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ORIGINAL ARTICLE

# Geochemistry of major and trace elements in Permian coal: with an emphasis on No. 8 coal seam of Zhuji coal mine, Huainan Coalfield, China

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**Abstract** A better understanding on geochemistry of elements in coal has both environmental and geological implications. In this study, 53 coal samples were collected from No. 8 coal seam of the Zhuji coal mine, Huainan Coalfield. The concentrations of 49 elements, ash yield, and total organic compound (TOC), as well as mineralogical phases in coal were determined. As compared with Chinese, the USA, and world coals, Si, K, Se, Cd, Sn, Sb, and W in studied coal seam are higher, whereas Zn, As, and Lu are lower. The enrichment factor and concentration coefficient show that Se, Cd, Sn, Sb, and W are preferably enriched in studied coals. The enrichment of Se and Cd is probably attributed to their higher proportions of organic forms. Most major and trace elements tend to concentrate in either the upper or lower sections of coal seams, which suggest that depositional micro-environment was important in controlling elements migration and enrichment. The correlation analysis of elements with ash yield shows that the behavior of elements in coal follows the periodic change of metallic activity. The modes of occurrence of major and trace elements are elaborated by statistical methods. Silicon is mainly in form of montmorillonite or presents as free quartz. Iron is associated with chlorite, siderite, lepidocrocite, and other iron-bearing minerals. Ti shows obviously organic association. Three groups of elements are divided in accordance with the cluster dendrogram: Group 1 (Sc–HREE–Be–Y–V–Co–Cu–P–Sr–B–Sn–Se–Bi–TOC–S–Ba–As), Group 2 (LREE–Zn–Al–Mn–Li–Na–Th–Cr–Fe–Mg) and Group 3 (Ca–Mo–Si–W–$A_d$–Ti–Pb–K). Many trace elements, including Li, Sc, V, Cr, Zn, Sr, La, Ce, Nd, Sm, Eu, Gd, Tb, Lu, Pb, Bi, and Th, correlate positively with Al, suggesting their occurrence mainly in clay such as kaolinite and chlorite. REE in the studied coalfield was primarily supplied by terrestrial clastics coming from North China Coal Basin. The differentiation of LREE and HREE is probably attributable to their different physicochemical characterisitcs and specific paleo-sedimentary environment. Various indexes (e.g., B content, Ash Index, C-value) and the existence of certain minerals suggest a reducing and anoxic sedimentary environment of coal swamp with a stable supply of terrigenous detrital materials in a moist environment. The origins of enriched elements are primarily derived from the source rock, sedimentary environment, and thermally contact metamorphism or possibly magmatic–hydrothermal fluids.

**Keywords** Element · Geochemistry · Depositional environment · Coal · TOC · Zhuji coal mine

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## Introduction

Coal plays an important role in energy sector. However, the environmentally sensitive trace elements emitted during coal utilization have posed a great threat to human health and caused the prevalence of endemic diseases such as arsenosis, fluorosis, selenosis in indigenous populations (Ando et al. 1998, 2001; Zheng et al. 1999; Swaine 2000; Finkelman et al. 2002; Liu et al. 2002, 2007; Fang et al. 2003; Dai et al. 2004, 2007, 2012a; Belkin et al. 2008; Luo et al. 2011; Li et al. 2012; Ernst 2012). These health problems are connected to burning of local coal seams that anomalously enriched hazardous trace elements such as Sb and Hg (Finkelman 1995; Dai et al. 2005; Qi et al. 2007; Zheng et al. 2008a, b).

The comprehensive information on concentration, distribution, mode of occurrence, and enrichment mechanisms may help understand the behavior of elements in coal mining, storage, combustion (Finkelman and Gross 1999; Zheng et al. 2008c). In Zhuji coal mine, the coal quality and its relationship with depositional environment, abundances and distribution of trace elements, and REE concentration affected by magmatic intrusion and coal-forming environment have been investigated previously (Sun et al. 2010a, b; Yang et al. 2012). No. 8 coal seam of Zhuji coal mine is a well developed and thick coal seam, with an estimated reserve of 154.3 Mt. As a terminated coal seam of Lower Shihezi Formation developed at a lower deltaic environment, No. 8 coal seam was deposited in a transition environment connecting to upper deltaic plain environment where Upper Shihezi Formation coals were developed. This coal seam is characterized by a high calorific value (~26 MJ/kg) and low moisture (1.46 %).

In the present study, we measured 49 elements along with ash yield and total organic compound (TOC) in 53 No. 8 coal samples. Our purposes are to: (1) explore whether the distribution of elements in coal is governed by their periodic properties at atomic level, (2) elucidate the dominant modes of occurrence of elements and (3) reveal the primary sources of elements enriched in coals.

## Geological setting

The Huainan Coalfield is located at the southeast corner of the North China Plate, and covers a total area of 3200 $km^2$. It has an elongated structure extending along NWW direction, with a mean length of 180 km and a mean width of 15–20 km. Zhuji coal mine is situated in the north of Huainan Coalfield and covers an area of 45 $km^2$ (Fig. 1). The overall geological structure of this mine is controlled by Zhuji-Tangji Anticline in the north and Shangtang-Gencun Syncline in the south.

The depositional environment of Huainan coals was shifted from a subaqueous deltaic plain, through a lower deltaic plain, and finally to a upper deltaic plain. The No. 8 coal seam with a mean thickness of 3 m was deposited in the transition environment between lower and upper deltaic plain.

The magmatic rocks in coal-bearing strata of Huainan Coalfield have been identified in the forms of dykes and sills. The Rb/Sr isotope age of intrusive magmatic rock is ~110 Ma (Yang et al. 2012), belonging to the Yanshan Movement period (tectonic events occurring in eastern China from Early Cretaceous to Late Jurassic) (Dong et al. 2008). The No.8 coal seam influenced by magmatic intrusion accounts for 7.8 % of total the mining area.

## Sampling and methods

A total of 55 samples, comprising 53 coal samples, one coal roof and one coal floor (both mudstone), were collected from 18 borehole cores of No. 8 coal seam in the Zhuji mine during exploration stage (Fig. 2). Generally, three coal samples were taken from each borehole according to their relative positions in coal seam: upper, middle, and lower portions.

All the studied coal samples were air-dried, pulverized to pass through 200-mesh sieve and preserved in plastic bags. The powder samples were digested using an acid mixture of $HNO_3$: HCl: HF (3:1:1) in a microwave oven before geochemical analysis. Ash yield ($A_d$) and volatile matter were determined according to ASTM standard (1997). X-ray fluorescence spectrometric analysis (XRF) was used to determine the concentrations of major elements including Si, P, S, Na, Mg, Al, K, Ca, Ti, Mn, and Fe. Inductively couple-plasma optical emission spectrometry (ICP-OES) was used to determine the concentrations of trace elements, except for Pr, Eu, Tb, Ho, Er, Tm, Lu, Th, which were determined by inductively coupled-plasma mass spectrometry (ICP-MS).

Elemental analyzer was used to determine the carbon content in coal samples, following the Chinese Standard Determination of TOC in Sedimentary rocks (GB/T 19145-2003). All samples were digested by excess HCl (37 wt%) to remove carbonate and evaporated for >2 h. The digested samples were then washed with deionized water to neutrality and dried in 60–80 °C. The mineralogical phases of raw coal samples were identified by a powder X-ray diffraction (XRD) with a Cu $K_\alpha$ radiation and a scintillation detector. Diffraction patterns were registered in a $2\theta$ interval of 5°–80° with a step of 0.02°/s.

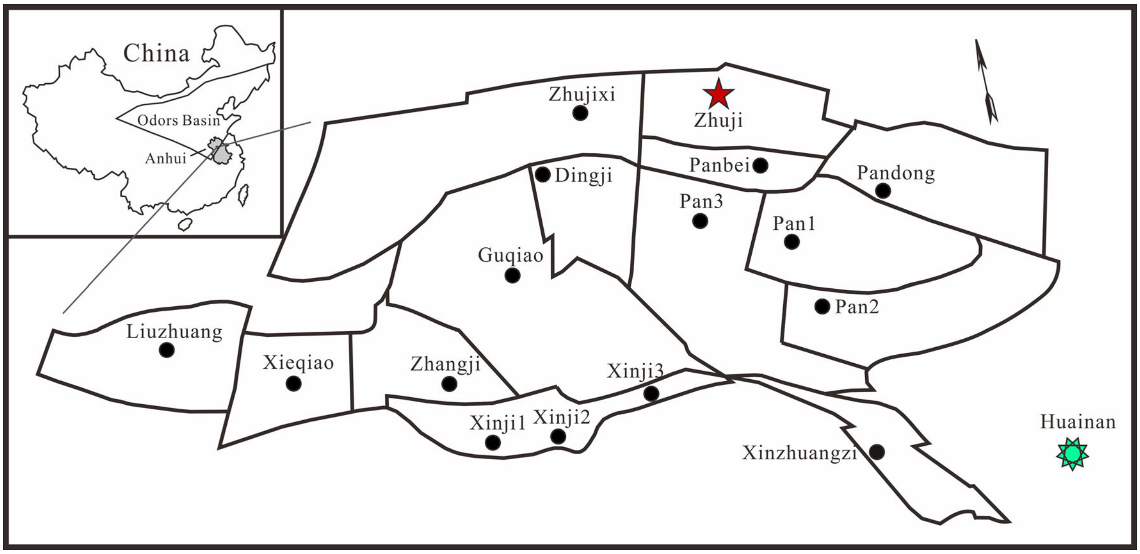


**Fig. 1** Locations of the coal mines in Huainan Coalfield showing the studied Zhuji coal mine (modified after Sun et al. 2010a, b)

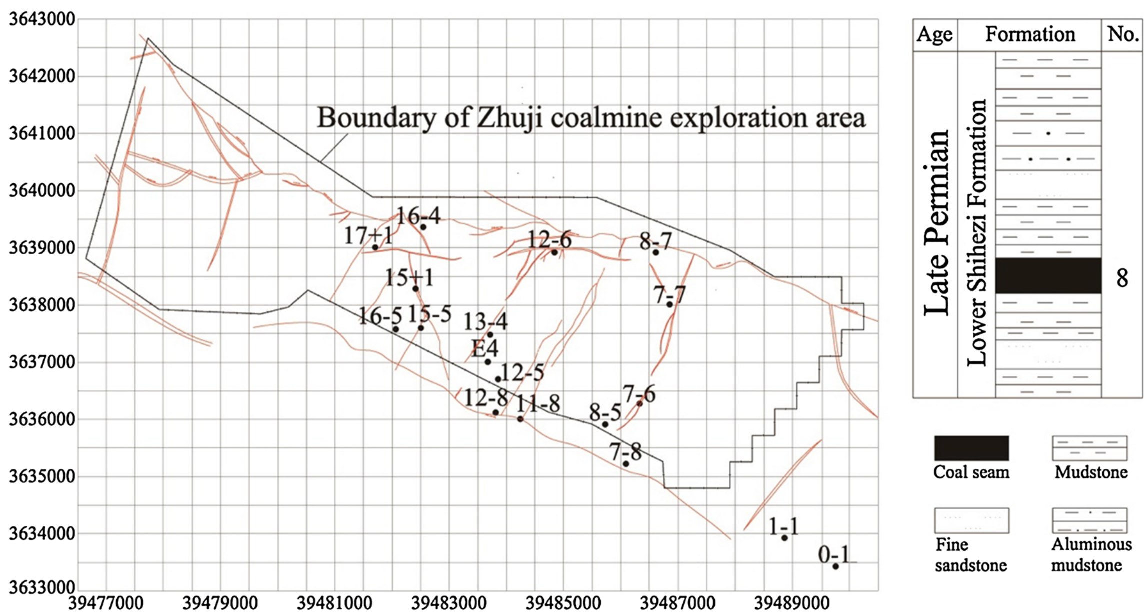


**Fig. 2** Distribution of 18 boreholes and general stratigraphic column and lithological characteristics of coal-bearing strata of coal seam 8 in Zhuji coal mine. The major faults are noted in red lines. The numbers in *X*, *Y* axis mean geographic coordinate

## Results and discussion

### Concentrations, distribution and a general pattern of elements in coal

*Concentrations of elements in No. 8 coal seam*

The concentrations of 9 major elements and 40 trace elements (including rare earth elements), and TOC and ash yield in upper, middle and lower sections of No. 8 coal seam are listed in Table 1. Table 1 also contains arithmetic and geometric means of 49 elements in different sections of coal seam. In order to evaluate the levels of elements in the coal seam, comparisons with Chinese, the USA, and world coals are shown in Table 2.

