



Enrichment of U-Re-V-Cr-Se and rare earth elements in the Late Permian coals of the Moxinpo Coalfield, Chongqing, China: Genetic implications from geochemical and mineralogical data



Shifeng Dai ^{a,b}, Panpan Xie ^{a,b}, Shaohui Jia ^{a,b}, Colin R. Ward ^c, James C. Hower ^{d,*}, Xiaoyun Yan ^{a,b}, David French ^c

^a College of Geoscience and Survey Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

^b State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology (Beijing), Beijing 100083, China

^c School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW 2052, Australia

^d University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, United States

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ABSTRACT

Rare metals in coal deposits have attracted much attention in recent years because of their potential economic significance. This paper reports the abundance and enrichment origin of rare metals in the Late Permian coals (K1 and K2 Coals) of the Moxinpo Coalfield, Chongqing, southwestern China. The K1 Coal is characterized by highly-elevated concentrations of U-Re-V-Cr-Se and Nb(Ta)-Zr(Hf)-REE assemblages; the latter assemblage is also enriched in the K2 Coal. The high temperature ash (815 °C) of the K1 Coal is enriched in V, Cr, Se, Re, U and REE; the ash of the K2 Coal, and also the floor strata of each seam, are enriched in REE, potentially making all of the units economically viable sources for these elements.

The minerals in the K1 Coal are mainly represented by kaolinite, illite and mixed-layer illite/smectite, and pyrite, while the minerals in the K2 Coal consist mainly of kaolinite and tobelite $[(\text{NH}_4\text{K})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]$. Authigenic roscelite $[\text{K}(\text{V}^{3+}, \text{Al})_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]$ is commonly observed in the K1 Coal under the SEM, and was probably formed by interaction of kaolinite with V derived from permeating U-Re-V-Cr-Se-rich solutions during early diagenesis. The tobelite enriched in the K2 Coal was formed by reaction between kaolinite already present in the coal and NH_4^{4+} derived from decomposition of the organic matter during hydrothermal alteration at a relatively high temperature.

The mafic tuffs directly underlying the K1 Coal and containing limestone residual breccias not only served as the substrate for coal accumulation but also as the source of sediment from the uplifted areas around the coal basin. The latter is indicated by low $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (from 10.09 to 14.24), positive Eu anomalies enrichment of medium rare earths (relative to upper continental crust), and detrital calcite of terrigenous origin. The highly-elevated concentrations of U-Re-V-Cr-Se assemblages in the coal were derived from exfiltrational hydrothermal solutions and were then deposited in a euxinic environment. The terrigenous materials in the K2 Coal, however, were derived from felsic-intermediate rocks at the top of the Kangdian Upland, although the elevated concentrations of Nb(Ta)-Zr(Hf)-REE assemblages are attributed to the input of hydrothermal solutions.

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1. Introduction

Rare metals in coal, e.g., V, Ge, Ga, rare earth elements and Y (REY, or REE if Y is not included), Sc, Se, Zr, Hf, Nb, Ta, Au, Re, and U, as well as the base metal Al, have attracted much attention in recent years (e.g., Seredin and Dai, 2012; Li et al., 2014b,c; Jiang et al., 2015; Hower et al., 2016a,b; Sorokin et al., 2013) as the concentrations of these metals in the ashes of some coals, and in some rocks adjacent to the coal seams, are equal to or even higher than those found in conventional types of rare metal ores (Seredin and Finkelman, 2008; Seredin and Dai, 2012;

Seredin et al., 2013). Coal, and especially coal combustion byproducts, can offer an opportunity to acquire valuable resources without the costs and environmental impacts of traditional mining and with the added benefit of reducing the amount of byproducts to dispose of. An enrichment assemblage of U, Re, V, Se, and Mo has been found in coals preserved within marine carbonate successions (Dai et al., 2015c; Zeng et al., 2005; Shao et al., 2003; Li et al., 2013; Liu et al., 2015) and in coals connected with sandstone-hosted roll-type uranium deposits (Seredin and Finkelman, 2008; Dai et al., 2015b). Uranium is also found to be enriched in coal-hosted Ge ore deposits with highly-elevated concentrations of Ge-W-Bi-Nb-U and As-Sb assemblages (Dai et al., 2015a; Hu et al., 2009; Seredin et al., 2006). The enrichment assemblage of Nb(Ta), Zr(Hf), and REY in coal has been found to be

* Corresponding author.

E-mail address: james.hower@uky.edu (J.C. Hower).

derived from alkali volcanic ashes (Dai et al., 2016a; Zou et al., 2014; Arbuzov et al., 2014, 2016), hydrothermal solutions, or a mixed process involving both alkali volcanic ashes and hydrothermal solutions (Dai et al., 2016a). However, a few studies (e.g., Zhuang et al., 2012) have attributed such enrichment of rare metals mainly to the sediment-source and, to a lesser extent, the input of volcanic ash.

Although two types of metalliferous coal deposits, namely the Nb(Ta)-Zr(Hf)-REE and U(Mo,Se)-REE ores in South China and Primorye of Russia have previously been recognized (Dai et al., 2016a), the occurrence of two mineralization types in the same coalfield has seldom been observed. For example, coal-hosted U(Mo,Se)-REE ores in South China generally occur within marine carbonate successions. However, where coal-hosted Nb(Ta)-Zr(Hf)-REE ores occur, limestone is absent and the ores either overlie the Emeishan basalts and are interbedded with epiclastic sedimentary rocks, or occur in the lowermost Late-Permian coal seams which contain either intra-seam alkali tonsteins (Zhou et al., 2000; Dai et al. 2014b; Zou et al., 2014) or were subjected to hydrothermal solutions (Dai et al., 2016a). In this paper, we report geochemical and mineralogical data on the Late Permian bituminous coals (Nos. K1 and K2 Coals) and associated roof and floor strata from the Moxinpo Coalfield, Chongqing, China, and discuss possible mechanisms to explain the joint enrichment of U-Re-V-Cr-Se and Nb(Ta)-Zr(Hf)-REY assemblages in the coals, with emphasis on U-Re-V-Cr-Se mineralization in the K1 Coal, which is quite different to mineralization previously-reported by Seredin and Finkelman (2008), Shao et al. (2003), Zeng et al. (2005), and Dai et al. (2015a,b,c), the latter of which is characterized by the enrichment of U-Mo-V-Cr-Se or U-Mo-V-Cr-Se-REY and by the normal concentrations of Nb(Ta)-Zr(Hf).

2. Geological setting

The Moxinpo Coalfield is located in Chongqing Municipality of southwestern China (Fig. 1A). The coal-bearing sequences of the coalfield are the Late Permian Longtan Formation (Fig. 2B; China Coal Geology Bureau, 1996), which has a thickness from 127.2 to 151.9 m, with an average of 138.8 m. The Longtan Formation has a disconformable contact with the underlying Middle Permian Maokou Formation, and is conformably overlain by the Late Permian Changxing Formation (Fig. 2B). The Longtan Formation contains ten coal seams, which are numbered as K1 to K10 from bottom to top (Fig. 2). Five separate intervals (P_3I^1 to P_3I^5) can be identified in the Longtan Formation of the Moxinpo Coalfield, based on their lithological compositions (Zhong

et al., 2011). The ten coal seams are located in the P_3I^1 (K1 to K4) and P_3I^3 (K5–K10) intervals.

The lowermost interval (P_3I^1) of the Longtan Formation, as previously described by Zhong et al. (2011), has a thickness of 31.82 to 45.68 m (average 35.90 m) and is mainly composed of mudstone, siltstone, sandy mudstone, and fine-medium sandstone, with four coal seams (K1 to K4). The lowermost portion of this interval is a mafic tuff, which has a thickness of 0.11–5.50 m (average 2.76 m) and contains abundant pyrite and residual breccias mainly composed of limestones. The mafic tuff layer is one of the marker beds in the coalfield (numbered as B1, Fig. 1B). A thick siliceous limestone layer, with an average thickness of 2.41 m, forming a marker bed (B2; Fig. 1B), is interbedded in the middle portion of this interval and contains traces of bioclasts. The K1 Coal, which is the lowermost coal seam of the Late Permian sequence and is locally minable (40-cm thick, on average), directly overlies the mafic tuff. The K2 Coal is a minable coal seam with a thickness varying from 1.54 to 5.16 m and averaging 3.25 m. Both the K3 and K4 Coals are also locally minable. The K1 Coal described in this study is laterally equivalent to the No. 25 coal in the Guxu Coalfield (Dai et al., 2015e), the K1 Coal in the Huayingshan Coalfield (Dai et al., 2014b) and the No. 12 Coal in the Songzao Coalfield (Dai et al., 2010), all located in southwestern China.

The second unit (P_3I^2) is mainly dominated by a thick layer of grey limestone, with an average thickness of 15.66 m (ranging from 12.88 to 21.57 m). The limestone layer contains flint nodules and is rich in *Fusulinida*?, *Brachiopoda*, *Cephalopoda*, and *Lamellibranchiata*. The third unit (P_3I^3) has a thickness of 48.31–54.65 m and consists mainly of silty mudstone, siltstone, fine sandstone, mudstone, and argillaceous limestone. The P_3I^3 unit is rich in pyrite and siderite nodules, and contains six coal seams (K5 to K10). The K5 Coal is directly overlain by an argillaceous limestone, which has a thickness of 0.81 m and forms a marker bed numbered as B3. Two marker beds, numbered as B4 and B5, both dominated by argillaceous limestone, are located in the middle portion of this unit.

The fourth unit (P_3I^4), with a thickness of 9.37–29.62 m (15.84 m on average), is mainly composed of thick micrite and, locally, siliceous limestone. The micrite contains *Fusulinida*, *Brachiopoda*, and *Lamellibranchiata*. A mudstone layer, with a thickness of 0.62–1.91 m, is interbedded in the middle portion of this unit and contains pyrite. The topmost unit (P_3I^5) consists mainly of mudstone, silty mudstone, calcareous mudstone, fine sandstone, pelitic sandstone, and siltstone. One to three limestone layers, all <4-m thick, are interbedded in the lower portion of this unit. This unit locally contains *Brachiopoda* and *Lamellibranchiata*.

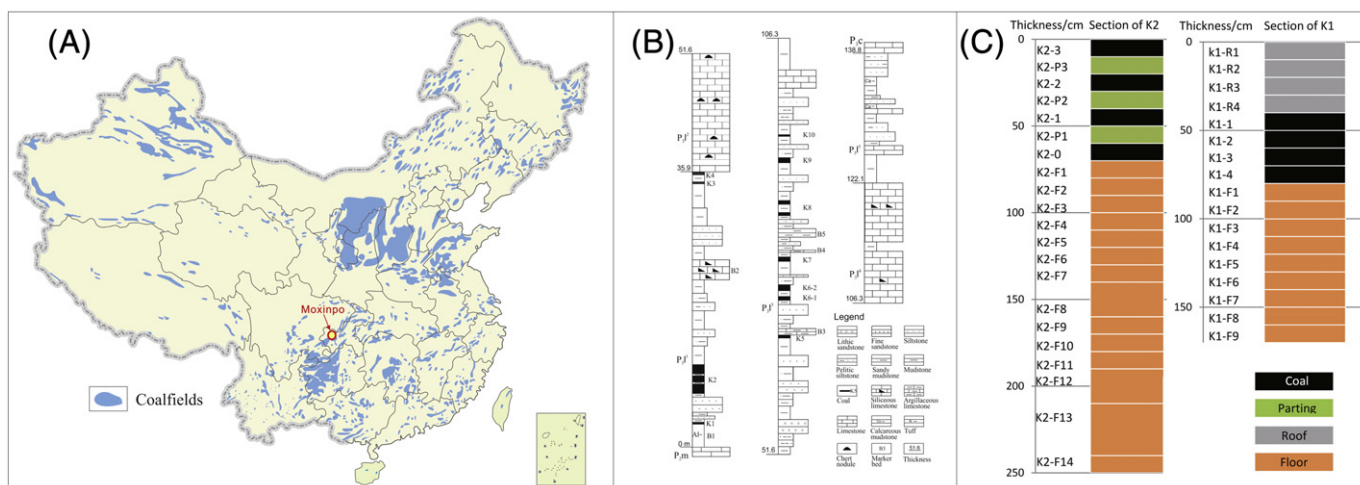


Fig. 1. Location (A), sedimentary sequences (B), and coal-seam sections (C) of the Moxinpo Coalfield.

