

Significant enrichment of Ga, Rb, Cs, REEs and Y in the Jurassic No. 6 coal in the Iqe Coalfield, northern Qaidam Basin, China—A hidden gem



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ABSTRACT

This paper presents new data concerning the mineralogy and trace element geochemistry of the enriched rare metals in the Jurassic No. 6 coal from the Iqe Coalfield, Qaidam Basin, China. The conclusions of this study are based on new data and evidence that suggest the considerable enrichment of Ga-Rb-Cs-REEs and Y in the No. 6 coal of the Iqe Coalfield may be a hidden treasure with yet-to-be-realized additional economic potential, if such rare metal enrichment is proven across the whole area of Iqe Coalfield.

The No. 6 Coal is enriched in Al_2O_3 , SiO_2 , Na_2O , MgO , P_2O_5 , K_2O , TiO_2 , Rb, Cs, Ga, Sc, V, Cr, Cu, Ba, W, Pb, Th, and REY, especially in Ga, Rb, Cs and H-REY, compared to world coals. The average contents of Ga, Cs, Rb, and REY are 3.1, 12.3, 6.0 and 3.5 times higher than those of world bituminous coals, respectively. Ga may occur in clay minerals (e.g., kaolinite), particularly in K-rich clay minerals (e.g., illite), which are thought to be derived from the Qilian Mountain Range. These minerals are probably the hosting phases for both Rb and Cs in the coal studied. REEs and Y in the coal are more likely to be associated with phosphates. The combustion products (e.g., fly and bottom ash) derived from those coals may be further enriched in these valuable rare metals and have economic potential in terms of the recovery of Ga, Rb, Cs, REEs and Y, providing additional economic value to this coal deposit.

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1. Introduction

Under some specific geological conditions, some valuable elements (e.g., Al, Li, Rb, Cs, Ga, Ge, Nb, Zr, U, Y and lanthanides, Au, Ag, and Pt) can be significantly enriched in coals or in coal-bearing strata, reaching levels equal to or even higher than their concentrations in many conventional types of respective ores (Qin et al., 2015; Dai et al., 2015; Lin et al., 2013; Sun et al., 2012, 2015; Zhao et al., 2009). Seredin and Finkelman (2008) noted that “metalliferous coal” is typically applied to coals with unusually high concentrations of potentially valuable trace elements, at least 10-times higher than the respective averages for the same elements in world coals.

Metalliferous coal deposits containing high concentrations of Ge, Ga, REE and Y, Li, Sc, Zr, Hf, Nb, and Ta have recently attracted

significant attention as a new source for the extraction of these rare metals, which are becoming increasingly important raw materials in various high-technology applications (Arbuzov et al., 2014; Seredin et al., 2013; Sun et al., 2016). For example, as early as 100 years ago, Au and Ag have been recovered from Wyoming and Utah coals (Stone, 1912). In the middle of the 20th century, a combined facility (Coal-uranium breeder) was developed for extracting U from U-bearing coal (Smith, 1977). Currently, more than 50% of the total annual industrial Ge production in the world is extracted from Ge-bearing coal deposits (Dai et al., 2015; Seredin et al., 2013). At the beginning of 2011, a pilot plant specifically designed for the extraction of Ga and Al from coal combustion products (fly ashes) was built at the Jungar coal mine, Inner Mongolia, China (Dai et al., 2015).

Sun et al. reported the concentrations of rare metal elements, rare-scattered elements and rare earth elements that are anomalously enriched in the No. 7 coal seam, which is located approximately 80 m below the No. 6 coal seam, in the Iqe Coalfield (Sun et al., 2015). However, the occurrence and origin of these elements require further detailed study. In this paper, new data and evidence

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for Ga, Rb, Cs, REEs and Y enrichment were obtained in the Jurassic coal in the Iqe Coalfield. With the high market value and concentrations of Ga, Rb, Cs, and REY, special emphasis is placed on the modes of occurrence of these elements.

2. Geological setting

The Qaidam Basin is located at the northeast margin of the Tibet Plateau and belongs to the south of the Tarim-Sino-Korean Plate (Fig. 1 A) (Hanson et al., 2001; Zhu et al., 2005). The Qaidam Basin is the third-largest inland basin of China. Sitting on the Proterozoic metamorphosed crystalline basement and Paleozoic fold deformation basement, the Qaidam Basin is a Mesozoic and Cenozoic sedimentary basin, which was developed after the Indosinian Orogenic movement. A group of small-scale intracontinental foreland basins have been developed bearing Jurassic deposits due to active tectonic contraction effects by the folded-fault belt of the Qilian Mountain Ranges and the northern faulted folds within the basin (Dai et al., 2009; Wang et al., 2015).

The Iqe Coalfield is an elongated continental basin with a narrow width and is located in the northeast part of the Qaidam Basin (Fig. 1B). The basement of the Iqe Coalfield is composed of a metamorphic series of the Lower Proterozoic; a flysch formation of the Ordovician; clastic rocks of continental and transitional facies and limestones of the Carboniferous; and ultra, mafic, intermediate-felsic intrusive and volcanic rocks of the Caledonian (Dai et al., 2009; Wang et al., 2005). The coal-bearing sequences in the Iqe Coalfield include the Dameigou and Shimengou Formations of the Middle Jurassic, with an average total thickness of ~110 m.

3. Sampling and analytical procedures

A total of 6 bench samples, including 5 coal samples and one parting (samples ID: 3059 to 3064), were collected from the ZK36-8 drill core intersecting the No. 6 coal in the Iqe Coalfield.

All collected samples were immediately sealed and stored in plastic bags to minimize contamination and oxidation. All analyses were performed in the Key Laboratory of Resource Exploration Research of Hebei Province. Samples were crushed and ground to pass the 200 mesh sieve for proximate, XRD, XRF, and ICP-MS analyses.

A proximate analysis was conducted following ASTM Standards D3173-03 (ASTM Standard D3173-11, 2011), D3174-04 (ASTM Standard D3174-11, 2011), and D3175-02 (ASTM Standard D3175-11, 2011). The total sulfur was determined following ASTM Standard D3177-02 (ASTM Standard D3177-02, 2002). A subset of samples was also prepared as polished blocks for microscopic analysis under reflected light following ASTM Standard D2797-04 (ASTM Standard D2797-04, 2005). Random vitrinite reflectance ($R_{o, \text{ran}}$) was measured using a Leica DM2500P reflected light microscope fitted with a halogen lamp (oil lens 32/0.65, 548 nm, $3 \times 3 \mu\text{m}$, EMI9592 S-11; calibrated with a glass standard from Leitz, $R_o = 0.889\%$), following ASTM D2798-05 (ASTM Standard D2798-05, 2005).

The mineralogical composition was determined by X-ray diffraction (XRD) and optical microscopic observation. Low-temperature ashing of coal was performed on an EMITECH K1050X plasma Asher. The temperature for low-temperature ashing was kept lower than 200 °C (75 W power). XRD analyses on the resultant low-temperature ashes and the parting samples were performed on a D/max-2500/PC powder diffractometer with Ni-filtered Cu-K α radiation and a scintillation detector. The XRD patterns were recorded over a 2θ interval of 2.6–70°, with a step size of 0.01°.

A scanning electron microscope (HITACHI UHR FE-SEM, SU8220) equipped with an energy-dispersive X-ray spectrometer (SEM-EDS) was used to study the distribution characteristics of the minerals, and the distribution patterns of some elements of interests in the coal.

Each coal and non-coal sample was also high temperature ashed at 815 °C, and loss on ignition was calculated. X-ray fluores-

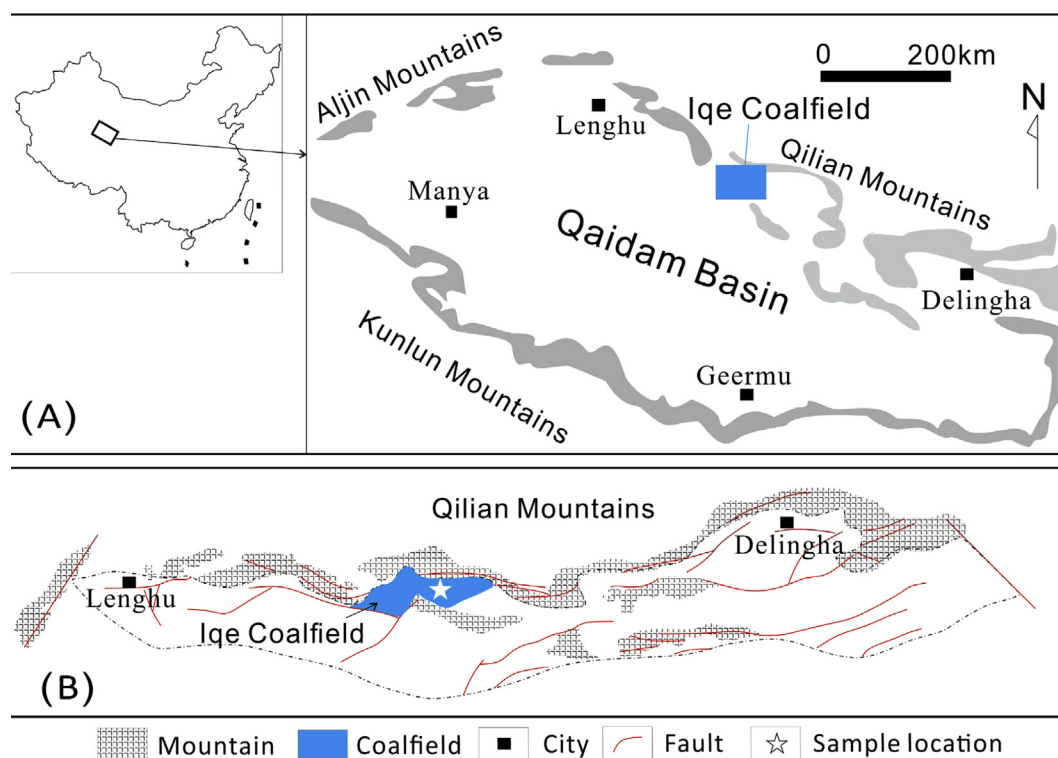


Fig. 1. Location and geological map of Iqe Coalfield. (A) Location of the Iqe Coalfield; (B) Geological map of the Iqe Coalfield.

