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ORIGINAL ARTICLE

# Characteristics of trace elements of the No. 9 coal seam from the Anjialing Mine, Ningwu coalfield, China

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**Abstract** Trace elements of the No. 9 coal seam from Aanjialing mine were measured by ICP–MS. The results indicated that Li, Ga, Cr, Sr, Zr and Pb are significantly enriched in the No. 9 coal seam. The Li and Ga contents in most of the coal seam samples reached an economically valuable level. Most trace elements were enriched near the roof and floor. The data from the Sr/Ba, V/Zn, Th/U, V/Zr and V/Ni ratios reveal that during this period, the peat swamp from this area was formed in swamp water, which was influenced by sea-water or, in an sea-land transition environment, where the ancient water salinity was slightly high. The Eu negative anomaly obviously shows that the rare earth elements are consistent with the terrigenous rocks, so we deduced that the rare earth elements contained in the mineral may mainly come from terrestrial detritus.

**Keywords** Anjialing Mine · Trace elements · Geochemistry · Coal

## 1 Introduction

The study of trace elements in coal is an important research direction in coal geology. The valuable elements of coals have been studied by many geologists (Qin et al. 2005; Deng and Sun 2011; Dai et al. 2011; Wang et al. 2013; Seredin et al. 2013). In the Pingshuo mine district, Ningwu Coalfield, coal resources are abundant. Many have focused on the trace elements in coal from this area (Qin et al. 2005; Sun et al. 2010; Lin and Tian 2011; Wang et al. 2013). The Li, Ga and Al content in the coal from the Pingshuo mining district have reached industrial grade levels (Sun et al. 2013b, 2014). However, the origin, enrichment mechanisms of trace elements and relationship between trace elements and peat moors are still unclear. The Anjialing mine belongs to the Pingshuo mine district. The purpose of this paper is to study the characteristics of trace elements from the No. 9 coal seam from the Anjialing Mine and to further study the enrichment mechanisms of trace elements in the Ningwu coalfield.

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## 2 Geological setting

The Anjialing coal mine is located in the north part of the Shanxi province. The mine district is 6.56 km long (N–S) and 7.84 km wide (W–E), with a total area of 28.88 km$^2$. It belongs to the Ningwu Coalfield, which is in the Ningwu Syncline Basin (Lin and Tian 2011; Sun et al. 2013a). The geological setting of the Ningwu Coalfield has been reviewed in detail by Tang and Liu (1996) and Lin and Tian (2011). This paper only discusses the characteristics of the trace elements from the Coal Seam 9 in the Anjialing Mine. The base rocks of the basin are metamorphic rocks of the Archean Eonothem (Tang and Liu 1996). From the Cambrian to Ordovician, the basin was in the marine environment. Since the Middle Ordovician, the basin was uplifted like the entire northern China and went through a weathering and corroding period of 150 million years. Until the Pennsylvanian, the basin began to receive the Benxi Formation sediments (Fig. 1).

In the Late Carboniferous, this area was in a semi-enclosed bay environment. The sources of the sediment mainly

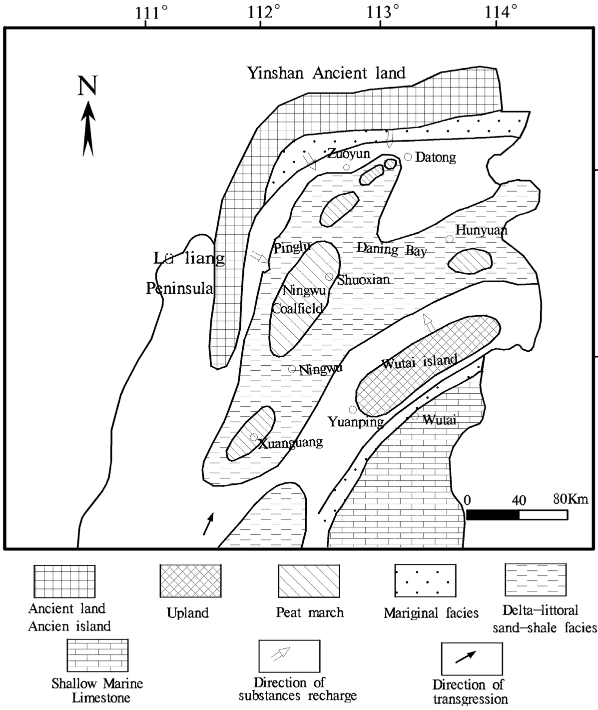


**Fig. 1** Paleogeographic map of the Late Paleozoic in the study area (After Sun et al. 2013a)

came from north of the ancient Yinshan Oldland, west of the Lvliang Peninsula and southeast of the Wutai Island. The transgression mainly came from the south (Fig. 1). The alluvial system had developed before the No.9 coal formed in the southwest and west of this area. This district was mainly composed of delta, coastal tidal flat, littoral subtidal zone and the lagoon. The micro-brackish water peat bogs developed on the leading edge of the delta and the basis of the abandoned tidal flat (Zhuang 1998).

The coal-bearing sequences include the Benxi Formation (Carboniferous), Taiyuan Formation (Carboniferous–Permian) and Shanxi Formation (Lower Permian) with a total thickness of 450–550 m. The Taiyuan Formation is the main coal bearing strata in this mine. There are 10 coal seams. Coal Seam 9 with a thickness between 11.6 and 22.4 m is main seam. The coal reserves of Coal Seam 9 in the Anjialing Mine amount to 450 Mt (Li 2011).

