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Mineralogy, distribution, occurrence and removability of trace elements during the coal preparation of No. 6 coal from Heidaigou mine

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Abstract Optical microscopy and scanning electron microscopy in conjunction with energy dispersed X-ray spectrometry (SEM–EDX) were used to study the minerals and the concentrations of 33 trace elements in No. 6 coal from Heidaigou mine. The distributions, organic affinity and removability of 18 trace elements were studied by float-sink experiments. A determination of the maceral groups was also undertaken. A high mineral content, dominated by kaolinite, was found in No. 6 coal from Heidaigou mine. The bauxite content was relatively high and it was mainly present as individual particles in fusinite lumens or was intimately intergrown with carbonate minerals. The pyrite and quartz contents were low. Some marcasite with a parallel twin structure was observed by cross-polar reflected light. A small amount of bean-like goyazite was present in the calcite. The weighted trace element content in Heidaigou formations is relatively low, which is beneficial for coal processing and utilization. The concentrations of Ga, Hg, Pb, Se, Th, Ta are relatively high compared with the average values of Chinese coals. As, Hg, Mo, Ge, Ga, Ta, Ti, W, Mn are mainly present in minerals while B, Be, Th, P, Sc, Sr, V, Y, Yb are mainly found in organic matter. As, Ge, Hg, Mo are mainly present in sulfides and Be, Th, P, Sc, Sr, Y, Yb are mainly present in inertinite. B and V are mainly present in vitrinite. The high organic affinity and the low theoretical removability of most trace elements cause difficulties in removing them during coal preparation.

Keywords Trace elements · Occurrence · Organic affinity · Removability · Heidaigou coal

1 Introduction

The Heidaigou coal mine is located in the middle of the Junger coalfield in the Inner Mongolia Autonomous Region. More than 30 million tons of raw coal is produced every year. As a preferred feedstock for power plants Heidaigou coal is primarily used for the generation of electricity. A low degree of anogenic metamorphism is the main coalification type. The main mineable coal bed, the No. 6 coal seam, was formed during the drying terrestrial delta deposition environment of the late Carboniferous period (Mao and Xu 1999).

Research into minimizing the hazards caused by trace elements is an important part of coal utilization technologies. Studies into the distribution and the occurrence of trace elements in coal are important. Bench samples from a drill core of the No. 6 coal seam were used to study the distributions and occurrence of trace elements in Heidaigou coal. It was found that Ga, Se, Sr, Zr, Hg, Pb, Th and REEs were relatively abundant while the Ga concentration was sufficient for industrial use. Ga, Th and REEs were found to be mainly distributed in boehmite in the No. 6 coal (Dai et al. 2006a). Their relative abundance in boehmite comes from the periodic drying of peat because of changes in the water table during the coal forming period (Dai et al.

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2007). It has been shown that high concentrations of Ga in weathered coal come from the absorption of humic acid (Wang et al. 2011). Lead and selenium are mainly present in galena, clausthalite, and selenio-galena while Hg is mainly found in clausthalite and sulfides. High concentrations of Zr are attributed to the presence of zircon and Sr is present in goyazite (Dai et al. 2006b, c; Li and Ren 2006). No. 6 coal from the Haerwusu surface mine that adjoins Heidaigou is enriched in Li, F, Ga, Se, Sr, Zr, REEs, Pb, and Th while Ga and F were mainly found in the clay minerals and partially in organic matter. Se and Pb are mainly present in the epigenetic clausthalite that fills the fractures. Sr and P may share the same carriers (Dai et al. 2008).

As a low-cost and mature technology coal preparation effectively reduces the amount of harmful elements in addition to improving the calorific values and lowering the ash and sulfur content of coal (Martinez-Tarazona et al. 1992). Coal preparation is thus believed to be an effective method to lower the concentrations of trace elements. This reduces the amount of environmental pollution by the trace elements (Pires et al. 1997; Klika et al. 1997, 2000; Tang et al. 2005; Song et al. 2010).

The geological setting of Heidaigou mine has been reported (Dai et al. 2006c). Production samples were used to study the coal's mineral composition. The distributions, occurrence and removability of trace elements from No. 6 coal were determined using float-sink experiments, petrological and statistical methods in this study. Correlation analysis was conducted to study the relationship among the trace elements and between the trace elements and the maceral groups, the ash content and the sulfur content. The theoretical content of trace elements in the macerals and minerals were then calculated using linear equations and the organic affinities of the trace elements are discussed. The removabilities of the trace elements were determined to provide guidance for the clean and environmentally-friendly use of Heidaigou coal.

2 Experiments

2.1 Characteristics of the samples

The samples were obtained from the No. 6 coal seam at the Heidaigou surface mine according to GB/T 481-1993 (production coal sampling method). Proximate analyses (GB/T 212-2008), ultimate analyses (GB/T 476-2008,GB/T 19227-2008), total sulfur (GB/T 214-2007) and forms of sulfur (GB/T 215-2003), ash composition (GB/T 1574-2007), the fusibility of ash (GB/T 219-2008), the maceral groups (GB/T 8899-2008), the microlithotype composition (GB/T 15590-2008), and the mean maximum reflectance of the vitrinite (GB/T 6948-2008) were determined following Chinese standards and the results are listed in Tables 1, 2, 3, 4, 5 and 6.

Heidaigou coal is a low-rank bituminous coal with a high ash content. The sulfur content is low and dominated by pyritic sulfur. The Al_2O_3 content is high while SiO_2 is relatively low in the ash. This results a high ash fusion temperature. The mine is located at the north edge of the carboniferous-permian coal accumulation basin in Northern China. The vitrinite content is lower than the average of the area while the inertinite and liptinite contents are higher

Table 1 Results of the proximate and ultimate analyses (wt%)

Proximate analysis				Ultimate analysis				
M_{ad}	A_d	V_{daf}	FC_d	C_{daf}	H_{daf}	N_{daf}	O_{daf}	S_{daf}
8.65	24.67	38.50	46.33	81.52	4.51	1.30	12.02	0.65

Table 2 Total sulfur and forms of sulfur in the coal (wt%)

$S_{t,d}$	Forms of sulfur		
	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$
0.49	0.33	0.00	0.16

Table 3 Ash composition analysis (wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	P_2O_5	Na_2O	K_2O
23.84	57.18	3.58	5.12	0.43	0.72	2.48	0.18	0.24	0.81

Table 4 Fusibility of the coal ash (°C)

DT	ST	HT	FT
1,380	>1,500	>1,500	>1,500

Table 5 Maceral groups and the mean maximum reflectance of vitrinite

Maceral group (vol%)				R^o_{max} (%)
Vitrinite	Inertinite	Liptinite	Mineral	
31.87	44.88	8.78	14.48	0.52

Table 6 Microlithotypes in Heidaigou coal (vol%)

Vitrite	Clarite	Inertrite	Vitrinertite	Trimacerite	Liptite	Durite	Minerite
11.33	4.30	17.38	12.11	13.48	0.00	29.88	11.52

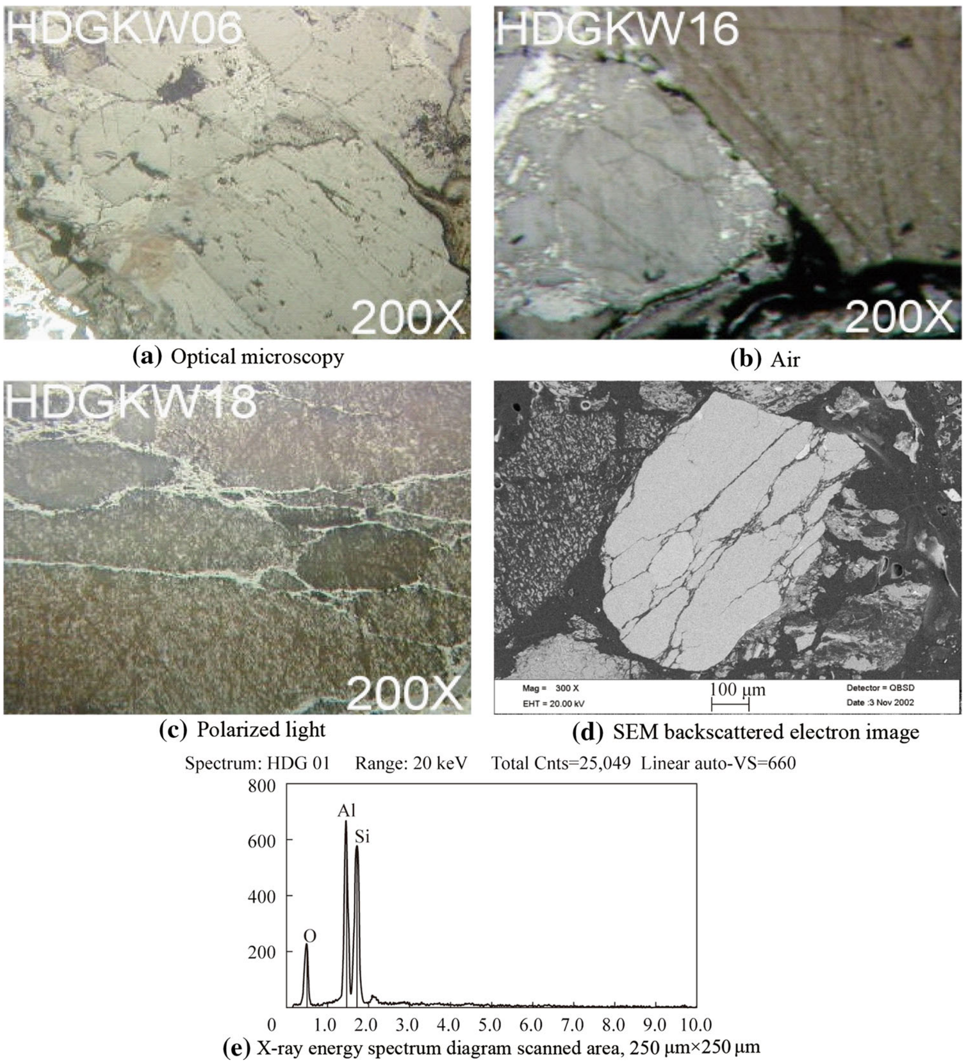


Fig. 1 Kaolinite in Heidaigou coal

(Han 1996). The dominant vitrinite macerals are telocollinite and desmocollinite. A small amount of telinite is also present. The liptinite group is mainly represented by sporinite, which disperses in the desmocollinite and in the matrix of the inertinite in the bedding direction. Fragmental fusinite usually mixes with semifusinite. The main microlithotypes are vitrite, trimacerite and durite while a small amount of clarite, inertrite and vitrinertite are present. Vitrite is usually uniform while trimacerite is fragmental or of lineation shape. Durite is composed of an inertinite matrix and a clastic texture.

