condition (Yu et al. 1990).

The elemental associations of the Adaohai coals were studied by R cluster analysis. In the barycenter clustering method, spacing for the Pearson correlation and the standard conversion of the maximum value of 1 was used in the analysis. Three groups of elemental association was identified (Fig. 4).

Group 1 This group includes Rb, Cs, Li, Cu, Cd, V, Cr, Zn, Co, Ni and Tl. Rb, Cs, Li, V and Cr are lithophile elements that probably occur in aluminosilicate minerals. Cu, Cd, Zn, Co, Ni and Tl are chalcophile elements. The high correlation coefficients of Cu–Cd (0.81), Cu–V (0.77), Zn–Cd (0.75), Zn–V (0.84), Zn–Cr (0.81), Cr–Co (0.86), Co–Ni (0.9), Ni–Tl (0.49) suggest that Cu, Cd, Zn, Co, Ni and Tl occur in the sulfide minerals.

Group 2 This group includes the elements Se–Pb–Be–Ga–In–Bi–Ag–U. Most elements in Group 2 are chalcophile elements (with the exceptions of Be and U), suggesting they most likely occur in sulfide minerals.

Group 3 consists of Sr and Ba. Sr and Ba are chalcophile elements with a high correlation coefficient of 0.8. Dai et al. (2012a, b) confirmed that Ba in the Adaohai coal probably occurs in barite and gorceixite.

4.5 The relationship between trace elements and maceral

The trace elements of the distribution and combination state in maceral is closely related to the structure and composition of maceral. Eskenzy et al. (1986) proved that vitrinite was mainly enriched in Pb and Ni, Co, Mo, Sn and

Table 5 Correlation between trace elements and macrcels

Element	Li	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Se	Rb
R_v	0.0	−0.6	−0.4	−0.3	−0.2	−0.2	−0.2	−0.2	−0.3	−0.6	0.1
R_e	0.1	0.0	−0.1	−0.1	−0.2	−0.2	−0.1	−0.1	−0.1	−0.1	0.1
R_i	0.0	0.4	0.2	0.2	−0.1	0.2	0.1	0.0	0.2	0.5	−0.3
R_m	0.0	0.5	0.4	0.3	0.3	0.2	0.3	0.2	0.2	0.3	0.1
Element	**Sr**	**Ag**	**Cd**	**In**	**Cs**	**Ba**	**Tl**	**Pb**	**Bi**	**U**	
R_v	0.2	−0.4	−0.2	−0.5	−0.1	0.1	0.1	−0.6	−0.3	−0.5	
R_e	−0.2	−0.1	0.0	−0.1	0.0	−0.1	−0.3	−0.1	−0.2	0.0	
R_i	0.0	0.2	0.0	0.3	−0.2	0.0	−0.3	0.3	0.2	0.4	
R_m	−0.1	0.3	0.2	0.4	0.3	−0.1	0.2	0.5	0.2	0.3	

R_v is the correlation coefficient between vitrinite and trace elements, R_e is the correlation coefficient between exinite and trace elements, R_i is the correlation coefficient between inertinite and trace elements, R_m is the correlation coefficient between mineral and trace elements

Ge, gelinite was mainly enriched of Ag, Co, As, Mo, Ge and Sn, followed by Zn and Pb and fusinite was mainly enriched of Y and Yb, followed by Sc, Mn, Ba and Cu.

The correlation between trace elements in coal and maceral were analyzed (Table 5). Elements V, Cr, Co, Cu, Zn, Ag, In and Pb in coal had a low or negative correlation coefficients with organic matter, but a positive correlation coefficients with minerals, indicating that these trace elements probably occurred in minerals. Li, Be, Ni, Ga, Se, Rb, Sr and U had positive correlation coefficients with organic matter as well as minerals, indicating both an organic and inorganic affinity.

4.6 Sedimentary environment significance of trace elements

Sr and Ba are significant to a sedimentary environment. Sr content is low when in a damp climate, while high when in a drought environment. A Sr/Ba ratio greater than 1 indicates that the aqueous medium is salt water, and a Sr/Ba ratio less than 1 reflects that the water medium is fresh water (Liu and Zhou 2007). The Sr/Ba values of Cu2 coal in the Adaohai Mine varied from 0 to 2.1 (Table 2), indicating the Cu2 coal was influenced both by sea water and fresh water during the coal forming process. But, only four Sr/Ba values of the coal layers (A10, A11, A18 and A23) were greater than 1, suggesting the coal forming environment of Cu2 coal was mainly influenced by fresh water.

5 Conclusions

1. The maceral content in the Adaohai Cu2 coal is dominated by vitrinite (57 % on average), followed by inertinite (30.6 % on average). Liptinite is rare.
2. The Adaohai Cu2 coal is significantly enriched in Se, Ag, Pb and Bi (concentration coefficients are 96.1, 27.5, 2.2 and 3.1, respectively). Compared to Chinese coals, the coals from Adaohai Mine are higher in V, Cr, Cu, Zn, Ga, Se, Ag, Cd, In, Ba, Pb and U. Compared to world hard coals, the elements of V, Cu, Zn, Ga, Se, Sr, Ag, Cd, In, Ba and U are enriched.
3. Trace elements V, Ni, Ga, Se and Pb are enriched near the roof. Most of the trace elements are also enriched in the immediate overlying and underlying partings, and most of the trace element content in the upper part of the coal seam is higher.
4. The elements in the coal may be classified into three groups of association according to their modes of occurrence. Group 1 includes Rb, Cs, Li, Cu, Cd, V, Cr, Zn, Co, Ni and Tl. Elements Li, Rb and Cs probably have the same carrier. Group 2 includes Se, Pb, Be, Ga, In, Bi, Ag and U. Group 3 consists of Sr and Ba. Elements Cu, Cd, Zn, Co, Ni and Tl in Group 1 probably also occurred in sulfide minerals. Most of the elements in Group 2 are chalcophile elements. Sr and Ba have a high correlation coefficient of 0.8.
5. Elements V, Cr, Co, Cu, Zn, Ag, In and Pb probably occured in minerals. Elements Li, Be, Ni, Ga, Se, Rb, Sr and U probably occurred in both minerals and organic matter.
6. The values of Sr/Ba show that the coal forming environment was influenced by both sea and fresh water.

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