As compared with the world coal (Ketris and Yudovich 2009), the mean concentrations of most elements are higher or nearly equivalent, especially Sc, Ti, V, Cr, Co, Se, Cu, Cd, Sn, Sb, Y, La, Dy, and W with concentration coefficient (CC, ratio of elemental concentration in studied coal to world coal) above 2. The remaining elements, including Zn, As, Tb, and Lu, have lower mean concentrations as

Table 1 Concentrations of major and trace elements, TOC and $A_d$ in No. 8 coal seam of the Zhujidong coal mine (unit in μg/g unless noted as %)

| Elements | E4 | | | 1-1 | | | 7-6 | | | 7-7 | | | 7-8 | | | 8-5 | | | 8-7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L |
| Li | 9.00 | 9.93 | 12.31 | 25.73 | 26.41 | 37.15 | 57.54 | 46.75 | 44.72 | 22.46 | 1.83 | 17.58 | 16.90 | 16.84 | 24.90 | 33.13 | 10.61 | 42.61 | 30.49 | 22.34 | 33.60 |
| Be | 2.39 | 9.02 | 3.46 | 1.76 | 1.62 | 1.71 | 2.70 | 3.57 | 3.88 | 1.68 | 1.69 | 1.58 | 8.97 | 3.10 | 3.15 | 2.89 | 2.92 | 2.84 | 2.17 | 1.92 | 1.64 |
| B | 105 | 32.52 | 114 | 67.51 | 73.26 | 80.04 | 41.19 | 28.74 | 48.53 | 19.42 | 0.60 | 33.09 | 44.63 | 165 | 163 | 122 | 111 | 133 | 20.09 | 29.95 | 23.97 |
| Na, % | 0.32 | 0.16 | 0.42 | 0.17 | 0.14 | 0.27 | 0.27 | nd | 0.43 | 0.01 | 0.01 | 0.15 | 0.18 | 0.26 | 0.26 | 0.26 | 0.15 | 0.22 | 0.23 | 0.24 | 0.22 |
| Mg, % | 0.12 | 0.08 | 0.16 | 0.06 | 0.03 | 0.07 | 0.07 | 0.27 | 0.19 | 0.03 | 0.01 | 0.07 | 0.11 | 0.08 | 0.12 | 0.17 | 0.13 | 0.16 | 0.09 | 0.10 | 0.08 |
| Al, % | nd | nd | nd | nd | nd | nd | 5.57 | 8.32 | 4.98 | nd | 0.34 | nd | 3.61 | 2.96 | 3.60 | nd | nd | nd | nd | nd | nd |
| Si, % | 7.56 | 13.27 | 13.27 | 2.76 | 1.85 | 5.77 | 8.03 | 13.58 | 4.24 | 7.44 | 3.86 | 5.02 | 6.04 | 8.26 | 13.00 | 30.09 | 10.37 | 23.07 | 10.01 | 7.82 | 10.78 |
| P | 45.48 | 107 | 56.14 | 33.97 | 63.61 | 159 | 79.40 | 186 | 270 | 146 | 149 | 340 | 55.73 | 62.23 | 444 | 424 | 60.36 | 140 | 468 | 307 | 610 |
| $S_{t,d}$, % | 0.17 | 0.22 | 0.17 | 0.14 | 0.18 | 0.16 | 0.17 | 0.21 | 0.29 | 0.26 | 0.07 | 0.27 | 0.33 | 0.28 | 0.26 | 0.25 | 0.35 | 0.24 | 0.07 | 0.11 | 0.09 |
| K, % | 0.58 | 0.38 | 1.00 | 0.57 | 0.26 | 1.52 | 0.47 | nd | 1.30 | 0.25 | 0.06 | 0.42 | 0.59 | 0.49 | 0.55 | 0.92 | 0.33 | 0.56 | 0.28 | 0.54 | 0.31 |
| Ca, % | 0.25 | 0.24 | 2.40 | 1.50 | 1.92 | 2.48 | 0.32 | 0.49 | 0.71 | 1.06 | 0.65 | 3.80 | 0.44 | 0.30 | 0.35 | 3.13 | nd | 1.19 | 0.32 | 0.92 | 0.66 |
| Sc | 9.45 | 12.17 | 7.96 | 4.88 | 4.80 | 10.72 | 8.01 | 11.06 | 9.90 | 6.62 | 0.87 | 5.96 | 13.67 | 7.61 | 9.53 | 9.54 | 7.31 | 9.48 | 5.26 | 6.11 | 4.39 |
| Ti, % | 0.37 | 0.40 | 0.37 | 0.25 | 0.26 | 0.19 | 0.40 | 0.42 | 0.60 | 0.30 | 0.04 | 0.29 | 0.46 | 0.46 | 0.48 | 0.63 | 0.57 | 0.57 | 0.35 | 0.51 | 0.48 |
| V | 61.91 | 95.68 | 96.52 | 25.77 | 24.03 | 82.20 | 30.04 | 142 | 81.22 | 38.14 | 7.51 | 41.74 | nd | 74.67 | 79.81 | 57.80 | 159 | 43.76 | 20.19 | 62.67 | 19.87 |
| Cr | 102 | 36.51 | 30.90 | 31.23 | 26.30 | 53.66 | 40.44 | 58.77 | 47.74 | 40.61 | 15.82 | 40.58 | 34.54 | 16.85 | 27.70 | nd | 60.67 | 90.07 | 9.80 | 13.55 | 15.62 |
| Mn | 24.44 | 19.38 | 33.30 | 36.28 | 11.31 | 29.81 | 24.60 | 41.30 | 53.56 | 21.03 | 8.05 | 46.78 | 8.25 | 17.43 | 20.22 | 125 | 113 | 58.49 | 23.94 | 13.90 | 13.65 |
| Fe, % | 0.86 | 0.65 | 0.85 | 3.08 | 1.53 | 3.14 | 1.64 | nd | 3.86 | 0.76 | 0.32 | 2.21 | 1.83 | 1.81 | 2.42 | 1.22 | 0.74 | 0.99 | 1.54 | 1.46 | 1.23 |
| Co | 19.63 | 25.23 | 18.94 | 8.91 | 8.27 | 8.14 | 7.06 | 10.84 | 22.88 | 9.38 | 1.87 | 14.82 | 29.31 | 22.25 | 22.85 | 21.74 | 17.44 | 26.23 | 2.33 | 4.05 | 2.09 |
| Ni | 14.20 | 31.30 | 11.39 | 18.02 | 17.31 | 23.63 | 13.86 | 24.43 | 28.50 | 21.73 | 11.71 | 21.82 | 22.12 | 17.68 | 24.85 | 21.79 | 22.52 | 20.96 | 7.31 | 11.27 | 8.88 |
| Cu | 32.31 | 57.71 | 42.96 | 33.44 | 55.77 | 110.87 | 17.21 | 29.63 | 38.25 | 111.71 | 10.96 | 54.11 | 38.59 | 39.86 | 38.99 | 28.71 | 28.67 | 22.25 | 9.64 | 23.47 | 15.25 |
| Zn | nd | 1.25 | nd | 6.77 | 4.00 | 11.24 | 4.72 | 15.20 | 9.29 | 11.62 | 3.95 | 9.50 | 15.43 | 3.75 | 8.57 | nd | nd | nd | nd | nd | nd |
| As | 1.42 | 3.10 | 1.89 | 1.30 | 2.05 | 2.71 | nd | 1.72 | 1.96 | 1.11 | nd | 3.43 | 4.18 | 1.62 | 1.45 | nd | 0.24 | 1.76 | 0.74 | 1.71 | 2.30 |
| Se | 6.84 | 9.64 | 7.80 | 10.69 | 12.89 | 16.96 | 3.85 | 5.23 | 5.30 | 21.78 | 1.95 | 18.25 | 6.44 | 7.19 | 7.84 | 11.08 | 9.24 | 10.63 | 1.08 | 0.87 | 1.04 |
| Sr | nd | nd | nd | 70.67 | nd | nd | 98.91 | 235 | 172 | 33.68 | 33.01 | 79.17 | 69.07 | 147 | 281 | nd | nd | nd | nd | nd | nd |
| Y | 15.48 | nd | 23.23 | 23.43 | 19.58 | 21.56 | 11.83 | 18.68 | 15.39 | 27.56 | 6.23 | 34.92 | 43.78 | 19.19 | 22.58 | 21.17 | 36.63 | 25.42 | 19.17 | 12.35 | 9.73 |
| Mo | nd | 1.37 | nd | nd | 0.52 | nd | nd | nd | 4.66 | nd | nd | 2.15 | 1.84 | 1.47 | 0.74 | nd | 10.82 | nd | nd | 0.66 | 0.12 |
| Cd | nd | nd | nd | nd | nd | 0.02 | nd | nd | nd | 0.03 | nd | 0.10 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Sn | 3.35 | 2.19 | 2.80 | 2.82 | 2.69 | 3.36 | 4.72 | 5.51 | 3.22 | 3.05 | nd | 3.20 | 7.36 | 5.55 | 5.74 | 6.73 | 6.10 | 6.84 | 10.02 | 10.66 | 7.95 |
| Sb | nd | nd | nd | nd | nd | nd | 3.01 | nd | nd | nd | nd | nd | 1.11 | nd | nd | nd | nd | nd | nd | nd | nd |
| Ba | 111 | 206 | 173 | 104 | 109 | 163 | 126 | 254 | 215 | 76.55 | 45.58 | 130 | 49.84 | 636 | 266 | 205 | 145 | 165 | 192 | 152 | 233 |
| La | 21.50 | 55.02 | 30.72 | 12.07 | 16.69 | 22.73 | 11.53 | 34.50 | 35.07 | 9.38 | 5.00 | 29.20 | 16.37 | 12.72 | 20.20 | 17.09 | 15.26 | 22.84 | 39.79 | 14.69 | 13.96 |
| Ce | 41.03 | nd | 60.77 | 20.30 | 22.65 | 34.08 | 21.80 | 62.34 | 63.39 | 14.72 | 7.19 | 38.11 | 30.21 | 24.89 | 34.82 | 34.44 | 28.26 | 38.60 | 53.16 | 24.76 | 22.58 |
| Pr | 3.63 | nd | 4.68 | 2.53 | 2.48 | 4.23 | 1.37 | 5.67 | 5.56 | 1.67 | 0.56 | 4.60 | 2.56 | 2.09 | 2.94 | 1.95 | 1.08 | 2.86 | 4.66 | 1.56 | 1.35 |
| Nd | 18.06 | nd | 28.00 | 14.16 | 12.20 | 19.04 | 9.36 | 28.83 | 30.06 | 9.14 | 4.11 | 21.12 | 15.70 | 12.47 | 15.86 | 16.35 | 16.96 | 19.58 | 20.43 | 12.38 | 9.84 |

**Table 1** continued

| Elements | E4 | | | 1-1 | | | 7-6 | | | 7-7 | | | 7-8 | | | 8-5 | | | 8-7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L |
| Sm | 3.81 | nd | 5.90 | 4.19 | 3.87 | 6.08 | 2.01 | 5.98 | 6.24 | 3.05 | 1.16 | 5.57 | 4.07 | 3.04 | 3.69 | 3.79 | 4.07 | 4.20 | 5.10 | 3.30 | 2.42 |
| Eu | 0.63 | nd | 1.03 | 0.65 | 0.57 | 0.94 | 0.41 | 0.92 | 0.96 | 0.58 | 0.21 | 1.05 | 0.82 | 0.54 | 0.67 | 0.65 | 0.86 | 0.68 | 0.53 | 0.41 | 0.29 |
| Gd | 2.95 | nd | 5.10 | 2.92 | 2.20 | 3.42 | 1.79 | 5.81 | 5.90 | 2.18 | 0.85 | 4.10 | 5.56 | 3.26 | 4.11 | 3.46 | 5.00 | 4.13 | 5.05 | 3.37 | 2.43 |
| Tb | 0.11 | 0.46 | 0.17 | 0.09 | 0.04 | 0.11 | 0.24 | 0.36 | 0.34 | 0.03 | nd | 0.12 | 0.27 | 0.17 | 0.20 | 0.12 | 0.19 | 0.17 | 0.07 | 0.05 | 0.01 |
| Dy | 2.84 | 9.35 | 4.15 | 5.09 | 4.25 | 4.85 | 2.01 | 4.33 | 3.19 | 4.24 | 1.10 | 5.92 | nd | 5.33 | 6.20 | 3.68 | 4.61 | 4.27 | 6.33 | 4.13 | 3.15 |
| Ho | 1.16 | nd | 1.58 | 0.93 | 0.83 | 0.90 | 0.65 | 1.03 | 0.85 | 0.93 | 0.68 | 1.04 | 3.03 | 1.39 | 1.66 | 1.31 | 1.88 | 1.60 | 0.57 | 0.39 | 0.34 |
| Er | 1.31 | 4.68 | 1.82 | 1.76 | 1.46 | 1.60 | nd | 0.42 | nd | 1.86 | 0.33 | 2.24 | 3.44 | 1.42 | 1.72 | 1.79 | 2.73 | 2.14 | 2.07 | 1.37 | 1.14 |
| Tm | nd | nd | nd | 0.28 | 0.21 | 0.33 | nd | 0.05 | nd | 0.20 | 0.79 | 0.15 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Yb | 1.37 | nd | 1.84 | 1.91 | 1.67 | 1.98 | 0.96 | 1.47 | 1.28 | 2.50 | 0.14 | 2.79 | nd | 1.76 | 2.10 | 2.04 | 3.06 | 2.40 | 2.45 | 1.86 | 1.54 |
| Lu | 0.07 | 0.20 | 0.08 | 0.06 | 0.04 | 0.06 | 0.09 | 0.13 | 0.12 | 0.05 | 0.01 | 0.06 | 0.17 | 0.08 | 0.10 | 0.11 | 0.13 | 0.11 | 0.07 | 0.05 | 0.05 |
| REE | 98.47 | 69.71 | 145.84 | 66.94 | 69.16 | 100 | 52.22 | 151 | 152 | 50.53 | 22.13 | 116 | 82.2 | 69.16 | 94.27 | 86.78 | 84.09 | 103 | 140 | 68.32 | 59.1 |
| W | nd | nd | nd | nd | nd | 0.42 | 29.99 | 29.95 | nd | 0.72 | nd | 0.63 | 26.98 | 26.80 | 26.23 | 142.23 | nd | nd | nd | nd | nd |
| Re | nd | nd | nd | nd | nd | nd | 0.20 | 0.25 | 0.06 | nd | nd | nd | 0.06 | 0.14 | 0.20 | nd | nd | nd | nd | nd | nd |
| Pb | 2.46 | 14.59 | 3.75 | 10.15 | 8.74 | 19.83 | 9.58 | 16.60 | 12.37 | 13.50 | 0.41 | 10.05 | 17.27 | 9.99 | 13.09 | 10.77 | 5.69 | 8.80 | 2.60 | 2.65 | nd |
| Bi | nd | nd | nd | nd | nd | nd | 3.34 | 3.07 | 4.07 | nd | 0.07 | nd | 3.34 | 3.32 | 3.80 | nd | nd | nd | nd | nd | nd |
| Th | 4.00 | 3.32 | 3.68 | 2.94 | 2.38 | 4.30 | 5.22 | 7.19 | 5.90 | 2.41 | 0.33 | 3.29 | 3.62 | 3.16 | 4.08 | 5.30 | 3.23 | 4.80 | 2.49 | 2.32 | 2.59 |
| TOC, % | 69.41 | 71.93 | 69.75 | 67.16 | 54.39 | 52.10 | 49.13 | 66.40 | 63.49 | 65.06 | 68.16 | 64.37 | 66.80 | 73.02 | 69.86 | 65.16 | 74.85 | 69.92 | 69.59 | 70.87 | 69.41 |
| $A_d$, % | 16.50 | 13.51 | 17.91 | 19.71 | 15.61 | 36.19 | 22.23 | 38.32 | 23.10 | 20.36 | 17.16 | 19.20 | 19.34 | 12.14 | 15.01 | 21.50 | 14.26 | 16.43 | 21.89 | 15.75 | 16.73 |