2.2 Mineral analysis

Minerals are the main carriers of most trace elements in coal. The distributions, occurrence and removability of the

Table 7 Si/Al ratio of the clay minerals

Sample No.	Scanning area (μm × μm)	Acquisition time (s)	Si/Al ratio
1	250 × 250	50	1.04
2	250 × 250	50	1.06
3	100 × 80	50	0.90
4	250 × 250	50	1.01

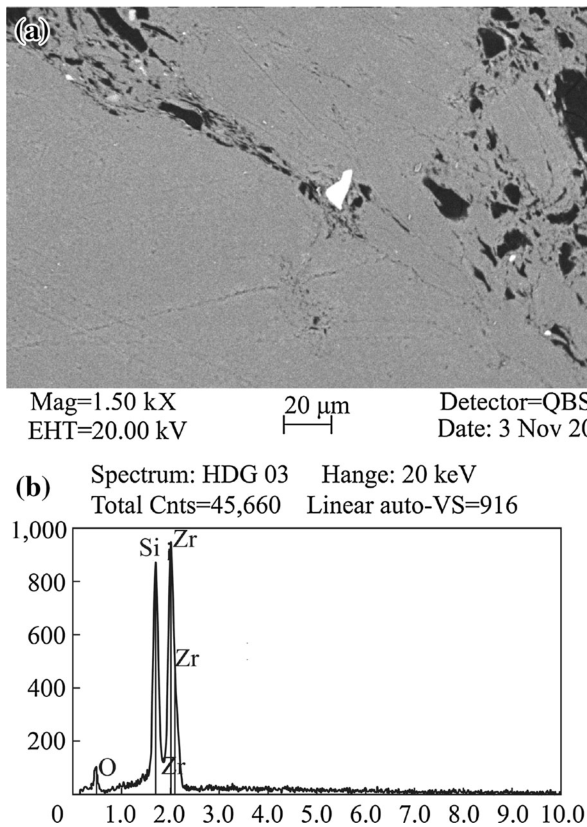


Fig. 2 Fine-grain zircon in the kaolinite

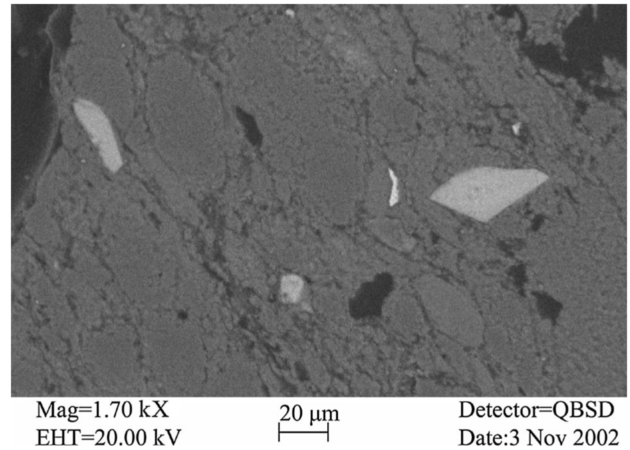


Fig. 3 Fine-grain rutile in the kaolinite (SEM backscattered electron image)

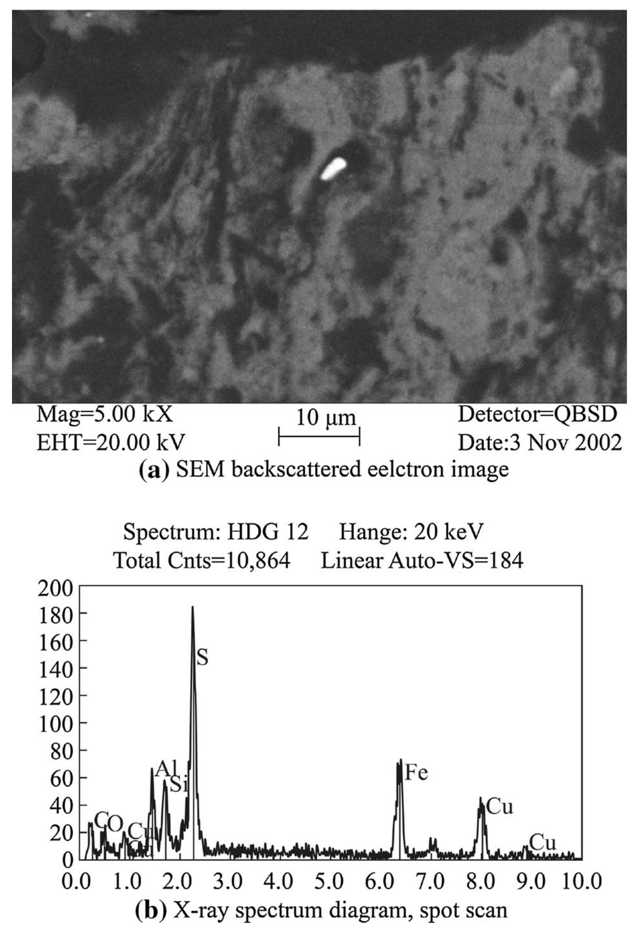


Fig. 4 Fine grain chalcopyrite in the kaolinite

trace elements are largely affected by the presence of minerals. They are closely related to each other in terms of their genesis. Samples were prepared for microscopic analysis (ZEISS AXIOSKOP 40 optical microscope) according to the Chinese standard (GB/T 16773-2008). The optical characteristics of the minerals are described below and photographs were taken. A scanning electron microscope in conjunction with energy-dispersive X-ray spectrometry (SEM–EDS) was used to study the characteristics of the minerals and also to determine the distributions of elements in the macerals and in the minerals by spot and area scanning. Backscattered electron images (BSE) of the minerals were then obtained. The mineral compositions were determined by EDS both qualitatively and

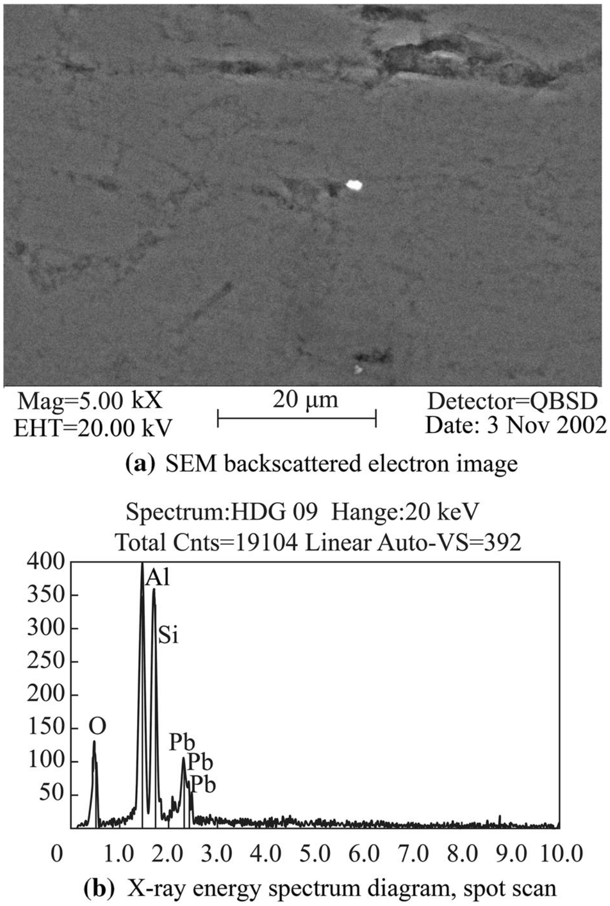


Fig. 5 Pb-bearing minerals in the kaolinite

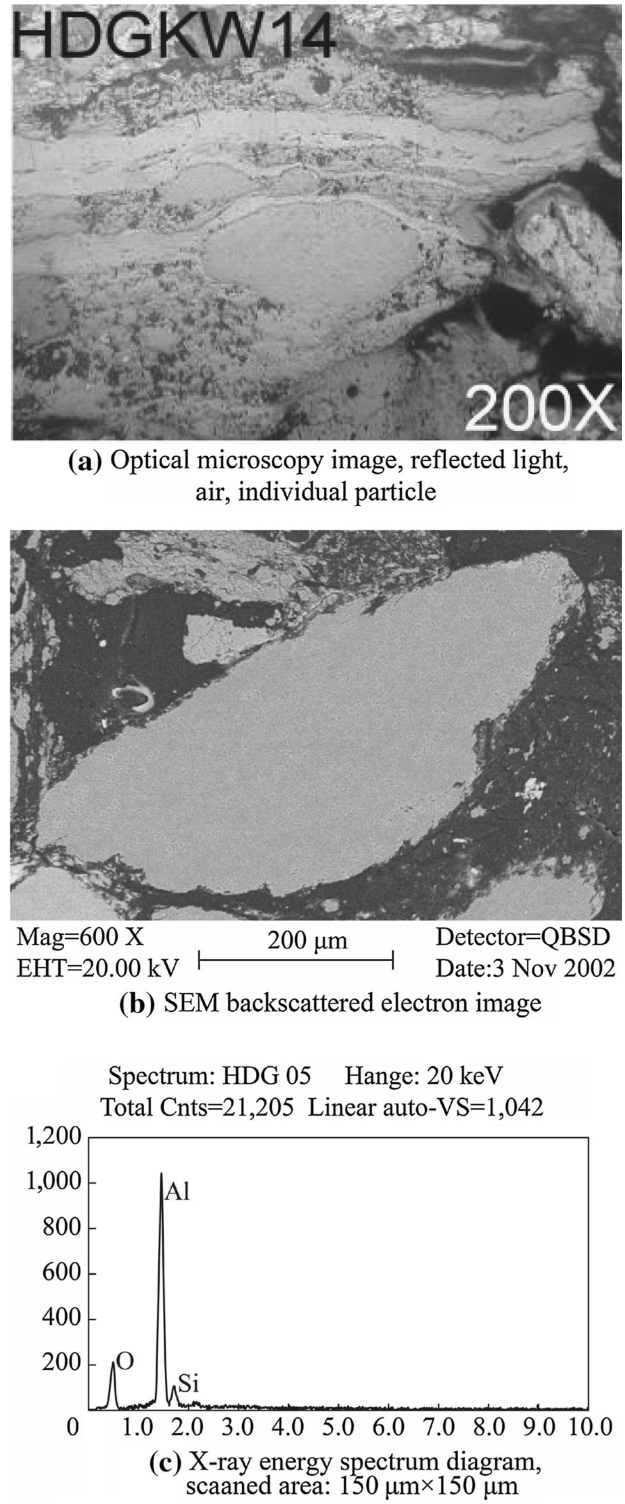


Fig. 6 Bauxite in Heidaigou coal

quantitatively. The acquisition time for the EDS analysis was 50 s and the scanned areas were determined by the size and morphology of the mineral particles.