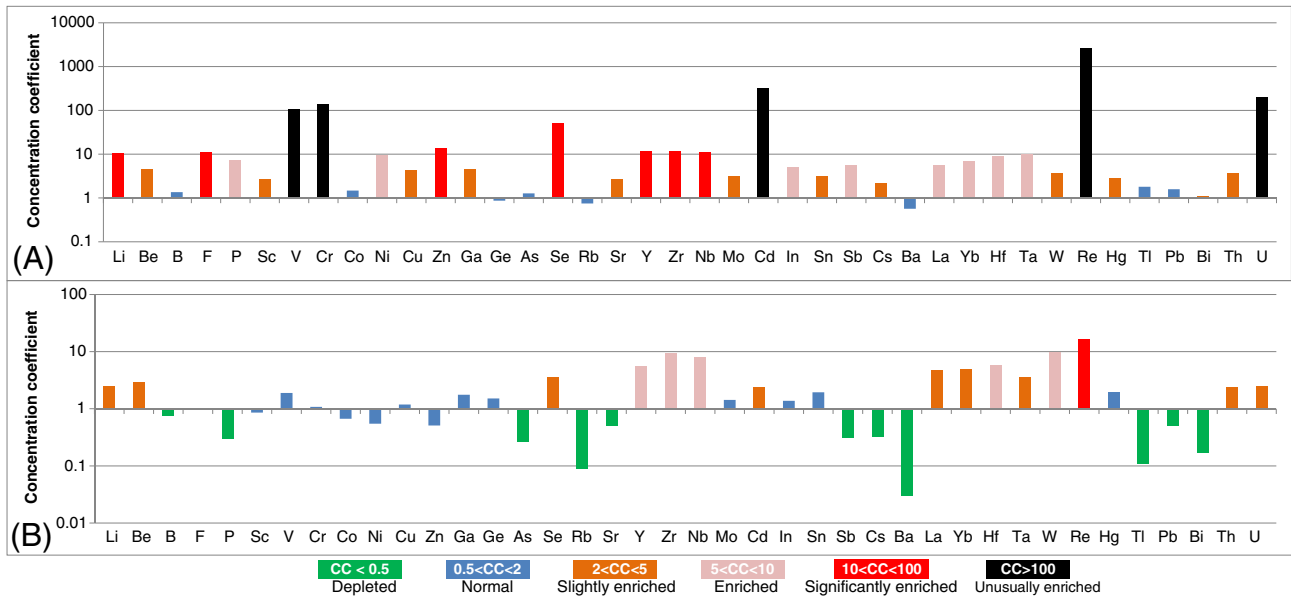


Fig. 2. Concentration coefficients (CC) of trace elements in the coals from the Moxinpo Coalfield. (CC, the ratio of trace element concentration in coal samples investigated vs. averages for world hard coals). Average concentrations of trace elements for world hard coals are from Ketris and Yudovich (2009). (A), K1 Coal; (B), K2 Coal.

3. Sample collection and analytical methods

3.1. Sample collection

A total of 38 bench samples (including four coal benches for each coal seam, three parting samples in the K2 Coal, four roof and nine floor samples for the K1 Coal, and 14 floor samples for the K1 Coal) were collected from underground workings in the Moxinpo Coalfield. Each coal bench sample was cut over a volume of 10-cm wide, 10-cm deep, and 10–30 cm high. The coal samples are numbered as K1–1 to K1–4 from top to bottom (K1 Coal) and as K2–0 to K2–3 from bottom to top (K2 Coal). The roof and floor samples for the K1 Coal are respectively numbered as K1-R1 to K1-R4 and as K1-F1 to K1-F9 (from top to bottom). The floor samples for the K2 Coal are numbered as K2-F1 to K2-F14 from top to bottom. The partings for the K2 Coal are numbered as K2-P1 to K2-P3. The upper portion of the K2 Coal could not be accessed due to slurry sealing after coal mining; therefore, the thickness of the uncollected upper portion of the seam section is unknown. The sample numbers and their thickness are shown in Fig. 1C.

3.2. Analytical methods

Proximate analysis was carried out based on ASTM Standards D3173-11 (2011); D3175-11 (2011), and D3174-11 (2011). The total sulfur content was analyzed following ASTM Standard D3177-02 (2002). Petrographic examination of the coals was conducted on epoxy-bound particulate pellets, prepared to a final 0.05- μ m alumina polish, using Leitz Orthoplan or Leica DM4500P microscopes equipped with 50 $\times$, oil-immersion, and reflected light objectives. Petrographic nomenclature followed the guidelines of ICCP (1998, 2001). Vitrinite reflectance was measured using incident light passing through a 546-nm band filter on the path to the photomultiplier. The reflectance was calibrated against a series of glass standards of known reflectance.

X-ray powder diffraction (XRD) analysis was carried out using a D/max-2500/PC powder diffractometer (with Ni-filtered Cu-K α radiation and a scintillation detector) to determine the mineral compositions of low-temperature ashes (LTAs) prepared from the coals, and also of the powdered host rocks (roof, parting, and floor samples). Each XRD pattern was recorded over a 2θ interval of 2.6–70°, with a step size of 0.01°. Prior to XRD analysis, the powdered coal samples were ashed at low-temperature (<120 °C) using an EMITECH K1050X plasma asher.

Quantitative mineralogical analysis was carried out on the X-ray diffractograms of both the coal LTAs and the host rocks using the Rietveld-based Siroquant™ software developed by Taylor (1991).

Mineralogical analysis was supplemented by examination of the polished sections using a field emission-scanning electron microscope (FE-SEM, FEI Quanta™ 650 FEG) in conjunction with an energy-dispersive X-ray spectrometer (EDS; Genesis Apex 4). The samples were not coated for low-vacuum SEM working conditions (60 bars). The working distance of the FE-SEM-EDS was 10 mm, beam voltage 20.0 kV, aperture 6, and spot size 5. Images were captured via a retractable solid state back-scattered electron detector.

The oxides of major elements, including SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, MnO, Na₂O, K₂O, and P₂O₅, were determined by X-ray fluorescence spectrometry (XRF; ARL ADVANTXP+). Prior to the XRF analysis, samples were ashed at a temperature of 815 °C; the loss on ignition (LOI) was also determined at this temperature. Except for Hg and F, the concentrations of trace elements in the samples were determined by inductively coupled plasma mass spectrometry (Thermo Fisher, X series II ICP-MS). Prior to ICP-MS analysis, 50 mg samples of each coal and each non-coal rock were digested without ashing using an UltraClave Microwave High Pressure Reactor (Milestone). The digestion reagents were 5-ml 65% HNO₃ and 2-ml 40% HF for coal samples and 2-ml 65% HNO₃ and 5-ml 40% HF for non-coal samples. The Guaranteed-Reagent HNO₃ and HF for sample digestion were further purified by sub-boiling distillation. Inorganic Ventures standard references (CCS-1, CCS-4, CCS-5, and CCS-6) were used for calibration of trace element concentrations. In order to avoid interference by polyatomic ions, the collision/reaction cell technology of ICP-MS was performed to determine concentrations of As and Se in the samples (Li et al., 2014a).

A Milestone DMA-80 analyzer, with a detection limit of 0.005 ng, was used to determine Hg concentrations in each 100-mg sample without ashing. Following the method of ASTM D5987-96 (2002), fluorine was determined by pyrohydrolysis in conjunction with an ion-selective electrode.

4. Results

4.1. Coal chemistry and petrology

The average sulfur content in the K1 and K2 Coals is 4.03% and 1.75%, respectively (Table 1), suggesting classification as high- and medium-

Table 1

Proximate analysis (%), vitrinite reflectance (%), and thickness (cm) of coal benches in the Moxinpo Coalfield.

Coal seam	Sample no.	Thickness	M _{ad}	A _d	V _{daf}	S _{t,d}	R _{o,max}	R _{o,ran}
K2	K2–3	10	0.57	7.48	20.23	0.89	1.49	1.40
	K2–2	10	0.70	12.28	20.94	1.03	1.39	1.28
	K2–1	10	0.48	8.61	19.90	1.11	1.44	1.37
	K2–0	10	0.72	20.09	21.85	3.96	1.52	1.35
K1	K1–1	10	1.08	40.31	28.30	4.20	1.21	1.15
	K1–2	10	1.17	38.81	27.36	4.91	1.20	1.15
	K1–3	10	1.13	37.07	27.19	2.85	1.17	1.11
	K1–4	10	1.25	49.96	31.77	4.17	1.17	1.13
K2	Av	40 ^a	0.62	12.12	20.73	1.75	1.46	1.35
K1	Av	40 ^b	1.16	41.54	28.66	4.03	1.19	1.14

M, moisture; A, ash yield; V, volatile matter; S_t, total sulfur; ad, as-received basis; d, dry basis; daf, dry and ash-free basis; R_{o,max}, vitrinite maximum reflectance; R_{o,ran}, vitrinite random reflectance; Av, average.

^a Part thickness of the coal seam.

^b Total thickness.

sulfur coals (Chou, 2012). The volatile matter yields and vitrinite reflectance (Table 1) indicate that the K1 and K2 Coals are medium and low volatile bituminous coals, respectively (ASTM D388-12, 2012). The ash yield of the K1 Coal (41.54%) is much higher than that of the K2 Coal (12.12%), probably due to more input of terrigenous materials during peat accumulation for the K1 Coal.

The K2 Coal has a total vitrinite content of 65.5–76.9% (mineral-free basis), dominated by telovitrinite varieties, and a significant proportion of inertinite, dominated by fusinite and semifusinite as shown in Supplementary Electronic File (SEF) 1. The K1 Coal has 45.3–70.7% vitrinite (SEF 2), with a higher proportion of detrovitrinite than the K2 Coal. Examples of the detrovitrinite-bearing assemblages are shown in SEF 2C, E. Fusinite and semifusinite dominate the inertinite macerals, with minor amounts of secretinite (SEF 2D) and macrinite. The cells of telinite and fusinite generally are filled with clay minerals (SEF 2F) and pyrite (SEF 2G, H). Sphalerite (Sph) is sometimes observed in the secretinite lumens (SEF 2I).

4.2. Geochemistry

The percentages of major-element oxides and the concentrations of trace elements in the Moxinpo coal bench samples, as well as the average values for Chinese coals (Dai et al., 2012) and world hard coals (Ketris and Yudovich, 2009), are listed in Table 2 (on a whole coal basis). The geochemical data for the host rocks (roof, floor and partings) are presented in SEF 3. With the exception of MnO, the K1 Coal has higher major-element oxide concentrations than common Chinese coals (Table 2), owing mainly to its high ash yield (41.54% on average). By contrast, all the major-element oxides have lower concentrations in the K2 Coal than in common Chinese coals (Table 2).

Based on the enrichment classification of Dai et al. (2015c), the concentrations of trace elements in coal can be classified into six categories (on a whole coal basis): unusually enriched (concentration coefficient CC > 100, CC is the ratio of trace-elements in samples investigated vs. averages for world hard coals), significantly enriched (10 < CC < 100), enriched (5 < CC < 10), slightly enriched (2 < CC < 5), normal (0.5 < CC < 2), and depleted (CC < 0.5). The elements V (2962 µg/g on average), Cr (2342 µg/g), Cd (61.9 µg/g), Re (2.55 µg/g), and U (376 µg/g) are unusually enriched in the K1 Coal, with CC > 100 (Fig. 2); elements Li, F, Zn, Se, Y, Zr, and Nb are significantly enriched (10 < CC < 100); elements P, Ni, In, Sb, La, Yb, Hf, and Ta are enriched (5 < CC < 10); the remaining elements are either slightly enriched (2 < CC < 5) or are close to (0.5 < CC < 2) the averages for world hard coals reported by Ketris and Yudovich (2009). In contrast, concentrations of a number of trace elements in the K2 Coal are either close to or depleted in comparison with the corresponding averages for world hard coals, with the exceptions of Re (CC = 16.5); Y, Zr, Nb, Hf, and W (5 < CC < 10); and Li, Be, Se, La, Yb, Ta, Th, and U (2 < CC < 5) (Fig. 2).

Overall, the K1 Coal is characterized by the enrichment of a U-Re-V-Cr-Se assemblage and both the K1 and K2 Coals are characterized by the enrichment of a Nb(Ta)-Zr(Hf)-REE assemblage. Note that Mo in the K1 and K2 Coals is slightly enriched and at a normal concentration level, respectively.