| Elements | 11-8 | | | 12-5 | | | 12-6 | | | 12-8 | | | 13-4 | | | 15-5 | | | 15 + 1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L |
| Li | 41.15 | 29.38 | 32.18 | 22.63 | 29.38 | 18.60 | 38.74 | 11.46 | 15.83 | 12.65 | 8.79 | 6.19 | 45.45 | 7.28 | 8.07 | 30.99 | 11.43 | 10.40 | 18.21 | 17.39 | 11.72 |
| Be | 3.15 | 3.36 | 3.20 | 4.80 | 5.15 | 4.90 | 3.64 | 3.57 | 3.15 | 2.40 | 1.78 | 4.92 | 2.76 | 1.63 | 1.62 | 5.10 | 4.67 | 4.81 | 7.94 | 0.70 | 0.30 |
| B | 55.25 | 53.68 | 51.75 | 26.99 | 23.01 | 24.41 | 215 | 164 | 159 | 2.31 | 31.69 | 44.69 | 36.78 | 65.43 | 42.05 | 62.19 | 39.18 | 37.02 | 19.74 | 23.42 | 21.19 |
| Na, % | 0.35 | 0.28 | 0.28 | 0.28 | 0.33 | 0.28 | nd | 0.32 | 0.28 | 0.19 | 0.19 | 0.10 | 0.27 | nd | 0.25 | 0.48 | 0.23 | 0.21 | 0.15 | 0.20 | 0.11 |
| Mg, % | 0.12 | 0.09 | 0.09 | 0.13 | 0.17 | 0.16 | 0.11 | 0.23 | 0.15 | 0.07 | 0.07 | 0.12 | 0.19 | 0.25 | 0.25 | 0.11 | 0.10 | 0.11 | 0.06 | 0.11 | 0.05 |
| Al, % | 3.67 | 3.86 | 3.99 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 3.57 | 3.81 | 2.31 |
| Si, % | 9.00 | 7.01 | 6.95 | 59.74 | 65.72 | 67.09 | 11.89 | 8.17 | 8.64 | 3.25 | 3.50 | 3.19 | 22.67 | 2.59 | 1.96 | 73.43 | 57.13 | 43.71 | 41.88 | 47.08 | 37.29 |
| P | nd | 93.96 | 100 | 97.19 | 134 | 83.25 | 170 | 114 | 91.80 | 419 | 32.73 | 42.79 | 77.53 | 55.62 | 66.92 | 100 | 65.49 | 55.79 | 64.02 | 48.20 | 48.43 |
| $S_{t,d}$, % | 0.16 | 0.21 | 0.19 | 0.11 | 0.09 | 0.14 | 0.19 | 0.28 | 0.30 | 0.29 | 0.23 | 0.30 | 0.15 | 0.26 | 0.32 | 0.09 | 0.13 | 0.16 | 0.25 | 0.23 | nd |
| K, % | 0.40 | 0.43 | 0.42 | 0.70 | 0.76 | 1.07 | 0.81 | 1.30 | 0.73 | 0.27 | 0.34 | 0.24 | 0.22 | 0.96 | 0.78 | 0.79 | 0.36 | 0.45 | 0.43 | 0.73 | 0.36 |
| Ca, % | 1.24 | 0.56 | 0.53 | 0.54 | 0.53 | 0.45 | 0.16 | 0.81 | 0.42 | 0.12 | 0.09 | 0.09 | 0.37 | nd | nd | 0.13 | 0.35 | 0.29 | 0.40 | 1.00 | 0.20 |
| Sc | 6.57 | 8.16 | 7.68 | 8.34 | 9.51 | 6.58 | 15.64 | 9.31 | 9.29 | 5.71 | 8.43 | 7.04 | 9.96 | 4.61 | 5.51 | 13.29 | 6.76 | 5.94 | 9.14 | 7.07 | 5.31 |
| Ti, % | 0.43 | 0.47 | 0.45 | 0.47 | 0.54 | 0.51 | 0.33 | 0.56 | 0.57 | 0.48 | 0.48 | 0.44 | 0.56 | 0.17 | 0.19 | 0.40 | 0.66 | 0.75 | 0.54 | 0.51 | 0.50 |

**Table 1** continued

| Elements | 11-8 | | | 12-5 | | | 12-6 | | | 12-8 | | | 13-4 | | | 15-5 | | | 15 + 1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L |
| V | 29.01 | 49.17 | 44.13 | 44.92 | 48.20 | 54.57 | 45.48 | 71.43 | 61.16 | 74.93 | 55.93 | 93.36 | 62.86 | 52.74 | 64.89 | 54.26 | 46.59 | 38.51 | 57.80 | 45.12 | 36.68 |
| Cr | 35.12 | 39.69 | 32.76 | 24.59 | 40.43 | 30.06 | 42.06 | 75.75 | 76.41 | 27.94 | 38.37 | 26.83 | 20.98 | 36.52 | 44.46 | 23.15 | 24.09 | 25.65 | 15.81 | 27.27 | 21.12 |
| Mn | 60.31 | 40.89 | 37.81 | 57.77 | 98.16 | 66.51 | 21.37 | 25.08 | 25.50 | 18.46 | 14.54 | 26.37 | 19.69 | 39.16 | 38.55 | 26.18 | 22.12 | 20.46 | 20.20 | 34.13 | 26.31 |
| Fe, % | 2.72 | 2.33 | 2.32 | 2.37 | 3.25 | 3.08 | 0.68 | 1.43 | 1.14 | 1.55 | 1.54 | 2.18 | 0.55 | 3.34 | 3.30 | 1.57 | 1.99 | 2.34 | 1.39 | 2.14 | 1.13 |
| Co | 9.99 | 12.71 | 11.56 | 8.73 | 7.37 | 10.81 | 11.23 | 39.26 | 36.97 | 9.99 | 15.42 | 20.92 | 9.68 | 9.99 | 11.97 | 5.06 | 12.07 | 16.88 | 18.53 | 13.58 | 3.67 |
| Ni | 17.21 | 18.47 | 18.55 | 11.14 | 12.62 | 14.57 | 21.46 | 21.89 | 23.03 | 11.12 | 14.85 | 17.26 | 9.08 | 21.72 | 22.11 | 6.81 | 12.94 | 21.26 | 22.22 | 17.30 | 5.93 |
| Cu | 14.22 | 32.45 | 27.08 | 22.74 | 22.30 | 28.21 | 30.20 | 50.57 | 40.25 | 26.62 | 27.76 | 45.19 | 29.83 | 100.86 | nd | 35.73 | 24.14 | 20.41 | 39.70 | 24.58 | 16.41 |
| Zn | 13.95 | 12.20 | 11.53 | 0.50 | 3.45 | 3.93 | nd | 7.53 | 5.28 | nd | nd | 4.66 | 0.88 | 11.64 | 8.65 | nd | nd | 0.06 | 11.50 | 8.82 | 3.99 |
| As | 0.09 | 0.14 | 0.71 | nd | nd | 0.04 | 0.53 | 2.90 | 0.60 | nd | nd | nd | nd | 1.68 | 2.02 | nd | nd | nd | 1.74 | 0.93 | 0.41 |
| Se | 4.53 | 4.48 | 6.21 | 1.64 | 1.80 | 1.65 | 11.50 | 12.65 | 12.58 | 3.30 | 1.46 | 1.29 | 3.27 | 17.33 | 15.09 | 3.25 | 1.87 | 2.39 | 4.27 | 3.63 | 3.15 |
| Sr | nd | 140 | 132 | 100 | 108 | 76.83 | nd | nd | nd | 110 | 105 | 78.30 | 55.93 | nd | nd | 90.85 | 91.28 | 90.44 | 99.59 | 165 | nd |
| Y | 28.56 | 20.17 | 17.21 | 19.62 | 22.94 | 15.40 | 21.13 | 25.19 | 17.88 | 14.69 | 12.25 | 36.80 | 19.48 | 34.89 | 40.38 | 25.40 | 15.19 | 14.47 | 27.53 | 17.91 | 15.27 |
| Mo | 1.52 | 0.85 | 0.41 | nd | nd | nd | nd | nd | nd | nd | nd | 5.11 | nd | 1.62 | 0.35 | nd | nd | nd | 3.45 | 4.77 | 1.23 |
| Cd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 0.07 | 0.01 | nd | nd | nd | nd | nd | nd |
| Sn | 3.37 | 3.18 | 3.53 | 7.42 | 7.09 | 5.63 | 8.85 | 7.41 | 7.06 | 2.94 | 2.33 | 1.96 | 10.45 | 2.12 | 4.22 | 12.43 | 6.96 | 0.28 | 0.95 | 2.28 | nd |
| Sb | nd | nd | 3.55 | 0.86 | 13.84 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Ba | 319 | 166 | 138 | 140 | 197 | 126 | 250 | 234 | 199 | 166 | 90.52 | 54.09 | 100 | nd | 605 | 168 | 98.16 | 104 | 104 | 125 | 117 |
| La | nd | 24.14 | 22.05 | 20.62 | 25.17 | 16.55 | 42.78 | 43.40 | 23.99 | 17.09 | 11.88 | 17.42 | 39.64 | 23.35 | 25.56 | 38.55 | 17.15 | 13.92 | 27.36 | 16.36 | 12.51 |
| Ce | 85.38 | 44.12 | 41.39 | 38.04 | 45.06 | 31.72 | 74.69 | 83.50 | 42.06 | 27.98 | 21.19 | 30.03 | 70.81 | 31.99 | 37.11 | 65.05 | 31.05 | 24.76 | 51.05 | 29.65 | 23.46 |
| Pr | 7.40 | 3.50 | 3.20 | 2.74 | 3.46 | 2.07 | 6.87 | 7.74 | 3.51 | 2.35 | 1.61 | 2.73 | 1.23 | 3.41 | 4.37 | 6.08 | 2.17 | 1.52 | 4.47 | 1.92 | 2.14 |
| Nd | 32.88 | 19.88 | 17.83 | 16.05 | 18.95 | 13.34 | 27.23 | 39.04 | 17.39 | 13.75 | 10.19 | 16.51 | 30.44 | 18.40 | 22.21 | 25.04 | 13.17 | 10.65 | 23.62 | 14.49 | 11.64 |
| Sm | 6.98 | 4.20 | 3.70 | 4.71 | 5.88 | 3.82 | 5.28 | 8.04 | 3.84 | 2.94 | 2.35 | 3.77 | 6.37 | 5.19 | 6.23 | 6.79 | 3.81 | 3.49 | 5.60 | 3.19 | 2.30 |
| Eu | 0.93 | 0.70 | 0.67 | nd | nd | nd | 0.79 | 1.29 | 0.63 | 0.39 | 0.35 | 0.56 | 1.21 | 0.90 | 1.10 | nd | nd | nd | 0.81 | nd | nd |
| Gd | 7.47 | 4.17 | 3.76 | 3.70 | 4.30 | 2.77 | 4.01 | 6.28 | 3.13 | 2.90 | 2.34 | 5.14 | 5.14 | 4.36 | 4.97 | 4.76 | 2.19 | 2.10 | 4.05 | 2.46 | 1.48 |
| Tb | 0.41 | 0.32 | 0.31 | 0.17 | 0.20 | 0.16 | 0.10 | 0.21 | 0.11 | nd | nd | 0.05 | 0.16 | 0.11 | 0.15 | 0.19 | 0.12 | 0.13 | 0.13 | 0.06 | nd |
| Dy | 6.53 | 3.73 | 3.56 | 5.77 | 7.22 | 4.27 | 3.93 | 4.71 | 3.21 | 3.14 | 2.68 | 6.31 | 3.93 | 5.28 | 6.54 | 8.39 | 4.49 | 4.09 | 4.71 | 2.89 | 1.55 |
| Ho | 1.61 | 1.21 | 0.99 | nd | nd | nd | 1.57 | 1.34 | 1.03 | 1.22 | 1.18 | 2.23 | 0.12 | 1.01 | 1.12 | nd | nd | nd | 0.18 | nd | nd |
| Er | 2.14 | 0.85 | nd | 1.20 | 1.58 | 0.67 | 1.78 | 1.89 | 1.46 | 5.01 | 4.32 | 0.95 | 1.52 | 2.28 | 2.67 | 1.79 | 0.60 | 0.46 | 2.35 | 1.42 | 1.05 |
| Tm | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 0.13 | 0.09 | 0.38 | 0.32 | nd | nd | nd | nd | nd | nd |
| Yb | 1.96 | 1.97 | 1.64 | 0.91 | 1.45 | 0.08 | 2.09 | 1.90 | 1.61 | 1.76 | 1.39 | 3.59 | 1.47 | 2.80 | 3.20 | 1.78 | nd | nd | 2.68 | 1.68 | 1.24 |
| Lu | 0.13 | 0.13 | 0.12 | 0.02 | 0.04 | nd | 0.09 | 0.10 | 0.09 | nd | nd | 0.13 | 0.07 | 0.08 | 0.08 | 0.02 | nd | nd | 0.15 | 0.11 | 0.08 |
| REE | 153 | 108 | 99.22 | 93.93 | 113 | 75.45 | 171 | 199 | 102 | 78.53 | 59.48 | 89.55 | 162 | 99.54 | 115 | 158 | 74.75 | 61.12 | 127 | 74.23 | 57.45 |
| W | 31.03 | 33.21 | 36.73 | 106 | 122 | 114 | nd | nd | nd | 34.84 | 33.68 | 24.22 | nd | 0.45 | 0.04 | 119 | 122 | 83.01 | 62.08 | 57.60 | 51.63 |
| Re | 0.44 | 0.33 | 0.43 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