2.3 Distributions and occurrence of the trace elements

2.3.1 Determination of the trace elements

The concentrations of Ag, As, B, Ba, Be, Cd, Co, Cr, Cs, Cu, F, Ga, Ge, Hg, Mn, Mo, Ni, P, Pb, Sb, Sc, Se, Sn, Sr, Ta, Th, Ti, U, V, W, Y, Yb, Zn in the No. 6 coal seam were determined.

The trace elements were determined by inductively coupled-plasma mass spectrometry (ICP-MS) except for As, F, Ge, Hg, Sb and Se. For ICP-MS analysis the samples were digested using a microwave high pressure reactor. F was determined by pyrohydrolysis in conjunction with a fluoride ion-selective electrode according to GB/T3558-1996. Hydride generation atomic fluorescence spectrometry analysis (HGAFS) was used to determine the concentrations of As, Ge, Sb and Se while cold-vapor atomic fluorescence spectrometry analysis (CVAFS) was used to determine the concentration of Hg.

2.3.2 Occurrence of the trace elements

The coal samples were crushed to less than 3 mm and fine particles of less than 0.5 mm were collected. Float-sink

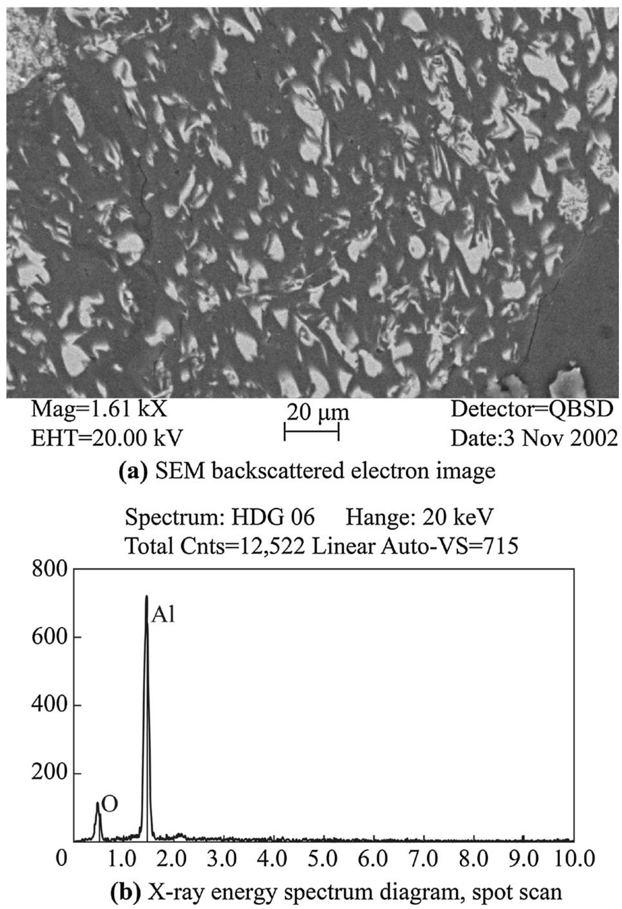


Fig. 7 Bauxite in the fusinite lumens

experiments were conducted using particles between 3 and 0.5 mm following the Chinese standard GB/T478-2008. The ash and sulfur content, the maceral groups and minerals (divided into clay minerals, pyrite, quartz and carbonates) and the contents of As, B, Be, Ga, Ge, Hg, Mn, Mo, P, Sc, Sr, Ta, Th, Ti, V, W, Y, Yb were determined in products of different densities and in the fines of particle size less than 0.5 mm. The precision of the float-sink experiment and the determination of the trace elements were evaluated by balancing the trace element content between the raw coal and the weighted mean values in the products of different densities in the float-sink experiments and in the fines of particle size less than 0.5 mm. The calculation was conducted according to Eq. (1):

$$R = \sum_{j=1}^{n} C_j W_j / C \tag{1}$$

where, R is the ratio of the weight mean trace element content in the products of different densities and of that in raw coal (%), C is the content of trace elements in the raw coal (μg/g), C_j is the content of trace elements in the products of a certain density including the fines of particle size less than 0.5 mm (μg/g), W_j is the yield of products of certain density including the fines of particle size less than 0.5 mm (%).

The dominant mineral components are clay minerals and the pyrite content is low resulting in a simple mineral composition for the Heidaigou coal. The coal can be divided into vitrinite, inertinite and various minerals in terms of coal petrology while liptinite is ignored. The mass fraction of organic matter that consists of vitrinite and inertinite, the minerals in the raw coal and the products of different densities can be calculated according to Eqs. (2) and (3).

$$MM = 1.1A_{\rm d} + 0.5S_{\rm p,d} \tag{2}$$

$$ORG = 100 - MM \tag{3}$$

where, MM is the mineral content of the coal (mass fraction), ORG is the organic matter in the coal (mass fraction), $A_{\rm d}$ is the yield of ash in the coal (%), $S_{\rm p,d}$ is the pyritic sulfur content of the coal (%).

Because the macerals and the minerals in the coal petrological analysis are expressed as volume fractions the densities of vitrinite, inertinite and the minerals were 1.33, 1.40 and 2.60 g/cm^3, respectively, for the calculation of mass fraction in this paper.

A linear relationship was found for the trace element content of the raw coal ($C_{\rm m}$) and for the different macerals and minerals ($C_{\rm mi}$). The theoretical trace element ($C_{\rm mi}$) content of the macerals and the minerals was calculated by multi-factor linear regression of the maceral and mineral compositions ($W_{\rm mi}$). The trace element ($C_{\rm m}$) content of the products of different densities were determined using Eq. (4):

$$C_{\rm m} = \sum_{i=1}^{n} C_{\rm mi} W_{\rm mi} \tag{4}$$

where, $C_{\rm m}$ is the content of a specific element in the coal (μg/g), $C_{\rm mi}$ is the theoretical content of a specific element in vitrinite, inertinite and in the minerals (μg/g), and $W_{\rm mi}$ is the maceral composition of the products of different densities (%).

The amount of trace elements in the organic matter of the coal can be expressed by organic affinity. The organic affinity index ($A_{\rm o}$) of different trace elements in the coal was calculated using Eq. (5):

$$A_o = C_o W_o / C \tag{5}$$

where, $C_{\rm o}$ is the average content of a specific trace element in the organic matter (μg/g), C is the content of trace elements in the raw coal (μg/g), and $W_{\rm o}$ is the content of organic matter in the coal (mass fraction).