## 3 Samples and methods

Eighteen samples were collected from two sections of the No. 9 Seam in the Anjialing Mine following the Chinese Standard Method GB482-1985. The petrologic composition was investigated on polished block samples in the Key Laboratory of Resource Exploration Research of the Hebei Province (Wang et al. 2011). The samples were cut over an area 10 cm wide and 15 m deep. Thirty-six samples were coal samples (in two sections from top to bottom, A1–A18 and B1–B18); two samples were floor mudstone samples (A Floor and B Floor) and the rest of the samples were parting samples: AP1 (between A3 and A4), AP2 (between A6 and A7), AP3 (between A14 and A15), BP1 and BP2 (between B6 and B7) and BP3 (between B17 and B14).

The samples were crushed and ground to less than 200 mesh. The contents of the 22 trace elements were determined by ICP–MS (inductively coupled plasma mass spectrometry) in the laboratory of the Beijing Research Institute of Uranium Geology and the Key Laboratory of the Resource Exploration Research of Hebei Province. The signal collection of the HR ICP–MS lasted 25 s, and the scanned mass ranges were set at 90–120 and 175–200 amu to cover the target elements (Zhao et al. 2009).

## 4 Results and discussion

### 4.1 General distribution characteristics of trace elements

The arithmetic mean values of the 44 trace elements in the No. 9 seam were compared with the Clark value of the upper crust arithmetic mean of the trace elements in Chinese coal, Late Paleozoic coal in North China and US coal. The results are shown in Table 1, from which we can get the characteristics of the 44 trace elements in the No. 9 coal.

(1) The enrichment factor (EF) is often used to evaluate the element dispersion and enrichment (Gluskoter et al. 1977). The EF values of each element can be seen in Table 1. The EF values of Li, Ga, Sr, Mo, Sb, Dy, Yb, Pb, Bi, Th, U, Zr and Hf are higher than 1, the others are lower than 1. Gluskoter et al. (1977) argued that the elements are enriched if their EF values are higher than 3. Among these 44 trace elements, Li and Sb are observably enriched, while the others are poorly enriched.

(2) Compared with the arithmetic mean of trace elements in Chinese coal statistics (Zhao et al. 2002; Dai et al. 2011), V, Cu, Zn, Y, Ba, La, Ce, Hf and Th are slightly enriched, while Li, Ga, Cr, Sr, Zr and Pb are highly enriched.

(3) Compared with the arithmetic mean of trace elements in North China coal statistics (Dai et al. 2004), Cu, Zn, Y, Pb, La, Ce, Hf and Th are slightly enriched, while Li, Ga, Cr, Sr and Zr are highly enriched.

(4) Compared with arithmetic mean of the trace elements in American coal statistics (Finkelman 1993),