cence spectrometry (ARL PERFORM'X) was used to determine the oxides of major elements, including SiO₂, Al₂O₃, CaO, K₂O, Na₂O, Fe₂O₃, MnO, MgO, TiO₂, and P₂O₅, in each ashed sample. OXSAS (Version 2.2), a “standard-less” methodology based on a set of fundamental parameters and unique algorithms, was used for matrix correction and calibration of the XRF data. Inductively coupled plasma mass spectrometry (X series II), in a pulse counting mode (three points per peak), was used to determine trace elements in the coal samples.

4. Results

4.1. Coal characteristics

Table 1 provides the results of proximate analysis, total sulfur content, and vitrinite reflectance data of the 6 samples from the Iqe coals. The vitrinite reflectances of all coal samples were determined. The coal is a high-ash and super-low-sulfur coal based on the Chinese Standards GB/T 15224.1-2010 (coals with an ash yield >40% are high-ash coal) (GB/T 15224.1-2010, 2011) and GB/T 15224.2-2010 (coals with a total sulfur content <0.5% are defined as super-low-sulfur coal) (GB/T 15224.2-2010, 2011). The average vitrinite reflectance and average volatile matter (daf) are 0.76% and 22.8%, respectively, indicating a medium volatile bituminous coal according to the ASTM classification (ASTM Standard D388-12, 2012).

4.2. Maceral composition

The maceral classification and terminology applied in the current study are based on the ICCP Maceral Classification System 1994 (ICCP, 1998, 2001) and Taylor et al. (1998).

The data concerning maceral composition of No. 6 coal from the Iqe Coalfield have been summarized and presented in Table 2. The maceral composition is dominated by vitrinites (ranges 50.5–67.6%; 61.7% on average), followed by inertinites (ranges 26.2–37.5%; 29.7% on average) and minor liptinites (only 0.8% on average). The vitrinite contents of the No. 6 coal are much lower than the Middle Jurassic coal in the Ningdong Coalfield, Ordos Basin (72.30% on average) (Zhao et al., 2014) but are higher than those

of other Early-Middle Jurassic coals in the Ordos Basin (which generally are 35–50% vitrinites) (Han et al., 1996); in contrast, the contents of inertinite and liptinite are much lower than those in the Early-Middle Jurassic coals of the Ordos Basin (which generally are 40–50% inertinites and ~5% liptinites) (Han et al., 1996).

The vitrinites are mainly composed of collotelinite (36.2% on average), collodetrinite (14.3% on average) and vitrodetrinite (10.0% on average), with minor amounts of telinite (1.7% on average) and corpogelinite (Table 2). Some of the endogenic crevices, developed in collotelinite and collodetrinite, have been filled with pyrite or calcite in some cases (Fig. 2A, B); the collodetrinite is always associated with fusinite, inertodetrinite and clay minerals (Fig. 2C).

The liptinite maceral is rare in the No. 6 coal, and only sporinite, liptodetrinite and cutinite are observed. Sporinite and liptodetrinite are distributed in the collodetrinite (Fig. 2D). The cutinite often borders the banded collotelinite and emits yellow-green fluorescence excited by blue light (Fig. 2E, F).

The inertinite maceral is represented by fusinite (15.1% on average), inertodetrinite (10.9% on average), and micrinite (2.3% on average), along with trace proportions of funginite, macrinite and semifusinite (Table 2). The fusinite sometimes shows well-preserved cell structures, but the cell walls often have been oxidized, showing possibly swelling (Fig. 2G) and signs of early fussionization. The cells are also filled with clay minerals in some cases. Micrinite sometimes is bedded as a lentoid or is intimately associated with clay minerals in vitrinite (Fig. 2H).

4.3. Geochemistry

4.3.1. Major elements

The abundances of major elements in the coal benches and parting sample, compared to the average values for Chinese coals, are listed in Table 3. The average major elements of the No. 6 coal in the Iqe Coalfield is dominated by Al₂O₃ (12.23%) and SiO₂ (23.99%); the No. 6 coal is also enriched in Na₂O (0.49%), MgO (0.32%), P₂O₅ (0.17%), K₂O (1.05%), and TiO₂ (0.48%), but other major element oxides (MnO, Fe₂O₃, and CaO) are lower than those of average Chinese coals (Table 3). The enrichment factor (EF = average element concentration ratio of coal samples investigated vs. averaged Chinese coals) of K₂O reached 5.54. The SiO₂/Al₂O₃ ratio of the coal (1.38 on average) is slightly lower than that of Chinese coals (1.42) (Dai et al., 2012a) but is higher than that of the theoretical SiO₂/Al₂O₃ ratio of kaolinite (1.18) (Dai et al., 2009).

4.3.2. Trace elements

The average abundances of trace elements from the No. 6 coal seam in the Iqe Coalfield compared with those of the world bituminous coals (Ketris and Yudovich, 2009) are presented in Table 4. Based on our results from this study, almost all trace elements in the No. 6 coal seam are higher than those of the respective averages of world bituminous coals, except Bi and Mo. The trace elements with significant enrichment factors of more than 5 times

Table 1
Proximate analyses of coal samples and parting sample from the Iqe Coalfield (%).

Sample	A ^d	V ^{daf}	W _{ad}	S _t ^d	R _o
3059(parting)	59.5	16.35	7.15	0.19	nd
3060	39.44	22.94	9.97	0.25	0.70
3061	42.97	21.9	11.5	0.17	0.75
3062	43.7	22.41	8.97	0.25	0.77
3063	30.57	26.7	3.41	0.52	0.74
3064	48.05	20.51	8.28	0.25	0.82
Ave.	40.9	22.8	8.42	0.29	0.76

Ave.: average of coal samples; nd: not determined; A: ash yield; W: moisture; V: volatile matter; S_t: total sulfur; ad: on air dry basis; daf: on dry and ash free basis.

Table 2
Maceral composition of the coal samples from Iqe Coalfield (vol.%; on mineral-free basis).

Sample	T	CT	CD	CG	VD	TV	Sp	Cu	TL	SF	F	Ma	Mi	Fg	ID	TI
3060	bdl	26.5	12.9	bdl	11.0	50.5	0.6	0.4	0.9	bdl	21.5	1.1	2.4	0.2	12.3	37.5
3061	bdl	44.5	14.3	bdl	8.4	67.2	0.9	bdl	0.9	bdl	15.2	0.5	0.9	0.5	9.1	26.2
3062	0.9	31.2	16.8	0.9	12.4	62.3	bdl	bdl	bdl	bdl	15.3	0.4	1.5	bdl	9.1	26.2
3063	3.8	45.2	17.1	bdl	1.5	67.6	bdl	bdl	bdl	1.0	12.3	0.2	3.3	bdl	10.1	26.9
3064	0.3	33.3	10.3	0.5	16.4	60.9	bdl	0.5	0.5	2.7	11.2	0.5	3.4	bdl	13.9	31.6
Ave.	1.7	36.2	14.3	0.7	10.0	61.7	0.7	0.4	0.8	1.9	15.1	0.5	2.3	0.4	10.9	29.7

T, telinite; CT, collotelinite; CD, collodetrinite; CG, corpogelinite; VD, vitrodetrinite; TV, total vitrinites; Sp, sporinite; Cu, cutinite; TL, total liptinites; SF, semifusinite; F, fusinite; Ma, macrinite; Mi, micrinite; Fg, funginite; ID, inertodetrinite; TI, total inertinites; bdl, below detection limit; Ave., average;