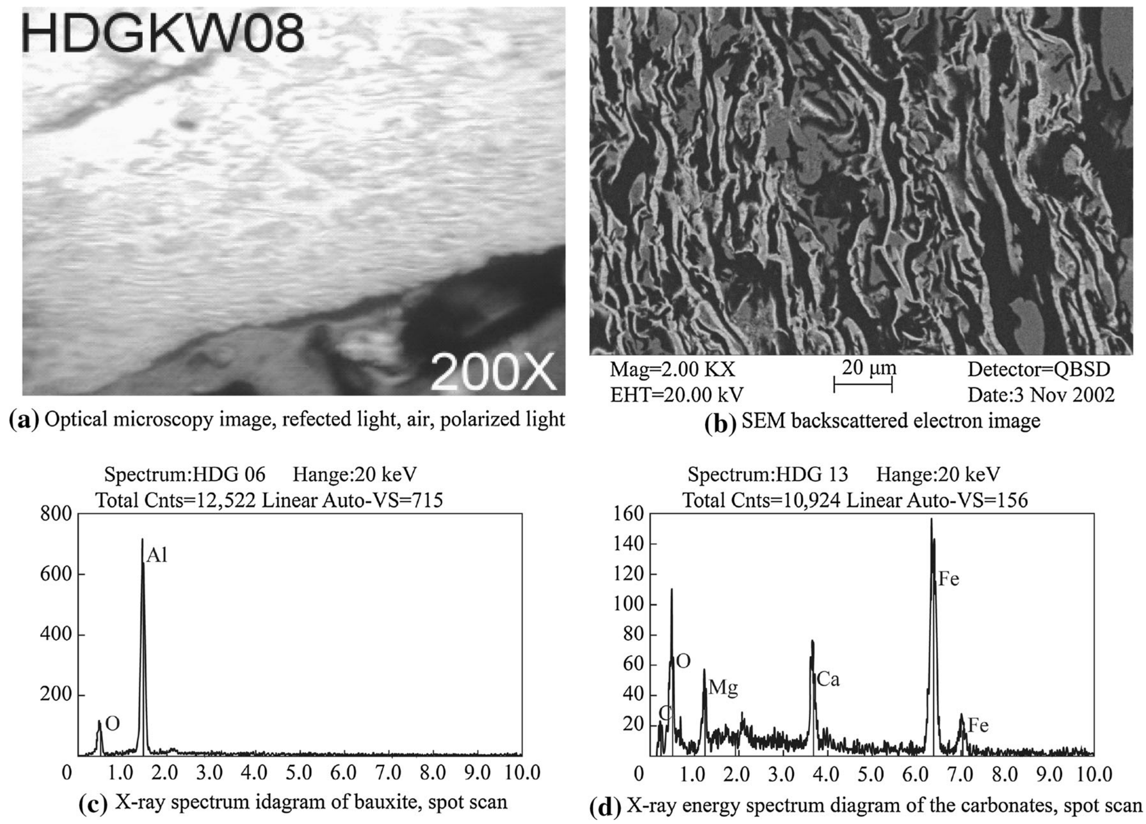


Fig. 8 Bauxite intergrown with carbonates

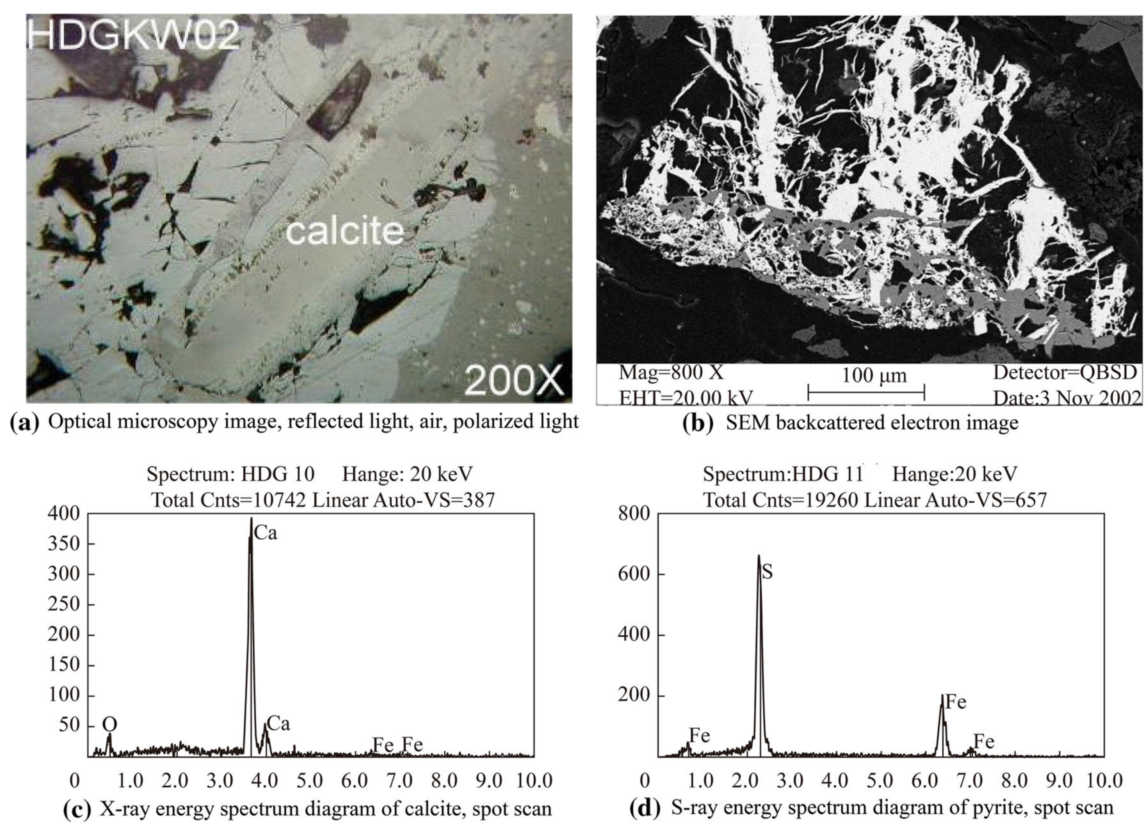


Fig. 9 Pyrite and calcite that fill fractures

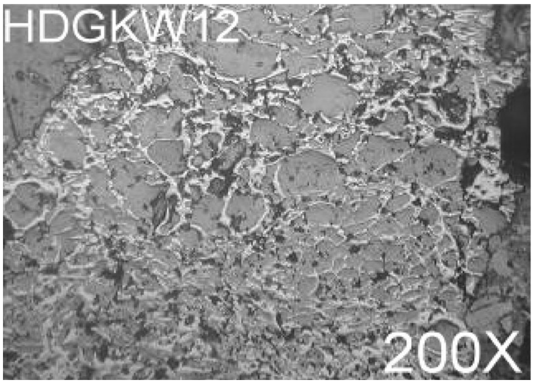


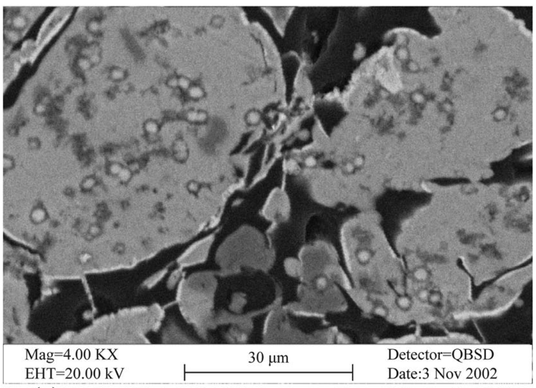
Fig. 10 Calcite in the fusinite lumens (reflected light; air; polarized light; ×200)

2.4 Removability of the trace elements

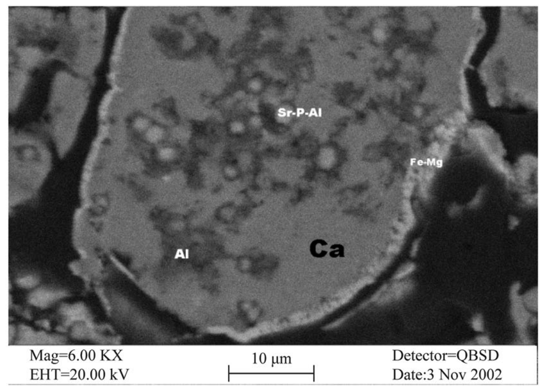
The theoretical degree of trace element removal depends on the organic affinity and on fine coal recovery. It is the ratio of trace element content in waste coal to that in raw coal. Suitable separation density and trace element washability was obtained by float-sink experiments. The theoretical degree of trace element removal from the coal preparation can be calculated using Eq. (6).

$$\lambda = (C - C_r \times FCR)/C \tag{6}$$

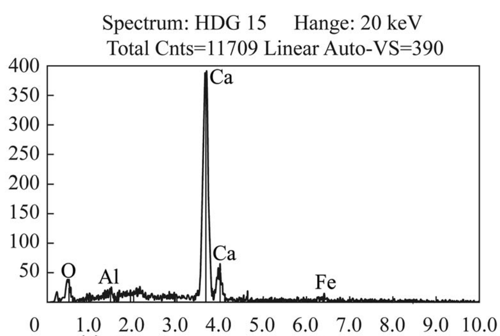
where, λ is the theoretical degree of trace element removal (%), C is the trace element content of the raw coal (μg/g),



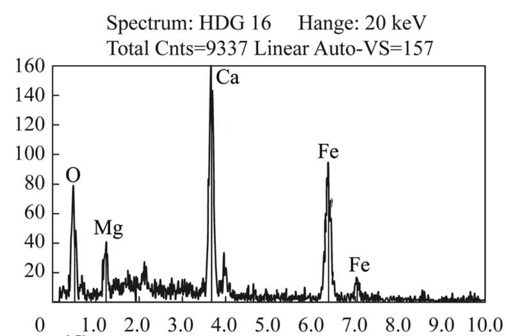
(a) Backscattered electron images of goyazite and calcite (Fe and Mg are enriched at the edge)



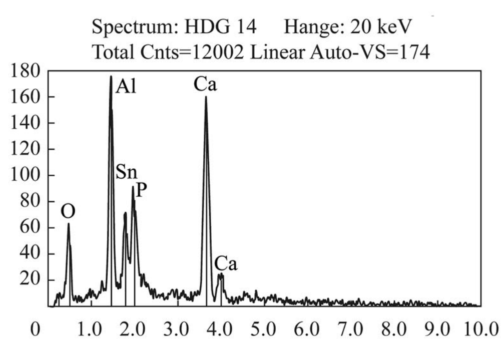
(b) Backscattered electron images of goyazite and calcite (Fe and Mg are enriched at the edge)



(c) X-ray energy spectrum diagram of caltite, scanned area 20μm×30 μm



(d) X-rya energy spectrum diagram of Fe and Ma at the edge of the calcite particle, spot scan



(e) X-ray energy spectrum diagram of goyazite in the calcite particle, spot scan

Fig. 11 Calcite and goyazite (bean-like) in the fusinite lumens

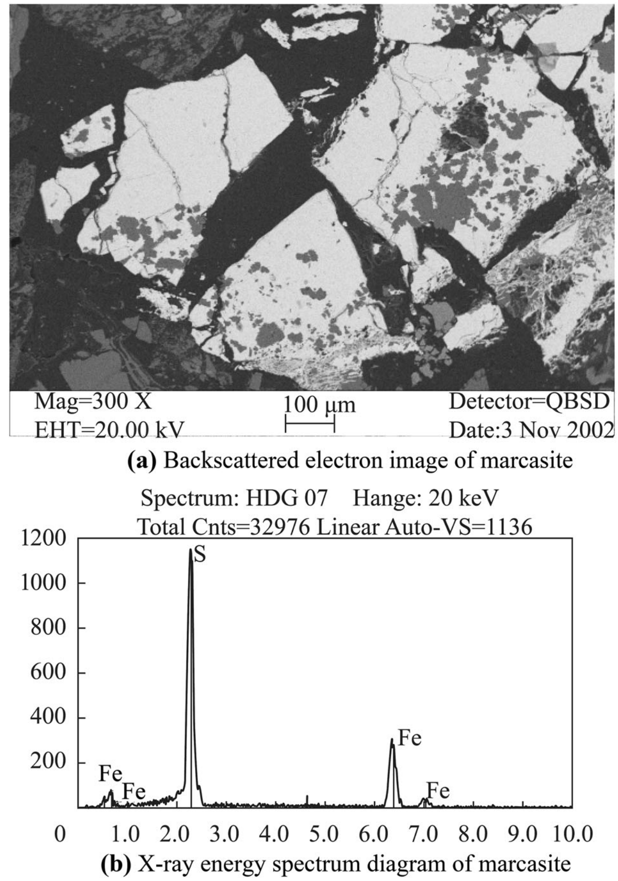


Fig. 12 Marcasite in Heidaigou coal

C_r is the trace element content of the clean coal (μg/g), *FCR* is the fine coal recovery (%).

3 Results and discussions

3.1 Mineralogical composition of No. 6 coal from Heidaigou mine

A high mineral content, dominated by kaolinite, was found in No. 6 coal from Heidaigou mine. Its bauxite content is relatively high while pyrite and quartz are low.

(1) *Clay minerals* Kaolinite is the main clay mineral in Heidaigou coal with some illite also present. Kaolinite is mainly dispersed in thin-layers or as individual particles (Fig. 1) and it is also found in the fusinite lumens. It appears uneven in reflected light with a gray–brown color and the kaolinite has a dim gray to yellow interference color under cross-polarized reflected light. The interference color changes slightly when the stage is rotated. The Si/Al ratio of Kaolinite is between 0.9 and 1.1 (Table 7) indicating a relatively high Al content and a comparatively low Si content. A low impurity content of zircon (Fig. 2), rutile (Fig. 3), chalcopyrite (Fig. 4) and Pb-bearing minerals (Fig. 5) was found in the Kaolinite by SEM–EDX analyses.

(2) *Bauxite* The presence of bauxite in Heidaigou coal results in a relatively high Al_2O_3 content for the coal ash (57.18 %) and a high coal ash fusion temperature (temperature higher than 1,500 °C). A gray reflection color and an uneven surface were found for bauxite while a dim gray–yellow or no interference color was found when using cross-polarized reflected light. The interference color does not change when the stage is rotated. Therefore, it is difficult to distinguish bauxite from kaolinite using optical microscopy. Individual particles (Fig. 6) are the main form of bauxite, which is also found in the fusinite lumens (Fig. 7) and it is intimately intergrown with carbonate minerals (Fig. 8).