**Table 1** Concentrations (μg/g) and statistical results of trace elements from the No. 9 coal of Anjialing Mine

| Element | Max | Min | AM | Clark value of upper crust[a] | Sample no. | EF | North China[b] | Chinese coal[c] | US coal[d] |
|---|---|---|---|---|---|---|---|---|---|
| Li | 408.00 | 43.00 | 140.50 | 20.00 | 18 | 7.02 | 14.00 | 14.00 | 16.00 |
| Be | 2.41 | 0.45 | 1.15 | 2.80 | 18 | 0.41 | 2.05 | 2.00 | 2.20 |
| Sc | 18.10 | 1.39 | 5.89 | 22.00 | 18 | 0.27 | 6.32 | 49.00 | 4.20 |
| V | 105.00 | 7.54 | 33.11 | 135.00 | 18 | 0.25 | 38.00 | 21.00 | 22.00 |
| Cr | 59.60 | 7.65 | 24.87 | 100.00 | 18 | 0.25 | 14.98 | 12.00 | 15.00 |
| Co | 6.77 | 0.49 | 1.93 | 25.00 | 18 | 0.08 | 6.00 | 7.00 | 6.10 |
| Ni | 11.60 | 1.71 | 4.99 | 75.00 | 18 | 0.07 | 18.00 | 14.00 | 14.00 |
| Cu | 42.20 | 3.30 | 18.75 | 55.00 | 18 | 0.34 | 18.00 | 13.00 | 16.00 |
| Zn | 199.00 | 4.01 | 46.35 | 70.00 | 18 | 0.66 | 30.00 | 35.00 | 53.00 |
| Ga | 82.80 | 3.46 | 24.80 | 15.00 | 18 | 1.65 | 12.57 | 9.00 | 5.70 |
| Rb | 45.60 | 0.09 | 5.75 | 90.00 | 18 | 0.06 | 6.00 | 8.00 | 21.00 |
| Sr | 4669.00 | 33.10 | 497.56 | 375.00 | 18 | 1.33 | 150.00 | 136.00 | 130.00 |
| Y | 42.20 | 4.86 | 16.38 | 33.00 | 18 | 0.50 | 9.00 | 8.00 | 8.50 |
| Nb | 50.60 | 1.40 | 13.97 | 20.00 | 18 | 0.70 | 28.00 | 14.00 | 2.00 |
| Mo | 5.96 | 0.61 | 2.07 | 1.50 | 18 | 1.38 | 4.00 | 4.00 | 3.30 |
| Cd | 0.42 | 0.02 | 0.11 | 0.20 | 18 | 0.54 | 0.50 | 0.20 | 0.47 |
| In | 0.17 | 0.01 | 0.06 | – | 18 | – | – | – | – |
| Sb | 3.09 | 0.13 | 0.82 | 0.20 | 18 | 4.08 | 0.60 | 2.00 | 1.20 |
| Cs | 4.30 | 0.01 | 0.48 | 3.00 | 18 | 0.16 | 1.00 | 1.00 | 1.10 |
| Ba | 311.00 | 15.00 | 84.92 | 425.00 | 18 | 0.20 | 94.00 | 82.00 | 170.00 |
| La | 114.00 | 1.78 | 29.25 | 30.00 | 18 | 0.98 | 26.07 | 24.00 | – |
| Ce | 168.00 | 2.89 | 49.15 | 60.00 | 18 | 0.82 | 47.62 | 45.00 | – |
| Pr | 22.10 | 0.39 | 5.87 | 8.20 | 18 | 0.72 | – | – | – |
| Nd | 76.20 | 1.64 | 20.87 | 28.00 | 18 | 0.75 | 21.78 | 21.18 | – |
| Sm | 11.40 | 0.47 | 3.61 | 6.00 | 18 | 0.60 | 3.99 | 3.80 | – |
| Eu | 2.43 | 0.10 | 0.68 | 1.20 | 18 | 0.57 | 0.72 | 0.74 | – |
| Gd | 9.75 | 0.63 | 3.15 | 5.40 | 18 | 0.58 | – | – | – |
| Tb | 1.53 | 0.15 | 0.59 | 5.40 | 18 | 0.11 | 0.30 | 0.54 | – |
| Dy | 8.24 | 0.90 | 3.28 | 3.00 | 18 | 1.09 | – | – | – |
| Ho | 1.53 | 0.18 | 0.61 | 1.20 | 18 | 0.51 | – | – | – |
| Er | 4.42 | 0.53 | 1.75 | 2.80 | 18 | 0.62 | – | – | – |
| Tm | 0.71 | 0.08 | 0.28 | 4.80 | 18 | 0.06 | – | – | – |
| Yb | 4.56 | 0.52 | 1.76 | 0.90 | 18 | 1.96 | 1.49 | 1.47 | – |
| Lu | 0.71 | 0.08 | 0.26 | 0.50 | 18 | 0.53 | 0.07 | 0.26 | – |
| Ta | 3.62 | 0.05 | 0.78 | 2.00 | 18 | 0.39 | 0.60 | 0.70 | 0.22 |
| W | 3.97 | 0.17 | 1.01 | 1.50 | 18 | 0.67 | 2.00 | 2.00 | 1.00 |
| Re | 0.003 | 0.00 | 0.00 | 0.10 | 18 | 0.01 | – | – | – |
| Tl | 0.49 | 0.01 | 0.10 | 0.43 | 18 | 0.22 | 0.40 | 0.40 | 1.20 |
| Pb | 61.30 | 4.67 | 21.42 | 12.50 | 18 | 1.71 | 21.00 | 13.00 | 11.00 |
| Bi | 1.47 | 0.06 | 0.42 | 0.17 | 18 | 2.45 | 0.80 | 0.80 | <1.00 |
| Th | 34.70 | 1.53 | 10.54 | 9.60 | 18 | 1.10 | 7.56 | 6.00 | 3.20 |
| U | 6.46 | 0.43 | 2.76 | 2.70 | 18 | 1.02 | 3.26 | 3.00 | 2.10 |
| Zr | 557.00 | 46.80 | 233.47 | 165.00 | 18 | 1.41 | 62.00 | 52.00 | 27.00 |
| Hf | 13.30 | 1.38 | 6.41 | 3.00 | 18 | 2.14 | 3.00 | 2.40 | 0.73 |

*AM* arithmetic mean, *EF* arithmetic mean/clark value, – not detected

[a] Taylor (1964)

[b] Dai et al. (2003)

[c] Zhao et al. (2002)

[d] Finkelman (1993)

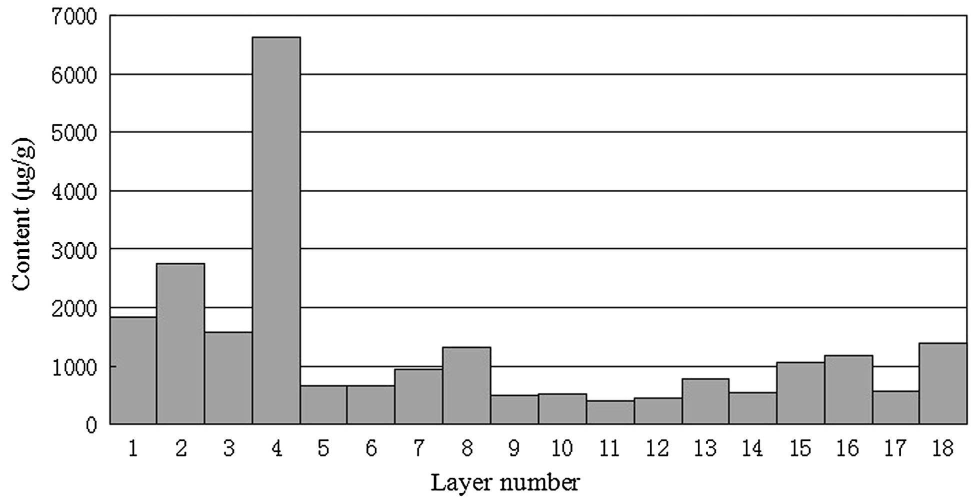


**Fig. 2** The content comparison of 44 selected trace elements from the 9th coal

Sc, V, Cu, Y and U are slightly enriched, while Li, Ga, Cr, Sr, Th, Pb, Zr and Hf and are highly enriched.

(5) The valuable Li and Ga contents are high in the No. 9 coal seam. Compared with the arithmetic mean of the trace elements in China coal, the content of harmful elements such as Sr, Sb, Th and U are high, and more attention should be paid to them.