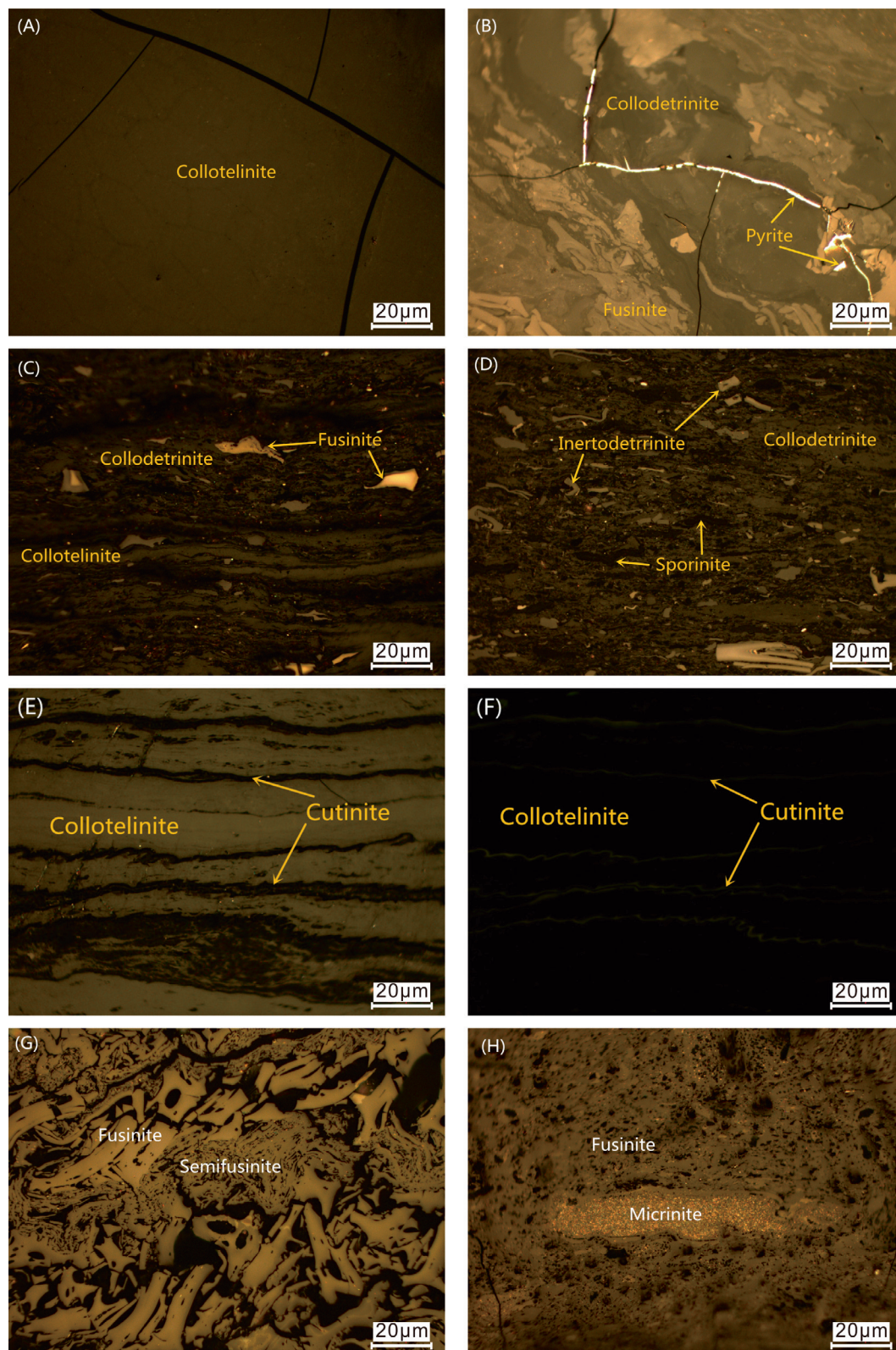


Fig. 2. Photomicrographs showing macerals in the No. 6 coal seam. (A) collotelinite, endogenic crevices developed; (B) collodetrinite, fusinite, and fracture-filling pyrite; (C) collotelinite, collodetrinite, and fusinite; (D) inertodetrinite, collodetrinite and sporinite; (E) cutinite and collotelinite; (F) cutinite, reflected fluorescent light under blue light irradiation; (G) fusinite and semifusinite; (H) fusinite and micrinite.

enrichment $CC > 5$ (CC = average concentrations of trace elements in the No. 6 coal seam in Iq vs. world bituminous coals) are limited to lithophile elements, such as Rb ($CC = 6.0$) and Cs ($CC = 12.3$);

most of the No. 6 coal seam is also enriched in Cs. The majority of the other trace elements studied are only slightly enriched ($CC = 2-5$)

Table 3

Concentrations of major oxides in the Iqe coal samples and parting sample, as well as their comparison with averages for Chinese coals (%).

Sample	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	Si/Al
3059(parting)	17.28	0.5	1.39	1.58	0.43	0.005	0.35	0.24	36.39	0.71	2.11
3060	11.19	0.73	1.34	1.06	0.32	0.005	0.52	0.22	22.98	0.44	2.05
3061	13.25	0.55	1.07	1.06	0.32	0.004	0.56	0.16	24.97	0.51	1.88
3062	12.58	0.69	1.27	1.13	0.36	0.007	0.7	0.15	25.59	0.5	2.03
3063	9.67	0.25	0.87	0.79	0.25	0.004	0.08	0.15	17.85	0.36	1.85
3064	14.48	0.5	1.19	1.22	0.37	0.005	0.57	0.16	28.54	0.57	1.97
Ave.	12.23	0.54	1.15	1.05	0.32	0.01	0.49	0.17	23.99	0.48	1.96
China*	5.98	1.23	4.85	0.19	0.22	0.015	0.16	0.092	8.47	0.33	1.42
EF	2.05	0.44	0.24	5.54	1.47	0.33	3.04	1.83	2.83	1.44	1.38

Ave., average of coal samples. EF (enrichment factor) = Ave./China.

* From Dai et al. (2012b).

Table 4

Concentrations of trace elements in the Iqe coal samples and parting, as well as their comparison with averages for world bituminous coals (μg/g).

Sample	3059(parting)	3060	3061	3062	3063	3064	Ave.	World*	CC
Ba	907	803.19	585.02	550.9	516.63	611.68	613.48	150	4.1
Be	3.32	3.8	2.95	3.06	5.51	3.41	3.75	1.6	2.3
Bi	0.89	0.75	0.64	0.7	0.8	0.67	0.71	0.97	0.7
Cd	0.3	0.26	0.36	0.38	0.47	0.34	0.36	0.22	1.6
Ce	109.68	85.28	70.57	65.12	103.67	73.53	79.63	23	3.5
Co	5.47	6.71	7.69	7.96	7.41	7.2	7.39	5.1	1.4
Cr	85.68	56.41	56.54	51.68	55.19	59.47	55.86	16	3.5
Cs	19.49	11.44	13.74	11.74	10.36	13.98	12.25	1	12.3
Cu	45.38	42.2	35.23	35.41	45.84	33.8	38.5	16	2.4
Dy	5.88	4.89	3.74	3.58	5.75	3.81	4.35	2.1	2.1
Er	3.33	2.72	2.18	2.1	3.35	2.27	2.52	0.93	2.7
Eu	1.86	1.36	1.07	0.99	1.52	1.15	1.22	0.47	2.6
Ga	27.05	16.59	18.9	17.16	17.35	21.04	18.21	5.8	3.1
Gd	7.75	6.17	4.76	4.48	7.36	5.09	5.57	2.7	2.1
Hf	3.36	2.23	2.4	2.39	2.09	2.68	2.36	1.2	2
Ho	1.22	1.03	0.78	0.76	1.21	0.83	0.92	0.54	1.7
La	56.01	41.94	37.15	34.03	55.2	38.58	41.38	11	3.8
Li	43.94	18.62	33.67	27.06	42.27	38.18	31.96	12	2.7
Lu	0.46	0.36	0.31	0.29	0.46	0.32	0.35	0.2	1.7
Mo	2.07	1.92	1.28	1.47	3.21	1.34	1.84	2.2	0.8
Nb	14.56	8.37	9.81	9.05	7.7	11.43	9.27	3.7	2.5
Nd	42.83	33.1	27.16	24.94	38.82	28.74	30.55	12	2.5
Ni	23.71	26.47	28.43	27.41	18.92	26.19	25.48	13	2
Pb	47.11	36.8	35.16	32.73	36.22	35.76	35.33	7.8	4.5
Pr	11.94	9.1	7.74	7.16	11.08	8.06	8.63	3.5	2.5
Rb	129.21	81.29	89.07	82.31	70.53	97.56	84.15	14	6
Sc	10.85	7.87	7.91	7.58	10.13	8.32	8.36	3.9	2.1
Sm	8.47	6.51	5.16	4.76	7.22	5.48	5.83	2	2.9
Sr	346.26	328.55	209.87	184.58	219.96	204.56	229.5	110	2.1
Ta	0.99	0.63	0.69	0.67	0.53	0.79	0.66	0.28	2.4
Tb	1.13	0.92	0.69	0.63	1.06	0.74	0.81	0.32	2.5
Th	17.6	13.37	13.95	13.71	14.11	14.56	13.94	3.3	4.2
Tm	0.51	0.42	0.33	0.33	0.52	0.36	0.39	0.31	1.3
U	4.92	3.87	4.03	3.94	5.22	4.11	4.23	2.4	1.8
V	131.49	83.01	84.9	75.68	89.49	86.17	83.85	25	3.4
W	3.78	5.57	2.6	2.33	2.89	2.85	3.25	1.1	3
Y	33.17	27.48	21.7	20.89	34	22.36	25.29	8.4	3
Yb	3.01	2.44	2.06	2.06	3.03	2.19	2.36	1	2.4
Zn	44.44	49.65	50.1	43.43	80.89	49.57	54.73	23	2.4
Zr	130.72	84.83	91.62	90.35	76.96	102.67	89.29	36	2.5

Ave., average of coal samples. CC (concentration coefficients) = Ave./world.