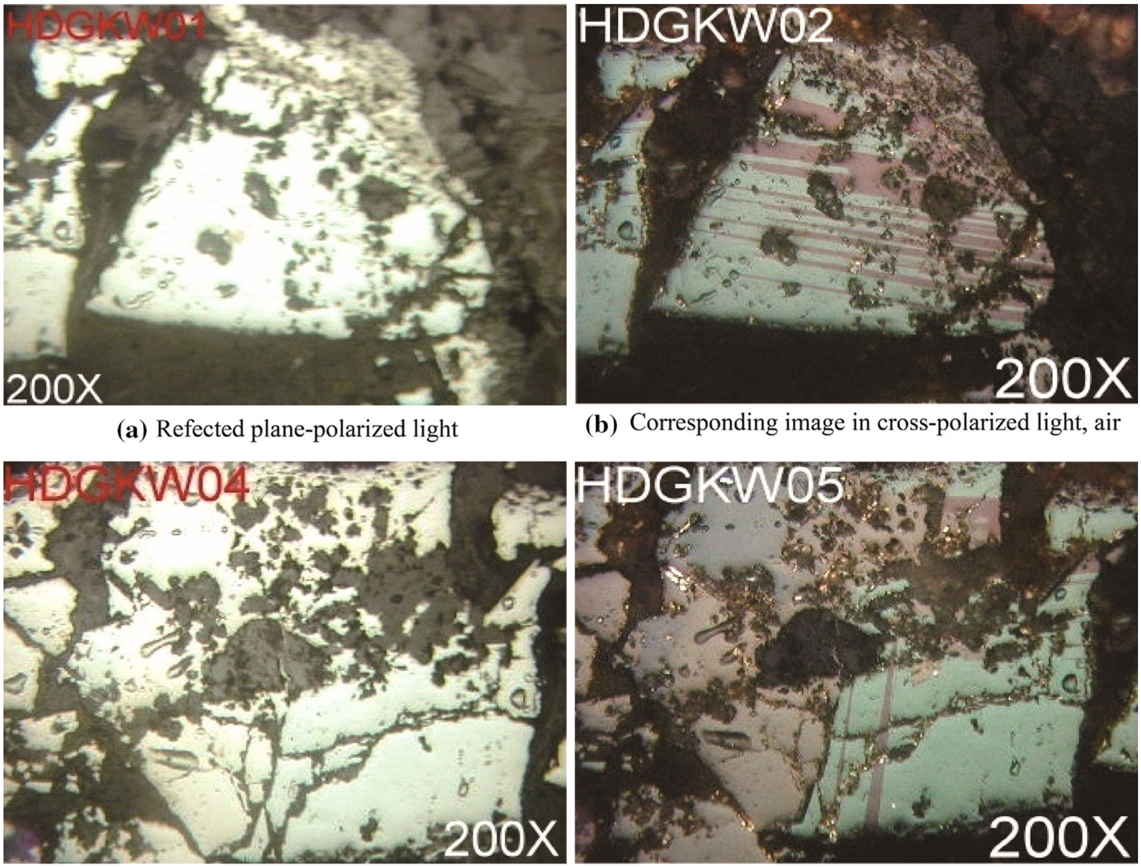
(3) *Carbonates* The carbonate mineral content is relatively high and the dominant mineral is calcite. Calcite mainly fills fractures (Fig. 9a) and cell cavities (Figs. 10, 11a, c). Some calcite was intimately intergrown with pyrite (Fig. 9b) and bauxite (Fig. 8). A significant amount of Fe and Mg that probably displaced Ca as isomorphs were found at the edge of the calcite (Fig. 11b, d). Small amounts of impure minerals such as irregular Al-bearing minerals and bean-like goyazite were found in the calcite particles (Fig. 11b, e).

(4) *Sulfides* The sulfide content mainly comes from sulfides such as pyrite and it is low in coal. The pyrite mainly fills fractures (Fig. 9b) or disseminates in the fine grains. Some marcasite is present in the coal (Fig. 12). A similar yellowish-white reflected color was obtained for marcasite and pyrite when subjected to polarized light and it is thus difficult to distinguish marcasite from pyrite. Marcasite presents obvious anisotropy and it has a parallel twin structure and a dim gray-shallow celadon interference color in cross-polarized reflected light, which is significantly different to that of pyrite (Fig. 13).

3.2 Distributions and occurrence of trace elements in No. 6 coal from Heidaigou mine

3.2.1 Trace element concentrations in the coal samples

The concentrations of 33 trace elements in No. 6 coal from Heidaigou mine were compared to average values of



(a) Refected plane-polarized light
(b) Corresponding image in cross-polarized light, air
(c) Refected plane-polarized light
(d) Corresponding image in cross-polarized light, air

Fig. 13 Comparison between marcasite upon receiving reflected plane-polarized light and cross-polarized light

these trace elements in Chinese and international coals and the data are listed in Table 8. Compared to the average values of trace elements in Chinese coals, the weighted value of the trace elements in Heidaigou coal is relatively low. The concentrations of Ta, Ga, Hg, Th, Se, Pb, U and Ti are 1.5–3 times higher than the average of these elements in Chinese coals while the W, Y, P, Sr contents are almost the same as the average concentrations in Chinese coals. The concentrations of the other trace elements are lower than those in Chinese coals. Compared to the average values of trace elements in international coals the concentrations of Se, Ta, Ti, Th, Hg, Pb, Ga are 3–5 times higher while Sr, Yb, and U are only slightly higher. Concentrations of Y, W, F, V, Sc, P, Be are almost the same as the average content of these elements in international coals. The concentrations of the other trace elements are lower than those in international coals. The ratios of these elemental concentrations in Heidaigou coal to Chinese coals and international coals are shown in Figs. 14 and 15.

3.2.2 *Occurrence of trace elements in No. 6 coal from Heidaigou mine*

The maceral composition and the content of 18 trace elements in the products from the float-sink experiments are listed in Table 9. The maceral compositions in the products of different densities are shown in Fig. 16. The precision of the float-sink experiments was in accordance with GB/T 478-2008, as shown by the balanced ash and sulfur content calculations. The *R* values of most trace elements were between 50 % and 150 %, which are acceptable for trace elements in float-sink experiments (Querol et al. 2001; Reed et al. 2001). The dark reflectance colors of clay minerals and quartz make a quantitative determination in oil immersed reflected light difficult, which results in deviations in the results of the balance calculations.

As shown in Table 9: As, Ga, Hg, Mn, Mo, Ta, Ti, W concentrate in the heavy density products and, therefore, these trace elements are probably present in the minerals. B, P, Sr, V, Y, Yb are mainly present in the organic matter.

Table 8 Element concentrations in No. 6 coal from Heidaigou mine (μg/g)

Element	Concentrations	China coal*	World coal**
Ag	0.02	0.04	0.095
As	1.34	4.09	8.3
B	32.21	53****	52
Ba	18.1	270	150
Be	1.51	1.75	1.6
Cd	0.06	0.81	0.22
Co	1.24	10.62	5.1
Cr	3.00	16.94	16
Cs	0.10	1.51	1.0
Cu	12.53	17.87	16
F	100	157	88
Ga	19.06	6.84	5.8
Ge	0.09	2.43	2.2
Hg	0.413	0.154	0.10
Mn	40.9	271.22****	50
Mo	1.31	2.70	2.2
Ni	3.13	14.44	13
P	219.90	216	230
Pb	31.63	16.64	7.8
Sb	0.09	0.71	0.92
Sc	3.90	4.40	3.9
Se	7.09	2.82	1.3
Sn	0.51	2.11***	1.1
Sr	178.0	195	110
Ta	1.42	0.40	0.28
Th	15.31	5.88	3.3
Ti	2,515	1,685****	500
U	3.51	2.33	2.4
V	27.59	51.18	25
W	1.28	1.05	1.1
Y	10.68	9.07	8.4
Yb	1.58	1.76	1.0
Zn	18.0	41.4***	23

* Bai et al. (2007)

** Ketris and Yudovich (2009)

*** Dai et al. (2012)

**** Ren et al. (1999)

B and V are mainly present in vitrinite while P, Sc, Sr, Y, Yb are present in inertinite. Be and Th are mainly present in inertinite with small amounts found in the minerals. Ge is evenly distributed in the minerals and in the organic matter.

The trace element content of the products of different densities of the No. 6 coal from Heidaigou mine is shown in Fig. 17. The contents of As and Hg in the products of different densities have the same trend as the change in density. This is also the case for Ga, Ta, W, Ti and Mn. The trend for these elements is the same as that of the minerals upon a change in density. Therefore, these trace elements are probably present in the minerals. As the density changes the B and V content of the products of different densities have the same trend as that of vitrinite. Therefore, these trace elements are probably present in the vitrinite. The Be, Th, P, Sc, Yb, Y and Sr content of the products of different densities have the same trend as the change in density. This is the same as the behavior of inertinite. Therefore, these trace elements are probably present in the inertinite.

(1) *Correlation analyses* The relationship between the trace element content and the maceral groups, the ash content, and the sulfur content are listed in Table 10 respectively. The content of trace elements, vitrinite, inertinite, clay minerals, pyrite, quartz, carbonates, ash and sulfur in the 6 products of different densities that were obtained from the float-sink experiments, raw coal and the fines of less than 0.5 mm were used to calculate the correlation coefficients. A significant positive correlation exists between As and the ash content, the sulfur content, the clay mineral content, and the pyrite at a confidence level of 95 % (critical correlation coefficient $R = 0.7068$). This is also the case for Hg and Mo. A significant positive correlation was found between Ga and the ash content, the clay mineral content, the quartz content and the carbonates content. It had a negative correlation with virtrinte and liptinite. This was also the case for Ta, Ti and W. A positive correlation was found between Mn and the carbonates content while a negative correlation exists between Mn and virtrinte. Significant negative correlations exist between Sr and the ash content, the sulfur content, the clay mineral content and the pyrite content. This was also the case for Y and Yb. A significant positive correlation existed between Be and inertinite and a negative correlation with the sulfur content. This was also the case for P, Sc and Th. A significant positive correlation existed between B and virtrinte and a negative correlation exists with inertinite. A significant positive correlation exists between V and virtrinte and a negative correlation exists with the minerals. A significant positive correlation exists between Ge and the sulfur content. The correlation coefficients of the trace elements are listed in Table 11. A significant positive correlation exists among As, Hg, Mo and Ge. This is also the case among Ga, Ta, Ti, W, Mn, among Be, Th, P, Sc, Sr, Y, Yb and between B and

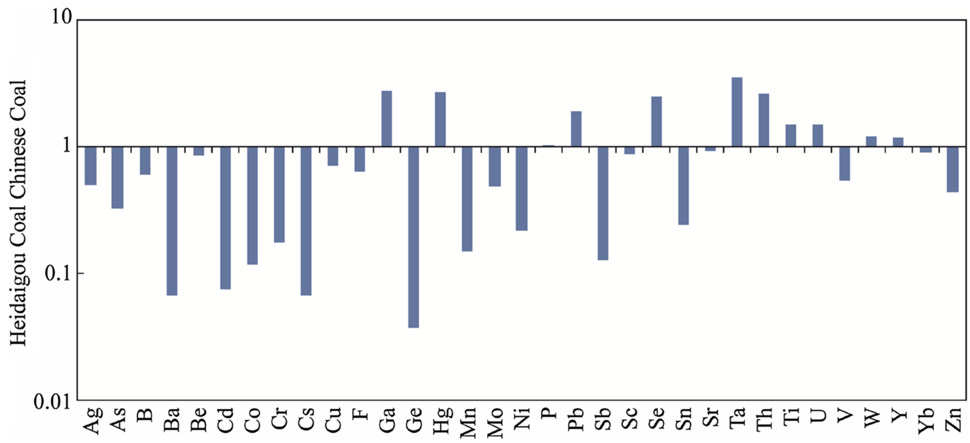


Fig. 14 Comparisons between the concentrations of trace elements in Heidaigou coal and those in other Chinese coals