(6) The total trace element contrast diagram used ICP data of all the samples of the No. 9 coal seam (Fig. 2). The change of trace elements in the vertical section can be seen from the figure. As a whole, it is relatively higher in the upper part. The elements in the fourth layer appear unusually high, which results from the extremely high content of Sr (The content of Sr is 1792 μg/g in the second layer and 4669 μg/g in the fourth layer). Contents of the elements are relatively stable in the lower parts.

## 4.2 Relationship among elements

In order to understand the relationship among the 23 elements in the No. 9 coal of Anjialing Mine, correlation analysis and cluster analysis are used in this study.

### *4.2.1 Correlation analysis*

Using correlation analysis and cluster analysis, combined with the geochemical properties of the elements, we indirectly discussed the occurrence of trace elements in coal. It is an important method to research the occurrence of trace elements in coal. After a standardizing pretreatment to the raw data, the resulting correlation analysis results of the trace elements are presented in Table 2.

A strong correlation exists between Li and Ta (0.81), Li and Th (0.81), Cr and Rb (0.83), Rb and Cs (0.985), Nb and Ta (0.84), Th (0.85), Zr (0.84) and Hf (0.86). All of these elements are lithophile elements. Relationships among Li, Rb, Th, Cr, Nb, Ta and Cs are probably associated with clay minerals.

There are also significant positive correlations between V and Ba (0.83), V and Ni (0.88), V and Cu (0.68), U and Ga (0.69), Ni and Ba (0.84), Cu and Cd (0.70), Zn and Cd (0.69), Ga and U (0.69). Most of them are thiophile elements. Relationships between them may be related to sulphide.

### *4.2.2 Cluster analysis*

Cluster analysis can provide quantifiable indicators to measure the similarity of elements. With these indicators, we divided the elements into different categories. Thus, the essential relationship among elements became apparent. We then classified and evaluated the elements (Chun 2007). According to results from the R cluster analysis based on the correlation matrix, elements were grouped by a calculated step by step mapping method (Hu 1984). Then a hierarchical tree structure figure of the 30 trace elements was made (Fig. 2).

From Fig. 3 we can see the 30 trace elements selected are divided into seven groups:

(1) Group 1 includes Zr, Hf, Nb, Ta, Th, Li, Pb, In and Bi, all of which show high values in the upper coal seam (Fig. 1). Studies showed that the clay minerals in coal were the main carrier of Li (Finkelman 1980). From our calculations we can see that the correlation coefficients of Li, Al and Si, Al are 0.802 and 0.828, respectively. The correlation coefficients of Pb, Bi, Th and Si are all above 0.7, showing that

**Table 2** Correlation matrix of trace elements from 9th in Anjialing Mine

| | Li | Be | Sc | V | Cr | Co | Ni | Cu | Zn | Ga | Rb | Y | Nb | Cd | Cs | Ba | REE | Ta | Pb | Th | U | Zr | Hf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 1.00 | | | | | | | | | | | | | | | | | | | | | | |
| Be | 0.61 | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| Sc | 0.52 | 0.82 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| V | 0.41 | 0.56 | 0.76 | 1.00 | | | | | | | | | | | | | | | | | | | |
| Cr | 0.59 | 0.57 | 0.76 | 0.69 | 1.00 | | | | | | | | | | | | | | | | | | |
| Co | -0.05 | 0.35 | 0.58 | 0.77 | 0.46 | 1.00 | | | | | | | | | | | | | | | | | |
| Ni | 0.36 | 0.45 | 0.68 | 0.88 | 0.70 | 0.81 | 1.00 | | | | | | | | | | | | | | | | |
| Cu | 0.48 | 0.55 | 0.60 | 0.68 | 0.54 | 0.44 | 0.56 | 1.00 | | | | | | | | | | | | | | | |
| Zn | 0.17 | 0.50 | 0.51 | 0.45 | 0.32 | 0.52 | 0.41 | 0.59 | 1.00 | | | | | | | | | | | | | | |
| Ga | 0.02 | 0.29 | 0.51 | 0.62 | 0.50 | 0.65 | 0.70 | 0.47 | 0.36 | 1.00 | | | | | | | | | | | | | |
| Rb | 0.54 | 0.61 | 0.79 | 0.76 | 0.83 | 0.63 | 0.69 | 0.52 | 0.42 | 0.30 | 1.00 | | | | | | | | | | | | |
| Y | 0.29 | 0.76 | 0.85 | 0.65 | 0.49 | 0.55 | 0.56 | 0.37 | 0.26 | 0.38 | 0.60 | 1.00 | | | | | | | | | | | |
| Nb | 0.60 | 0.44 | 0.71 | 0.62 | 0.71 | 0.30 | 0.53 | 0.43 | 0.22 | 0.47 | 0.61 | 0.55 | 1.00 | | | | | | | | | | |
| Cd | 0.43 | 0.62 | 0.70 | 0.65 | 0.45 | 0.45 | 0.47 | 0.70 | 0.69 | 0.47 | 0.50 | 0.47 | 0.60 | 1.00 | | | | | | | | | |
| Cs | 0.50 | 0.59 | 0.80 | 0.78 | 0.82 | 0.64 | 0.68 | 0.48 | 0.40 | 0.29 | 0.99 | 0.64 | 0.62 | 0.48 | 1.00 | | | | | | | | |
| Ba | 0.41 | 0.66 | 0.70 | 0.83 | 0.67 | 0.80 | 0.84 | 0.60 | 0.50 | 0.55 | 0.75 | 0.69 | 0.55 | 0.53 | 0.75 | 1.00 | | | | | | | |
| REE | 0.32 | 0.64 | 0.75 | 0.73 | 0.50 | 0.75 | 0.72 | 0.56 | 0.54 | 0.42 | 0.66 | 0.78 | 0.43 | 0.55 | 0.70 | 0.86 | 1.00 | | | | | | |
| Ta | 0.81 | 0.60 | 0.72 | 0.60 | 0.83 | 0.21 | 0.51 | 0.62 | 0.44 | 0.37 | 0.71 | 0.40 | 0.84 | 0.65 | 0.69 | 0.55 | 0.42 | 1.00 | | | | | |
| Pb | 0.88 | 0.57 | 0.56 | 0.48 | 0.53 | -0.01 | 0.31 | 0.60 | 0.18 | 0.10 | 0.49 | 0.35 | 0.71 | 0.60 | 0.46 | 0.39 | 0.35 | 0.77 | 1.00 | | | | |
| Th | 0.81 | 0.71 | 0.83 | 0.62 | 0.79 | 0.23 | 0.47 | 0.58 | 0.38 | 0.30 | 0.75 | 0.59 | 0.85 | 0.69 | 0.74 | 0.56 | 0.50 | 0.94 | 0.82 | 1.00 | | | |
| U | 0.24 | 0.63 | 0.82 | 0.57 | 0.54 | 0.48 | 0.48 | 0.51 | 0.32 | 0.69 | 0.46 | 0.78 | 0.62 | 0.59 | 0.49 | 0.52 | 0.62 | 0.52 | 0.34 | 0.63 | 1.00 | | |
| Zr | 0.58 | 0.52 | 0.76 | 0.68 | 0.72 | 0.33 | 0.53 | 0.45 | 0.42 | 0.48 | 0.63 | 0.46 | 0.84 | 0.69 | 0.63 | 0.44 | 0.39 | 0.83 | 0.68 | 0.83 | 0.57 | 1.00 | |
| Hf | 0.67 | 0.57 | 0.77 | 0.66 | 0.74 | 0.28 | 0.50 | 0.45 | 0.38 | 0.40 | 0.67 | 0.48 | 0.86 | 0.68 | 0.67 | 0.45 | 0.40 | 0.86 | 0.74 | 0.88 | 0.56 | 0.99 | 1.00 |