* From Ketris and Yudovich (2009).

4.4. Minerals in the coal

The XRD data of low temperature ashes and optical microscopy observations show that the No. 6 coal seam of the Iqe Coalfield is composed of the following minerals – mainly kaolinite, quartz and illite, and trace amount of pyrite, siderite, calcite, and rutile (Fig. 3).

4.4.1. Kaolinite

Kaolinite in the No. 6 coal occurs mainly as cell-fillings in telinite and fusinite (Fig. 4A). It is common observed in many other

coals and closely associated strata and may indicate formation during an authigenic processes. Some of the kaolinite is also impregnated and associated with collodetrinite or striped collotelinite (Fig. 4B). Kaolinite was also found under SEM observation (Fig. 5A), often distributed along the edges of illite.

During peat accumulation in the Iqe Coalfield, the peat bog was possibly very close to the provenance of the Qilian Mountain Range (Fig. 1), which mainly consisted of gneiss and granite. These rocks contain feldspar, quartz and mica (Huang et al., 2015; Yang et al., 2015). Feldspar and mica can be weathered or altered/degraded and then transformed into kaolinite and illite (Banfield and

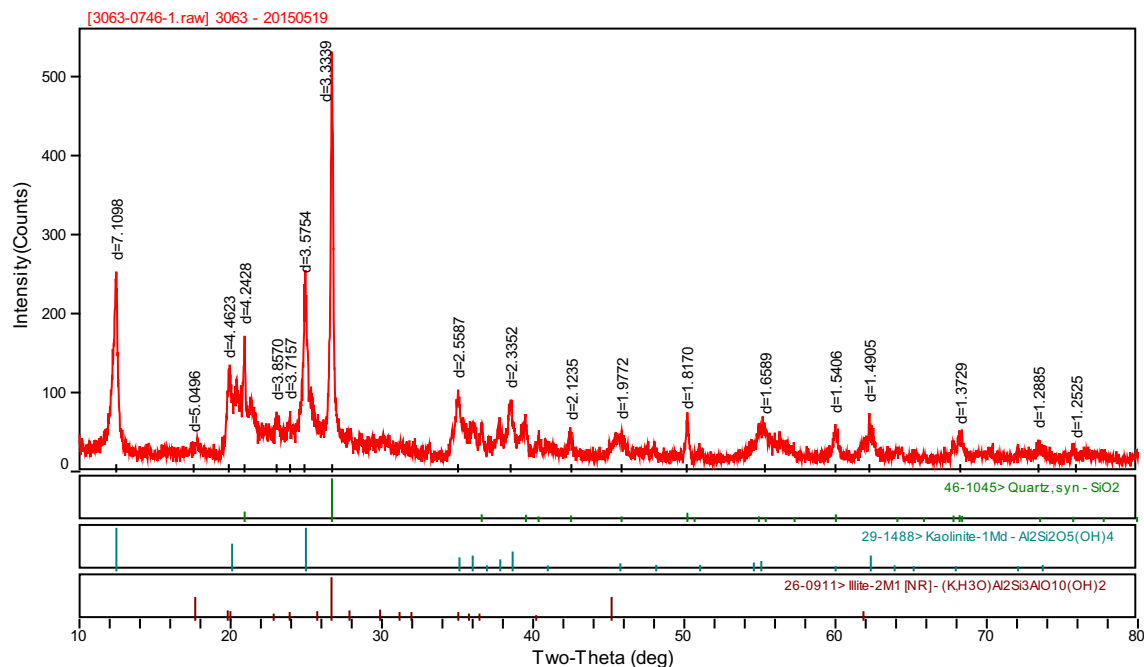


Fig. 3. Identification of minerals in the XRD pattern of the low temperature ashes (LTA) of the Iqe coal.

Eggleton, 1990; Ma and Liu, 2001; Perri, 2011; Perri et al., 2012, 2014a,b; Borrelli et al., 2014). Thus, the kaolinite in these samples is mostly derived from feldspar and mica, which have been weathered and transported into the peat bog during the depositional and diagenetic stages of its development.

4.4.2. Illite

Illite in the coal often occurs as thin laminar or parallel layers stacked together (Fig. 5B, C), associated with kaolinite and quartz (Fig. 5), and is widely and intimately distributed in the collodetrinite or filling in the cell structures in some cases.

Illite is mostly derived from the sediments of the Qilian Mountain Range. The Iqe coalfield is close to the source area; thus, it is not unreasonable to suggest that the illite of terrigenous origin in the No. 6 coal more than likely originated from the weathering of feldspar and mica in the Qilian Mountains.

4.4.3. Carbonate minerals

Carbonate minerals identified in the coal include calcite and siderite. Carbonate minerals are common in coal and are formed during the complete range of its petrogenesis from the authigenic to epigenetic and post-coalification stages (Kortenski, 1992). Calcite mainly occurs as cell- and fracture-infillings (Fig. 4A, F) in the No. 6 coal seam, indicating an authigenic and epigenetic origin.

Siderite was found in this coal as aggregates consisting of radiating crystal structures and small grains and is mostly associated with clay minerals and quartz (Fig. 6). The syngenetic siderite occurs as a typical radiating crystal structure, as well as infillings and replacements of the maceral components, and the epigenetic siderite mainly occurs as cleat-fillings (Zodrow and Cleal, 1999; Ward, 2002; Ward et al., 1999). The siderite in coals is paragenetic and associated with quartz particles during peat swamp accumulation.

4.4.4. Pyrite, quartz, apatite, and rutile

Pyrite is one of the most common sulfides occurring in coals (Taylor et al., 1998), but it is present only a minor component in the No. 6 coal seam; the average total sulfur content in this coal is only 0.27% because the peat swamp depositional environment

of the No. 6 coal seam has never been influenced by marine transgression. The main occurrence of pyrite is framboid and euhedral crystals (Fig. 4D), with some pyritized cell structures and a few fracture-fillings found in the coal (Fig. 4E), showing that pyrite can be of both syngenetic and epigenetic origin.

Quartz is one of the most common silicate minerals in coal. Generally, it is brought in, transported by water at the peat stage (Taylor et al., 1998). Quartz is commonly distributed in collodetrinite as irregular granules (Fig. 4C) and often associated with clay minerals (kaolinite and illite) (Fig. 5A, B), suggesting its terrigenous detrital origin.

Apatite is a rare mineral in the studied coal. This mineral is often below the detection limit of the XRD and it can be observed only under SEM. Apatite generally occurs as cell-infillings in fusinite (Fig. 7A), semifusinite or telinite, and in collodetrinite with kaolinite. The modes of occurrence of apatite indicate an authigenic origin. The apatite occurs as chlorapatite in this coal and is confirmed by SEM-EDS.

A traces of rutile has been found in the SEM-EDS analysis. It is usually associated with kaolinite or illite as irregular particles or it is distributed in the mixed-layer clay or within collodetrinite (Fig. 7B). Rutile is an important carrier of Ti in the No. 6 coal seam.

5. Discussion

5.1. Affinity of the elements

The correlation of element concentrations with ash yield may provide statistical evidence for the determination of their organic or inorganic affinity (Ketris and Yudovich, 2009; Eskenazy et al., 2010), and many scholars use the correlation analysis to discuss the occurrence, affinity and genesis of elements in coal (Wang et al., 2005; Spears and Zheng, 1999; Xu et al., 2011). The correlations between ash yield and selected element combinations are presented in Table 5. Five groups (Groups 1 to 5) of elements have been recognized in the present study according to their correlation coefficients with ash yield (Table 5).