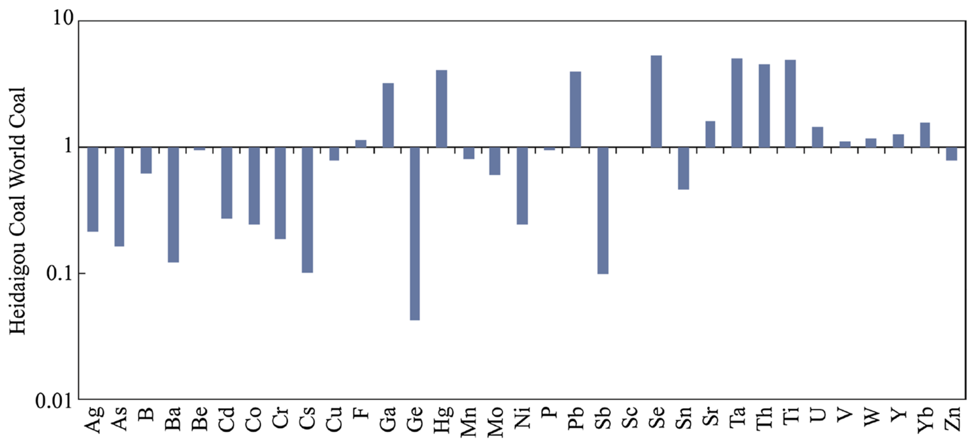


Fig. 15 Comparisons between the concentrations of trace elements in Heidaigou coal and those in international coals

V. High correlation coefficients indicate that these grouped elements have a similar occurrence. As, Hg, Mo, Ge, Ga, Ta, Ti, W, Mn are mainly concentrated in the minerals while Be, Th, P, Sc, Sr, Y, Yb, B, V are mainly found in the organic matter according to the correlation analyses of the trace elements and between the trace elements and the maceral groups.

(2) *Theoretical trace element content in the maceral groups and the minerals in No. 6 coal from Heidaigou mine* The trace element content of the maceral groups and of the minerals can be calculated using float-sink experiments and statistical methods, which is of great importance in determining the trace element occurrence and their behavior during coal processing and conversion. The theoretical content of trace elements in the maceral groups and in the minerals of No. 6 coal from Heidaigou mine are listed in Table 12. A ternary diagram showing the distribution of trace elements is given in Fig. 18. As, Ga, Hg, Mn, Mo, Ta, Ti, W are obviously concentrated in the minerals with low concentrations found in organic matter. B, Be, P, Sc, Sr, Th, V, Y, Yb are concentrated in the organic matter. B and V are mainly present in virtrinte while Be, P, Sc, Sr, Th, Y, Yb are present in inertinite. The Ge content of the minerals and of the organic matter is similar, which indicates an even distribution of Ge in the minerals and in the organic matter (no significant correlation from an F test).

(3) *Organic affinities of the trace elements in No. 6 coal from Heidaigou mine* The organic affinities of the trace elements in No. 6 coal from Heidaigou mine are listed in Table 13. The value for Ta in the raw coal was obtained from a weighted mean value of Ta in the different density products. As shown in Table 13, most of the trace elements are associated with the organics except for As, Hg, Mn, Ta, and W.

Table 9 Maceral compositions and concentrations of 18 trace elements in the products from the float-sink experiments

Size grade (mm)	3–0.5						<0.5	Raw coal	*R* (%)
Yield of production (%)	54.44						45.56		
Density level (kg/L)	−1.30	1.3–1.4	1.4–1.5	1.5–1.6	1.6–1.8	+1.80			
Yield of products of different density (%)	6.29	31.12	19.82	13.34	8.46	20.97			
Coal quality									
A_d (%)	2.62	7.13	14.47	23.89	34.67	68.11	23.15	24.67	99.36
$S_{t,d}$ (%)	0.53	0.46	0.34	0.27	0.33	0.85	0.44	0.49	94.91
Maceral group (vov%)									
Vitrinite	79.09	40.54	14.21	10.56	8.53	5.99	27.62	31.87	80.13
Inertinite	12.55	40.54	65.94	63.34	56.81	22.66	50.90	44.88	105.63
Liptinite	7.27	13.21	5.10	3.84	0.91	0.75	4.69	8.78	63.56
Clay mineral	0.55	4.82	12.75	17.66	28.13	59.93	15.16	11.87	156.17
Pyrite	0.18	0.18	0.18	0.38	0.36	5.81	0.36	0.65	142.70
Quartz	0.18	0.18	1.28	1.54	2.54	2.25	0.36	0.33	249.84
Carbonates	0.18	0.54	0.55	2.69	2.72	2.62	0.90	1.63	72.81
Concentrations of trace element (μg/g)									
As	0.95	0.95	0.95	0.95	0.95	5.97	0.95	1.34	113.97
B	51.77	31.63	23.94	28.53	27.74	26.60	31.80	32.21	94.96
Be	1.11	1.63	2.10	2.03	1.94	0.83	1.63	1.51	106.88
Ga	14.73	14.76	15.27	19.86	25.05	27.10	18.99	19.06	99.65
Ge	0.19	0.13	0.06	0.06	0.06	0.24	0.08	0.09	117.71
Hg	0.063	0.091	0.113	0.155	0.175	0.971	0.342	0.412	76.62
Mn	10.00	13.10	24.60	42.30	48.60	41.70	45.80	40.90	88.39
Mo	1.32	1.05	0.98	1.10	1.37	2.02	1.21	1.31	95.72
P	145.50	253.90	315.00	262.70	200.10	97.57	222.80	219.90	101.38
Sc	2.19	4.28	5.40	5.11	3.75	0.95	5.48	3.90	116.20
Sr	152.40	248.40	258.60	204.00	111.10	41.73	203.60	178.00	108.24
Ta	0.32	0.58	1.02	1.29	1.91	2.51	1.39	1.42	93.24
Th	4.90	14.10	21.33	17.57	16.07	8.21	15.73	15.31	97.83
Ti	1,325.00	1,661.00	2,292.00	2,632.00	3,221.00	3,298.00	2,571.00	2,515.00	97.87
V	48.11	30.81	27.60	28.05	29.86	16.51	29.75	27.59	104.01
W	0.18	0.46	0.89	1.33	1.98	2.19	1.19	1.28	90.70
Y	12.93	15.99	17.08	13.72	9.49	3.53	14.21	10.68	124.58
Yb	1.51	1.80	2.06	1.79	1.45	0.53	1.74	1.58	103.09

The balance calculations for the maceral groups are based on volume fraction

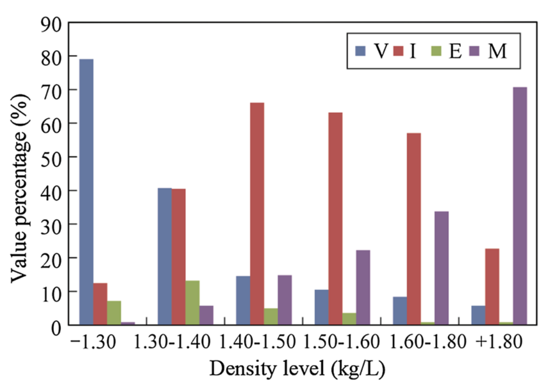


Fig. 16 Histogram of the maceral groups in the products of different densities

Their low organic affinity indicates that these elements are mainly integrated into an inorganic phase. It is worth noting that trace elements with high organic affinity are not necessary organically integrated because some trace elements were present in the fine grained minerals in the organic matter that filled the lumens.

3.3 Removal of trace elements during the coal preparation of No. 6 coal from Heidaigou mine

The washability curves of the trace elements were obtained during coal preparation of No. 6 coal from Heidaigou mine

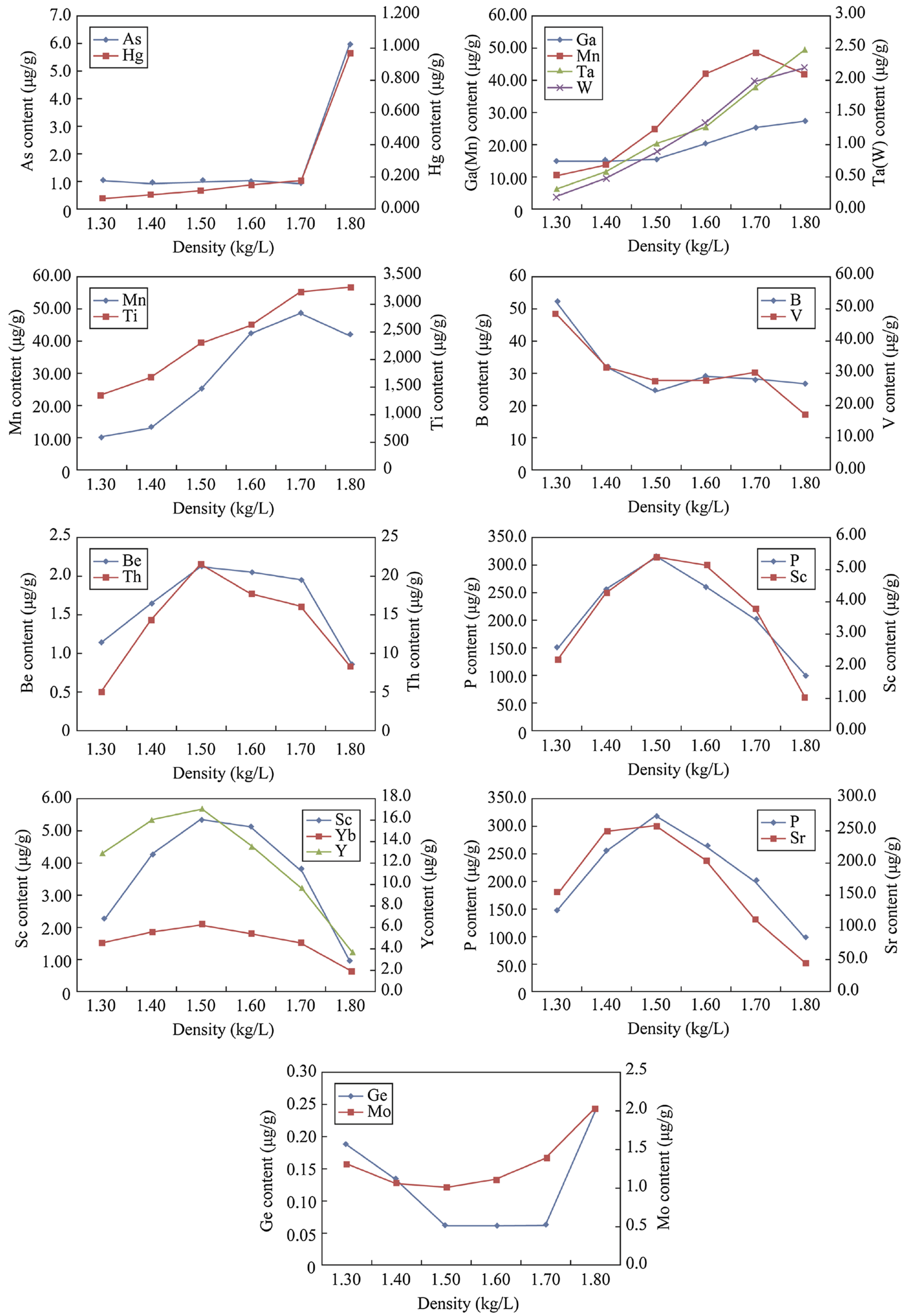


Fig. 17 Trace element content of the products of different densities from No. 6 coal from Heidaigou mine