N = 18

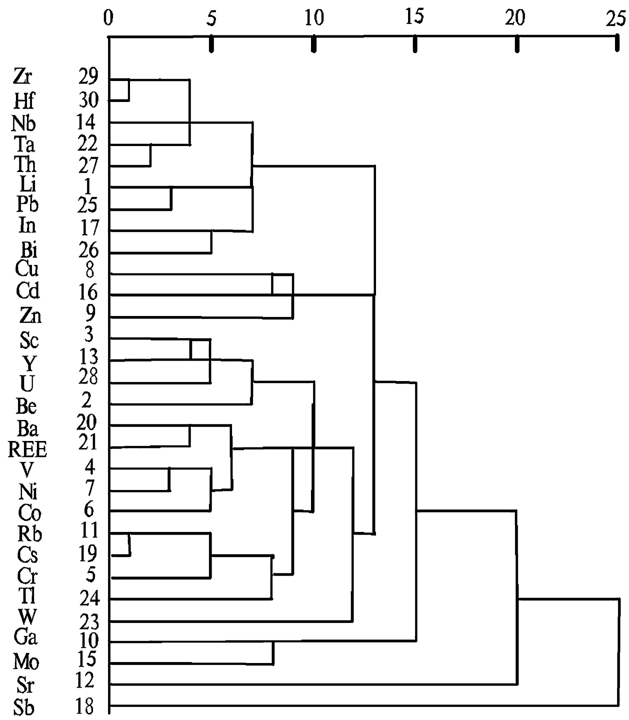


**Fig. 3** R cluster analysis of selected trace elements

these elements are related to clay minerals. The elements may mainly concentrate in clay mineral, which means clay mineral is their main carrier.

(2) Group 2 is composed of Cu, Cd and Zn, all of which are sulphophile elements. Their occurrence state associates with sulfide.

(3) Group 3 consisted of Sc, Y, U, Be, Ba, REE, V, Ni, Co, Rb, Cs, Cr and Tl. This group can be further divided into four sub-groups by the characteristics of the elements. Sc, Y, U, Be compose the first sub-group, which show a strong positive correlation with Si and Al and a strong negative correlation with Ga. This phenomenon reveals that the elements are mainly associated with terrigenous clay mineral. Ba and REE compose the second sub-group. The meteorites standardized curve of rare earth elements shows that the rare earth elements are in accordance with terrigenous rocks and are close to the source, but the supply is from a different sedimentary environment. Ba is a kind of continental element. V, Ni and Co compose the third sub-group, which are all thalassophile elements. Rb, Cs, Cr and Tl compose the forth sub-group. As a result of complex coal forming process, the trace elements in coal are affected by different factors, including inorganic factors and organic factors.

(4) W is the only element in the fourth group. The fifth group is comprised of Ga and Mo. Sr and Sb are, respectively, the only element in the sixth and seventh group. They both have no significant correlation with other elements.

In conclusion, elements which related to clay minerals include Th, Li, Nb, Ta, Pb, Bi, Sc, Y, U, Be, Ba, REE, Rb, Cs, Cr and T. Trace elements which are related to sulfide minerals mainly include Cu, Cd, Zn, V, Co, Ni and so on, among which Co and Ni are always present isomorphism interfused other thing. The state of elements in coal is related to the geochemical behavior of soil, rock and mineral. Thus, the elements were affected by seawater and terrigenous sediment, which reflected the characteristics of marine-continental transitional facies.