Group 1 includes the following: V, Cr, Ga, Rb, Zr, Nb, Cs, Hf, Ta, Th, MgO, K₂O, Al₂O₃, SiO₂, and Fe₂O₃. This group of elements is

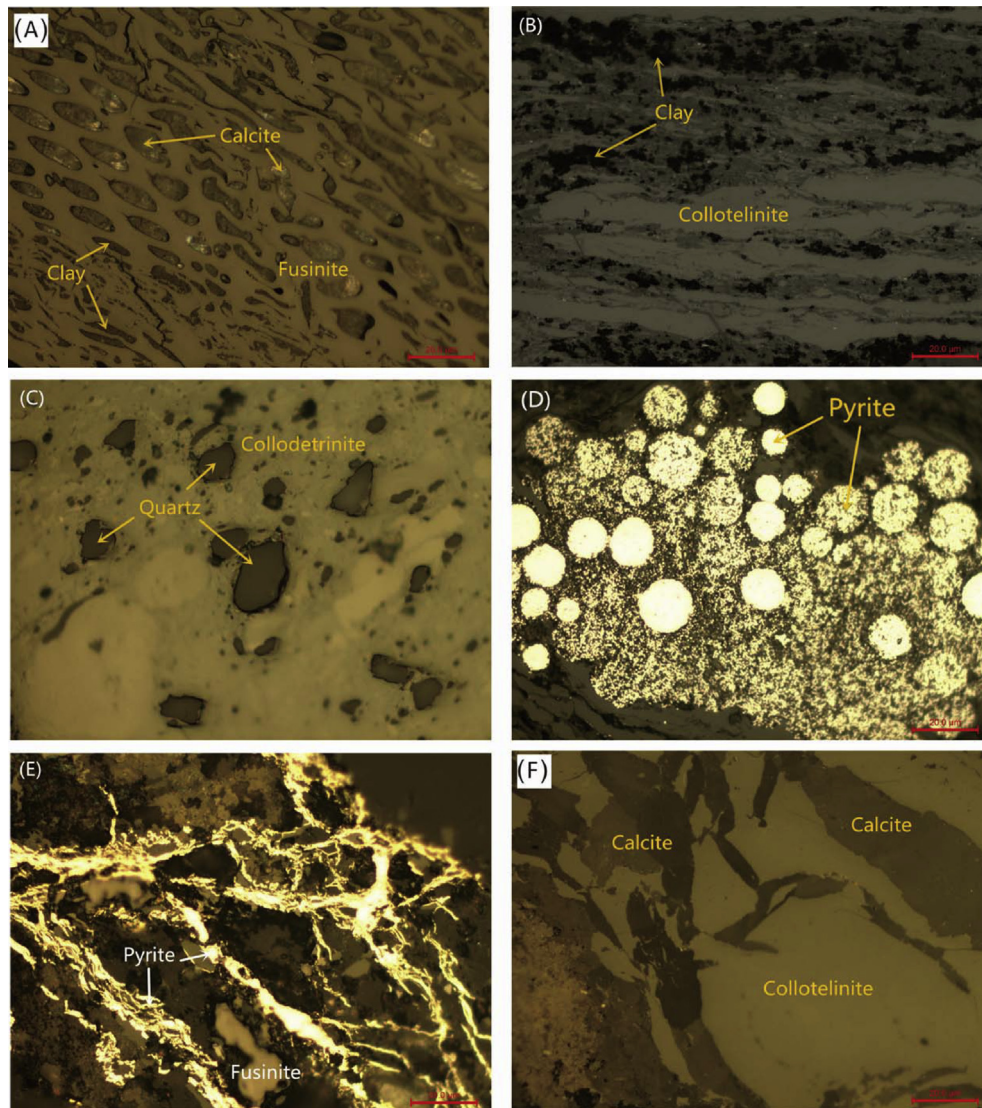


Fig. 4. Optical photomicrographs of minerals in the Iqe coals (reflected light). (A) cell-filling clay and calcite; (B) impregnated clay minerals associated with collotelinite; (C) quartz particles with subangular shape and detrital origin; (D) framboidal and euhedral pyrite 3; (E) pyrite veins; (F) calcite veins.

strongly correlated with ash yield ($r_{\text{ash}} = 0.7\text{--}1.0$). The correlation coefficient between ash yield and SiO_2 is 1.00, and that between ash yield and Al_2O_3 is 0.99. Silicon and aluminum are major constituents of the aluminosilicate (kaolinite) or silicate (quartz) minerals, which are the major minerals present in the coal samples. Other elements in this group (V, Cr, Ga, Rb, Zr, Nb, Cs, Hf, Ta, Th, and MgO) also have strong correlations with aluminosilicate affinity ($r_{\text{Al-Si}} > 0.7$; Table 5). In particular, Ga, Rb, Cs, and K_2O have high correlation coefficients with both Al_2O_3 and SiO_2 , which are Ga (0.91, 0.90), Rb (0.97, 0.97), Cs (0.96, 0.95), and K_2O (0.96, 0.99), respectively (Table 5). These lithophile elements are probably contained/hosted in the clay minerals or mica due to their high correlation coefficients with SiO_2 and Al_2O_3 .

Group 2 includes elements with a lower inorganic affinity than Group 1, but the elements still have a relatively high inorganic affinity (Table 5). Elements in this group, such as Ba, Pb, and P_2O_5 , are positively correlated with ash yield and correlation coefficient values between 0.50 and 0.69, and all of these elements have a relatively high aluminosilicate affinity ($r_{\text{Al-Si}} = 0.3\text{--}0.69$), suggesting an inorganic affinity for this group.

The elements of Group 3 only include Sr and MnO, which have correlation coefficients with an ash yield varying from 0.35 to 0.49.

These two elements also have a reasonable affinity with aluminosilicate, with correlation coefficients $r_{\text{Al-Si}} = 0.3\text{--}0.69$.

Group 4 includes Li, Sc, Ni, Cu, W, Bi, U, Na_2O , CaO, REEs, and Y. The correlation coefficients with ash yield for this group of elements range from -0.34 to 0.34 , indicating ambiguous organic or inorganic affinities. However, Ni and Na_2O show a strong affinity with carbonates, indicating that Ni and Na_2O may be more likely to be associated with carbonate minerals.

Group 5 includes Be, Co, Zn, Mo, Cd, and S, which have strong negative correlation coefficients with ash yield ($r_{\text{ash}} < -0.35$), indicating a dominant organic affinity.

5.2. Valuable trace elements in the coal

As valuable elements in coal, Ga, Cs, Rb, and REE + Y can be recovered as by-products from coal combustion residues if their concentrations are sufficiently high (Dai et al., 2015; Seredin et al., 2013).

5.2.1. Gallium

The Ga concentration in the coal samples varies from 16.6 to $21.0\text{ }\mu\text{g/g}$, with a weighted average of $18.21\text{ }\mu\text{g/g}$ (Table 3), which

is considerably higher than the average Ga in world bituminous coals (average 5.8 $\mu\text{g/g}$) (Ketris and Yudovich, 2009).

Gallium is one of the valuable and rare metals in coal. It is generally related to clay minerals in coal.¹ It can be deduced that Ga mainly occurs in inorganic associations based on the positive correlations of Ga-ash yield ($R^2 = 0.77$), Ga-Al ($R^2 = 0.83$), and Ga-Si ($R^2 = 0.81$). The correlation between Ga and Al ($r = 0.91$) is higher than that between Ga and Si ($r = 0.90$) (Table 5) because Ga has similar geochemical characteristics to Al and could isomorphously substitute Al in Al-bearing minerals (Kortenski and Sotirov, 2002; Dai et al., 2012b). Kaolinite is the main clay mineral in the studied coal and may be the major host mineral for Ga in the No. 6 coal seam of the Iqe Coalfield. Ga may also replace Zn in sphalerite (Swaine, 1990). However, in the absence of sphalerite, along with the low-sulfur content and the negative correlation coefficient of Ga-S ($r = -0.40$) in this coal, all of the evidence suggests that Ga is not related to sulfide in the studied coals.

5.2.2. Rubidium

The average Rb content in the No. 6 coal seam is 84.15 $\mu\text{g/g}$, which is much higher than that in world bituminous coals (average 14 $\mu\text{g/g}$) (Ketris and Yudovich, 2009). Such a high concentration of Rb in the No. 6 coals may potentially have additional economically significant values for Rb recovery during coal utilization.

Most previous studies show that Rb in coals displays an inorganic mode of occurrence. According to Seredin (2003), Rb was mainly adsorbed by clay minerals rather than associating with organic matter, and anomalous enrichment of Rb is due to its high content in volcanogenic Ge-bearing solutions circulating in rocks of the coal-bearing molasse. Ward et al. found that Rb exhibits a

very strong correlation with K in Permian coals (Ward et al., 1999). Yossifova (2007) studied the Pernik coal and found that Rb shows a distinctly inorganic mode of occurrence. Rb and Cs have very similar geochemical characteristics; the vertical variation trends of Rb and Cs (Fig. 8) in the No. 6 coal seam are almost identical. The correlation coefficients between Rb and Al_2O_3 , SiO_2 , ash yield, and K_2O are very high ($R^2 > 0.92$) in the No. 6 coal; such correlation coefficients are even higher than that with Cs. Such high correlation coefficient values suggest that Rb and Cs probably have the same carrier in the No. 6 coal, and illite is most probably the carrier for both Rb and Cs.

5.2.3. Cesium

The Cs concentration in the studied samples varies from 11.44 to 13.98 $\mu\text{g/g}$, with an average of 12.25 $\mu\text{g/g}$ (Table 3), and represents as much as 12.3 times that of world bituminous coals (average 1.0 $\mu\text{g/g}$) (Ketris and Yudovich, 2009).