**Table 1** continued

| Elements | 11-8 | | | 12-5 | | | 12-6 | | | 12-8 | | | 13-4 | | | 15-5 | | | 15 + 1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L | U | M | L |
| Pb | 10.25 | 11.56 | 12.98 | 9.88 | 14.00 | 10.85 | 8.46 | 10.99 | 13.69 | 8.82 | 7.88 | 10.26 | 10.08 | 14.01 | 13.42 | 16.88 | 7.01 | 9.28 | 14.24 | 13.63 | 8.88 |
| Bi | 2.87 | 3.21 | 3.39 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 0.99 | 0.73 | 1.00 |
| Th | 4.05 | 4.00 | 4.13 | 4.80 | 5.52 | 4.35 | nd | 5.71 | 4.78 | 2.93 | 2.89 | 2.49 | 6.18 | 2.86 | 3.38 | 6.92 | 3.38 | 3.27 | 2.93 | 3.08 | 2.00 |
| TOC, % | 69.06 | 68.73 | 68.45 | 65.09 | 61.02 | 64.78 | 57.10 | 67.76 | 69.53 | 68.95 | 72.93 | 75.83 | 76.07 | 71.80 | 72.16 | 59.29 | 70.78 | 67.79 | 68.89 | 70.26 | 73.46 |
| $A_d$, % | 18.60 | 16.36 | 16.97 | 20.85 | 26.05 | 20.67 | 28.61 | 18.18 | 15.45 | 15.93 | 12.04 | 9.18 | 10.83 | 17.52 | 17.38 | 27.66 | 14.64 | 16.69 | 16.94 | 20.55 | 12.78 |

| Elements | 16-4 | | | 16-5 | | | 17 + 1 | | | 0-1 | | | | AM | | | GM | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | R | U | D | F | U | M | L | U | M | L |
| Li | 33.78 | 29.99 | 7.88 | 36.11 | 9.64 | 11.35 | 30.86 | 17.45 | 25.66 | 19.09 | 18.02 | 74.00 | 25.76 | 29.75 | 17.05 | 21.22 | 27.07 | 14.52 | 17.73 |
| Be | 4.32 | 2.67 | 3.66 | 0.18 | nd | 1.95 | 2.02 | 1.84 | 2.04 | nd | 2.89 | 1.35 | 2.30 | 3.46 | 2.89 | 2.87 | 2.72 | 2.60 | 2.46 |
| B | 123 | 177 | 165 | 40.35 | 43.13 | 36.03 | 34.03 | 35.82 | 30.76 | 27.48 | 52.64 | 49.64 | 26.67 | 61.10 | 61.04 | 71.15 | 41.77 | 40.79 | 55.27 |
| Na, % | 0.34 | 0.34 | 0.14 | 0.27 | 0.22 | 0.27 | 0.22 | 0.21 | 0.18 | nd | 0.14 | nd | 0.35 | 0.25 | 0.21 | 0.24 | 0.21 | 0.18 | 0.22 |
| Mg, % | 0.21 | 0.27 | 0.28 | 0.08 | 0.09 | 0.10 | 0.09 | 0.10 | 0.08 | 0.23 | 0.09 | 0.03 | 0.11 | 0.11 | 0.12 | 0.13 | 0.10 | 0.10 | 0.12 |
| Al, % | nd | nd | 0.96 | 3.77 | 2.51 | 3.16 | nd | nd | nd | nd | 3.61 | 1.62 | 5.18 | 4.04 | 3.11 | 3.17 | 3.98 | 2.60 | 2.82 |
| Si, % | 6.84 | 11.00 | 3.76 | 33.78 | 31.25 | 37.91 | 11.58 | 16.35 | 11.89 | 60.05 | nd | 1.38 | 113.43 | 20.35 | 17.16 | 17.50 | 13.01 | 10.92 | 10.79 |
| P | 811 | nd | 64.85 | 2409 | 49.82 | 49.96 | 81.26 | 78.57 | 97.11 | 177 | 88.83 | 1246.00 | 57.99 | 207 | 94.77 | 160 | 134 | 84.84 | 110 |
| $S_{t,d}$, % | nd | 0.27 | 0.33 | 0.14 | 0.18 | 0.16 | 0.17 | 0.20 | 0.17 | 0.13 | 0.16 | 0.52 | 0.13 | 0.18 | 0.19 | 0.22 | 0.17 | 0.19 | 0.21 |
| K, % | 0.91 | 1.05 | 0.24 | 0.39 | 0.53 | 0.91 | 0.51 | 0.51 | 0.23 | nd | 0.42 | 0.14 | 0.89 | 0.53 | 0.53 | 0.65 | 0.49 | 0.47 | 0.55 |
| Ca, % | 1.75 | 1.04 | 1.10 | 0.24 | 0.22 | 0.20 | 0.02 | 0.03 | 0.03 | 2.92 | 0.67 | 0.62 | 0.93 | 0.71 | 0.57 | 0.93 | 0.39 | 0.42 | 0.50 |
| Sc | 9.60 | 9.14 | 7.03 | 6.92 | 7.03 | 7.08 | 9.24 | 7.12 | 6.65 | 12.08 | 5.73 | 4.67 | 7.95 | 8.93 | 7.06 | 7.41 | 8.48 | 6.72 | 7.20 |
| Ti, % | 0.46 | 0.62 | 0.57 | 0.57 | 0.85 | 0.64 | 0.53 | 0.67 | 0.60 | 0.14 | 0.54 | 2.78 | 0.43 | 0.44 | 0.46 | 0.48 | 0.43 | 0.42 | 0.45 |
| V | 91.72 | 63.26 | 84.87 | 35.34 | 52.43 | 55.49 | 52.27 | 49.14 | 39.82 | 75.20 | 29.02 | 17.00 | 51.17 | 48.90 | 61.12 | 59.92 | 45.32 | 54.33 | 55.44 |
| Cr | 113 | nd | 1.06 | 15.38 | 26.19 | 23.73 | 53.99 | 39.21 | 34.22 | 27.61 | 25.53 | 12.00 | 22.83 | 39.47 | 33.88 | 36.62 | 32.15 | 32.32 | 28.45 |
| Mn | 126 | 124 | 46.34 | 23.80 | 21.13 | 20.73 | 14.54 | 22.82 | 7.24 | nd | 20.06 | 33.00 | 24.67 | 38.36 | 37.10 | 33.63 | 28.96 | 28.44 | 29.52 |
| Fe, % | 2.22 | 2.28 | 1.37 | 1.55 | 2.08 | 1.88 | 1.50 | 1.88 | 1.24 | nd | 1.89 | 0.33 | 2.39 | 1.59 | 1.69 | 2.04 | 1.44 | 1.57 | 1.84 |
| Co | 28.31 | 32.42 | 31.21 | 11.95 | 20.90 | 21.59 | 24.37 | 30.95 | 27.58 | 8.95 | 12.70 | 6.00 | 12.32 | 13.89 | 15.81 | 18.18 | 11.61 | 13.31 | 14.89 |
| Ni | 25.46 | 23.07 | 21.67 | 15.65 | 17.34 | 15.21 | 16.00 | 17.13 | 14.43 | nd | 25.11 | 10.00 | 17.52 | 16.19 | 17.42 | 18.47 | 15.09 | 17.77 | 17.29 |
| Cu | 37.83 | 35.56 | 40.61 | 17.92 | 39.01 | 43.95 | 26.16 | 25.33 | 17.92 | nd | 24.04 | 51.00 | 32.10 | 32.50 | 34.92 | 37.67 | 28.13 | 32.83 | 32.96 |
| Zn | nd | 17.22 | nd | 7.21 | 5.58 | 8.62 | nd | 1.97 | nd | 8.30 | 6.17 | nd | 8.13 | 8.06 | 6.90 | 7.11 | 5.23 | 5.71 | 4.85 |
| As | nd | 3.15 | 2.55 | 1.56 | 1.58 | 0.78 | nd | nd | nd | 1.60 | 2.22 | nd | 0.39 | 1.41 | 1.60 | 1.62 | 0.98 | 1.30 | 1.13 |
| Se | 12.56 | 11.13 | 6.96 | 5.20 | 5.42 | 4.83 | 2.33 | 0.92 | 1.23 | 6.89 | 2.48 | nd | 2.51 | 6.68 | 5.98 | 7.25 | 5.06 | 4.35 | 5.04 |
| Sr | nd | nd | nd | 139 | 105 | 101 | 97.60 | 100 | 104 | 109 | 118 | 87.00 | 133 | 87.94 | 112 | 124 | 82.78 | 111 | 112 |
| Y | 23.09 | 20.57 | 17.59 | 14.65 | 12.89 | 17.90 | 16.56 | 13.31 | 16.86 | 32.83 | 23.11 | 4.87 | 16.03 | 21.95 | 18.12 | 21.33 | 20.91 | 17.72 | 19.94 |
| Mo | nd | 0.35 | 4.08 | 0.52 | 0.64 | 1.36 | nd | nd | nd | 1.08 | 3.38 | 1.07 | 2.04 | 1.83 | 2.10 | 2.02 | 1.50 | 1.27 | 1.16 |

**Table 1** continued

| Elements | 16-4 | | | 16-5 | | | 17 + 1 | | | 0-1 | | | | AM | | | GM | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | U | M | L | U | M | L | U | M | L | R | U | D | F | U | M | L | U | M | L |
| Cd | nd | nd | nd | 9.22 | 9.32 | 9.13 | nd | nd | nd | 5.32 | nd | 0.11 | nd | 4.63 | 3.13 | 2.32 | 0.53 | 0.81 | 0.12 |
| Sn | 7.02 | 6.89 | 6.78 | 0.72 | 2.18 | 1.75 | 4.06 | 1.92 | 3.75 | nd | 5.35 | 0.43 | 7.03 | 5.66 | 4.42 | 4.25 | 4.46 | 4.01 | 3.47 |
| Sb | 33.66 | nd | nd | 8.50 | 2.94 | 25.80 | nd | nd | nd | 4.04 | nd | 0.64 | 4.91 | 9.43 | 5.59 | 14.68 | 3.83 | 6.38 | 9.57 |
| Ba | 298 | 328 | 129 | 151 | 870 | 218 | 116 | 118 | 112 | 322 | 127 | 119 | 139 | 157 | 222 | 185 | 142 | 178 | 161 |
| La | 31.10 | 28.14 | 3.86 | 17.63 | 18.16 | 22.52 | 21.24 | 19.65 | 20.58 | 38.00 | 37.98 | 5.33 | 19.80 | 23.98 | 21.18 | 20.80 | 21.63 | 19.60 | 19.02 |
| Ce | 56.32 | 52.28 | 6.56 | 31.06 | 33.15 | 43.15 | 36.57 | 33.54 | 34.41 | 60.35 | 67.37 | 12.27 | 36.15 | 44.27 | 33.86 | 35.71 | 39.70 | 31.75 | 32.59 |
| Pr | 4.11 | 4.00 | nd | 2.57 | 2.86 | 3.91 | 3.81 | 3.25 | 3.45 | 5.02 | 6.17 | 1.24 | 2.55 | 3.53 | 2.79 | 3.32 | 3.09 | 2.49 | 3.09 |
| Nd | 25.12 | 22.37 | 4.26 | 13.34 | 14.74 | 19.58 | 15.35 | 15.00 | 14.87 | 31.34 | 30.23 | 11.72 | 14.96 | 19.18 | 16.07 | 17.16 | 17.96 | 15.38 | 15.81 |
| Sm | 5.17 | 4.69 | 1.13 | 2.63 | 2.96 | 3.91 | 3.46 | 3.10 | 3.38 | 5.36 | 7.00 | 2.32 | 2.30 | 4.47 | 3.81 | 4.10 | 4.23 | 3.73 | 3.80 |
| Eu | 0.85 | 0.74 | 0.27 | nd | nd | 0.30 | 0.45 | 0.42 | 0.42 | 0.67 | 0.66 | 0.23 | 0.31 | 0.69 | 0.61 | 0.68 | 0.66 | 0.59 | 0.62 |
| Gd | 4.89 | 4.36 | 2.18 | 1.91 | 1.90 | 2.49 | 3.17 | 2.82 | 3.32 | 8.23 | 5.54 | 2.28 | 2.30 | 3.88 | 3.27 | 3.56 | 3.62 | 3.13 | 3.34 |
| Tb | 0.20 | 0.20 | 0.07 | nd | nd | 0.16 | nd | nd | nd | 0.22 | 0.28 | 0.15 | 0.21 | 0.16 | 0.18 | 0.15 | 0.14 | 0.15 | 0.12 |
| Dy | 4.10 | 3.85 | 2.60 | 2.28 | 1.78 | 2.77 | 3.83 | 3.24 | 4.09 | 5.63 | 5.52 | 0.81 | 2.25 | 4.43 | 4.05 | 4.16 | 4.14 | 3.87 | 3.91 |
| Ho | 1.22 | 0.78 | 0.70 | 0.13 | 0.18 | 0.07 | 1.32 | 1.10 | 1.38 | 0.94 | 0.01 | 0.15 | 0.11 | 1.06 | 0.93 | 1.11 | 0.77 | 0.88 | 0.89 |
| Er | 2.07 | 1.75 | 1.39 | 1.20 | 1.04 | 1.38 | 5.61 | 4.47 | 5.67 | 2.90 | 1.61 | 0.44 | 1.12 | 2.31 | 1.81 | 1.76 | 2.07 | 1.49 | 1.48 |
| Tm | nd | nd | nd | 0.36 | 0.67 | 0.48 | nd | nd | nd | 0.36 | 0.08 | 0.05 | 0.03 | 0.23 | 0.35 | 0.28 | 0.21 | 0.29 | 0.25 |
| Yb | 2.36 | 1.82 | 1.59 | 1.37 | 1.26 | 1.57 | 1.69 | 1.33 | 1.78 | 1.29 | 0.94 | 0.36 | 0.63 | 1.83 | 1.60 | 1.89 | 1.75 | 1.48 | 1.57 |
| Lu | 0.14 | 0.13 | 0.09 | 0.12 | 0.12 | 0.13 | nd | nd | nd | 0.13 | 0.14 | 0.05 | 0.14 | 0.09 | 0.09 | 0.09 | 0.08 | 0.08 | 0.09 |
| REE | 137 | 125 | 24.7 | 74.6 | 78.82 | 102 | 96.5 | 87.92 | 93.35 | 160 | 163 | 37.4 | 82.86 | 107 | 86.44 | 93.71 | 100 | 83.34 | 87.25 |
| W | nd | nd | nd | 59.88 | 55.11 | 55.28 | 25.14 | 26.95 | 30.86 | 149 | 70.59 | 0.10 | 79.19 | 58.06 | 46.24 | 38.49 | 35.31 | 29.61 | 10.68 |
| Re | nd | nd | nd | 0.44 | 0.18 | 0.30 | nd | nd | nd | nd | nd | 0.17 | nd | 0.29 | 0.18 | 0.25 | 0.22 | 0.21 | 0.20 |
| Pb | 21.25 | 13.30 | 6.80 | 13.08 | 14.19 | 17.89 | 10.05 | 8.47 | 9.44 | 14.66 | 15.58 | 4.85 | 12.58 | 11.14 | 9.65 | 11.34 | 9.87 | 8.27 | 10.63 |
| Bi | nd | nd | nd | 0.72 | 0.69 | 0.52 | nd | nd | nd | nd | nd | 0.28 | nd | 2.25 | 1.58 | 2.56 | 1.87 | 1.02 | 1.94 |
| Th | 6.97 | 6.29 | 3.09 | 3.45 | 3.52 | 3.64 | 4.53 | 3.26 | 3.01 | 3.11 | 3.61 | 2.33 | 4.40 | 4.30 | 3.47 | 3.69 | 4.06 | 3.18 | 3.57 |
| TOC, % | 57.52 | 66.46 | 75.97 | 67.82 | 60.24 | 67.36 | 68.27 | 71.61 | 72.33 | 30.43 | 68.84 | 57.92 | 2.38 | 65.32 | 64.51 | 68.62 | 65.01 | 68.09 | 68.39 |
| $A_d$, % | 28.40 | 21.46 | 10.30 | 17.81 | 14.92 | 17.87 | 16.86 | 13.05 | 11.67 | 62.13 | 17.63 | 28.69 | 87.47 | 20.24 | 16.75 | 17.27 | 19.71 | 16.94 | 16.44 |