Seredin and Dai (2012) divided the REY into light, medium, and heavy fractions: LREY (La, Ce, Pr, Nd, and Sm), MREY (Eu, Gd, Tb, and Dy, plus Y), and HREY (Ho, Er, Tm, Yb, and Lu). Normalized to the upper continental crust concentrations (UCC, Taylor and McLennan, 1985), three enrichment patterns were also identified as 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) (Seredin and Dai, 2012). Additionally, anomalies of redox-sensitive Ce and Eu, and, in some cases, non-redox-sensitive La, Gd, and Y in coal, could develop or change under specific geochemical conditions (Dai et al., 2016b). In this study, the following formulae were used to quantify the decoupling of individual Ce, Eu, and Gd concentrations from the other REY in the distribution patterns (Bau and Dulski, 1996; Dai et al., 2016b). Eu_N/Eu_N^{*}, Ce_N/Ce_N^{*}, and Gd_N/Gd_N^{*} are expressed as the concentration anomalies of Eu, Ce, and Gd respectively decoupling from other REY.

$$\text{Eu}_N/\text{Eu}_N^* = \text{Eu}_N/[(\text{Sm}_N \times 0.67) + (\text{Tb}_N \times 0.33)] \quad (1)$$

$$\text{Ce}_N/\text{Ce}_N^* = \text{Ce}_N/(0.5\text{La}_N + 0.5\text{Pr}_N) \quad (2)$$

$$\text{Gd}_N/\text{Gd}_N^* = \text{Gd}_N/[(\text{Sm}_N \times 0.33) + (\text{Tb}_N \times 0.67)] \quad (3)$$

In order to avoid the interference of the Gd anomaly with the Eu anomaly, Tb but not Gd concentration was used in the Eu_N/Eu_N^{*} calculation. Similarly, Tb instead of Eu was used in the Gd_N/Gd_N^{*} calculation to avoid interference of the Eu anomaly with the Gd anomaly. The Y_N/Ho_N ratio in coal is used to represent the decoupling of the geochemical twins Y and Ho, which produces Y anomalies in REY patterns. Values for Y_N/Ho_N < 1 and > 1 represent negative and positive anomalies, respectively.

All four benches of the K1 Coal have an M-type enrichment pattern and are characterized by positive anomalies of Eu, Gd and Y (Table 3; Fig. 3) and negative Ce anomalies. In contrast, the LREY, MREY, and HREY in samples of K2 Coal are weakly fractionated, with the exception of sample K2–0 which is characterized by a H-type enrichment pattern. Eu in the K2 Coal shows distinctly negative (samples K2–0 and K2–2) and weakly negative (samples K2–1 and K2–3) anomalies. Except for sample K2–3 with a weak Gd anomaly, the samples of the K2 Coal show distinctly positive Gd anomalies. Yttrium in the K2 Coal shows weak anomalies.

4.3. Minerals

4.3.1. Minerals in coal and in host rocks

X-ray diffraction data show that the minerals in the LTAs of the K1 Coal are mainly represented by kaolinite, illite, mixed-layer illite/smectite, and pyrite, along with traces of quartz, calcite, apatite, florencite, anatase, and bassanite (Table 4). The illite and mixed-layer illite/smectite are grouped together in that table because of the difficulty in providing reliable discrimination between those two phases from the powder diffraction patterns.

In contrast, XRD studies show that the minerals in the LTAs of the K2 Coal are represented mainly by kaolinite (samples K2–0 and K2–3) or kaolinite-tobelite assemblages (samples K2–1 and K2–2). Tobelite (or ammonian illite) is a member of the illite group and has a formula (NH₄,K)Al₂(AlSi₃O₁₀)(OH)₂. Other minerals identified in the K2 Coal by XRD and Siroquant techniques include illite + I/S, pyrite, quartz, and calcite, as well as traces of anatase and bassanite.

A number of other phases, including chalcocopyrite and REY-bearing minerals (e.g. bastnäsite, xenotime, and rhabdophane [(Ce,La)PO₄·H₂O]), have also been identified from examination using SEM-EDS techniques. However, these are relatively rare in volumetric terms, and occur at

Table 2
Percentages of major-element oxides (%), concentrations of trace elements (µg/g; Hg in ng/g), and loss on ignition (LOI, %) in the K1 and K2 Coals from the Moxinpo Coalfield. Percentages of major-element oxides and concentrations of trace elements are 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	Li	Be	B	F	P	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr
K2-3	92.56	3.73	0.13	2.92	0.25	0.002	0.014	0.324	bdl	0.004	58.7	3.61	11.0	nd	54	2.43	17.1	10.3	1.85	3.63	5.32	4.01	7.49	1.76	0.04	2.09	0.01	52.4	17.3	112
K2-2	87.81	6.21	0.38	4.69	0.34	0.001	0.071	0.204	0.125	0.148	38.7	5.75	71.1	nd	95	4.65	40.2	31.6	5.94	15.9	13.4	18.1	13.0	3.28	0.41	3.51	5.23	66.7	49.7	180
K2-1	91.43	3.78	0.16	3.07	0.53	0.005	0.032	0.901	0.037	0.046	17.5	7.04	42.3	nd	36	2.89	120	16.6	4.05	5.02	31.8	22.2	6.20	4.68	0.72	3.52	0.02	35.2	20.2	76.6
K2-0	80.05	8.28	0.22	5.47	4.18	0.006	0.073	1.516	0.114	0.073	26.4	7.17	17.8	nd	112	2.73	33.8	14.9	4.20	13.1	25.5	12.8	15.7	4.87	7.91	9.42	1.55	45.8	97.0	977
Av-K2	87.96	5.50	0.22	4.04	1.32	0.004	0.048	0.736	0.069	0.068	35.3	5.89	35.5	nd	74	3.18	52.9	18.3	4.01	9.40	19.0	14.3	10.6	3.65	2.27	4.64	1.70	50.0	46.1	336
K1-1	60.12	16.09	0.82	11.64	8.09	0.005	0.357	1.445	0.356	0.594	96.9	6.46	59.9	1082	2079	11.1	2583	1983	15.3	105	51.0	94.4	23.9	2.12	16.9	63.6	11.3	246	110	506
K1-2	61.64	16.31	0.93	11.53	6.86	0.003	0.404	1.007	0.399	0.738	121	9.37	58.9	813	791	8.37	3360	2501	3.93	114	38.1	101	27.2	1.98	8.5	67.0	14.4	233	99.1	473
K1-3	63.35	17.07	1.16	11.69	3.48	0.002	0.483	1.372	0.305	0.896	178	10.7	67.2	891	851	9.60	3023	2899	6.95	145	86.0	38.1	28.8	1.95	6.0	52.0	15.9	225	70.8	252
K1-4	50.99	20.34	1.53	15.42	7.20	0.003	0.422	2.304	0.352	0.676	187	8.51	70.3	908	3392	9.83	2879	1984	9.39	270	98.7	1276	29.1	2.34	11.3	80.0	12.5	334	101	415
Av-K1	59.03	17.45	1.11	12.57	6.41	0.003	0.417	1.532	0.353	0.726	145.5	8.76	64.1	924	1778	9.7	2962	2342	8.89	158	68.4	377	27.2	2.10	10.7	65.6	13.5	260	95.3	411
World	n.d.	8.47 ^a	0.33 ^a	5.98 ^a	4.85 ^a	0.015 ^a	0.22 ^a	1.23 ^a	0.16 ^a	0.19 ^a	14	2	47	82	250	3.7	28	17	6	17	16	28	6	2.4	8.3	1.3	18	100	8.4	36

Sample	Nb	Mo	Cd	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Hg	Tl	Pb	Bi	Th	U
K2-3	24.3	0.41	0.15	0.07	2.09	0.13	0.01	1.36	6.24	12.70	1.41	5.07	1.04	0.10	1.59	0.33	2.55	0.54	1.70	0.23	1.42	0.19	2.60	0.57	1.97	0.000	110	bdl	1.77	0.42	3.63	2.34
K2-2	15.6	2.06	0.21	0.06	1.68	0.31	1.25	13.2	101	173	18.0	65.1	9.83	0.80	12.4	1.69	9.46	1.85	5.82	0.85	5.83	0.83	4.59	1.00	15.9	0.000	148	bdl	4.69	0.32	9.62	3.40
K2-1	8.49	2.75	0.22	0.02	1.15	0.23	0.04	1.91	18.3	31.0	3.77	15.7	2.68	0.52	3.45	0.49	3.04	0.65	1.97	0.28	1.86	0.27	1.67	0.43	0.24	0.020	125	bdl	1.86	0.01	5.65	2.93
K2-0	79.5	6.77	1.3	0.07	5.98	0.55	0.15	2.19	83.1	164	19.5	77.6	14.3	2.05	18.7	2.85	18.0	3.66	11.0	1.52	10.2	1.47	19.0	2.32	20.6	0.046	400	0.25	9.63	0.01	12.0	10.2
Av-K2	32.0	3.00	0.47	0.06	2.73	0.31	0.36	4.68	52.1	95.1	10.7	40.9	6.96	0.87	9.01	1.34	8.26	1.68	5.13	0.72	4.83	0.69	6.97	1.08	9.67	0.017	196	n.d.	4.49	0.19	7.72	4.71
K1-1	46.0	4.78	20.9	0.3	5.17	3.03	1.87	121.01	59.5	120	19.1	87.2	19.6	4.48	21.8	3.04	17.6	3.37	9.54	1.27	8.34	1.2	12.4	3.48	2.79	2.317	218	1.18	10.8	1.15	12.7	295
K1-2	54.0	6.01	33.8	0.17	4.95	6.71	2.3	90.41	77.4	117	17.1	70.2	13.9	3.16	15.5	2.24	13.5	2.70	7.81	1.03	6.51	0.94	12.4	3.31	2.46	1.587	337	0.69	10.4	1.31	11.0	364
K1-3	17.8	6.73	35.0	0.14	2.17	5.48	3.63	60.82	50.4	66.1	10.0	39.9	7.91	1.96	9.73	1.46	9.33	1.96	6.05	0.82	5.29	0.79	6.68	0.94	6.4	2.920	194	0.66	10.6	0.85	7.70	370
K1-4	54.3	8.28	158	0.20	4.68	6.99	1.82	67.34	61.8	127	19.6	87.3	18.1	4.18	19.4	2.67	15.4	2.91	8.21	1.05	6.59	0.95	10.9	3.88	3.04	3.385	366	1.66	25.3	1.37	14.6	476
Av-K1	43.0	6.45	61.9	0.20	4.24	5.55	2.41	84.9	62.3	107	16.5	71.1	14.9	3.45	16.6	2.35	14.0	2.74	7.90	1.04	6.68	0.97	10.6	2.90	3.67	2.55	279	1.05	14.3	1.17	11.5	376
World	4	2.1	0.2	0.04	1.4	1	1.1	150	11	23	3.4	12	2.2	0.43	2.7	0.31	2.1	0.57	1	0.3	1	0.2	1.2	0.3	0.99	0.001	100	0.58	9	1.1	3.2	1.9

World, world hard coals, data from Ketris and Yudovich (2009). nd, not determined. n.d., no data. bdl, below detection limit. Av, average concentration.

^a Major-element oxides in Chinese coals, data from Dai et al. (2012).

Table 3
Enrichment patterns and anomalies for individual REY in the Moxinpo coals.

Sample	La _N /Lu _N	La _N /Sm _N	Gd _N /Lu _N	Ce _N /Ce _N *	Eu _N /Eu _N *	Gd _N /Gd _N *	Y _N /Ho _N
K2-3	0.36	0.91	0.71	0.98	0.34	0.99	1.16
K2-2	1.29	1.54	1.25	0.92	0.39	1.31	0.98
K2-1	0.73	1.02	1.08	0.84	0.90	1.27	1.14
K2-0	0.60	0.87	1.07	0.93	0.65	1.22	0.96
K1-1	0.53	0.45	1.53	0.80	1.13	1.24	1.19
K1-2	0.88	0.83	1.39	0.73	1.11	1.21	1.33
K1-3	0.68	0.95	1.04	0.67	1.15	1.21	1.31
K1-4	0.69	0.51	1.72	0.82	1.17	1.24	1.27

Ce_N/Ce_N*, Eu_N/Eu_N*, and Gd_N/Gd_N* are the anomalies of Ce, Eu, and Gd respectively in the coal.

concentrations below the detection limit of the XRD and Siroquant techniques.

4.3.2. Comparison between mineralogy and chemical composition

Supplementary Electronic File 4A shows a comparison between the percentages of high-temperature ash (HTA) determined during proximate analysis and the LTA yields for the Moxinpo coal samples. The HTA and LTA yields for the Moxinpo coal samples are close to the diagonal equality line indicated in the plot, but the LTA percentage is slightly higher than the HTA for each sample, due to dehydration of the clay minerals, decomposition of carbonate minerals, and oxidation of the sulfides during the high-temperature ashing process (Ward, 2002).