### 4.3 The vertical distribution of trace elements

The elements content analysis (Fig. 4) shows that the trace elements relatively tend to concentrate near the bottom of the coal seams, mostly in the 8th layer. The element enrichment in the coal seam near the roof and floor may be caused by the exchange of elements between the roof and floor. The main factors of this phenomenon are downward infiltration of ore solution, groundwater, etc. during the period of mudstone deposit or the late diagenetic process. Mineral is the most likely host of trace elements, so the enrichment of trace elements can also explain why mineral components in coal are relatively high.

## 5 Sedimentary environment significance of trace elements

Some trace elements have the sedimentary environment indicator significance (Sun et al. 1995). Based on their affinity, they can be divided into continental elements (Ba, Ga, Zr, Ti, Th, Zn etc.) and thalassophile elements (Sr, B, Li, V, Ni, U, Cu etc.) (Qin et al. 2005).

Due to the geochemical differences between Sr and Ba in a supergene environment, the content of Sr is high and that of Ba is low in marine sediments. Therefore the Sr/Ba ratio can be used to judge the sedimentary environment of coal seam. The Sr/Ba ratio in freshwater sediments is usually lower than 1, but in marine sediments it is usually higher than 1 (Shi et al. 2003; Sun et al. 1997). The V/Ni radio is higher in marine deposits than in continental deposits, and it increases with the ancient water salinity (Tu 1982). The V/Zn radio is lower than 1.33 in continental deposits, higher than 3.59 in the marine deposit. In sea-land transitional deposit, it falls between 1.33 and 3.59 (Qin et al. 2005). The Th/U radio is higher than 7 in continental deposits and lower than 7 in marine deposits (Bouska 1981).

As Table 3 shows, all the Sr/Ba ratios in these samples are higher than 1 (except 9–1, 9–3 and 9–18). All the Th/U ratios in these samples are higher than 7 (except 9–3). All the V/Ni ratios in these samples are higher than 4. The average mean of the V/Ni ratios of the 18 samples is 6.77.

The above data reveals that the peat swamp in this area was formed in swamp water that was influenced by seawater or in a sea-land transition environment, where the ancient water salinity was slightly high. This corresponds to previous studies that pointed out that this area was in the delta sedimentary system during the Late Carboniferous (Guo et al. 1998; Sun et al. 2002).

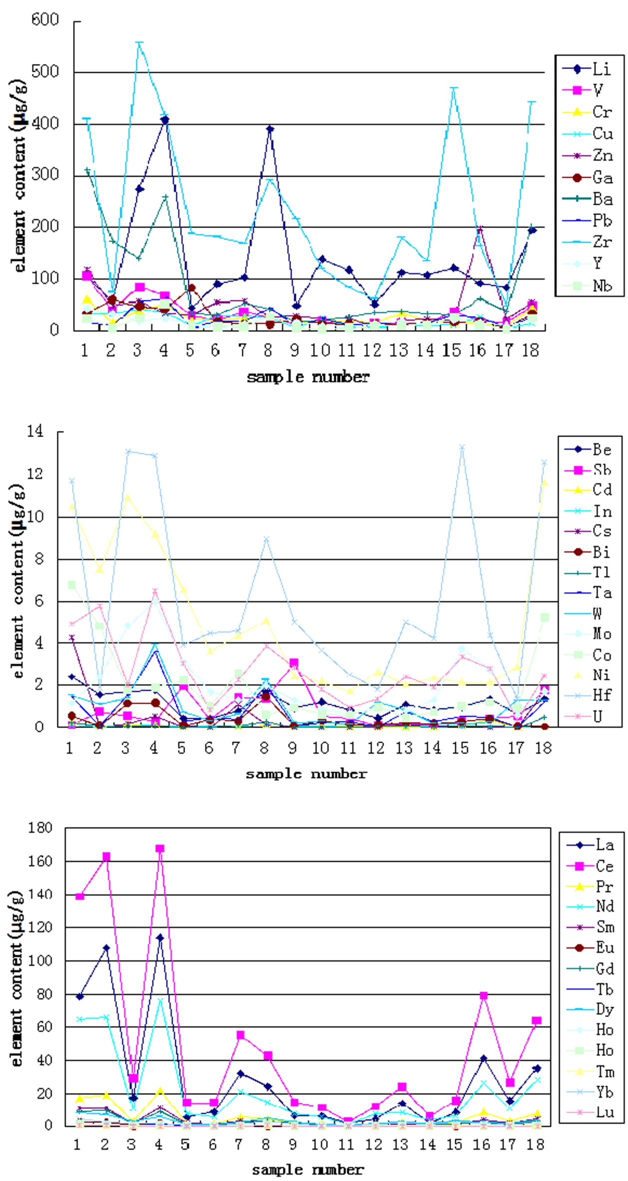


**Fig. 4** The content distribution of 43 trace elements selected from the 9# coal

## 6 Rare earth element

There are many geochemical parameters of rare earth elements, but ∑REE, LREE, HREE, LREE/HREE, $(La/Yb)_N$, δEu and δCe are commonly used to reflect their characteristics (Zhao et al. 2012). ∑REE reflects the total content of rare earth elements, LREE reflects the content of light rare earth elements, HREE reflects the content of heavy rare earth elements and LREE/HREE reflects the degree of enrichment of light rare earth element and heavy rare earth elements. The ratio is small, which means a relative depletion of light rare earth elements. $(La/Yb)_N$ is the ratio of La and Yb after standardized by chondrite, which reflects the relative degree of differentiation of rare earth elements. δEu and δCe reflect the extent of the Eu and Ce anomaly reaction. Usually, 1 is the dividing line: the ratio greater than 1 indicates a positive anomaly; otherwise, a negative anomaly.