The modes of occurrence of Cs in coal have been investigated in previous studies (Sun et al., 2012; Swaine, 1990; Seredin, 2003; Eskenazy, 2009). According to these studies, Cs is presumably adsorbed by both clay minerals and organic matter, and Cs could be exploited as a byproduct and has important economic significance in the Spetzugli Ge-bearing brown coal (Seredin, 2003). Cs generally occurs in K-bearing minerals (e.g., illite and smectite), partly because Cs can isomorphously substitute for K (Swaine, 1990). Eskenazy (2009) found a positive correlation between Cs and ash yield in the Dobrudza coal, Bulgaria. In this study, Cs in the No. 6 coal from the Iqe Coalfield not only has high correlation coefficients with Al_2O_3 ($r = 0.96$), SiO_2 ($r = 0.96$), ash yield ($r = 0.94$), and K_2O ($r = 0.93$) but also demonstrates almost the same vertical

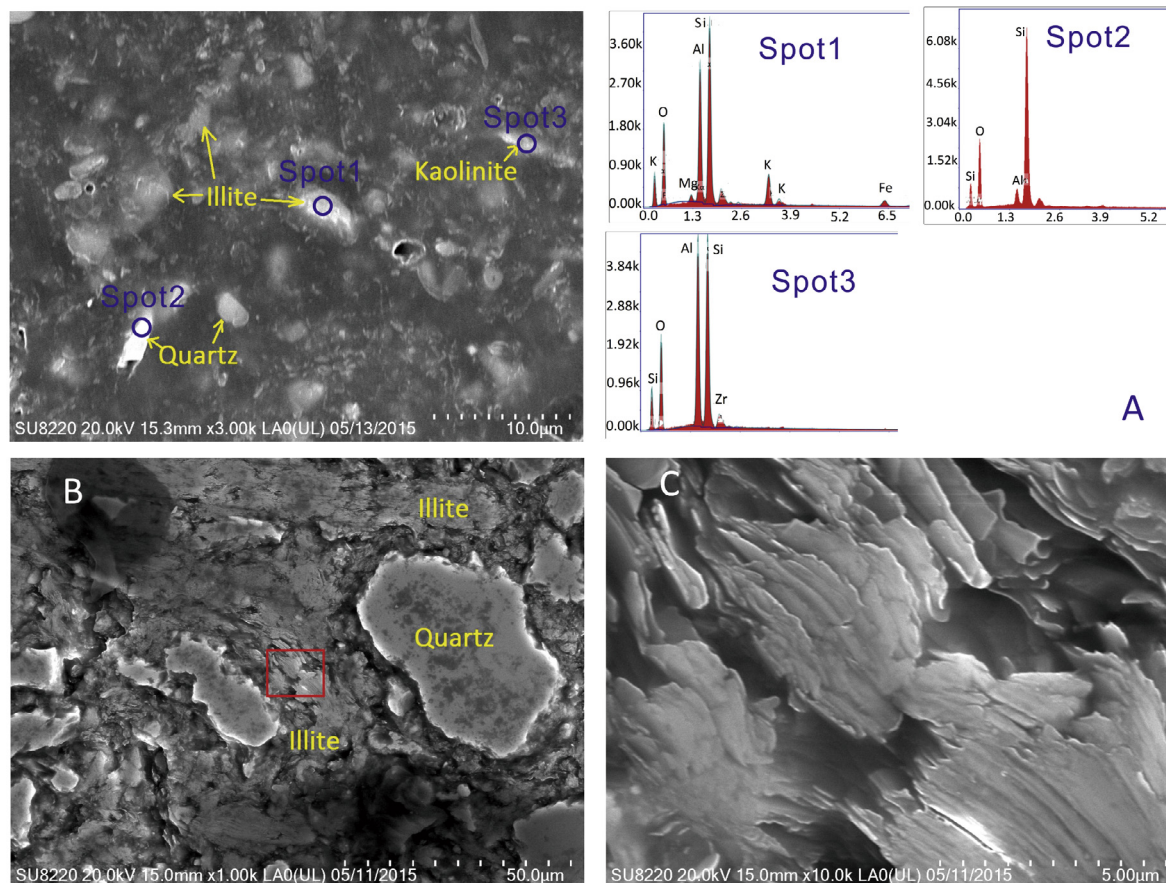


Fig. 5. SEM (back-scattered electron) images of kaolinite, illite, and quartz in the Iqe coals. (A) image of kaolinite, illite, and quartz with respective EDS spectras; (B) laminated sheet illite; (C) laminated illite, enlarge image of the marked area with red box.

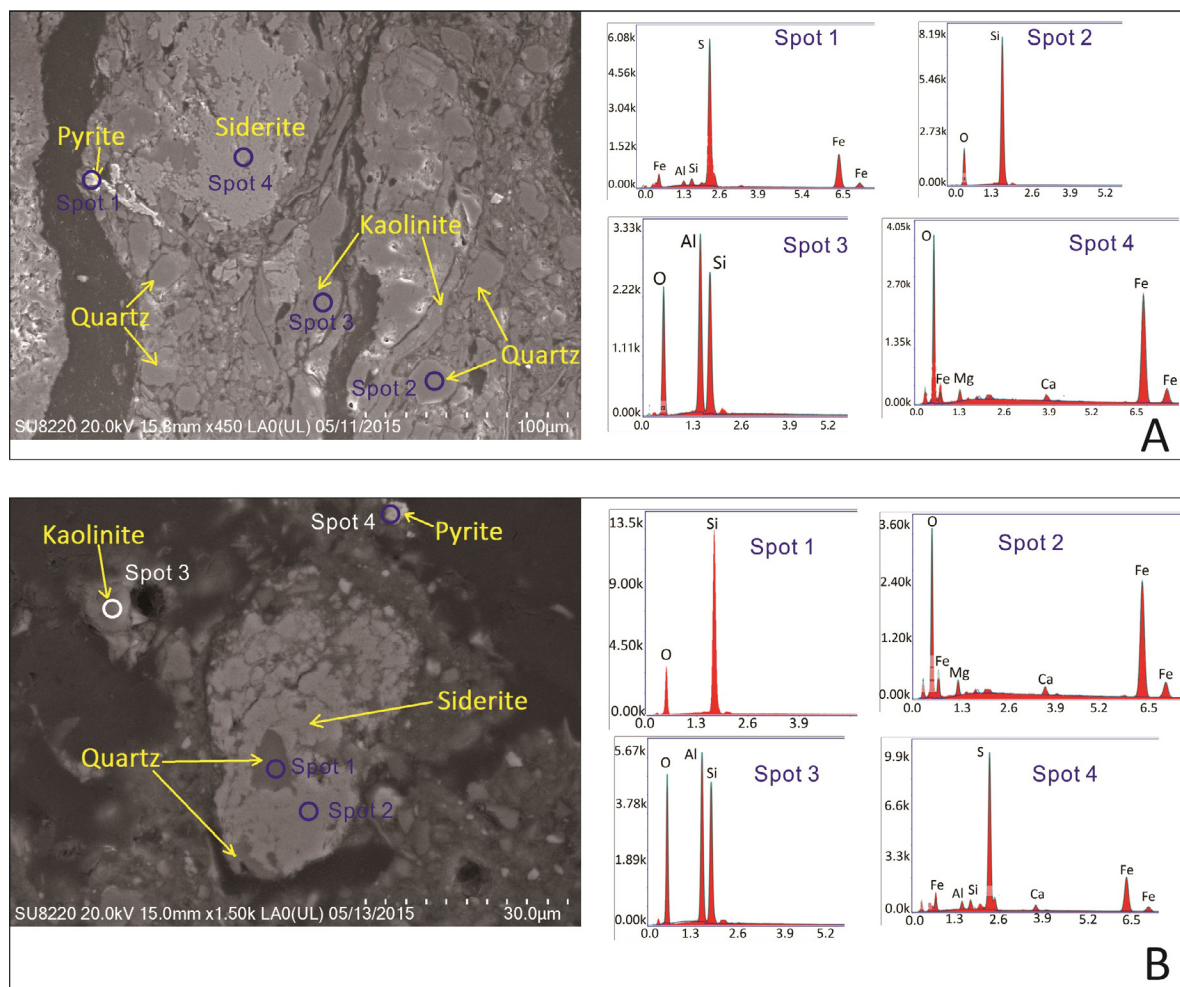


Fig. 6. SEM images (back-scattered electron) of kaolinite, pyrite, siderite and quartz and their EDS spectra in the Iqe coals.

variation patterns (Fig. 8), strongly indicating that Cs most probably occurs in the inorganic minerals, particularly in K-rich clay minerals (e.g., illite) in this coal.

5.2.4. Rare earth elements and yttrium (REY)

In this study, a threefold geochemical classification of REY was used: light (LREY: La, Ce, Pr, Nd, and Sm), medium (MREY: Eu, Gd, Tb, Dy, and Y), and heavy (HREY: Ho, Er, Tm, Yb, and Lu) (Seredin and Dai, 2012). Accordingly, three enrichment types are identified, L-type (light-REY: $La_N/Lu_N > 1$), M-type (medium-REY: $La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type (heavy REY: $La_N/Lu_N < 1$), compared with the upper continental crust (UCC).