Supplementary Electronic File 4B–H shows the relationship of the percentages of major element oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO, TiO₂, K₂O, and P₂O₅; all on a SO₃-free basis) inferred from the XRD analysis to the percentages of the same oxides (normalized, SO₃-free) derived from the XRF analysis data. The points in each plots are very close to the diagonal equality line, suggesting that the inferred percentages of these elements from the XRD results are compatible with the chemical analyses and adding confidence to the quantifications derived from the XRD data.

4.3.3. Modes of occurrence of minerals in coal

The modes of occurrence of minerals in the coals identified by XRD, as well as those observed only by SEM-EDS, are illustrated in Figs. 4–10.

Kaolinite occurs as cell-fillings, massive forms in collodetrinite, and rounded fine particles with a size of 1–3 μm (Fig. 4A). The rounded fine kaolinite particles are generally distributed along bedding planes and, in some cases, assembled as aggregates (Fig. 4B). EDS data show that the kaolinite in the K1 Coal contains traces of Ti, V, and Cr. Liu et al. (2015) found that the highly-elevated concentrations of V, Cr, Se, U, and Mo in coals preserved within carbonate successions are mainly associated with the organic matter of the coal, and to a lesser extent, are associated with illite or mixed-layer illite/smectite.

Roscoelite [K(V³⁺,Al)₂(AlSi₃O₁₀)(OH)₂], identified by SEM-EDS, occurs as cell-fillings (Fig. 4C) and also distributed along bedding planes (Fig. 4D), suggesting an authigenic origin. The roscoelite in the coal contains 13.59% V₂O₅ and 2.73% Cr₂O₃ on average (Fig. 4F). The areal distribution of elements (Fig. 5) shows that Si, Al, K, V, and Cr, have similar distributions, further indicating that the V and Cr occur within the aluminosilicate material. The modes of occurrence and chemical compositions of the roscoelite indicate that it was probably formed by reaction between kaolinite and V derived from U-Se-Re-V-Cr rich solutions during early diagenesis. Iron does not occur in the roscoelite but has similar distribution with S, as would be expected from occurrence as pyrite. The similar distributions of P and Ca indicate the possible occurrence of apatite in the coal (Fig. 5).

A high proportion of tobelite is identified in the K2 Coal by the XRD and Siroquant data (Table 5). The SEM-EDS data (Fig. 6) also present evidence for the occurrence of tobelite, including the variation in grey level on the BSE image (Fig. 6A–C; tobelite showing higher brightness than kaolinite in the BSE images), the textural relationships with kaolinite (Fig. 6A–C), and the presence of minor K in the spectra (Fig. 6E). In contrast, EDS spectra show that the kaolinite closely-related to the tobelite (Fig. 6A) does not contain K at all, and the mica (Fig. 6C) contains significant K plus minor Mg and Na (Fig. 6F).

Pyrite in the Moxinpo coals occurs as cell-fillings (Fig. 7A), framboidal forms in collodetrinite (Fig. 7B), discrete crystals in cavities of the organic matter (Fig. 7C), rounded forms (Fig. 7E, F) probably of bacteriogenic origin (cf. Kostava et al., 1996), or is distributed along the bedding planes. The modes of occurrence of pyrite in the coal suggest that it is of syngenetic or early-diagenetic origin.

Table 4
Low temperature ash yields (LTA, %) and percentages of minerals in coal LTAs (%).

Sample	LTA	Quartz	Kaolinite	Illite + I/S	Tobelite	Pyrite	Calcite	Apatite	Florencite	Anatase	Bassanite
K2-3	8.53	4.7	86.3	1.6		1.1	4.9				0.7
K2-2	14.33		53.8		41.8	3.0	0.5			0.9	
K2-1	9.23		45.1		37.6	7.0	9.8			0.4	
K2-0	25.07	9.7	51.8	7.8		18.6	9.1	1.4		0.3	1.2
K1-1	47.46	0.6	32.2	32.6		28.1	0.9	3.7	0.1	0.6	1.1
K1-2	48.05	0.1	36.1	40.8		17.3	1.0	0.5	0.2	1.9	2.1
K1-3	43.79	0.1	29.0	51.5		9.6	4.4	1.5		2.5	1.4
K1-4	58.29		40.4	28.3		16.8	5.3	3.6	0.3	3.0	2.3

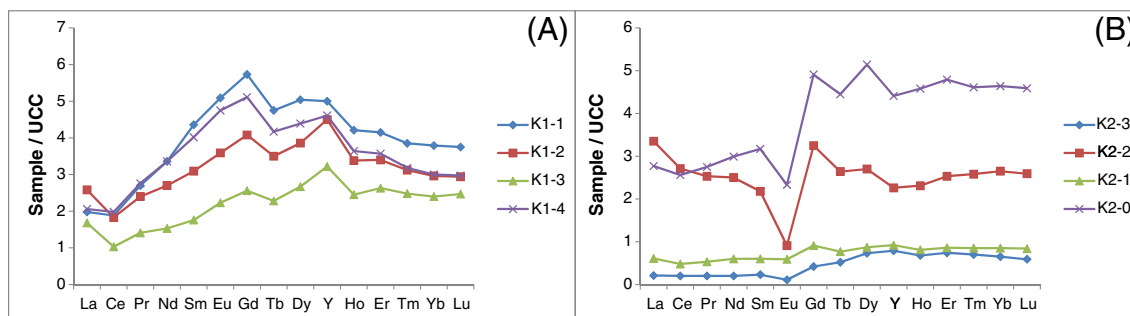


Fig. 3. REY distribution patterns for the Moxinpo coals. (A), K1 Coal; (B), K2 Coal. REY are normalized to the Upper Continental Crust (UCC) (Taylor and McLennan, 1985).

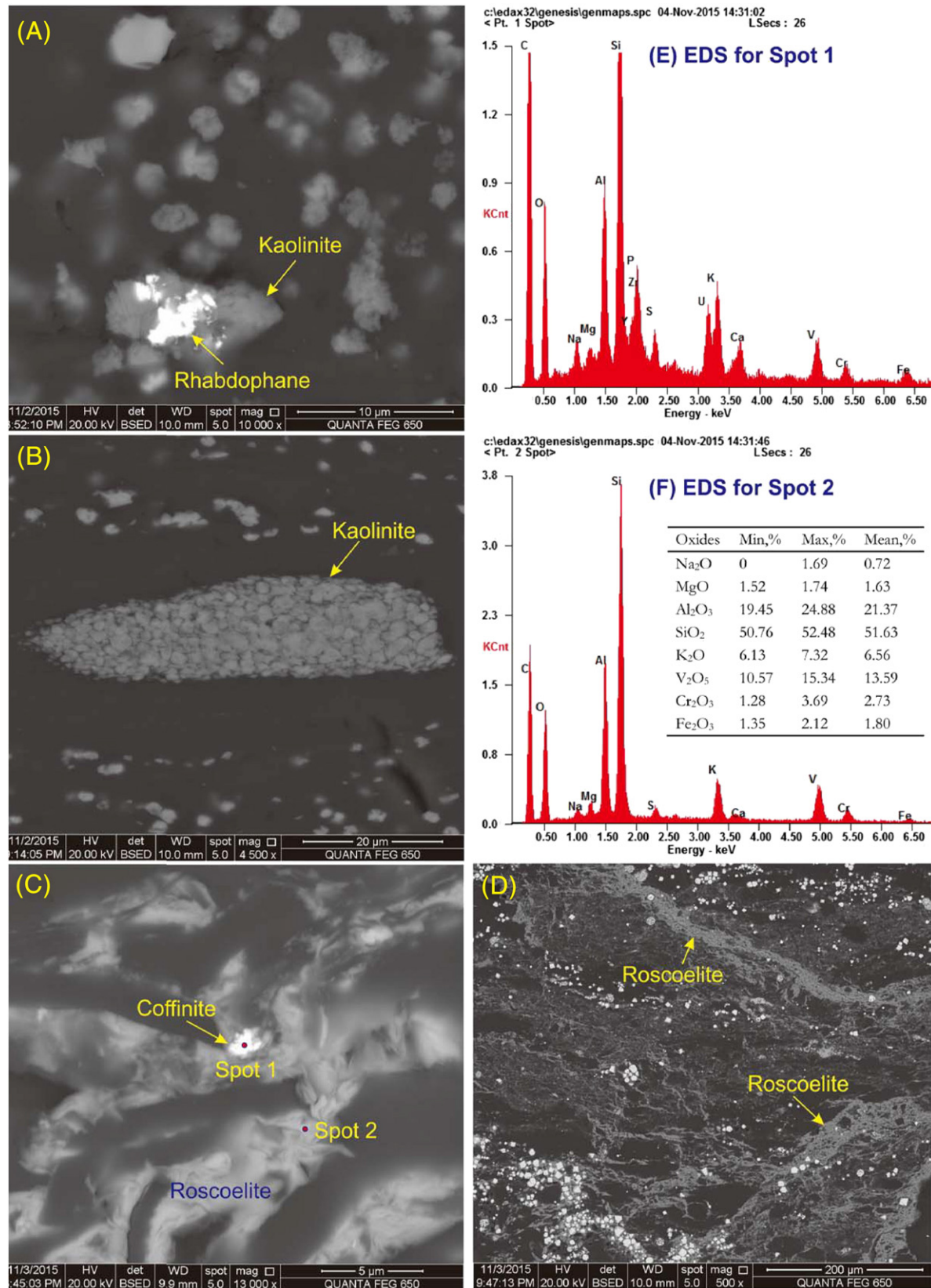


Fig. 4. SEM back-scattered electron images of kaolinite, roscoelite, rhabdophane, and coffinite in the K1 Coal. (A) and (B), kaolinite and rhabdophane in sample K1–3. (C) and (D), roscoelite and coffinite in sample K1–4. (E), EDS spectrum for coffinite in (C). (F), EDS spectrum for roscoelite in (C); EDS data for roscoelite are based on six test spots, expressed on H₂O-free basis.

Calcite in the K1 Coal has four modes of occurrence: 1) cavity-fillings in kaolinite (Fig. 8A), 2) discrete particles in collodetrinite (Fig. 8B), 3) cell-fillings in structured macerals (Fig. 8C), and 4) fracture-fillings.

The occurrences as cavity-, cell-, and fracture-fillings suggest an authigenic origin. However, the presence of discrete calcite particles in some cases (Fig. 8B) may indicate a detrital, possibly terrigenous, origin

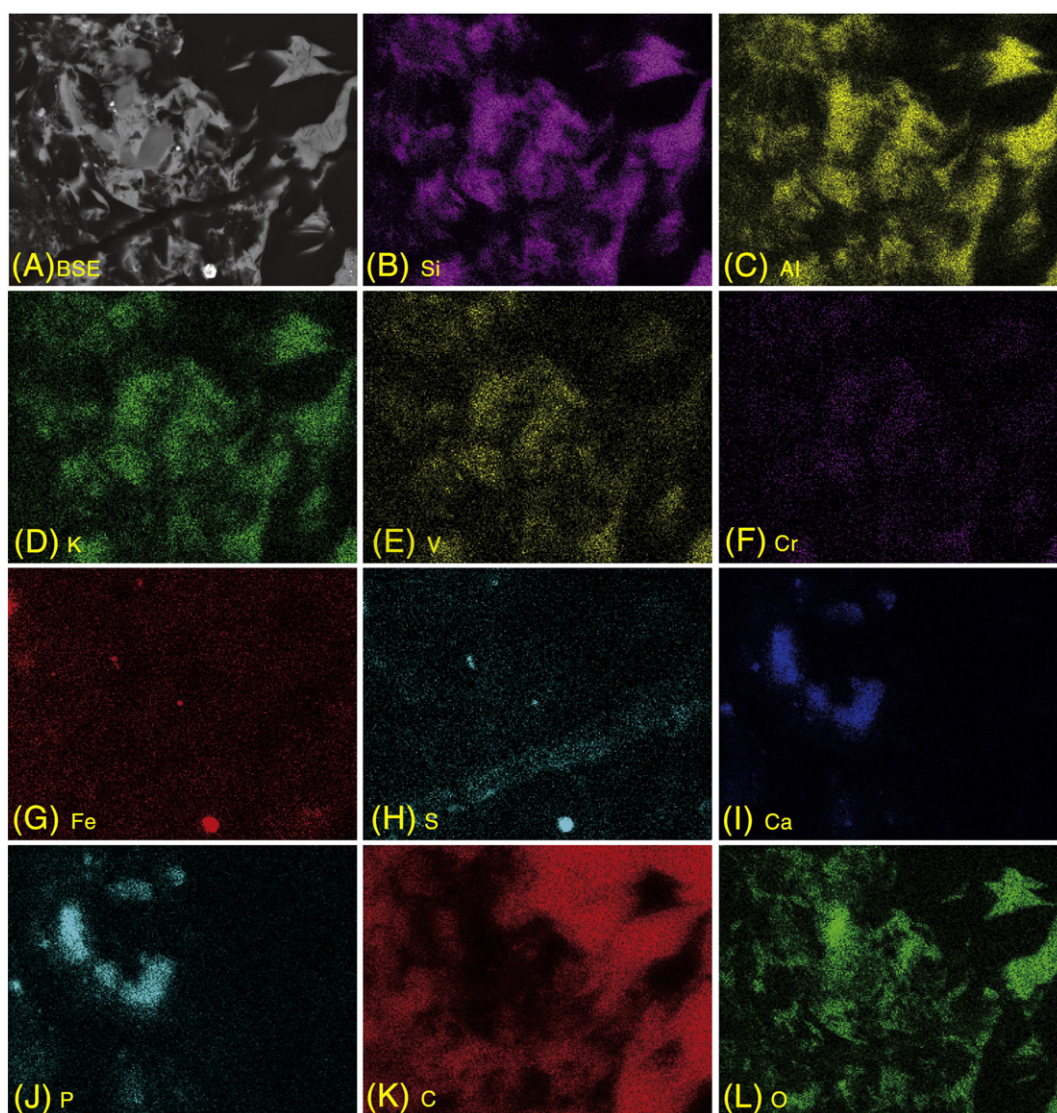


Fig. 5. Areal distributions of Si, Al, K, V, Cr, Fe, S, Ca, P, C, and O in sample K1–4.