According to the test on the content of rare earth elements, we deduced the corresponding parameters of the rare earth element (Table 4), and drew its distribution pattern (Fig. 5).

Table 4 shows that ΣREE concentrations of all the samples range from 10.34 to 415.65 μg/g, with a arithmetic average of 121.1 μg/g. This is higher than the average content in world coals (46.3) put forward by Valcovic (1983). The LREE concentration varied from 7.27 μg/g to 393.68 μg/g, the average was 109.43 μg/g. The HREE ranged from 3.07 to 30.78 μg/g, the average was 11.67 μg/g. The LREE/HREE ranged from 2.03 to 17.92 μg/g, the

**Table 3** Parameters of the trace elements

| Sample number | Sr/Ba | V/Zn | Th/U | V/Zr | V/Ni |
|---|---|---|---|---|---|
| 9–1 | 0.36 | 0.89 | 4.41 | 0.26 | 10.00 |
| 9–2 | 10.42 | 0.83 | 0.50 | 0.52 | 5.17 |
| 9–3 | 0.69 | 1.48 | 7.67 | 0.15 | 7.72 |
| 9–4 | 18.10 | 2.00 | 5.37 | 0.16 | 7.28 |
| 9–5 | 3.81 | 0.96 | 1.22 | 0.15 | 4.42 |
| 9–6 | 4.45 | 0.37 | 4.29 | 0.11 | 5.47 |
| 9–7 | 4.88 | 0.63 | 3.93 | 0.21 | 8.19 |
| 9–8 | 5.07 | 0.90 | 6.91 | 0.08 | 4.75 |
| 9–9 | 3.75 | 0.40 | 1.08 | 0.05 | 4.77 |
| 9–10 | 4.07 | 0.86 | 3.12 | 0.15 | 7.99 |
| 9–11 | 2.55 | 0.31 | 4.09 | 0.09 | 4.41 |
| 9–12 | 4.74 | 3.72 | 1.91 | 0.25 | 5.62 |
| 9–13 | 7.16 | 0.67 | 3.79 | 0.08 | 6.62 |
| 9–14 | 3.64 | 0.62 | 4.63 | 0.10 | 5.49 |
| 9–15 | 5.63 | 1.92 | 3.63 | 0.08 | 16.78 |
| 9–16 | 5.93 | 0.08 | 3.36 | 0.10 | 7.80 |
| 9–17 | 7.34 | 0.74 | 3.60 | 0.33 | 5.28 |
| 9–18 | 0.16 | 0.88 | 6.18 | 0.11 | 4.04 |

**Table 4** The parameters of REE (μg/g)

| Sample number | ΣREE | LREE | HREE | LREE/HREE | $(La/Yb)_N$ | δEu | δCe |
|---|---|---|---|---|---|---|---|
| 9–1 | 343.93 | 313.15 | 30.78 | 10.17 | 11.69 | 0.70 | 0.85 |
| 9–2 | 396.06 | 369.33 | 26.73 | 13.82 | 25.43 | 0.70 | 0.78 |
| 9–3 | 74.98 | 64.10 | 10.89 | 5.89 | 6.04 | 0.67 | 0.86 |
| 9–4 | 415.65 | 393.68 | 21.97 | 17.92 | 37.40 | 0.58 | 0.74 |
| 9–5 | 37.39 | 31.66 | 5.73 | 5.53 | 4.40 | 0.62 | 1.05 |
| 9–6 | 35.33 | 31.67 | 3.65 | 8.67 | 9.92 | 0.66 | 0.84 |
| 9–7 | 128.31 | 118.89 | 9.42 | 12.62 | 15.95 | 0.64 | 0.88 |
| 9–8 | 107.41 | 90.26 | 17.15 | 5.26 | 5.33 | 0.54 | 0.92 |
| 9–9 | 41.58 | 32.74 | 8.84 | 3.71 | 3.37 | 0.54 | 0.97 |
| 9–10 | 32.69 | 27.38 | 5.31 | 5.16 | 4.90 | 0.57 | 0.84 |
| 9–11 | 10.34 | 7.27 | 3.07 | 2.37 | 2.33 | 0.57 | 0.78 |
| 9–12 | 37.25 | 29.41 | 7.85 | 3.75 | 2.85 | 0.51 | 1.01 |
| 9–13 | 61.61 | 51.71 | 9.90 | 5.22 | 5.22 | 0.54 | 0.89 |
| 9–14 | 20.96 | 14.05 | 6.91 | 2.03 | 1.31 | 0.48 | 1.06 |
| 9–15 | 46.60 | 35.04 | 11.56 | 3.03 | 2.39 | 0.51 | 0.90 |
| 9–16 | 171.18 | 160.54 | 10.64 | 15.09 | 15.93 | 0.52 | 0.94 |
| 9–17 | 64.55 | 58.51 | 6.04 | 9.68 | 11.36 | 0.47 | 0.87 |
| 9–18 | 153.94 | 140.32 | 13.63 | 10.30 | 10.19 | 0.48 | 0.87 |
| Average | 121.10 | 109.43 | 11.67 | 7.79 | 9.78 | 0.57 | 0.89 |