*nd* no data, *U* upper portion, *M* middle portion, *L* lower portion, *AM* arithmetic mean, *GM* geometric mean

**Table 2** Comparison of elemental concentrations, TOC and $A_d$ from No. 8 coal seam of Zhujidong coal mine with Chinese, the US, and world coals (unit in μg/g unless noted as %)

| Elements | This study | | | Chinese coal[a] | | | | | World coal[e] | | | Clarke value of sedimentary rock[h] | CC | EF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | AM | Min | Max | AM[c] | Max | AM | Min | Max | AM[h] | | | |
| Li | 1.83 | 74.00 | 23.88 | 0.1 | 152 | 31.80 | 370 | 16 | 1.0 | 80 | 14 | 33 | 1.70 | 0.88 |
| Be | 0.18 | 9.02 | 3.10 | 0.1[b] | 72.8[b] | 2.11 | 330 | 2.2 | 0.1 | 15 | 2.0 | 1.9 | 1.54 | 1.97 |
| B | 0.10 | 215.56 | 58.50 | 6 | 997 | 53.00 | 1700 | 49 | 5.0 | 400 | 47 | 72 | 1.23 | 0.98 |
| Na, % | 0.01 | 0.48 | 0.23 | 0.015 | 0.94 | 0.12 | 1.4 | 0.08 | nd | nd | nd | nd | nd | nd |
| Mg, % | 0.01 | 0.28 | 0.12 | 0.001 | 1.45 | 0.13 | 1.5 | 0.11 | nd | nd | nd | nd | nd | nd |
| Al, % | 0.34 | 8.32 | 3.49 | 0.55 | 15.58 | 3.16 | 10.6 | 1.5 | nd | nd | nd | nd | nd | nd |
| Si, % | 1.38 | 73.43 | 18.34 | 0.54 | 16.69 | 3.96 | (13) | (2.4) | nd | nd | nd | nd | nd | nd |
| P | 32.73 | 1246 | 176.17 | bdl | 4192 | 401.51 | 58000 | 430 | 10 | 3000 | 250 | 670 | 0.70 | 0.32 |
| $S_{t,d}$, % | 0.07 | 0.52 | 0.21 | nd | nd | nd | (3) | (2.17) | nd | nd | nd | nd | nd | nd |
| K, % | 0.06 | 1.52 | 0.57 | 0.008 | 1.56 | 0.16 | 2 | 0.18 | nd | nd | nd | nd | nd | nd |
| Ca, % | 0.02 | 3.80 | 0.75 | 0.014 | 8.57 | 0.88 | 72 | 0.46 | nd | nd | nd | nd | nd | nd |
| Sc | 0.87 | 15.64 | 7.84 | 0.1 | 52.1 | 4.38 | 100 | 4.2 | 1.0 | 10 | 3.7 | 9.6 | 2.14 | 1.00 |
| Ti, % | 0.04 | 2.78 | 0.51 | 0.009 | 0.95 | 0.16 | 0.74 | 0.08 | 0.001 | 0.2 | 0.09 | 0.374 | 5.73 | 1.66 |
| V | 7.51 | 159.31 | 56.68 | 0.2[b] | 1405[b] | 35.10 | 370 | 22 | 2.0 | 100 | 28 | 91 | 2.03 | 0.76 |
| Cr | 1.06 | 113.43 | 36.62 | 0.1[b] | 943[b] | 15.40 | 250 | 15 | 0.5 | 60 | 17 | 58 | 2.13 | 0.76 |
| Mn | 7.24 | 126.21 | 36.69 | 0.2[b] | 8619[b] | 116.18 | 2500 | 43 | 5.0 | 300 | 71 | 830 | 0.51 | 0.05 |
| Fe, % | 0.32 | 3.86 | 1.78 | 0.014 | 14.29 | 3.39 | 24 | 1.3 | nd | nd | nd | nd | nd | nd |
| Co | 1.87 | 39.26 | 16.01 | 0.1[b] | 59.3[b] | 7.08 | 500 | 6.1 | 0.5 | 30 | 6 | 14 | 2.64 | 1.37 |
| Ni | 5.93 | 31.30 | 17.70 | 0.5[b] | 186[b] | 13.70 | 340 | 14 | 0.5 | 50 | 17 | 37 | 1.04 | 0.58 |
| Cu | 9.64 | 111.71 | 35.75 | 0.9[b] | 420[b] | 17.50 | 280 | 16 | 0.5 | 50 | 16 | 31 | 2.23 | 1.40 |
| Zn | 0.06 | 17.22 | 7.45 | 0.3[b] | 982[b] | 41.40 | 19000 | 53 | 5.0 | 300 | 28 | 43 | 0.27 | 0.21 |
| As | 0.04 | 4.18 | 1.62 | bdl[b] | 478.4[b] | 3.79 | 2200 | 24 | 0.5 | 80 | 9.0 | 7.6 | 0.18 | 0.25 |
| Se | 0.87 | 21.78 | 6.67 | 0.02[b] | 82.2[b] | 2.47 | 150 | 2.8 | 0.2[f] | 10[f] | 1.6 | 0.27 | 4.13 | 29.70 |
| Sr | 33.01 | 281.80 | 110.07 | 6 | 894 | 140.00 | 2800 | 130 | 15 | 500 | 100 | 270 | 1.11 | 0.50 |
| Y | 4.87 | 43.78 | 20.61 | 1.2 | 79.1 | 18.20 | 170 | 8.5 | 2.0 | 50 | 8.2 | 29 | 2.53 | 0.87 |
| Mo | 0.12 | 10.82 | 2.12 | 0.1[b] | 263[b] | 3.08 | 280 | 3.3 | 0.1 | 10 | 2.1 | 1.5 | 0.99 | 1.69 |
| Cd | 0.01 | 9.32 | 3.11 | bdl[b] | 5.4[b] | 0.25 | 170 | 0.47 | 0.1 | 3.0 | 0.2 | 0.8 | 16.65 | 5.06 |
| Sn | 0.28 | 12.43 | 4.81 | 0.1 | 25.9 | 2.11 | 140 | 1.3 | 1.0 | 10 | 1.4 | 2.9 | 3.46 | 2.03 |
| Sb | 0.64 | 33.66 | 9.39 | bdl[b] | 120[b] | 0.84 | 35 | 1.2 | 0.05 | 10 | 1.0 | 1.2 | 8.57 | 8.68 |
| Ba | 45.58 | 870.04 | 189.68 | 9 | 1458 | 159.00 | 22000 | 170 | 20 | 1000 | 150 | 410 | 1.27 | 0.57 |
| La | 3.86 | 55.02 | 22.35 | 2 | 350 | 22.50 | 300 | 12 | 1.0 | 40 | 11 | 32 | 2.05 | 0.86 |
| Ce | 6.56 | 85.38 | 38.75 | 3 | 459 | 46.70 | 700 | 21 | 2.0 | 70 | 23 | 52 | 1.70 | 0.91 |
| Pr | 0.56 | 7.74 | 3.29 | 0.8 | 43.9 | 6.42 | (65) | (4.8) | 1.0 | 10 | 3.4 | 6.8 | 0.97 | 0.59 |
| Nd | 4.11 | 39.04 | 17.94 | 2 | 169 | 22.30 | 230 | 10 | 3.0 | 30 | 12 | 24 | 1.51 | 0.92 |
| Sm | 1.13 | 8.04 | 4.23 | 0.8 | 27.4 | 4.07 | 18 | 1.7 | 0.5 | 6.0 | 2.2 | 5.5 | 1.91 | 0.93 |
| Eu | 0.21 | 1.29 | 0.67 | 0.09 | 51.22 | 0.84 | 4.8 | 0.4 | 0.1 | 2.0 | 0.43 | 0.94 | 1.53 | 0.85 |
| Gd | 0.85 | 7.47 | 3.65 | 0.8 | 20.3 | 4.65 | (21) | (1.5) | 0.4 | 4.0 | 2.7 | 4.0 | 1.37 | 1.13 |
| Tb | 0.01 | 0.46 | 0.17 | 0.12 | 3.7 | 0.62 | 3.9 | 0.3 | 0.1 | 1.0 | 0.31 | 0.69 | 0.55 | 0.30 |
| Dy | 0.81 | 9.35 | 4.25 | 0.7 | 12.8 | 3.74 | (28) | (1.5) | 0.5 | 4.0 | 2.1 | 3.6 | 2.02 | 1.43 |
| Ho | 0.01 | 3.03 | 1.01 | 0.14 | 2.57 | 0.96 | (12) | (0.47) | 0.1 | 2.0 | 0.57 | 0.92 | 1.74 | 1.31 |
| Er | 0.33 | 5.67 | 1.96 | 0.39 | 748 | 1.79 | (11) | (0.63) | 0.5 | 3.0 | 1.0 | 1.7 | 1.96 | 1.40 |
| Tm | 0.05 | 0.79 | 0.29 | 0.05 | 1.14 | 0.64 | (5.1) | (0.28) | nd | nd | 0.3 | 0.78 | 0.93 | 0.44 |
| Yb | 0.08 | 3.59 | 1.76 | 0.4 | 17.2 | 2.08 | 20 | 0.1 | 0.3 | 3.0 | 1.0 | 2.0 | 1.73 | 1.05 |
| Lu | 0.01 | 0.20 | 0.09 | 0.03 | 30 | 0.38 | nd | 0.14 | 0.03 | 1.0 | 0.2 | 0.44 | 0.50 | 0.28 |
| W | 0.04 | 142.23 | 48.28 | nd | nd | 1.08 | 400 | 1.0 | 0.5 | 6[g] | 0.99 | 2.0 | 52.47 | 31.56 |
| Re | 0.06 | 0.44 | 0.25 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

**Table 2** continued

| Elements | This study | | | Chinese coal[a] | | | | | World coal[e] | | | Clarke value of sedimentary rock[h] | CC | EF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | AM | Min | Max | AM[c] | Max | AM | Min | Max | AM[h] | | | |
| Pb | 0.41 | 21.25 | 10.86 | 0.2[b] | 790[b] | 15.10 | 1900 | 11 | 2.0 | 80 | 9 | 12 | 1.22 | 1.11 |
| Bi | 0.07 | 4.07 | 2.08 | 0.1 | 3.6 | 0.79 | 14 | <1.0 | <0.05 | nd | 1.1 | 0.26 | 1.89 | 9.72 |
| Th | 0.33 | 7.19 | 3.84 | 0.1[b] | 55.8[b] | 5.84 | 79 | 3.2 | 0.5 | 10 | 3.2 | 7.7 | 1.20 | 0.61 |
| TOC, % | 49.13 | 76.07 | 67.26 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| $A_d$, % | 9.18 | 38.32 | 18.59 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

CC-concentration coefficient = AM of this study/AM of world coal; EF-enrichment factor = AM of this study/Clarke value of sedimentary rock

*nd* no data, *bdl* below detection limit

[a] Dai et al. (2007, 2008), [b] Ren et al. (2006), [c] Dai et al. (2012a), [d] Finkelman (1993). Data in bracket were calculated from USGS CD-ROM (7430 samples), [e] Swaine (1990), [f] Swaine (1995), [g] Yudovich et al. (1985), [h] Ketris and Yudovich (2009)

compared to the corresponding elements in world coals (Fig. 3a). As compared with Chinese coals summarized by Dai et al. (2012a), mean concentrations of Si, K, Ti, Cd, Sb, W, Cr, Co, Cu, Se, and Bi in studied coals seam are higher, whereas the remainder elements are either lower (P, Mn, Zn, As, Gd, Tm, and Lu) or equivalent. Approximately half of elements have average concentrations approaching to the USA coals (Finkelman 1993), except that Na, Al, Si, K, Ti, V, Cr, Co, Cu, Y, Cd, Sn, Sb, Sm, Gd, Dy, Ho, Er, Yb, and W are higher, and P, S, Zn, and As are lower. High concentrations for Se, Sb, Cd, and W are considered to be resulted from magma-derived hydrothermal fluids in many coal mines (Zhao 1997; Finkelman et al. 1998). These elements are all enriched in No. 8 coal seam of Zhuji mine with enrichment factors of 2.7, 11.2, 12.4, and 47.7 compared to Chinese coals. In addition, magmatic rocks are discovered locally from boreholes during exploration. This suggested that part of coal seam was possibly affected by magmatic hydrothermal fluids in Zhuji coal mine. Note that the concentration ranges of potentially hazardous elements (e.g., Cr, As, Cd) are very wide, and are elevated in specific locations (e.g., Cr in borehole #16-4). Great attention should be given as these localized coals are utilized in industrial applications.

EF (enrichment factor) is a useful parameter of identifying and quantifying human interference with global element cycles and natural fractionation of elements (Reimann and Caritat 2000). The EF is calculated by

$$EF = \frac{A_i/B}{C_i/D}$$

where $A_i$ = the mean concentration of element $i$ in coals of this study (Table 2), $B$ = the mean concentration of Sc in coals of this study (7.84 μg/g, Table 2), $C_i$ = the clarke value of element $i$ in sedimentary rock (black shale) (Ketris and Yudovich 2009), $D$ = the clarke value of Sc in sedimentary rock (black shale) (9.6 μg/g, Ketris and Yudovich 2009).