and a derivation from the mafic tuff. The mafic tuff layer (China Coal Geology Bureau, 1996), which could serve as terrigenous input for the K1 Coal as mentioned below, contains residual breccias made up mainly of limestones. Detrital calcite only occurs in the K1 Coal and is more abundant in the lower coal benches of the coal seam section; such discrete detrital calcite, however, was not observed in the K2 Coal.

Bassanite occurs in some of the LTA residues (Table 4), especially in the LTAs of the K1 Coal samples. Although bassanite may represent an artefact derived from interaction of non-mineral Ca with organic S during plasma ashing (Ward, 2002), it may represent gypsum occurring in the present coal samples (Fig. 8E, F) that was partly dehydrated by the ashing process. This is because the non-mineral Ca effectively disappears from the macerals at a rank of vitrinite reflectance around 0.6% (Li et al., 2010); the vitrinite in the K1 Coal has a reflectance of 1.14% ($R_{o,ran}$) (Table 1). SEM study shows that gypsum is found along or near fractures in the organic matter of the K1 Coal samples (Fig. 8E, F). Such occurrences may possibly have been produced by reactions between calcite and the sulfuric acid derived from oxidation of pyrite in the coal (cf. Rao and Gluskoter 1973; Pearson and Kwong 1979), either with exposure in the mine or during sample storage.

The REY-bearing minerals identified in the K2 Coal by SEM studies are bastnäsite, xenotime [(Y(PO₄)), and rhabdophane

[(Ce,La,Nd)(PO₄)·H₂O] (Fig. 9). One grain of bastnäsite has a composition between that of bastnäsite-(Ce), -(La), -(Nd), and -(Y) with a formula of (Ce_{0.44}Nd_{0.30}La_{0.18}Y_{0.08})CO₃F, also containing traces of Pr, Sm, and Gd (Fig. 9A, D). Another grain of bastnäsite has a composition between that of bastnäsite-(Ce), -(La), and -(Nd) with a formula of (Ce_{0.42}Nd_{0.41}La_{0.17})CO₃F, containing traces of Y, Pr, Sm, and Gd (Fig. 9B, E). The occurrences of bastnäsite, xenotime, and rhabdophane identified by SEM-EDS techniques closely coexist with kaolinite in the coal samples.

The apatite occurs as discrete particles and lath-like form in collodetrinite (Fig. 10), with the long-axes of the laths aligned along the bedding planes (Fig. 10B, C, D) suggesting detrital materials of terrigenous origin. Some of the apatite may also represent shell fragments and thus be of biogenic origin (Fig. 10B). In some cases, the cavities of apatite are filled with syngenetic, authigenic kaolinite (Fig. 10D). SEM-EDS data show that the apatite, in a few cases, contains a trace of F, and thus can be identified as fluorapatite. Other studies indicate that the apatite in coal mostly occurs as cell-fillings in structured macerals, and thus represents material syngenetically precipitated in the peat bed (e.g., Ward et al., 1996; Rao and Walsh, 1999; Dai et al., 2015d). The phosphorus precipitated in this way may have been released from decay of the peat-forming plant tissues, or possibly from contemporaneous input of volcanic material. Apatite in some other coals may also occur as cleat- and fracture-fillings; these may

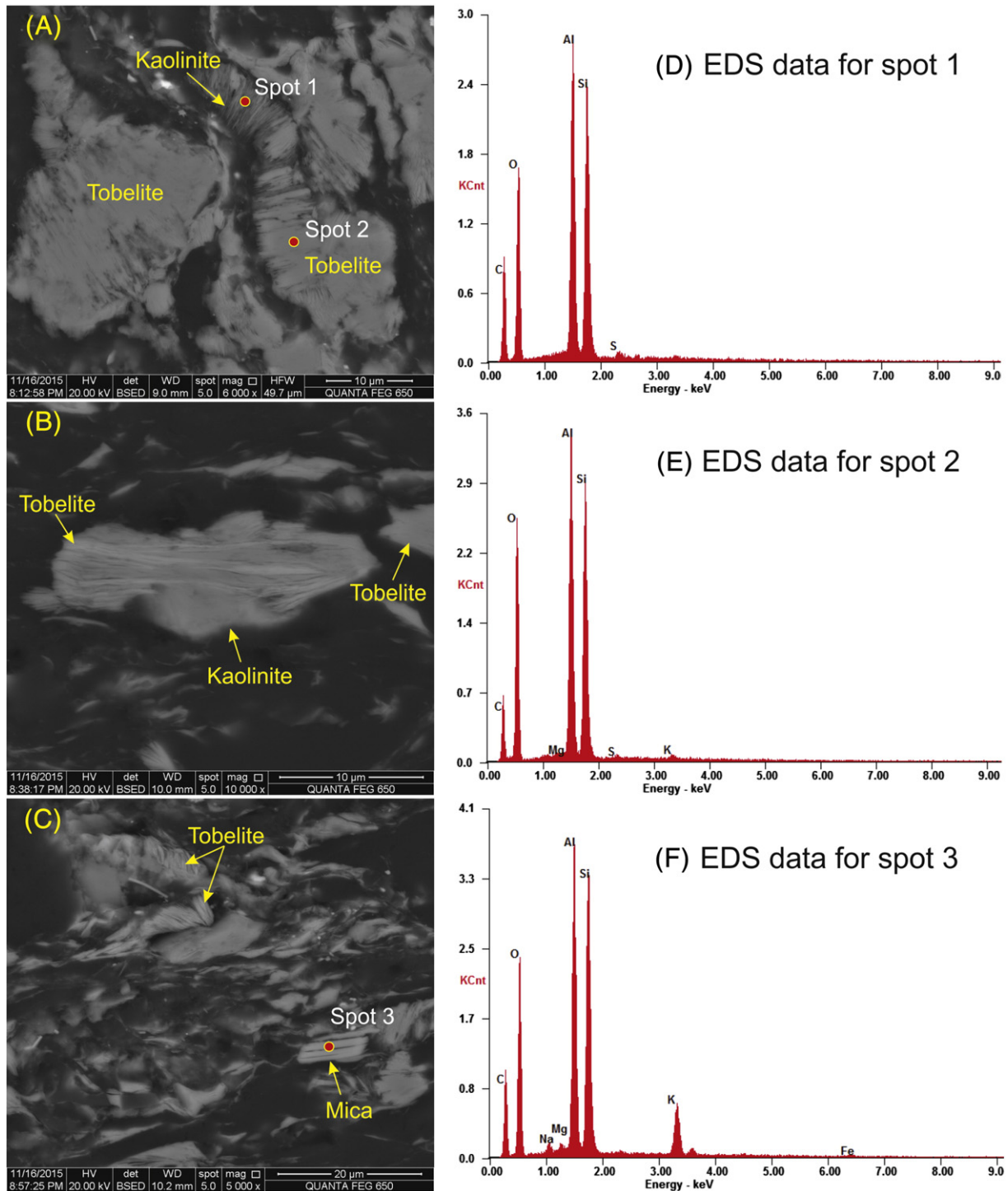


Fig. 6. SEM back-scattered electron images and EDS data for tobelite, kaolinite, and mica in sample K2–2. (A) and (B), alternations of tobelite and kaolinite. (C), tobelite and mica. (D), (E), and (F), EDS spectra for spots 1, 2, and 3 on SEM images.

either be formed by migration of low-temperature solutions (Davis et al., 2006; Permana et al., 2013), or from local remobilization of phosphate formed earlier within the coal seam or associated strata (Ward et al., 1996; Dai et al., 2015d).

Traces of chalcopyrite (Fig. 8D) and coffinite (Fig. 4C) were also observed in the Moxinpo coals by SEM. The chalcopyrite occurs mainly as cell-fillings in fusinite and the coffinite contains traces of Zr, P, and Y.

The minerals in the roof and floor strata of the K1 Coal are similar overall to those in the coal LTAs (Supplementary Electronic File 5). However, the floor samples have higher proportions of kaolinite, florencite, and anatase, and lower proportions of illite + I/S and pyrite (all on ash basis), than the roof samples and the coal LTAs. The minerals in the floor samples of the K2 Coal are also similar to those in the LTAs of the K2 Coal, with the exception that tobelite was not observed in the floor samples.

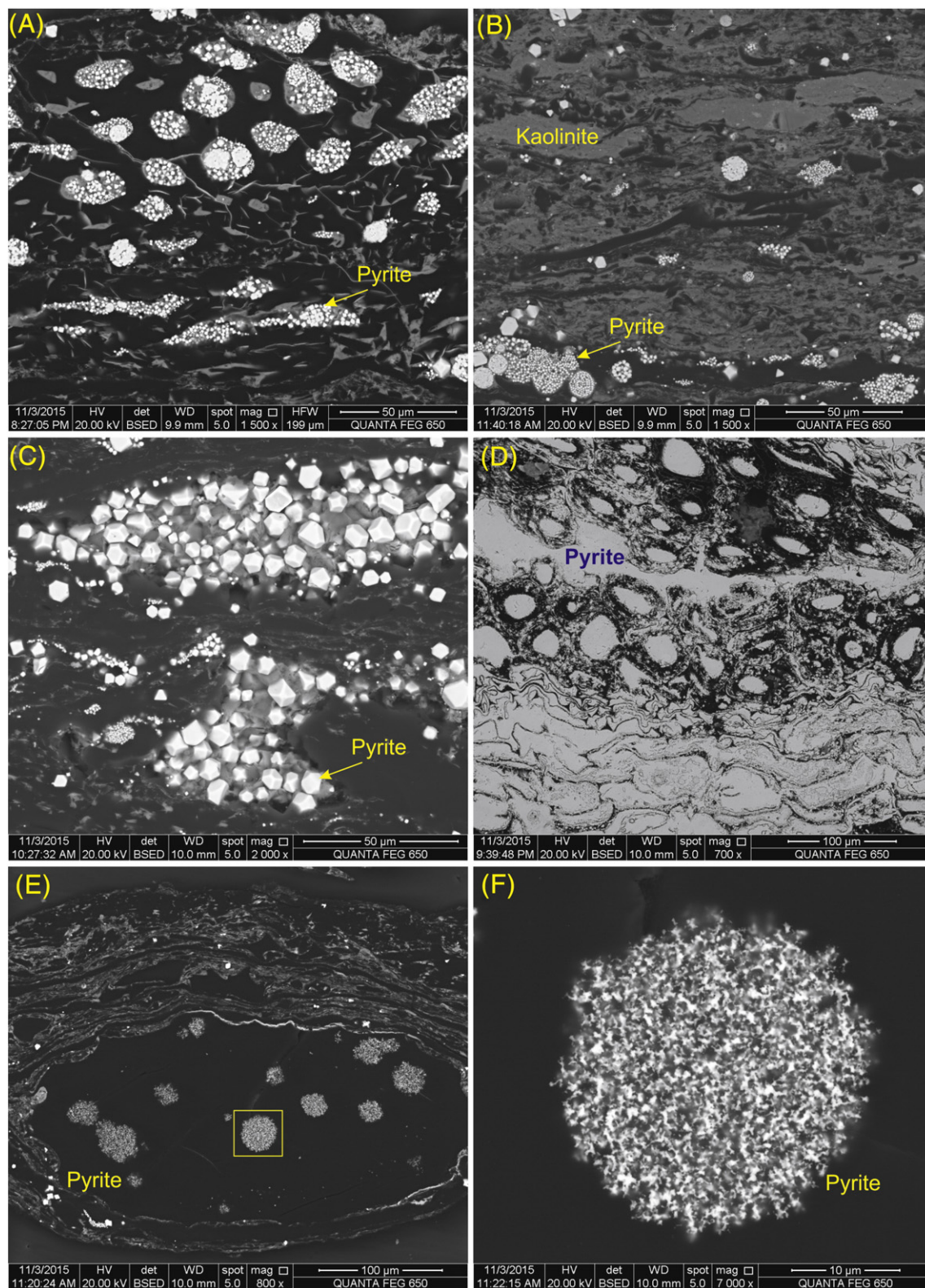


Fig. 7. Backscattered electron images of pyrite in the coals from the Moxinpo Coalfield. (A), pyrite as cell-fillings in sample K1-4. (B), framboidal pyrite in collodetrinite, and massive kaolinite distributed along bedding planes in sample K1-2. (C), discrete crystals of pyrite in cavities in sample K1-1 (D), pyrite as cell-fillings and structured maceral significantly pyritized; sample K1-4. (E), bacteriogenic pyrite in organic matter in sample K1-2. (F) is the enlargement of square in (E).