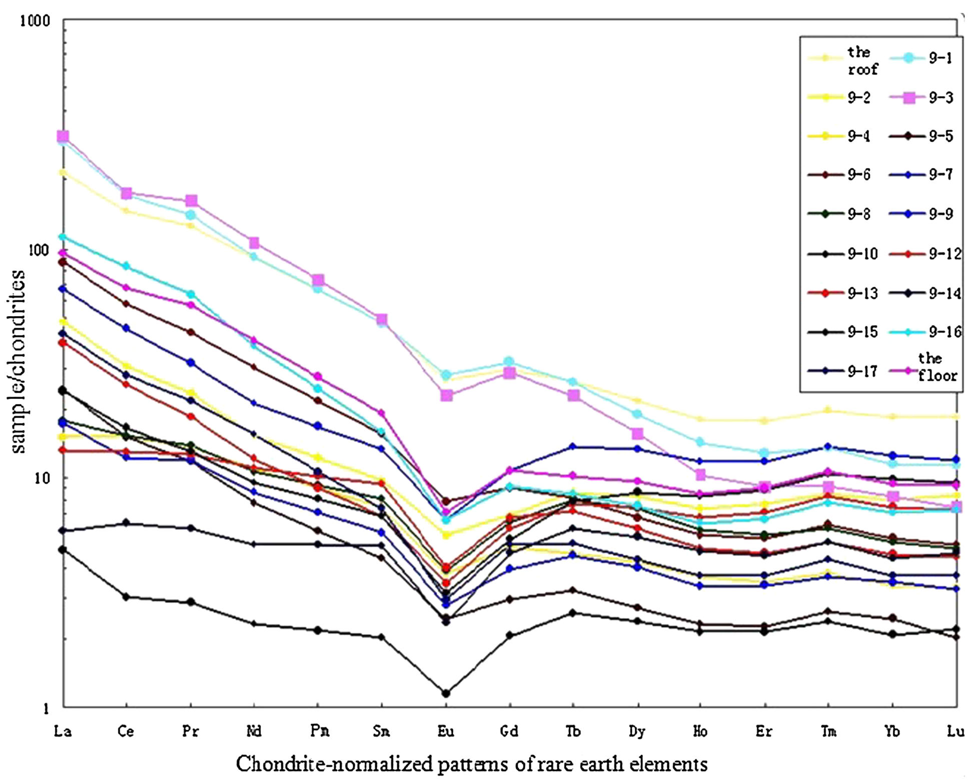


**Fig. 5** REE distribution patterns in 9th coal seam

average was 7.79 μg/g. The $(La/Yb)_N$ ranged from 1.31 to 37.4 μg/g, the average was 9.78 μg/g, which indicated the LREE was obviously concentrated, and HREE depleted relatively. The δEu ranged from 0.47 to 0.7 μg/g, the average was 0.57 μg/g. The Eu was a negative anomaly. Previous studies said that Eu anomalies are used directly by source rock (Birk and White 1991; Zhao et al. 2000). The δCe ranged from 0.74 to 1.06 μg/g, the average was

0.89 μg/g. Previous studies showed (Valkovic 1983) that Ce negative anomalies occur in the Marine sedimentary environment. In the edge of the sea, shallow sea and the Back Bay, Ce's concentration is normal, the loss of which is not serious. A lot of loss of Ce reflects an open ocean environment. From Table 4, samples show a weak negative anomaly. It means that the coal-forming environment had weak oxidation–reduction.

From the rare earth elements distribution patterns we can see: the left of the distribution curve is high and right is low, looking like a "V" as a whole. The La-Eu curve is steep, and its slope is big. The Gd–Lu curve is relatively slow, and its slope is small. The standardization of LREE value declines at a rate slightly greater than HREE's. The Eu presents z "valley", which means the Eu negative anomaly exists.

Above all, the Ce in the No.9 coal seam presents a weak negative anomaly. This reflects that the coal seams formed in shallow or enclosed seas. The Eu negative anomaly obviously shows that rare earth elements are consistent with the terrigenous rocks. Rare earth elements contained in mineral may mainly come from terrestrial detritus.

## 7 Conclusions

(1) Compared with the Clark value of the Upper Crust, Chinese coal, North China coal and US coal, Li and Ga are greatly enriched in the No. 9 coal in the Anjialing Mine, and the Arithmetic Mean reaches 140.5 and 24.8, respectively. In addition, Yb, Pb, Bi, Hf and Sr are slightly enriched. Most other trace elements are at normal or low levels.

(2) Through correlation analysis and cluster analysis, these 30 elements can generally be divided into 4 groups. Rb and Cs, Nb and Ta have a significant positive correlation in the research area, with correlation coefficients of 0.99 and 0.84, respectively. Element Li, which enriches in the coal seam, is significantly correlated with Ta and Th, with correlation coefficients of 0.809 and 0.807, respectively.

(3) As can be seen from the vertical distribution figure (Fig. 4), most trace elements are enriched near the roof and floor. Li, Zr and Hf are enriched in the middle of the coal seam.

(4) The content ratios of Sr and Ba, V and Ni, V and Zn might indicate that the peat swamp of this area was formed in swamp water, which is influenced by seawater, or in a sea-land transition environment. The data of the Sr/Ba, V/Zn, Th/U, V/Zr, V/Ni reveal that the peat swamp of this area formed in swamp water which was influenced by seawater or in a sea-land transition environment, where the ancient water salinity was slightly high.

(5) The Eu negative anomaly obviously shows that the rare earth elements are consistent with terrigenous rocks, which means the rare earth elements contained in the mineral may mainly come from terrestrial detritus.

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