Figure 3b shows that Be, Se, Cd, Sn, Sb, W, and Bi,are higher in studied coals, with EF values >2. The concentrations of P, Mn, Zn, As, Sr, Tb, Tm, and Lu studied coals are lower than corresponding elements in black shales. Sediments and sedimentary rocks (shale and coal) with high TOC are generally enriched in specific trace elements, such as P, U, Mo, V, Re, Se, Zn, Hg, Cu, Ni (Brumsack and Thurow 1986; Dean and Arthur 1986; Ketris and Yudovich 2009). The enrichment of Se and Cd in the analyzed coals is probably attributed to their higher TOC than black shale.

*The vertical variation of elements in coal seam*

Figure 4 summarizes the variation of elements among three sections of No. 8 coal seam. In total, 31 elements in the upper coal section and 27 elements in the lower section of coal seam exceed the arithmetic mean of the whole coal. Therefore, we draw a preliminary conclusion that most major and trace elements in No. 8 coal seam were concentrated in the upper or lower coal sections. This is consistent with the observations on coals from other regions (Gentzis and Goodarzi 1997; Liu et al. 2004).

The significant variation of elemental concentrations in different sections of a single coal seam points to the importance of depositional micro-environment in controlling elemental migration in the stages of peat accumulation and humification-gelification. The enrichment of seawater-derived elements such as B, Mg, K, Sr, Mo, and V in the lower coal section and their decreased trends from lower to upper coal sections suggest that the seawater regressed with the deposition of No. 8 coal seam. It is in line with the observation of Sun et al. (2010b). The REE is slightly concentrated in the upper coal section, and positively correlates with the distribution of ash yield, suggesting an

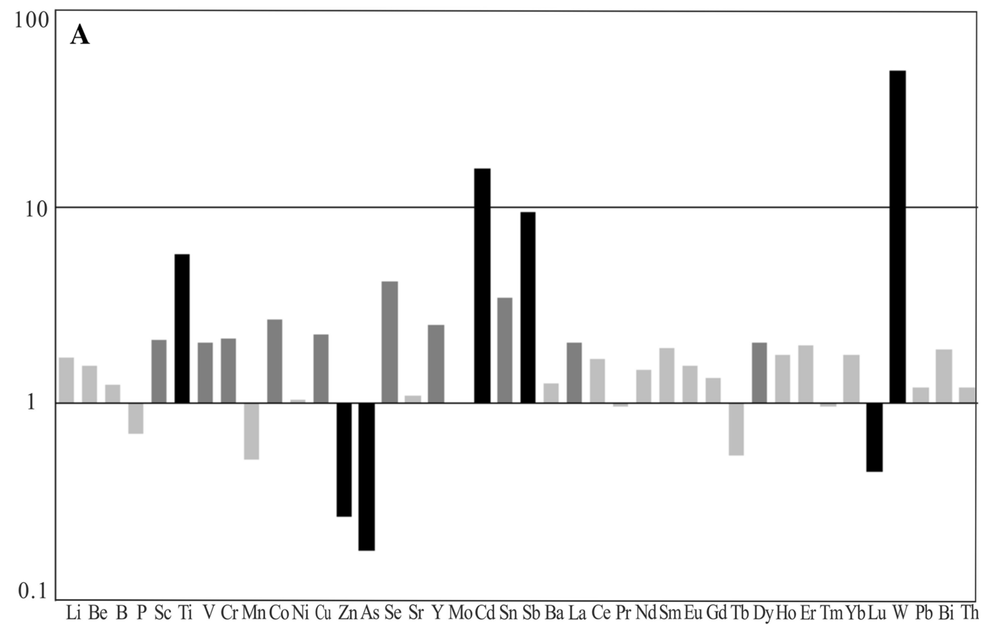


**Fig. 3** Ratios of element concentrations in No. 8 coal seam of Zhuji coal mine and world coals (**a**) and sedimentary rocks (*black shale*) (**b**)

increased input of REE from detrital materials in the late deposition stage of No. 8 coal seam.

*A general pattern of element geochemistry in coal seam*

Yang (2011) proposed that the abundance, distribution, and occurrence of elements in coal are generally governed by the periodic law of elemental properties, especially for coal seams accumulated in a stable depositional environment. For coal seams gathered with interruption from the epigenetic processes, this periodic law of elemental behavior will be invalid. This periodic law is assessed by correlating the first ionization energy (FIE) or electronegativity (EP) of elements with the correlation coefficients between elements and ash yield ($r_{\text{element-ash yield}}$). Trends of FIE versus $r_{\text{element-ash yield}}$ and EP versus $r_{\text{element-ash yield}}$ are shown in Fig. 5. It shows a negative correlation between $r_{\text{element-ash yield}}$ and FIE of elements.

## Modes of occurrence

Modes of occurrence of an element indicate how this element is chemically bound or physically distributed in the whole coal (Finkelman 1994). Because many of the

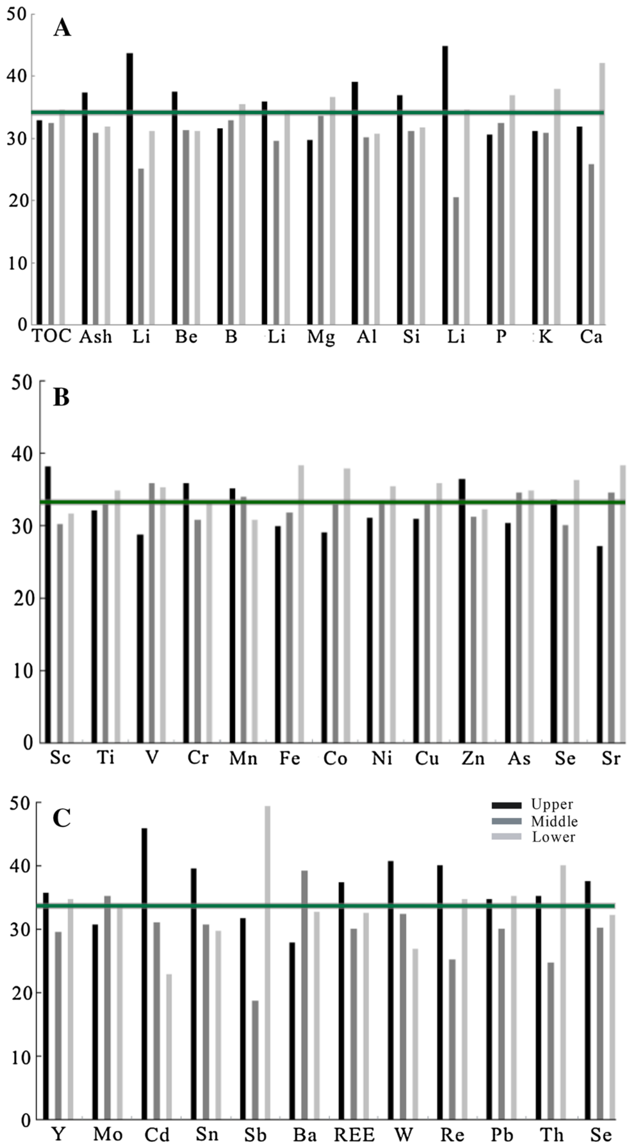


**Fig. 4** Vertical variation of elements in No. 8 coal seam of Zhuji coal mine. The blue line between 30 and 40 means one-third line

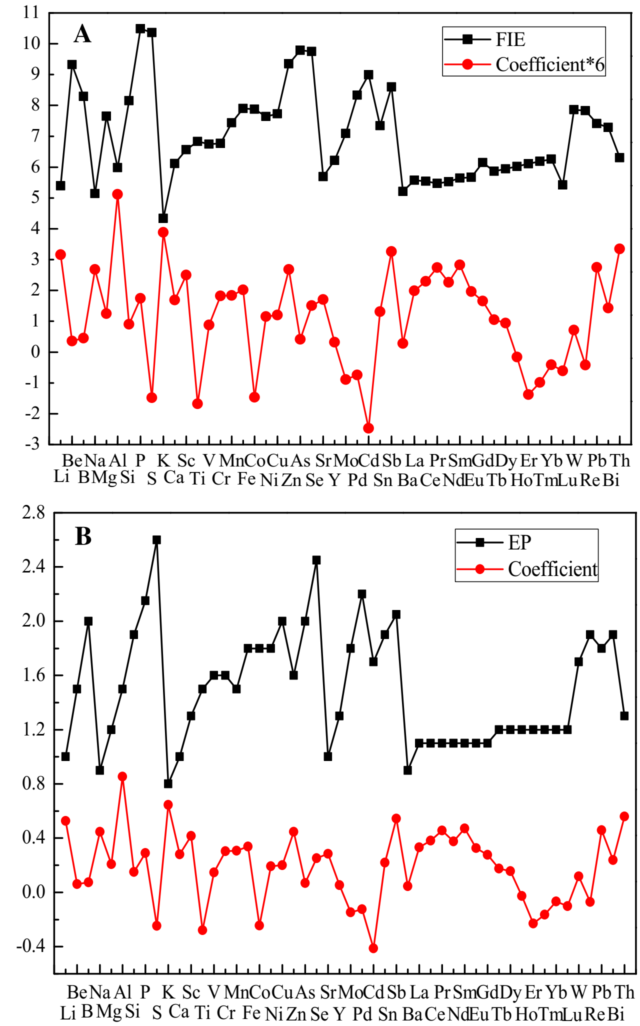


**Fig. 5** Trends between first ionization energy (FIE) (**a**) electronegativity (EP) (**b**) of 50 elements and correlation coefficients of elements with ash yield. in No. 8 coal seam of Zhuji coal mine

environmental and health problems are attributed to coal utilization (Finkelman and Gross 1999), the detail information on the modes of occurrence, including the specific minerals that an element forms, dispersion of elements within a particular host mineral, and the oxidation state that an element occurs (Vejahati et al. 2010), of potentially toxic elements are significantly important.

Many statistical methods, such as correlation, cluster analysis and factor analysis, have been applied to determine the modes of occurrence of elements in coal (Finkelman and Gluskoter 1983; Finkelman 1994; Warwick et al. 1997; Dai et al. 2005, 2008, 2012b; Song et al. 2007; Vesper et al. 2008; Wang et al. 2008; Zheng et al. 2008a; Životić et al. 2008; Sun et al. 2010a, b; Arbuzov et al. 2011). Correlation analysis was used in present study to interpret elemental modes in coals. Pearson correlation coefficients of elements with TOC and ash yield, and of trace elements with Si, Al, and Fe are tabulated in Table 3.

*Major elements*

Major elements (e.g., Si, Al, Fe, and Ca) are the basic components of coal minerals such as quartz, clay minerals, and carbonate. X-ray diffraction (XRD) results reveal that the major minerals in studied coal samples are quartz, kaolinite, and chlorite, with less fraction of siderite, montmorillonite, lepidocrocite and glauconite, and trace proportion of calcite, muscovite, and pyrite (Fig. 6).

The major components in six representative coal ashes are $SiO_2$ followed by $Al_2O_3$, $Fe_2O_3$, and CaO. These

**Table 3** Pearson correlation coefficients of elements with TOC, ash yield, Si, Al, and Fe

| | | | | |
|---|---|---|---|---|
| Correlation coefficient with TOC | | | | |
| $r_{TOC–Ad} = -0.685$** | $r_{TOC–Li} = -0.493$** | $r_{TOC–K} = -0.403$** | $r_{TOC–Ca} = -0.296$* | $r_{TOC–Pb} = -0.359$* |
| $r_{TOC–Th} = -0.366$** | $r_{TOC–S} = 0.297$* | | | |
| Correlation coefficient with Ad yield | | | | |
| $r_{Ad–REE} = 0.419$** | $r_{Ad–Li} = 0.527$** | $r_{Ad–Na} = 0.446$** | $r_{Ad–Al} = 0.853$** | $r_{Ad–P} = 0.290$* |
| $r_{Ad–K} = 0.646$** | $r_{Ad–Sc} = 0.416$** | $r_{Ad–Cr} = 0.304$* | $r_{Ad–Mn} = 0.307$* | $r_{Ad–Fe} = 0.337$* |
| $r_{Ad–Zn} = 0.446$** | $r_{Ad–LREE} = 0.433$** | $r_{Ad–La} = 0.332$* | $r_{Ad–Ce} = 0.381$** | $r_{Ad–Pr} = 0.456$** |
| $r_{Ad–Nd} = 0.377$** | $r_{Ad–Sm} = 0.472$** | $r_{Ad–Eu} = 0.326$* | $r_{Ad–Pb} = 0.458$** | $r_{Ad–Th} = 0.559$** |
| $r_{Ad–Ti} = -0.280$* | | | | |
| Correlation coefficient with Si | | | | |
| $r_{Si–S} = -0.435$** | $r_{Si–Ni} = -0.356$* | $r_{Si–Zn} = -0.377$* | $r_{Si–As} = -0.358$* | $r_{Si–Se} = -0.397$** |
| $r_{Si–Ho} = -0.413$** | $r_{Si–Er} = -0.295$* | $r_{Si–Yb} = -0.343$* | $r_{Si–Bi} = -0.733$** | $r_{Si–W} = 0.872$** |
| $r_{Si–Ti} = 0.398$** | $r_{Si–Pd} = 0.981$** | $r_{Si–Cd} = 0.986$** | | |
| Correlation coefficient with Al | | | | |
| $r_{Al–Ad} = 0.853$** | $r_{Al–REE} = 0.672$** | $r_{Al–Li} = 0.818$** | $r_{Al–Na} = 0.764$** | $r_{Al–K} = 0.582$* |
| $r_{Al–Sc} = 0.635$** | $r_{Al–V} = 0.558$* | $r_{Al–Cr} = 0.844$** | $r_{Al–Fe} = 0.661$** | $r_{Al–Zn} = 0.530$* |
| $r_{Al–Sr} = 0.565$* | $r_{Al–Pd} = 1.000$** | $r_{Al–LREE} = 0.685$** | $r_{Al–La} = 0.738$** | $r_{Al–Ce} = 0.589$* |
| $r_{Al–Nd} = 0.632$** | $r_{Al–Sm} = 0.603$* | $r_{Al–Eu} = 0.639$* | $r_{Al–Gd} = 0.535$* | $r_{Al–Tb} = 0.571$* |
| $r_{Al–Lu} = 0.502$* | $r_{Al–Pb} = 0.591$* | $r_{Al–Bi} = 0.541$* | $r_{Al–Th} = 0.903$** | $r_{Al–Tm} = -0.969$** |
| Correlation coefficient with Fe | | | | |
| $r_{Fe–Ad} = 0.337$* | $r_{Fe–Na} = 0.378$** | $r_{Fe–Mg} = 0.300$* | $r_{Fe–Al} = 0.661$** | $r_{Fe–K} = 0.486$** |
| $r_{Fe–Sr} = 0.418$* | $r_{Fe–Sm} = 0.338$* | $r_{Fe–Pb} = 0.436$** | $r_{Fe–Bi} = 0.646$** | |

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

components account for >90 wt% of minerals in coal ash (Table 4). The calculated correlations of Al ($r = 0.853$), K ($r = 0.646$), Na ($r = 0.446$), Fe ($r = 0.337$), and Ti ($r = 0.280$) with ash yield show their associations with minerals in coal. Potassium correlated negatively with TOC ($r = -0.403$), which also supports the point above.