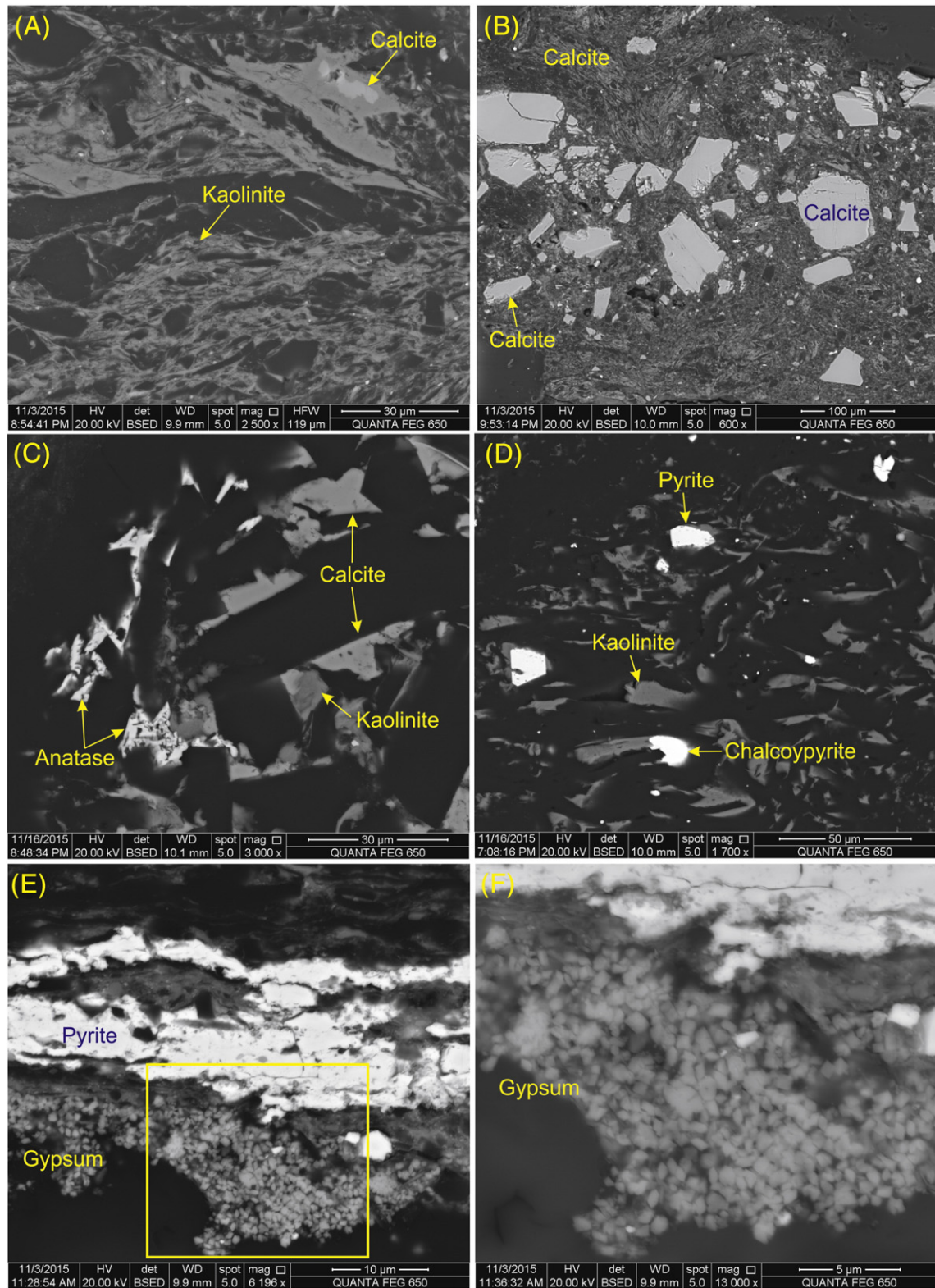


Fig. 8. SEM back-scattered electron images of calcite, gypsum, anatase, and chalcocypirite in the K1 and K2 Coals. (A), calcite as cavities of kaolinite in sample K1-4. (B), discrete calcite particles in clay minerals in sample K1-4. (C), cell-filling anatase and calcite in sample K2-1. (D), cell-filling chalcocypirite, pyrite, and kaolinite in sample K2-2. (E), gypsum and pyrite in sample K1-2. (F), enlargement of the yellow square in (E).

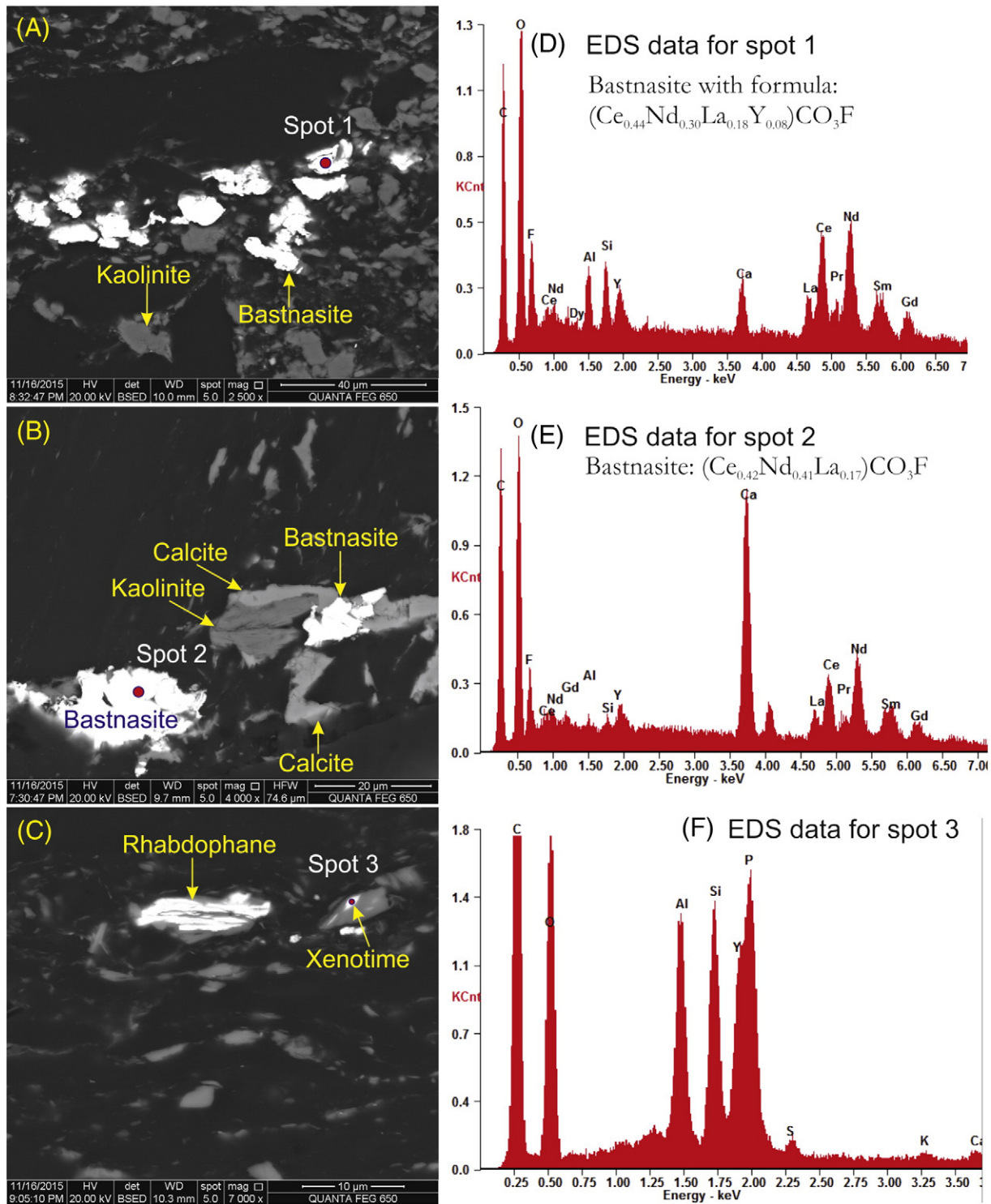


Fig. 9. REY-bearing minerals in the K2 Coal. (A)–(C), SEM back-scattered electron images of bastnasite, xenotime, rhabdophane, kaolinite, and calcite. (D)–(F), EDS data for REY-bearing minerals. (A) and (C), sample K2–2. (B), sample K2–1.

5. Discussion

5.1. Source of terrigenous mineral matter in the coals

A large number of studies have shown that the major source region supplying terrigenous sediment to the Late Permian coals in southwestern China was the Kangdian Upland (Zhuang et al., 2000, 2012; Zhao

et al. 2013, 2015; Wang et al., 2012, 2015; Chen et al., 2015; Li et al., 2016), which in turn was derived from the Emeishan mantle plume and consists mainly of massive flood basalts with numerous contemporaneous mafic and felsic intrusions (He et al., 2010; Chung and Jahn, 1995; Xiao et al., 2004). The terrigenous materials for most of the Late Permian coals in southwestern China are tholeiitic basalts (China Coal Geology Bureau, 1996; Zhuang et al., 2012). Recent studies by Dai