The concentrations of total REY (from La to Lu plus Y) in coal samples and the partings are averaged at 209.81 $\mu\text{g/g}$ and 287.24 $\mu\text{g/g}$, respectively (Table 6), and they are much higher than that of world bituminous coals (60 $\mu\text{g/g}$) (Ketris and Yudovich, 2009). The REY enrichment in the coal falls into L-type ($La_N/Lu_N = 1.27$, Table 6). Although the REY distribution patterns for the coal samples are similar to that of the partings (Fig. 9), the partings have a higher average REY concentration than the coals, with a slightly positive Eu-anomaly (average $Eu/Eu^* = 1.01$).

REY in coal is often positively correlated with ash yield and is generally related to minerals, primarily clay minerals and phosphates, and is partly associated with the organic compounds in coal (Seredin and Dai, 2012). The positive but very low correlation coefficients of REY-ash, REY- SiO_2 , and REY- Al_2O_3 (Table 5) indicate that the REEs and Y show no clear association with inorganic

or organic matter in the No. 6 coal seam of the Iqe Coalfield. However, the relatively high correlation coefficients of REE- P_2O_5 (0.55) suggest that the mode of REE and Y occurrence for the coal are more likely to be associated with phosphates, such as apatite in this coal.

The H-REY in the No. 6 coal may mainly occur in the organic matter; this is deduced based on the weak correlation between H-REY and ash yields. The correlation between ash yield and L-REY and M-REY is also low but positive, with the exception of Y, and is relatively higher than that with H-REY, indicating that L-REY and M-REY may occur in both inorganic and organic matter.

5.3. Estimation of the prospective of rare metal recovery as by-products

The market price of Ga, Rb, Ce, REEs and Y is very high, and the demand for such rare metal resources has been sharply increasing in recent years (USGS, 2013). The coal deposits with high concentrations of such rare metals serve as an alternative source of rare metals (Swaine, 2000), and some resource department officials and researchers have taken notice and advocated for such alternative resource recovery ideas in recent years. For example, GB/T-25832 has proposed with provisions that the industrial grade of Ga associated with coal is 30 $\mu\text{g/g}$ (GB/T 25283-2010, 2011); Dai et al. (2012b) proposed that if the thickness of the coal seam is greater than 5 m, the cut-off grades for Ga and REY in coal ash could be set at >50 $\mu\text{g/g}$ and >800–900 $\mu\text{g/g}$, respectively. Sun

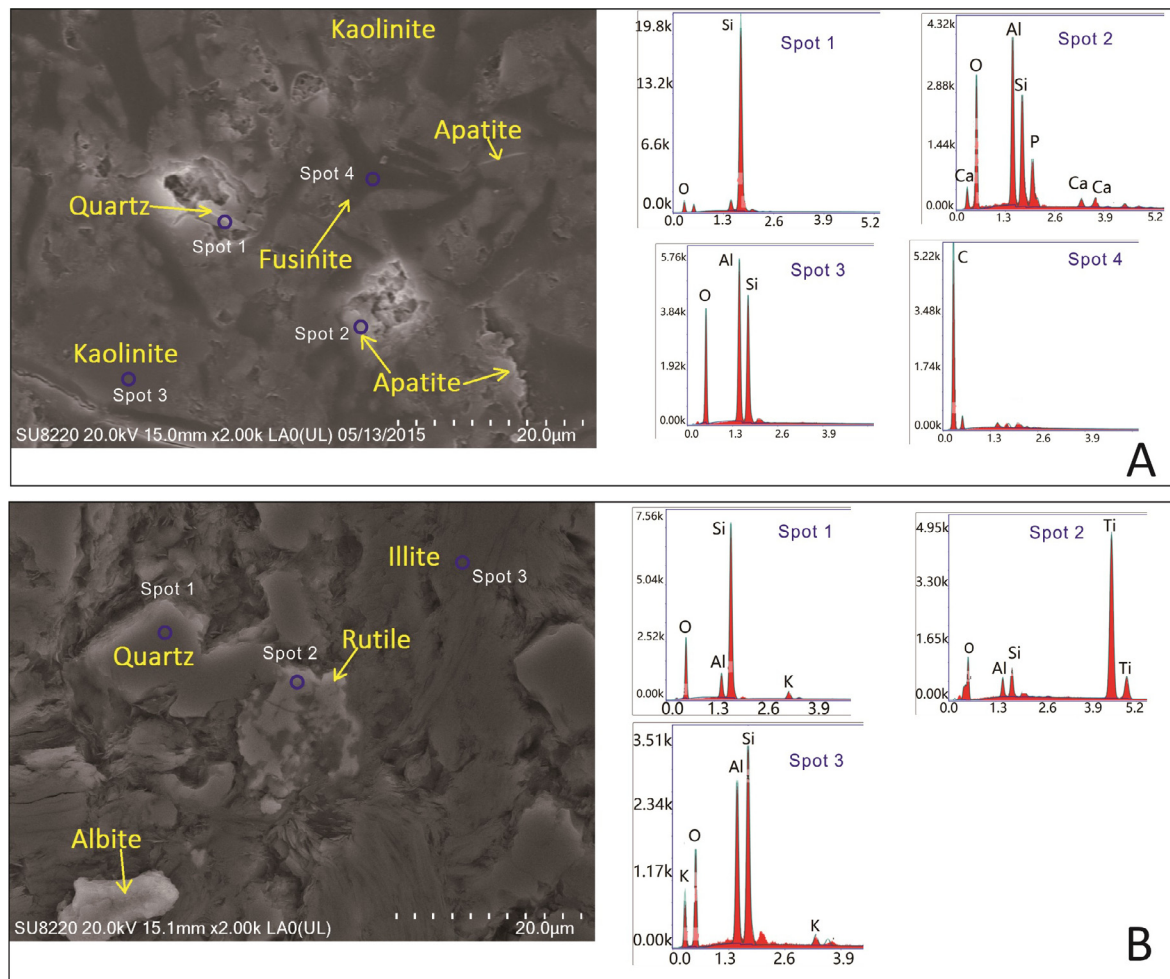


Fig. 7. SEM images (back-scattered electron) of kaolinite, illite, apatite, rutile, albite, and quartz and their EDS spectra in the Iq coals.

Table 5

Element affinities deduced from calculation of Pearson's correlation coefficients between the concentration of each element in the coal and ash yield or selected elements.

Correlation with ash yield

Group 1: $r_{\text{ash}} = 0.7$ to 1.0 V (0.71), Cr (0.81), Ga (0.88), Rb (0.96), Zr (0.97), Nb (0.96), Cs (0.94), Hf (0.96), Ta (0.99), Th (0.80), MgO (0.98), K_2O (0.99), Al_2O_3 (0.99), SiO_2 (1.00), Fe_2O_3 (0.74)

Group 2: $r_{\text{ash}} = 0.50$ to 0.69 Ba (0.67), Pb (0.69), P_2O_5 (0.62)

Group 3: $r_{\text{ash}} = 0.35$ to 0.49 Sr (0.42), MnO (0.44)

Group 4: $r_{\text{ash}} = -0.34$ to 0.34 , Li (0.29), Sc (0.27), Ni (0.34), Cu (-0.09), W (0.03), Bi (0.28), U (-0.04), Na_2O (0.328), CaO (0.27), REY (0.10)

Group 5: $r_{\text{ash}} = -1.0$ to -0.35 Be (-0.68), Co (-0.66), Zn (-0.75), Mo (-0.48), Cd (-0.59), S (-0.74).

Aluminosilicate affinity

$r > 0.7$ V (0.72, 0.74), Cr (0.81, 0.84), Ga (0.91, 0.90), Rb (0.97, 0.97), Zr (0.97, 0.98), Nb (0.98, 0.97), Cs (0.96, 0.95), Hf (0.97, 0.98), Ta (0.99, 0.99), Th (0.82, 0.83), MgO (0.94, 0.97), K_2O (0.96, 0.99), TiO_2 (0.96, 0.99)

$r = 0.3$ to 0.69 Li (0.40, 0.32), Sc (0.31, 0.32), Sr (0.35, 0.45), Ba (0.60, 0.68), Pb (0.68, 0.73), P_2O_5 (0.54, 0.64), MnO (0.34, 0.43), Fe_2O_3 (0.62, 0.73)

(Note: the first number and the second number is the correlation coefficient of elements with Al_2O_3 and SiO_2 respectively).