The average ratio of $SiO_2/Al_2O_3$ for the coal ashes is 1.55, which is slightly higher than the theoretical $SiO_2/Al_2O_3$ ratio of kaolinite (1.18) and compiled Chinese coal (1.42) (Dai et al. 2012a), indicating the existence of free $SiO_2$ (Dai et al. 2013). The abundant $SiO_2$ in No. 8 coal seam of Zhuji is a main feature to distinguish this coal from other No. 8 coal of Huainan Coalfield with average $SiO_2$ of 0.45 wt%. No correlations were observed in either Si versus TOC or Si versus ash yield or other major elements, indicating that the quartz was dispersed in organic matrix of coal. In the plot of Si versus Al, the scatter points distribute in two distinct areas with average value Si/Al ratio of 12.14 and 2.19, respectively. The calculated correlation coefficient of the scatter point group with higher Si/Al ratio is 0.646, which supports the above argument that free quartz presents in coal. The lower Si/Al ratio with a correlation coefficient of 0.910 approaches to the theoretical Si/Al ratio of 2.48 in montmorillonite, which may suggest that Si and Al in corresponding samples are in the form of montmorillonite (Fig. 7).

Strong linkage between Fe and S for pyrite-rich coal was thought to be governed by a seawater depositional environment (Wang et al. 2008). S is the only element that has a positive correlation ($r = 0.297$) with TOC in this study. However, its relationships with Fe and ash yield are absent. This suggests that pyrite is lacked and S is mainly bound to the organic matter in No. 8 coal seam of the Zhuji mine. Iron is thought to be generally controlled by sulfide in high-sulfur coal, mainly pyrite. Considering the rare occurrence of pyrite, Fe in No. 8 coal seam of Zhuji is thought to exist in carbonate, oxide, and hydroxide such as chlorite, siderite, and lepidocrocite or other iron-bearing minerals (Ren et al. 2006; Wang et al. 2008). Titanium has a negative correlation with ash yield, indicating its organic association, although Ti is mainly carried into coal basin via weathering of oxide and clay minerals (Tang and Huang 2004). Swaine (1990) pointed out that Ti has the possibility to be associated with organic matter in low-rank coal. Huggins and Huffman (1995, 1996, 2004) reported that Ti has both organic and mineral associations in coals. Calcium may be present as calcite as described by the results of X-ray diffraction (Fig. 6a). Sodium correlates well with Al

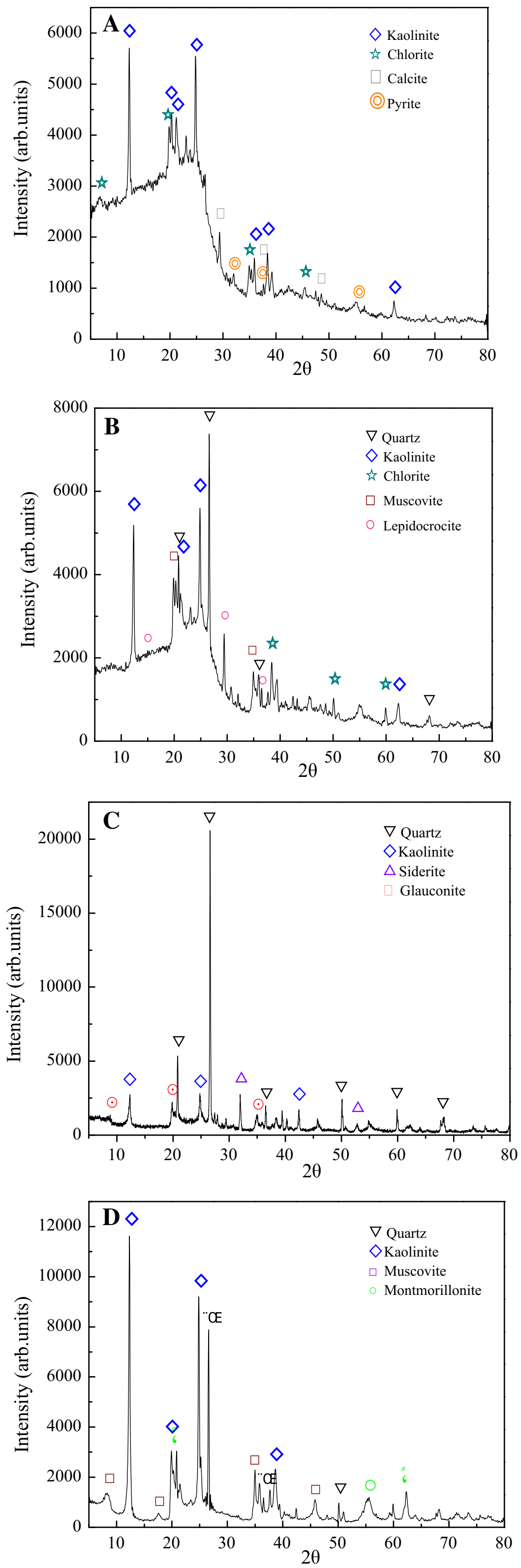


**Fig. 6** Powder X-ray diffraction patterns of coal samples from No. 8 coal seam in the Zhuji coal mine

($r = 0.764$) and Fe ($r = 0.378$), suggesting its possible associations with clay minerals.

*Trace elements*

Many authors (Finkelman 1994, 1995; Querol et al. 1995; Huggins and Huffman 1996; Davidson and Clarke 1996; Finkelman and Gross 1999; Goodarzi 2002; Huggins et al. 2002; Huggins and Huffman 2004; Dai et al. 2005; Wang et al. 2008; Zheng et al. 2008a, b, c; Spears and Tewalt 2009; Chen et al. 2011) did a voluminous of work to identify the modes of occurrence of trace elements in coal. However, the modes of occurrence of trace elements are so complex, researchers obtained different results due to the contrasting geological setting of the coal and different techniques they used (Ward 2002). Modes of occurrence of trace elements in this study are deduced by several indirect evidences: correlation with ash yield and TOC; correlation with selected major elements Si, Al, Fe, and Ca; correlation among the trace elements; and presence of minerals which carry some of the trace elements (Eskenazy 2009). Trace elements including Cd, Sb, and Re are not included due to their limited number of data.

According to the dendrogram shown in Fig. 8, three large groups of elements could be classified with the choice of a distance of 20 as a benchmark. Group 1 is divided into three subgroups: Group 1A, 1B, and 1C. Group 1A comprises Sc, Ni, HREE, Be, Y, V, Co, and Cu. Phosphorus and Sr constitute Group 1B. Group 1C is made up of B, Sn, Se, Bi, TOC, S, and Ba. Half of elements in Group 1 are negatively correlated with TOC, while the rest of elements are positively correlated to TOC, with correlation coefficients. HREE clusters together with TOC, which may indicates their organic affinities relative to LREE. Group 2 can also be divided into three subgroups: Group 2A, 2B, and 2C. LREE and Zn constitute Group 2A. Group 2B covers Al, Mn, and Li. Group 2C is made up of Na, Th, Cr, Fe, and Mg. Elements in this group have relatively high correlations with Al with correlation coefficients ranging from 0.33 to 0.90. LREE correlated highly with inorganic matter, which contrast with HREE. Group 3 includes two subgroups: Ca and Mo in Group 3A, and Si, W, Ti, Pb, and K in Group 3B along with ash yield. The correlation coefficients of the elements with ash yield in this Group 3 range from −0.280 to 0.646.

The relationship between trace elements and Al is thought to indicate their associations with aluminosilicate or clay minerals. In the studied coal samples, 17 out of 41 trace elements, including Li, Sc, V, Cr, Zn, Sr, La, Ce, Nd, Sm, Eu, Gd, Tb, Lu, Pb, Bi, and Th, positively correlate

**Table 4** Major oxide compositions in 8 typical coal ashes from No. 8 coal seam of Zhuji coal mine

| Sample no. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $TiO_2$ | $K_2O$ | $Na_2O$ | $P_2O_5$ | MnO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0-1-r | 44.15 | 23.76 | 6.59 | 7.86 | 4.23 | 5.52 | 1.261 | 1.22 | 0.83 | 0.04 | 0.058 | 95.519 |
| 0-1-u | 48.34 | 35.0 | 3.41 | 3.46 | 1.20 | 1.69 | 1.234 | 0.69 | 0.62 | 0.052 | 0.030 | 95.726 |
| 0-1-l | 55.76 | 31.18 | 2.91 | 2.95 | 1.04 | 1.00 | 1.375 | 0.80 | 0.62 | 0.036 | 0.032 | 97.703 |
| 0-1-f | 53.74 | 36.73 | 2.18 | 0.10 | 1.03 | 0.10 | 0.89 | 1.54 | 0.12 | 0.031 | 0.027 | 96.488 |
| 7-6-m | 49.46 | 36.64 | 3.97 | 1.19 | 1.51 | 0.20 | 1.50 | 1.60 | 1.08 | 0.052 | 0.031 | 97.233 |
| 12-8-d | 45.27 | 34.29 | 8.15 | 3.74 | 1.68 | 3.58 | 1.202 | 0.88 | 0.52 | 0.04 | 0.054 | 99.406 |
| 13-4-u | 44.56 | 23.78 | 6.67 | 8.12 | 4.32 | 5.20 | 1.248 | 1.33 | 2.18 | 0.045 | 0.053 | 97.506 |
| 16-5-d | 53.67 | 34.3 | 3.55 | 1.05 | 1.42 | 0.05 | 2.88 | 1.80 | 0.93 | 0.04 | 0.039 | 99.729 |

with Al, possibly indicating their occurrence in clay such as kaolinite and chlorite. Ti, Cd, and W positively correlate with Si but not Al, suggesting they are not associated with clay minerals. The relationship between trace elements and Fe is indicative of their associations with iron-bearing clay minerals in low-sulfur coal. Only Sr, Sm, Pb, and Bi have significant positive correlations with Fe in this study. The relationship between trace elements and Ca can be implicative for the associations of trace elements with carbonate in medium rank coal, e.g., high-volatile bituminous coal in this study. Mn, Cu, Se, As, Y, Cd, and Eu all correlate well with Ca.

## REE geochemistry

Rare earth elements in coal contain abundant and dependable information about the basinal structure of coal-accumulation and depositional environment. The application of REE to research clastic sediment provenance and as a tracer for seawater, groundwater, and fluid processes during diagenesis has been well established (Schatzel and Stewart 2003; Zheng et al. 2007).

### *General features and distribution pattern*

The arithmetic mean of REE concentration of No. 8 coal samples from Zhuji is 98 μg/g, ranging from 22 to 199 μg/g. The average REE concentration is lower than Huainan coals reported by Zheng et al. (1999) and Chinese coals by Dai et al. (2012a), but much higher than the world coals by Ketris and Yudovich (2009) (Table 5). The mean LREE/HREE ratio is 7.00, which is higher than those of Huainan, Chinese, and world coals, reflecting a greater discrepancy between LREE and HREE. All the samples show negative Eu anomalies and slightly positive Ce anomalies when they were chondrite-normalized, indicating a weak seawater influence on coal swamp.

Figure 9 shows REE distribution patterns, which are characterized by a "V" shape curve with significant Eu negative anomalies and the enrichment of LREE relative to HREE. An apparent "V" shape of REE distribution with a Eu negative anomaly was also observed in Neopaleozoic coal-bearing kaolinite rocks and north China Paleozoic coals. Europium is thought to be inherited from source rocks of coal basin (Eskenazy 1987). Zheng et al. (2008b) reported that the supply of terrigenous materials into coal basin was extremely stable during the formation of Late Paleozoic Carboniferous-Permian coals in North China. Huainan Coalfield is located at southeast of North China Paleozoic coal Basin. Samples from borehole #0-1 include one roof, two coal layers and one floor. Their REE distribution patterns are analogical and exhibit comparable Eu anomalies indicating their same provenance.