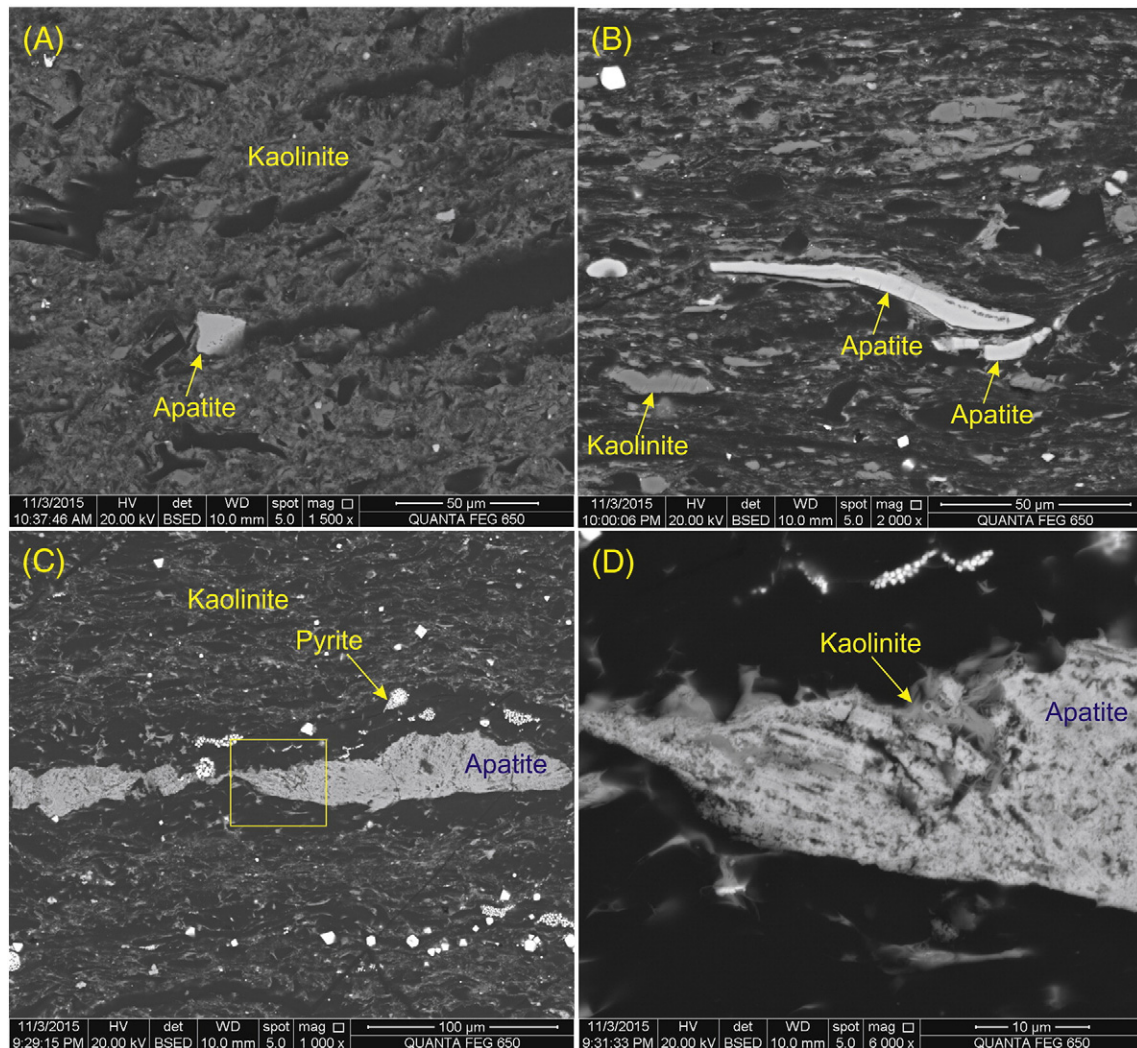


Fig. 10. SEM back-scattered electron images of apatite in the K1 Coal. (A), discrete apatite and kaolinite in sample K1-1. (B), apatite in sample K1-4 distributed along bedding planes. (C), apatite in sample K1-4 distributed along bedding planes; apatite in cavities filled with kaolinite. (D) enlargement of the yellow square in (C).

et al. (2015e) and Wang et al. (2015), however, have shown that terrigenous materials for some coal seams in this area were derived from the felsic-intermediate rocks at the top of the Kangdian Upland succession.

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio has been widely used as a useful provenance indicator for sedimentary rocks (Hayashi et al., 1997; He et al., 2010) and for the sediment-source region of coal deposits (Dai et al., 2015b,c; Hower et al., 2015). Typical $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios are 3–8, 8–21, and 21–70 for sediments derived from mafic, intermediate, and felsic igneous rocks, respectively (Hayashi et al., 1997).

The mafic tuff underlying the lowermost late-Permian coal seam (K1 Coal in this study) was deposited on the eroded limestone surface of the middle-Permian Maokou Formation, and then served as the substrate for the coal deposits. Residual breccias made up mainly of limestones of the Maokou Formation generally occur in the mafic tuff layer (China Coal Geology Bureau, 1996). The occurrence of discrete calcite particles in the lowermost bench K1-1 of the present study, as well as the variable size of the calcite particles (from ~1 to ~100 μm), indicate that the calcite was derived from the mafic tuff and was transported only a short distance into the peat mire. Based on the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio (from bottom to top ranging from 10.09, through 10.12 and 12.34, to 14.24), positive Eu anomalies (Fig. 3A; Table 3), M-type enrichment patterns of the REY (Fig. 3A; Table 3), and the presence of apparently

detrital calcite (Fig. 8), it can be deduced that the terrigenous materials were mainly derived from the mafic tuffs located in the secondary uplifted areas around the coal basin at the early stage of peat accumulation. At later stages of peat accumulation, additional terrigenous materials were input from the felsic-intermediate rocks at the top of the Emeishan basalt sequence, indicated by the increasing $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios from bottom to top of the seam section.

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios for samples K2-0 (25.44), K2-1 (19.61), K2-2 (12.33), and K2-3 (22.63) suggest that the inorganic materials in the K2 Coal were dominantly derived from the felsic-intermediate terrigenous rocks at the top of the Emeishan basalt sequence. The low concentrations of V, Sc, Co, Ni, Cu, and Zn (Fig. 2B), as well as the negative Eu anomalies for the K2 Coal (Fig. 3B), are also indicative of parent rocks with felsic-intermediate compositions (Dai et al., 2016b). Detrital calcite of terrigenous origin was not observed in the K2 Coal, further indicating different terrigenous source materials for the two coal beds.

5.2. Enrichment origin of U-Re-Se-V-Cr and REY in the coals: hydrothermal solution

The highly-elevated concentrations of trace elements in the Late Permian coals of southwestern China are generally attributed to low-

Table 5
Rare metals in the coal ashes and coal-seam host rocks of the Moxinpo Coalfield (μg/g).

Sample	LOI	V ₂ O ₅	Cr ₂ O ₃	Ga	Se	Re	U	REO
K2-3	92.56	410	201	100.7	28.1	bdl	31.5	846
K2-P3	18.71	19	9.1	80.6	10.8	bdl	8.0	158
K2-2	87.81	588	378	106.7	28.8	bdl	27.9	4488
K2-P2	15.96	11	6.0	97.5	4.3	bdl	8.5	650
K2-1	91.43	2506	283	72.4	41.1	0.23	34.2	1459
K2-P1	16.44	13	3.2	91.0	3.8	0.01	9.6	1616
K2-0	80.05	302	109	78.5	47.2	0.23	51.0	3156
K2-F1	17.57	1214	316	67.7	10.2	0.03	30.7	694
K2-F2	16.92	873	284	69.2	4.1	0.02	14.2	638
K2-F3	15.88	797	289	74.3	3.8	0.01	11.9	945
K2-F4	18.38	651	276	67.4	2.6	0.01	10.6	1056
K2-F5	22.43	501	148	81.6	3.2	0.05	14.3	2012
K2-F6	38.68	516	81	84.4	10.9	0.14	18.5	2835
K2-F7	61.71	1395	277	62.9	28.7	0.45	83.1	2052
K2-F8	61.84	1351	267	59.0	30.3	0.42	75.7	1728
K2-F9	32.11	1511	366	71.2	16.6	0.20	87.4	1159
K2-F10	18.15	1056	306	64.4	10.0	0.11	32.9	721
K2-F11	15.13	1194	372	61.1	4.9	0.08	21.0	836
K2-F12	15.76	961	392	64.0	2.2	0.02	18.7	996
K2-F13	15.29	812	374	58.1	0.7	0.01	11.4	864
K2-F14	17.68	770	472	53.0	0.9	0.02	8.8	852
K1-R1	22.44	335	283	27.9	14.8	0.01	32.9	832
K1-R2	15.96	805	567	50.6	1.2	0.04	36.7	571
K1-R3	26.24	1293	1078	49.8	31.0	0.39	196	636
K1-R4	39.68	3042	3566	58.3	85.0	1.40	392	1371
K1-1	60.12	11,558	7268	60.0	159	5.81	740	1463
K1-2	61.64	15,631	9530	70.8	175	4.14	948	1402
K1-3	63.35	14,720	11,562	78.5	142	7.97	1011	925
K1-4	50.99	10,482	5916	59.3	163	6.91	971	1166
K1-F1	22.01	3528	5139	58.0	54.9	0.93	431	1112
K1-F2	16.1	1648	6080	61.6	89.1	0.38	213	1027
K1-F3	13.77	1476	4936	57.3	37.4	0.18	165	1488
K1-F4	14.14	1797	4470	55.6	33.6	0.20	133	1175
K1-F5	15.8	2203	3484	56.5	46.6	0.16	77.7	1223
K1-F6	16.61	2562	3833	63.4	25.1	0.25	81.3	1513
K1-F7	16.92	2242	3431	48.2	23.5	0.10	39.5	704
K1-F8	15.7	2630	3695	44.9	18.2	0.05	33.9	862
K1-F9	15.97	2467	3626	45.6	19.8	0.08	34.2	713
Av-K1	59.03	13,098	8569	67.1	160	6.21	917	1239
Av-K2	88.0	952	243	89.5	36.3	0.12	36.1	2487

bdl, below detection limit.

Table 6
Enrichment types of U in coal.

Enrichment stage	Solution type	Host rocks or mineralization condition	Elemental association	Examples
Epigenetic	Infiltration	U-rich rocks surrounded; Coarse sediments as host rocks (e.g., roof), arid climate.	U-Se-Mo-Re-V (in some cases, As-Hg)	Coals connected with sandstone-hosted uranium deposits
Syngenetic or early diagenetic	Exfiltration	Roof and/or floor are impermeable rocks (e.g., clays or limestones)	U-Se-Mo-Re-V-Cr	Coals preserved within carbonate successions
Early diagenetic	Exfiltration	U-rich rocks surrounded	U-Ge-Be, As-Sb, Cs	Coal-hosted Ge ore deposits
	Exfiltration	Well-developed syndepositional faults	Joint enrichment of U-Re-V-Cr-Se and Nb(Ta)-Zr(Hf)-REY	This study

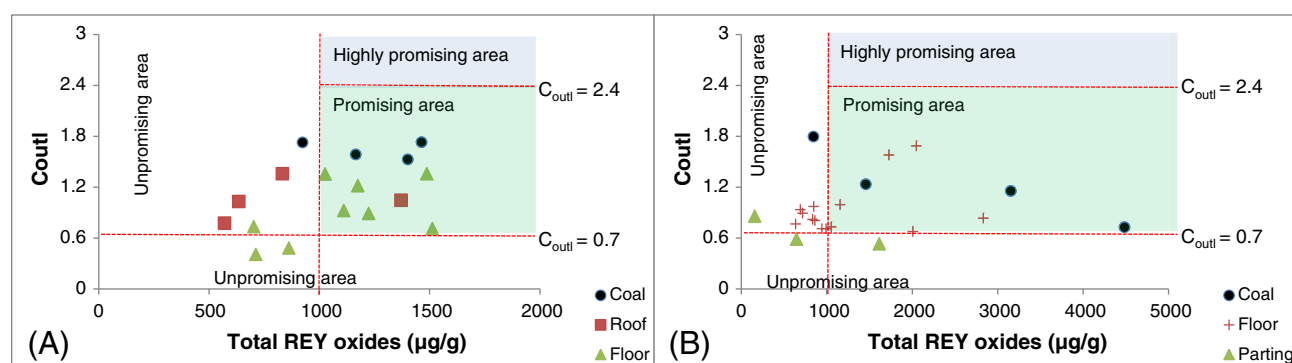


Fig. 11. Evaluation of REY in coal ash and host rocks from the Moxinpo Coalfield. (A), K1 Coal and its host rocks. (B), K2 Coal and its host rocks.

temperature-hydrothermal fluids, submarine exhalation, groundwater movement, and contemporaneous volcanic ash (Dai et al., 2012, 2016a; Wang et al., 2012, 2015; Zhao et al., 2015).

Two enrichment types of U (usually accompanied by Re and Se, and in some cases, V, Cr, and Mo) in coal have been identified (Seredin and Finkelman, 2008), namely an epigenetic infiltration type (type I) and a syngenetic or early diagenetic exfiltration type (type II). Type I is usually characterized by enrichment assemblage of U, Re, Mo, and Se; and is related to sandstone-hosted roll-type uranium deposits; the coal deposits in this case were surrounded by igneous rocks enriched in U and the climate was arid during the epigenetic infiltration process (X.-C. Wang et al., 2006; Y. Wang et al., 2006). Coarse sediments usually occur as the roof strata and served as channels for migration of the U-bearing solutions (Seredin and Finkelman, 2008; Dai et al., 2015b). The elements U, Re, Mo, and Se usually are enriched in the upper portion of the coal seam, which is in direct contact with a sandstone-hosted uranium deposit. Type II accumulations can be divided into two subtypes (subtypes-1 and 2). Subtype-1 is characterized by enrichment assemblage of U, Re, Mo, Se, V, and Cr; and is usually interlayered between impermeable clays (Seredin and Finkelman, 2008) or limestones (Dai et al., 2015c). The elevated concentration of these trace elements is consistent throughout the seam section. Subtype-2 is characterized by enrichment of Be-Nb-U and Ge-W assemblages (Seredin et al., 2006; Dai et al., 2015a), although other elements, including V, Cr, Mo, and Se, are depleted in the coals. Associated U- and Ge-rich granites served as both the basement for the coal-bearing sequences and as the sediment-source materials (Dai et al., 2015a) (see Table 6).