Table 10 Relationship between trace element content and the maceral group content, the mineral content, the ash content and the sulfur content

Element	A_d	$S_{t,d}$	Vitrinite	Inertinite	Liptinite	Clay mineral	Pyrite	Quartz	Carbonates
As	0.8676	0.8810	−0.3512	−0.4,729	−0.4488	0.8905	0.9990	0.4708	0.4366
B	−0.5092	0.1370	0.9445	−0.7056	0.3505	−0.5078	−0.2594	−0.5762	−0.5163
Be	−0.3976	−0.9342	−0.3833	0.9369	0.0176	−0.3967	−0.6935	0.1181	0.0530
Ga	0.9323	0.4011	−0.6666	−0.0220	−0.7861	0.9056	0.7019	0.8163	0.8776
Ge	0.3744	0.9143	0.3432	−0.9200	−0.0179	0.4243	0.7266	−0.0155	−0.0705
Hg	0.9047	0.8304	−0.4204	−0.3560	−0.4554	0.8706	0.9392	0.3875	0.4869
Mn	0.6685	−0.0540	−0.7474	0.4421	−0.6863	0.5763	0.2755	0.5761	0.7903
Mo	0.8581	0.8630	−0.2093	−0.5941	−0.5389	0.8525	0.9184	0.4830	0.5038
P	−0.5626	−0.8124	−0.2050	0.8307	0.3495	−0.5597	−0.6967	−0.2154	−0.2674
Sc	−0.5142	−0.8395	−0.2097	0.8488	0.2303	−0.5431	−0.7325	−0.2555	−0.2096
Sr	−0.7936	−0.6761	0.1861	0.5303	0.6482	−0.7859	−0.7616	−0.5937	−0.6070
Ta	0.9636	0.4143	−0.7827	0.1020	−0.7567	0.9269	0.7338	0.7698	0.8166
Th	−0.1508	−0.7180	−0.6006	0.9756	−0.0224	−0.1736	−0.4434	0.1487	0.1118
Ti	0.8685	0.1581	−0.8751	0.3399	−0.7930	0.8275	0.5445	0.8169	0.8605
V	−0.7908	−0.3102	0.8760	−0.3295	0.3959	−0.7678	−0.6451	−0.5563	−0.6161
W	0.9155	0.2631	−0.8241	0.2135	−0.7847	0.8774	0.6260	0.8311	0.8875
Y	−0.8823	−0.7275	0.3110	0.4600	0.5839	−0.8518	−0.8419	−0.5803	−0.6737
Yb	−0.8354	−0.8647	0.1817	0.6264	0.4864	−0.8381	−0.9148	−0.4778	−0.5081

and are shown in Fig. 19. The theoretical removal of the trace elements is listed in Table 14. The value for Ta in the raw coal was obtained as a weighted mean value of Ta in the different density products.

The washability curves of As and Hg are similar, which is also the case for Ga and W, Mn, Ta and Ti. High removal rates were obtained for these elements during coal preparation because sharp washability curves were obtained. The elements with flat washability curves are evenly distributed in the organic matter and in the minerals and they cannot be effectively removed during coal preparation.

The ash and sulfur content of the clean coal were 9.18 % and 0.43 %, respectively, and poor washability was obtained for No. 6 coal. The recovery of trace elements is closely related to their washability, as shown in Table 14. Only Hg, Mn, W, Ta, As, Ti, Ga, Mo have high washability. The relationship between organic affinity and the theoretical removal rate of trace elements in No. 6 coal from Heidaigou mine are shown in Fig. 20. The theoretical removal rates of the trace elements decrease as the organic affinity increases. Most trace elements are closely related to the organic matter in No. 6 coal from Heidaigou mine. This is also shown by the correlation analyses and the theoretical concentration calculations of the trace elements in the maceral groups and in the minerals. Therefore, it is difficult to remove these trace elements during coal preparation.

4 Conclusions

Optical microscopy and SEM were used to study the characteristics of minerals and the concentrations of 33 trace elements in No. 6 coal from Heidaigou mine. The distribution of trace elements in the macerals and in the minerals as well as the organic affinity and removability of the trace elements are also discussed.

1. A high mineral content dominated by kaolinite clay minerals was found in No. 6 coal from Heidaigou mine. Bauxite was mainly present as individual particles in the fusinite lumens or was intimately intergrown with carbonate minerals. Its content was relatively high while that of pyrite and quartz was low. Some marcasite with a parallel twin structure, as observed by cross-polarized reflected light, was also

Table 11 Correlation coefficients for the trace elements in No. 6 coal from Heidaigou mine

	As	B	Be	Ga	Ge	Hg	Mn	Mo	P
As	1.0000								
B	−0.2441	1.0000							
Be	−0.7076	−0.4683	−1.0000						
Ga	0.6751	−0.4453	−0.2534	1.0000					
Ge	0.7448	0.4102	−0.9481	0.2056	1.0000				
Hg	0.9333	−0.3136	−0.6535	0.7304	0.5841	1.0000			
Mn	0.2380	−0.5743	0.1855	0.7763	−0.3424	0.4713	1.0000		
Mo	0.9135	−0.0241	−0.7859	0.7817	0.7459	0.8911	0.3393	1.0000	
P	−0.6954	−0.4054	0.8931	−0.5561	−0.8303	−0.6481	−0.0941	−0.8931	1.0000
Sc	−0.7446	−0.3534	0.8758	−0.4517	−0.9009	−0.5996	0.1326	−0.8568	0.9151
Sr	−0.7499	−0.0606	0.6605	−0.8360	−0.6126	−0.7218	−0.4080	−0.9413	0.8986
Ta	0.7099	−0.6181	−0.1930	0.9544	0.1326	0.8090	0.8206	0.7341	−0.4150
Th	−0.4555	−0.7285	0.9033	−0.1204	−0.8875	−0.3329	0.3456	−0.6225	0.8822
Ti	0.5146	−0.7107	0.−637	0.9164	−0.1225	0.6360	0.9053	0.5445	−0.2121
V	−0.6319	0.8771	−0.0125	−0.6477	0.0007	−0.7142	−0.6184	−0.4314	0.0028
W	0.5981	−0.6440	−0.0556	0.9620	0.0024	0.6957	0.8654	0.6463	−0.3345
Y	−0.8313	0.1007	0.6532	−0.8739	−0.5889	−0.8436	−0.4854	−0.9636	0.8363
Yb	−0.9107	0.0012	0.7972	−0.7671	−0.7791	−0.8612	−0.2830	−0.9921	0.9039

	Sc	Sr	Ta	Th	Ti	V	W	Y	Yb
As									
B									
Be									
Ga									
Ge									
Hg									
Mn									
Mo									
P									
Sc	1.0000								
Sr	0.8338	1.0000							
Ta	−0.3262	−0.7140	1.0000						
Th	0.8587	0.6142	0.0500	1.0000					
Ti	−0.1068	−0.5763	0.9640	0.2653	1.0000				
V	0.0285	0.2709	−0.8117	−0.3619	−0.7888	1.0000			
W	−0.2455	−0.6787	0.9829	0.1363	0.9885	−0.7744	1.0000		
Y	0.7964	0.9637	−0.8063	0.5133	−0.6593	0.4673	−0.7581	1.0000	
Yb	0.8845	0.9376	−0.6972	0.6595	−0.5025	0.4100	−0.6146	0.9572	1.0000

Table 12 Theoretical trace element content in the maceral groups and in the minerals of No. 6 coal from Heidaigou mine, calculated values (in μg/g)

Element	Component			Sample amount	Significance testing			
	Vitrinite	Inertinite	Minerals		R	F	$F_{0.05}$ (3, n−4)	Significance
As	1.82	−3.01	7.01	8	0.93	10.73	6.59	Significant
B	54.45	16.34	29.29	8	0.94	12.61	6.59	Significant
Be	0.69	3.19	0.52	8	0.96	18.23	6.59	Significant
Ga	14.37	12.8	31.83	8	0.94	12.42	6.59	Significant
Ge	0.04	0.04	0.04	8	0.97	24.12	6.59	Significant
Hg	0.128	0.114	0.413	7	0.32	0.15	9.28	Non-significant
Mn	11.58	2.78	109.33	7	0.89	5.09	9.28	Non-significant
Mo	1.47	0.28	2.35	8	0.99	72.63	6.59	Significant
P	105.8	460.94	20.28	8	0.56	0.77	6.59	Non-significant
Sc	1.23	9.63	−0.56	8	0.96	22.45	6.59	Significant
Sr	138.63	388.46	−48.11	8	0.94	12.29	6.59	Significant
Ta	0.27	0.66	3.04	8	0.97	24.06	6.59	Significant
Th	1.17	32.64	4.01	8	0.99	82.17	6.59	Significant
Ti	1,082.59	2,404.66	3,738.02	8	0.96	17.89	6.59	Significant
V	46.93	27.65	16.46	8	0.88	5.86	6.59	Significant
W	0.03	0.81	2.71	8	0.96	17.64	6.59	Significant
Y	11.43	24.04	−1.27	8	0.95	15.28	6.59	Significant
Yb	1.26	3.03	0.06	8	0.99	137.42	6.59	Significant

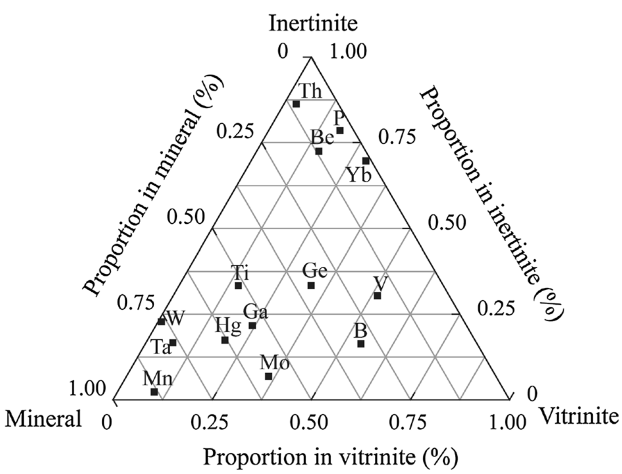


Fig. 18 Ternary diagram showing the distribution of trace elements in No.6 coal

found. A small proportion of bean-like goyazite was found in the calcite.