Carbonate affinity

$r_{\text{Ca}} > 0.7$ Ni (0.84), Na_2O (0.85), Fe_2O_3 (0.75)

$r_{\text{Ca}} = 0.3$ to 0.69 Ba (0.32), W (0.38), MgO (0.40), MnO (0.62)

Sulfur affinity

$r_{\text{S}} > 0.7$ Be (0.96), Zn (0.94), Mo (0.86), Cd (0.77)

$r_{\text{S}} = 0.3$ to 0.69 Sc (0.36), Cu (0.49), U (0.63), REY (0.43)

Correlation coefficients between selected elements

Rb- Al_2O_3 (0.97), Rb- SiO_2 (0.97), Rb-MgO (0.89), Rb- K_2O (0.97), Rb- TiO_2 (0.97), Rb-V (0.86), Rb-Cr (0.93), Rb-Ga (0.97), Rb-Zr (0.99), Rb-Nb (0.99), Rb-Cs (0.99), Rb-Ba (0.74), Rb-Hf (0.99), Rb-Ta (0.99), Rb-Pb (0.85), Rb-Th (0.92)

Cs- Al_2O_3 (0.96), Cs- SiO_2 (0.96), Cs-MgO (0.84), Cs- K_2O (0.93), Cs- TiO_2 (0.95), Cs-V (0.88), Cs-Cr (0.94), Cs-Ga (0.97), Cs-Zr (0.98), Cs-Nb (0.98), Cs-Hf (0.98), Cs-Ta (0.97), Cs-Pb (0.85), Cs-Th (0.93)

Ga- Al_2O_3 (0.91), Ga- SiO_2 (0.90), Ga-S (-0.40), Al_2O_3 - SiO_2 (0.99), Al_2O_3 - K_2O (0.97), SiO_2 - K_2O (0.99), Ba- P_2O_5 (1.00), Ba-Sr (0.95), Cr- K_2O (0.85), REY- SiO_2 (0.99), REY- Al_2O_3 (0.99), REY- P_2O_5 (0.55)

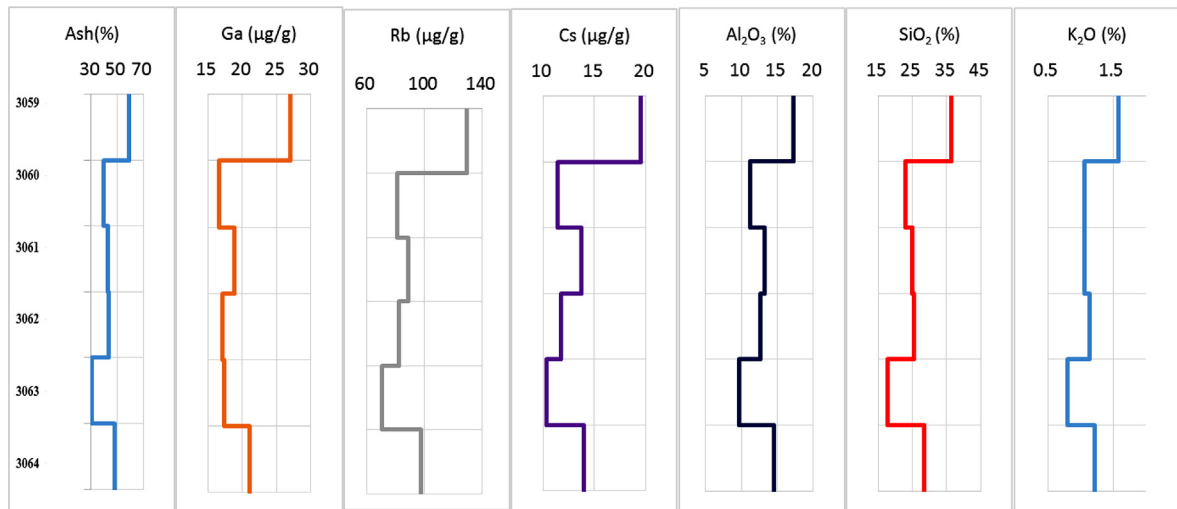


Fig. 8. Variations of Ga, Rb, Cs, Al_2O_3 , SiO_2 , and K_2O concentrations, as well as ash yield content, through the No.6 coal-seam section.

Table 6

REY parameters of the coal samples and parting from Iqe Coalfield.

Sample	REY	LREY	MREY	HREY	$(\text{La}/\text{Lu})_N$	$(\text{La}/\text{Sm})_N$	$(\text{Gd}/\text{Lu})_N$	$(\text{La}/\text{Yb})_N$	Eu/Eu^*	Ce/Ce^*
3059(parting)	287.24	228.92	49.79	8.53	1.3	0.99	1.43	1.37	1.08	1.03
3060	223.72	175.94	40.82	6.96	1.25	0.97	1.46	1.26	1.01	1.06
3061	185.42	147.79	31.97	5.66	1.29	1.08	1.31	1.32	1.02	1.01
3062	172.13	136.02	30.58	5.53	1.25	1.07	1.29	1.21	1.01	1.01
3063	274.25	215.99	49.69	8.57	1.28	1.15	1.34	1.34	0.98	1.02
3064	193.51	154.39	33.15	5.97	1.29	1.06	1.35	1.29	1.02	1.01
Ave.	209.81	166.03	37.24	6.54	1.27	1.07	1.35	1.28	1.01	1.02

Ave. average of coal samples. $\text{Eu}/\text{Eu}^* = 2\text{Eu}_N / (\text{Sm}_N + \text{Gd}_N)$; $\text{Ce}/\text{Ce}^* = 2\text{Ce}_N / (\text{La}_N + \text{Pr}_N)$; REY are normalized by Upper Continental Crust (UCC) when $(\text{La}/\text{Lu})_N$, $(\text{La}_N/\text{Sm})_N$, $(\text{Gd}/\text{Lu})_N$, $(\text{La}/\text{Yb})_N$, Eu/Eu^* , and Ce/Ce^* are calculated.

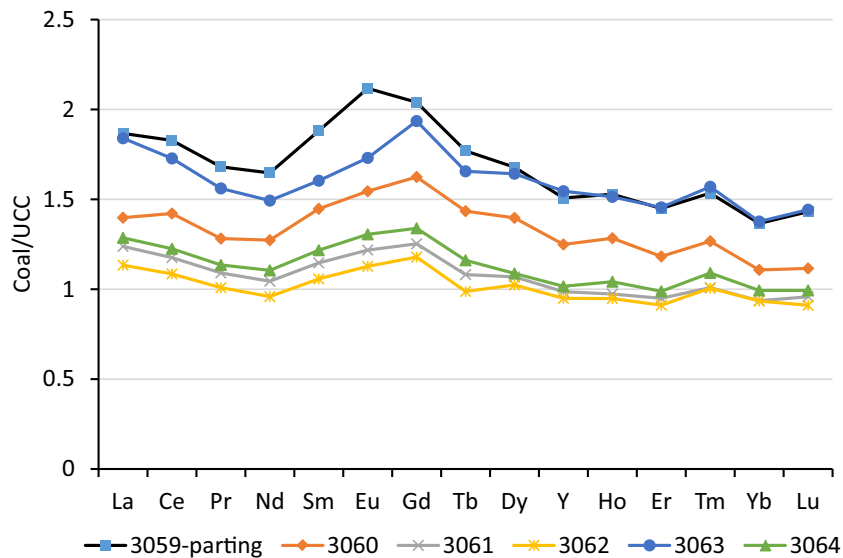


Fig. 9. Distribution patterns of rare earth elements and yttrium in the Iqe samples. REY are normalized by Upper Continental Crust (UCC).

et al. (2014) suggested that the minimum minable grades for Li, U, Th and REE should be set at 120, 40, 150 and 300 $\mu\text{g}/\text{g}$ in Chinese coal, respectively. Although no one has set the exact and affirmative cut-off grades of Cs and Rb in coal, it is reasonable to propose that if the Cs and Rb concentrations are 5 times higher than the averages of world coal (Yudovich and Ketris, 2006), they may have potential economic significance for recovery.

As mentioned above, the No. 6 coal seam of the Iqe coal field is significantly enriched in rare metals, including Ga, Rb, Cs, and REY, and can be further enriched in coal combustion products because they are not classified as volatile elements (Meij and Winkel, 2009; Clarke and Sloss, 1992). Therefore, the fly ash and bottom ash should be considered as potential sources for the economic recovery of Ga, Rb, Cs, and REY.

6. Conclusions

The No. 6 coal of the Middle Jurassic in the Iqe Coalfield is classified as a medium volatile (22.8%) bituminous coal, high-ash (40.9%), low-sulfur (0.27%), and $R_{o, \text{ran}} = 0.76\%$. Inorganic matter consists of the following minerals – kaolinite, illite, quartz and siderite, which are the main minerals in studied coals and trace amounts of dolomite, rutile, and pyrite.

Based on the statistical analysis among elements and the correlation coefficient analysis of specific elements with ash yield, SiO_2 , and Al_2O_3 , the inorganic and organic affinity of elements are determined. Ga is found to be associated with K-rich clay minerals (e.g., illite), which is probably derived from the Qilian Mountains during the accumulation stage of peat formation; these clay minerals are most likely the carriers of both elements Rb and Cs in studied coal samples. In contrast, REY elements most probably associated with phosphates, such as apatite, L-REY and M-REY may occur in both inorganic and organic matter, whereas H-REY may be mainly associated with organic matter. The No. 6 coal seam of the Iqe Coalfield is found to be enormously enriched in Ga, Rb, Cs, REEs, and Y and can be further enriched in their combustion products (e.g., fly ash and bottom ash). The results of this study strongly indicate that Ga, Rb, Cs, REEs, and Y in the No. 6 coal seam may have potential significant economic value for the recovery of these rare elements during coal utilization.

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