The K1 Coal of the Moxinpo Coalfield was deposited on mafic tuff, and no U-rich rocks (e.g., granite) have been observed surrounding the coalfield. Thus, the enrichment of U, as well as Re, Se, V, and Cr, cannot be categorized into any of the enrichment types described above. Additionally, Mo is only slightly enriched in the K1 Coal but is significantly enriched in the U-rich coals belonging to the type-1 and subtype-1 categories.

Based on previous studies (e.g., Zeng et al. 2005; Shao et al. 2003; Li et al. 2013; Dai et al., 2015c; Hou et al. 1995; Lei et al. 1994), the Late Permian U-rich coals were exclusively preserved within marine

carbonate successions and are characterized by extremely-high organic sulfur contents. Some studies have variously attributed the highly elevated sulfur and concentrations of trace elements (e.g., U, Se, Mo, Re and V) to a marine transgressive environment (Shao et al., 2003; Li et al., 2013) or to the formation of soil horizons prior to peat accumulation (Zeng et al., 2005). However, a recent study by Dai et al. (2015c) attributed these elevated elements to the injection of exfiltrational hydrothermal solutions during peat accumulation, which were then deposited in an euxinic environment.

The highly-elevated concentrations of U-Re-Se-V-Cr and Zr(Hf)-Nb(Ta)-REE in the K1 Coal, as well as Zr(Hf)-Nb(Ta)-REE in the K2 Coal, in the Moxinpo coals can also be attributed to exfiltrational hydrothermal solutions for the following reasons:

- (1). As described above, the sediment-source materials for the K1 Coal were mafic tuffs. These contain 5.44- $\mu\text{g/g}$ U, 3.19- $\mu\text{g/g}$ Se, 246- $\mu\text{g/g}$ V, and 177- $\mu\text{g/g}$ Cr (Dai et al., 2014b), values higher than those of average world clays (Grigoriev, 2009), but still cannot account for the highly-elevated concentrations of these elements in the K1 Coal (Tables 2 and 5). The high-Ti basalts in the Kangdian Upland, the major sediment-source for the Late Permian coals and for other sediments in southwestern China, contain 374- $\mu\text{g/g}$ V, 71- $\mu\text{g/g}$ Cr, and 1.41- $\mu\text{g/g}$ U (Xiao et al., 2004). The non-coal detrital sediments (888 samples) derived from the Kangdian Upland in southern Sichuan province surrounding Chongqing contain 441- $\mu\text{g/g}$ V and 206- $\mu\text{g/g}$ Cr (Hong, 1993). The mafic tuff below the K1 Coal and the basalts of the Kangdian Upland, both derived from the Emeishan mantle plume, have a similar magmatic source and similar trace-element assemblages (Dai et al., 2014a).
- (2). The occurrence of roscelite in the K1 Coal, suggests injection of V-Cr-rich solutions during early diagenesis of the coal seam. Roscelite has rarely been reported in coal. For example, Papanicolaou et al. (2004) reported highly-elevated concentrations of U (33–313 $\mu\text{g/g}$) and V (116–737 $\mu\text{g/g}$) in coal ash from the Drama Basin, Greece, which suggested the possibility of carnotite and/or roscelite and/or vivianite minerals. Such minerals may be attributed to intense volcanic activity along with geothermal fluid circulation (Ashworth et al., 1985; Fytikas et al., 1984). XAFS studies on the Kentucky No. 9 (Springfield) seam, with a concentration of 1800 $\mu\text{g/g}$ V, showed that two distinct forms of V in the coal, roscelite and V^{4+} in a pyramidal or distorted octahedral structure (Huggins and Huffman, 1996).

Tobelite occurs only in coal benches K2–1 and K2–2. It may have resulted from interaction of NH_4^+ ions with kaolinite during hydrothermal alteration at a relatively high temperature, which is supported by the higher vitrinite reflectance for the K2 Coal than the K1 Coal (Table 1). The K2 Coal has been subjected to alteration by hydrothermal solutions, leading to the enrichment of Nb(Ta)-Zr(Hf)-REE, as described below. Coal benches K2–0 and K2–3 do not contain tobelite, probably due to the low permeability of the associated clay partings, K2-P1 and K2-P2, which may have prevented hydrothermal solutions penetrating into the overlying and underlying coal benches. Other studies indicate that tobelite in coal may have been formed at relatively high temperatures (e.g., $>200^\circ\text{C}$) by interaction of kaolinite with nitrogen released from the organic matter in coal during rank advance, or during metamorphism caused by igneous intrusions (Daniels and Altaner, 1990, 1993; Ward and Christie, 1994; Sucha et al., 1994; Nieto, 2002; Boudou et al., 2008). Juster et al. (1987) suggested that the starting temperature for the formation of ammonian illite associated with coal is 250°C . It therefore seems that ammonian illite or tobelite, when present, mostly occurs in relatively high-rank coals or in their intra-seam partings, including coals in which hot solutions have permeated through the seam (Permana et al., 2013).

- (3). The U concentrations decrease from top to bottom in the floor strata but from bottom to top in the roof succession (Supplementary Electronic File 3), suggesting that U permeated into the adjacent roof and floor strata from the coal bed during early diagenesis.

The U-Re-Mo-Se-V-Cr-rich hydrothermal solutions could have been injected into the unconsolidated peat deposit during early diagenesis along syndepositional faults, which were well and widely developed in the study area (China Coal Geology Bureau, 1996). This mineralization type is similar to the enrichment origin of U, Se, Mo, Re, and V in coals preserved within marine carbonate successions as proposed by Dai et al. (2015c), and also indicates that all coals with highly-elevated concentrations of U, Se, Re, and V are not necessarily those preserved within marine carbonate successions. Overall, based on prior studies (e.g., Shao et al., 2003; Zeng et al., 2005; Seredin and Finkelman, 2008; Dai et al., 2015a,b) and geochemical and mineralogical data present in this study, the types of U enrichment in coal can be summarized as presented in Table 5.

- (4). Seredin and Dai (2012) have identified four main genetic types of REY enrichment in coals, namely, terrigenous, tuffaceous, infiltrational, and hydrothermal. Three mineralization types in coal deposits have been identified in southwestern China, tuffaceous, hydrothermal-fluid, and mixed tuffaceous-hydrothermal types. In this study, the K1 Coal hosts not only U(Re, Se, V, Cr) but also Zr(Hf)-Nb(Ta)-REE assemblages and the K2 Coal hosts Zr(Hf)-Nb(Ta)-REE. The modes of occurrence of REE-bearing minerals (bastnäsite, xenotime, and rhabdophane) indicate that they are of authigenic origin and were in-situ deposited from REY-rich solutions.

The K1 Coal samples all show a Gd-maximum (Fig. 3A); such patterns are due to hydrothermal fluids and other waters (Shand et al., 2005; Dai et al., 2016b). The K1 Coals also show significant positive Y anomalies (Fig. 3A), with Y_N/Ho_N values 1.19–1.33 (Table 3). For comparison, the Y_N/Ho_N values of average Chinese and world coals are 0.93 (Dai et al., 2012) and 0.56 (Ketris and Yudovich, 2009), respectively. Infiltration of hydrothermal solutions is one of the main factors that could cause such positive Y anomalies in coal (Dai et al., 2016b).

The mafic tuffs in the study area (e.g., the weakly-hydrothermally altered mafic tuffs of samples K1-5F to K1-9F; Supplementary Electronic File 6) show weakly negative Y anomalies. The non-coal sediments and the coals containing terrigenous materials derived from the high-Ti basalts in the Kangdian Upland, as well as the high-Ti basaltic volcanic ashes in southwestern China generally, all show negative or very weak negative Y anomalies (Dai et al., 2014a). Thus, the significant positive Y anomalies in the K1 Coal cannot be attributed to the terrigenous materials.

6. Evaluation of rare metals in the Moxinpo coals and host rocks

The criteria of Seredin and Dai for preliminary assessment of the REY in coal ashes as economic raw materials (Seredin and Dai, 2012) include the REY grade and the overall element composition, although a relatively full assessment should include a number of factors that may be taken into account, such as the resources of the rare metals, the minable tonnage of the coal, the modes of occurrence of rare metals in the coal and coal combustion productions, extraction methods, environmental issues, and the relation between demand and supply of rare metals (Dai et al., 2016c). A REO content $\geq 1000 \mu\text{g/g}$ in the ash is considered as the cut-off grade for beneficial recovery (REO: oxides of rare earth elements and yttrium). The second criterion is the $\text{REY}_{\text{def, rel-Coutl}}$ graph, where REY_{def} is the percentage of critical elements in the total REY and the Coutl (outlook coefficient) is the ratio of the relative amount

of critical REY metals in the total REY to the relative amount of excessive REY, calculated according to the following formula:

$$C_{\text{outl}} = \frac{(\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y}) / \sum \text{REY}}{(\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu}) / \sum \text{REY}} \quad (4)$$

Sources of REY with $0.7 \leq C_{\text{outl}} \leq 1.9$ and $C_{\text{outl}} > 2.4$ are considered as promising and highly promising, respectively. Based on the relation between cut-off grade and C_{outl} (Fig. 11), the K1 Coal (1239 $\mu\text{g/g}$ REO on average), the floor strata of the K1 Coal (1091 $\mu\text{g/g}$ REO on average), the K2 Coal (2487 $\mu\text{g/g}$ REO on average), and the floor strata of the K2 Coal (1242 $\mu\text{g/g}$ on average) fall within the promising area (all on ash basis, 815 °C; Fig. 11; Table 5). However, most samples of the K1 roof strata, some samples of the K2 floor strata, and the partings in the K2 Coal do not reach the cut-off grade and, thus, are considered to be unpromising.

In addition to the rare earth elements and yttrium in the coals and their host rocks, other rare metals in the K1 Coal, including V_2O_5 (13,098 $\mu\text{g/g}$ on average), Cr_2O_3 (8596 $\mu\text{g/g}$), Ga (67.1), Se (160 $\mu\text{g/g}$), Re (6.21 $\mu\text{g/g}$), and U (917 $\mu\text{g/g}$) (all on ash basis, 815 °C; Table 5) have potential economic significance. The cut-off grades for V and U in coal ashes are both 1000 $\mu\text{g/g}$, and that of Re in coal is 1 $\mu\text{g/g}$ (Seredin, 2004).

7. Conclusion

Previous studies have shown that the highly-elevated concentrations of U-Mo-Re-V-Cr-Se and Nb(Ta)-Zr(Hf)-REE assemblages in the Late Permian coals of southwestern China are respectively distributed in different coal deposits, with the former usually being preserved within carbonate successions. In this study, both of these elevated trace-element assemblages (with the exception of Mo that is not enriched) occur in the K1 Coal, which was deposited on a substrate of a mafic tuff. The mafic tuffs, rather than the Kangdian Upland (the dominant sediment-source region for most Late Permian coals in southwestern China), also served as a source of terrigenous sediment for the K1 Coal.

The elevated concentrations of U-Re-V-Cr-Se and Nb(Ta)-Zr(Hf)-REE in the Moxinpo coals are attributed to influx of hydrothermal solutions. The enhanced U-Re-V-Cr-Se assemblage in the coal therefore indicates that enhancement of these trace elements does not necessarily occur only in coals preserved within carbonate successions, and that the highly-elevated concentrations were not necessarily derived from seawater.

The ash of the K1 Coal, with highly-elevated concentrations of V_2O_5 , Cr_2O_3 , Se, Re, and REE oxides, as well as the ash of the K2 Coal and the floor strata of both seams are also rich in REY and may be considered as promising sources for these rare metals.

Roscoelite and tobelite, which are uncommon in other coals, were identified in the K1 and K2 Coals, respectively. The roscoelite is of authigenic origin and was probably derived from interaction between V derived from permeating U-Re-V-Cr-Se-rich solutions and kaolinite already present in the coal during an early stage of the diagenetic process. The tobelite probably resulted from interaction between kaolinite already present in the coal and NH_4^{+} ions derived from decomposition of the organic matter at a relatively high temperature during hydrothermal alteration.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.oregeorev.2016.06.015>.

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