2. The weighted content of trace elements in Heidaigou formations is relatively low, which is beneficial for coal processing and utilization. The concentrations of Ga, Hg, Pb, Se, Th, Ta are relatively high compared to the average values of Chinese coals.
3. As, Hg, Mo, Ge, Ga, Ta, Ti, W, Mn are mainly concentrated in the minerals while B, Be, Th, P, Sc, Sr, V, Y, Yb are mainly found in the organic matter in No. 6 coal from Heidaigou mine. As, Ge, Hg, Mo are mainly present in sulfides, Be, Th, P, Sc, Sr, Y, Yb are mainly present in inertinite while B and V are mainly present in vitrinite.

Table 13 Organic affinity of the trace elements in No. 6 coal from Heidaigou mine

Element	As	B	Be	Ga	Ge	Hg	Mn	Mo	P
A_o	26.66	77.75	92.11	56.05	–	–	–	51.61	–
Element	**Sc**	**Sr**	**Ta**	**Th**	**Ti**	**V**	**W**	**Y**	**Yb**
A_o	100	100	32.05	93.07	58.93	86.98	33.05	100	99.10

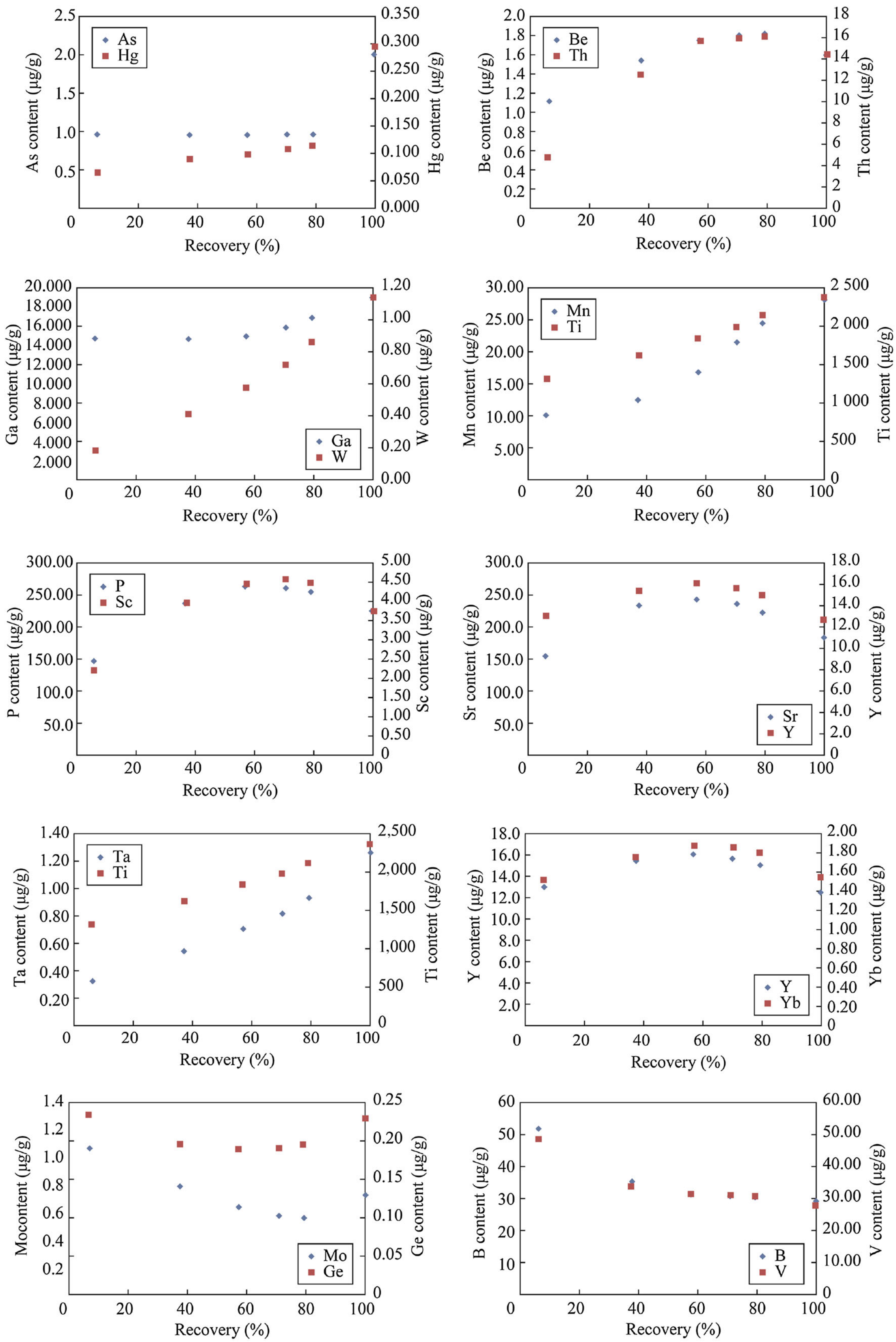


Fig. 19 Washability curves for the trace elements in No. 6 coal from Heidaigou mine

Table 14 Theoretical removal of trace elements in No. 6 coal from Heidaigou mine (Recovery of clean coal was 57.23 % at a separation density of 1.50 kg/L)

Element	As	B	Be	Ga	Ge	Hg	Mn	Mo	P
Theoretical removal rate (%)	59.29	44.60	34.28	55.16	28.64	86.70	76.57	53.92	31.51
Element	Sc	Sr	Ta	Th	Ti	V	W	Y	Yb
Theoretical removal rate (%)	34.87	22.39	71.55	41.71	58.07	34.45	74.05	14.10	32.72

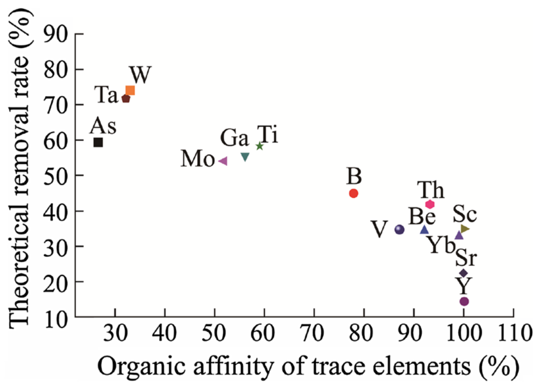


Fig. 20 Relationship between organic affinity and theoretical trace element removal rate in No. 6 coal from Heidaigou mine

4. The high organic affinity and low theoretical removability of most trace elements causes difficulties in their removal during coal preparation.

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References

Bai XF, Li WH, Chen YF, Jiang Y (2007) The general distributions of trace elements in Chinese coals. Coal Qual Technol 1:1–4

Dai SF, Ren DY, Li SS, Chou CL (2006a) A discovery of extremely-enriched Boehmite from coal in the Junger coalfield, the Northeastern Ordos Basin. Acta Geol Sin 80(2):294–300

Dai SF, Ren DY, Li SS (2006b) Discovery of ultra-large gallium deposit in the Junger Coalfield Inner Mongolia. Chin Sci Bull 51(2):177–185

Dai SF, Ren DY, Chou CL, Li SS, Jiang YF (2006c) Mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. Int J Coal Geol 66:253–270

Dai SF, Ren DY, Li SS, Zhao L, Zhang Y (2007) Succession characteristics of coal facies of the main coal seam in Heidaigou mine from the Jungar Coalfield, Inner Mongolia. China Earth Sci D 37(supp.):119–126

Dai SF, Li D, Chou CL, Zhao L, Zhang Y, Ren DY, Ma YW, Sun YY (2008) Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. Int J Coal Geol 74:185–202

Dai SF, Ren DY, Chou CL, Finkelman RB, Seredin VV, Zhou YP (2012) Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. Int J Coal Geol 94:3–21

Han DX (editor in chief) (1996). Coal petrology of China. China University of Mining and Technology Press, Xuzhou

Ketris MP, Yudovich YE (2009) Estimations of Clarkes for carbonaceous biolithes: world averages for trace element contents in black shales and coals. Int J Coal Geol 78:135–148

Klika Z, Kolonaznik I (2000) New concept for the calculation of the trace element affinity in coal. Fuel 79:659–670

Klika Z, Weiss Z, Roubicek V (1997) Calculation of element distributions between inorganic and organic parts of coal. Fuel 76(14/15):1537–1544

Li SS, Ren DY (2006) Analysis of anomalous high concentration of lead and selenium and their origin in the main minable coal seam in the Junger Coalfield. J China Univ Min Technol 35(5): 612–616

Mao JH, Xu HL (1999) Prediction and evaluation of coal resources in China. Science Press, Beijing

Martinez-Tarazona MR, Spears DA, Tascon JMD (1992) Organic affinity of trace elements in Asturian bituminous coals. Fuel 71:909–917

Pires M, Fiedler H, Teixeira EC (1997) Geochemical distribution of trace elements in coal: modeling and environmental aspects. Fuel 76(14/15):1425–1437

Querol X, Klika Z, Weiss Z, Finkelman RB, Alastueya A, Juana R, López-Solera A, Plana F, Kolker A, Chenery SRN (2001) Determination of element affinities by density fractionation of bulk coal samples. Fuel 80:83–96

Reed GP, Ergüdenler A, Grace JR, Watkinson AP, Herod AA, Dugwell D, Kandiyoti R (2001) Control of gasifier mercury emissions in a hot gas filter: the effect of temperature. Fuel 80(5):623–634

Ren DY, Zhao FH, Wang YQ, Yang SJ (1999) Distributions of minor and trace elements in Chinese coals. Int J Coal Geol 40:109–118

Song DY, Zhang XK, Zhang JY, Zheng CG (2010) Migration characteristics of hazardous trace elements in coal in the process of flotation. J China Coal Soc 35(7):1170–1176

Tang YG, Chang CX, Zhang YZ (2005) Migration and distribution of fifteen toxic trace elements during the coal washing of the Kailuan Coalfield Hebei Province. Geochimica 34(4):366–372

Wang WF, Qin Y, Liu XH, Zhao JL, Wang JY, Wu DG, Liu JT (2011) Distribution, occurrence and enrichment causes of gallium in coals from the Jungar Coalfield Inner Mongolia. Sci China Earth Sci 41(2):181–196