### *Differentiation of LREE and HREE*

The detrital materials, especially clay, are the main suppliers of REE in the peat basin (Eskenazy 1999). REE in coal mainly combines with silicate derived from terrestrial clastics, although certain proportion of REE is associated with organic matter (Eskenazy 1987; Finkelman 1993). In addition, sulfide and carbonate, to a less extent, contribute to the overall REE budget (Schatzel and Stewart 2003). In this study, REE shows significant correlations with ash yield ($r = 0.42$) and Al ($r = 0.67$), which suggests their association with aluminosilicate. Furthermore, correlation coefficients of LREE with ash yield and Al are greater than those of HREE. This indicates that HREE has a stronger organic association than LREE, in accordance with the conclusion of Querol et al. (1995). LREE and HREE fractionate each other mainly as a function of their different physicochemical properties, such as dissolubility, precipitation, adsorbability and complicated abilities. A proportion of REE would be dissolved and desorbed from terrestrial clastic materials and enter into coal swamp under a slightly acid aqoues environment. With the ascent of atomic number of REE, their abilities to complex with organic matters increase but their adsorbabilities onto clay

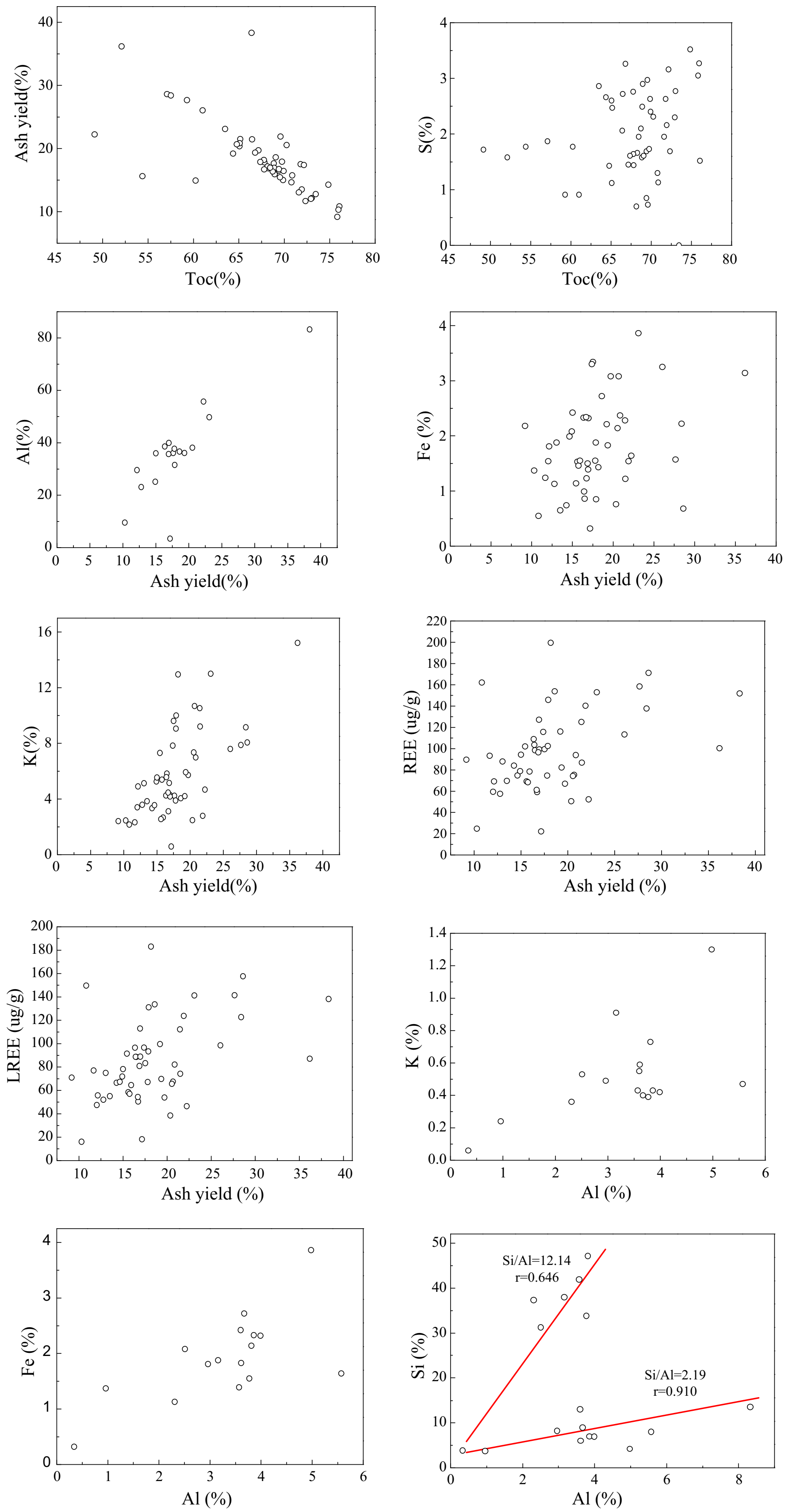


**Fig. 7** Correlations of between TOC (total organic carbon), ash yield, and selected major elements

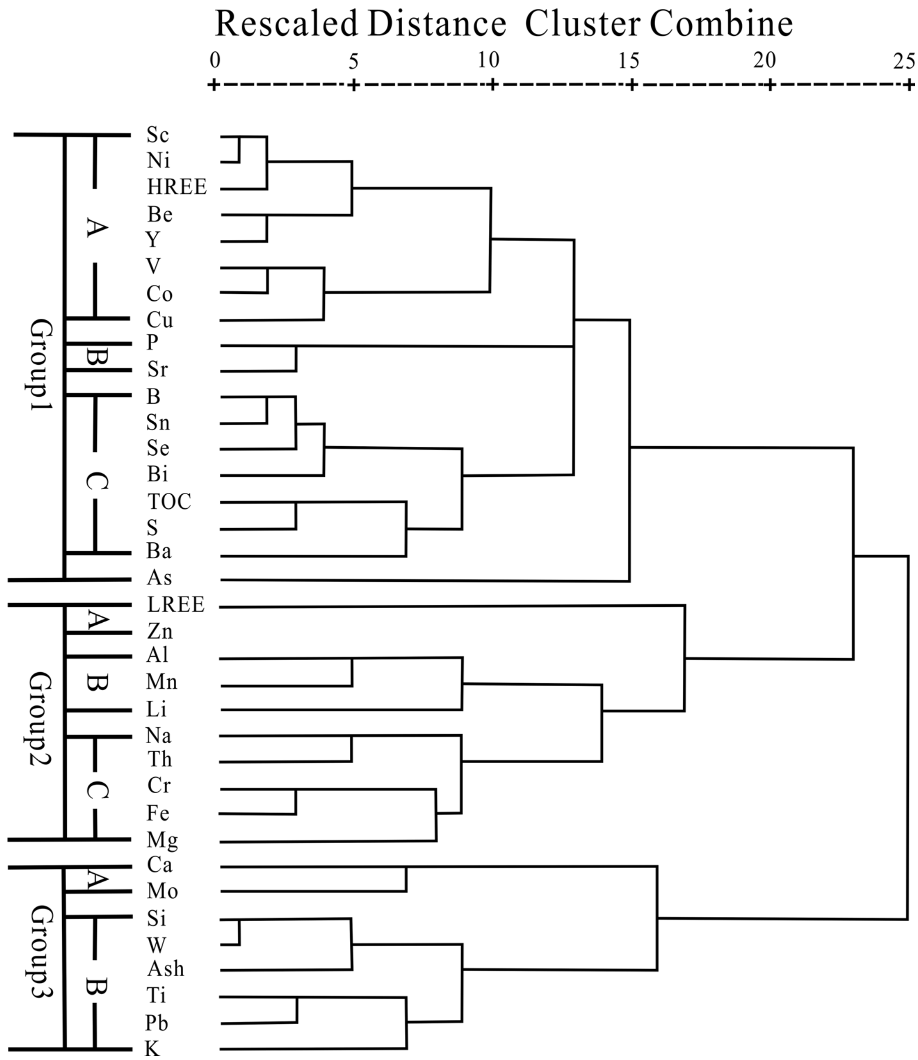


**Fig. 8** Dendrogram produced by hierarchical cluster analysis of data (cluster method: between groups linkage; interval: pearson correlation; transform values: standardize range 0–1)

minerals decrease (Liu and Cao 1987). Thus, HREE bound to minerals are more easily transported and dissolved into ambient solutions due to their small ion radii when coal-accumulating swamp was invaded by seawater (Huang et al. 2000).

## Depositional environment of No. 8 coal seam of the Zhuji coal mine

Table 6 lists B concentration (Goodarzi 1994; Goodarzi and Swaine 1994), δCe/δEu (Ren et al. 2006), Ash Index (AI), Acid Alkali Index (AAI), and Salinity Index (SI) (Zhao 1991) of coal ash, and C-value, V/(V + Ni), V/Cr, Ni/Co, Cu/Zn (Cao et al. 2012) of mudstone, reflecting the degrees of marine influence, environment of peat swamp, paleoclimate, and redox condition, respectively.

The average B concentration in studied coals is 58.5 μg/g, varying between 40 and110 μg/g, indicating a mildly brackish water-influenced sedimentary environment (Goodarzi and Swaine 1994). δCe/δEu is >1, which demonstrates an acidic-reducing dominant environment of coal deposition. Chlorite was abundant in coal, roof, and floor, which also demonstrates a reducing sedimentary environment. Pyrite was not preferably formed in the sub-deltaic environment with a reducing condition and limited supply of sulfur. This is in line with the rare occurrence of pyrite in the No. 8 coal seam. However, the discovery of glauconite that is considered to be formed in the interface of marine sediments with water (Odin and Matter 1981) indicates the complex control factors and a variable sedimentary environment during the deposition of coal. All kinds of Ash Indexes including AI, AAI, and SI support a weak reducing, high salinity peat swamp severing as a favorable medium for the activities of anaerobic bacteria (Spears and Tewalt 2009). The paleo-climate index C-value is 1.04, indicating a moist paleo-climate (Zheng et al. 2008b), whereas V/(V + Ni), V/Cr, Ni/Co, Cu/Zn all reflect an anoxic condition.

**Table 5** REE concentrations (μg/g) and related parameters of 8 representative coal sample and arithmetic means of No. 8 coals of Zhujidong coal mine, Huainan, Chinese, world coals

| Sample no. | REE | $La_N/Lu_N$ | $La_N/Sm_N$ | $Gd_N/Lu_N$ | δCe | δEu | δY | Type REE |
|---|---|---|---|---|---|---|---|---|
| 0-1-r | 193.27 | 3.12 | 1.06 | 5.33 | 1.00 | 0.47 | 1.09 | L |
| 0-1-u | 186.64 | 2.89 | 0.81 | 3.33 | 1.00 | 0.50 | 7.48 | M |
| 0-1-l | 42.27 | 1.14 | 0.34 | 3.84 | 1.09 | 0.47 | 1.06 | M |
| 0-1-f | 98.89 | 1.51 | 1.29 | 1.38 | 1.16 | 0.63 | 2.45 | L |
| 7-6-m | 170.44 | 2.83 | 0.87 | 3.76 | 1.02 | 0.73 | 0.67 | M |
| 12-8-d | 126.35 | 1.43 | 0.69 | 3.33 | 0.99 | 0.60 | 0.75 | M |
| 13-4-u | 181.6 | 6.04 | 0.93 | 6.18 | 2.31 | 0.99 | 2.15 | M |
| 16-5-d | 120.32 | 1.85 | 0.86 | 1.61 | 1.05 | 0.45 | 3.09 | M |
| Up | 132.06 | 2.65 | 0.79 | 3.42 | 1.10 | 0.78 | 0.77 | M |
| Middle | 108.72 | 2.84 | 0.80 | 3.63 | 1.00 | 0.81 | 0.71 | M |
| Down | 116.10 | 2.51 | 0.83 | 3.06 | 0.98 | 0.84 | 0.75 | M |
| Average[a] | 121.02 | 2.47 | 0.76 | 3.33 | 1.03 | 0.80 | 0.76 | M |
| Huainan[b] | 177.70 | 0.48 | 1.09 | 0.58 | 1.09 | 0.95 | nd | H |
| Chinese[c] | 135.89 | 0.63 | 0.83 | 1.03 | 0.89 | 0.91 | 0.73 | H |
| World[d] | 68.61 | 0.59 | 0.75 | 1.14 | 0.86 | 0.83 | 0.58 | H |

$\delta Ce = Ce_N/(La_N{*}Pr_N)^{1/2}$; $\delta Eu\text{–}Eu = Eu_N/(Sm_N{*}Gd_N)^{1/2}$; $\delta Y\text{–}Y = Y_N/(Dy_N{*}Ho_N)^{1/2}$

[a] This study, [b] cited by Zheng et al. (1999), [c] cited by Dai et al. (2012a), [d] cited by Ketris and Yudovich (2009)

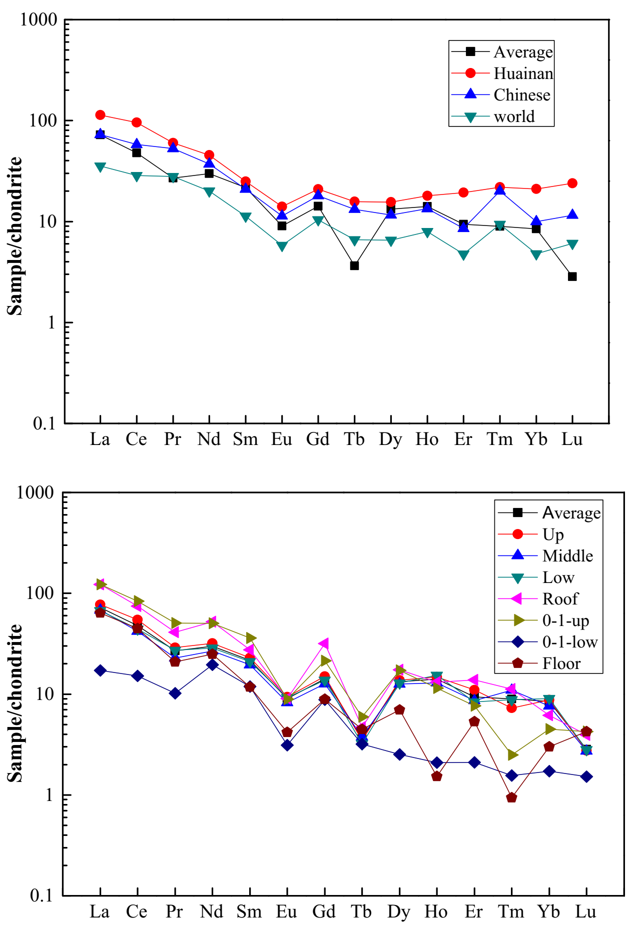


**Fig. 9** Chondrite-normalized REE distribution patterns of No. 8 coals of Zhujidong and Huainan, Chinese and world coals

**Table 6** Geochemistry indexes related to depositional environment for Zhujidong coal mine

| Index | B content (μg/g) | δCe/δEu | AI | AAI | SI |
|---|---|---|---|---|---|
| Values | 58.50 | 2.06 | 0.12 | 10.01 | 0.06 |
| Index | C-value | V/(V + Ni) | V/Cr | Ni/Co | Cu/Zn |
| Values | 1.04 | 0.74 | 2.24 | 1.42 | 3.95 |

$AAI = \frac{Fe_2O_3+MgO+CaO}{SiO_2+Al_2O_3}$, $AAI = \frac{SiO_2+Al_2O_3}{MgO+CaO}$, $SI = \frac{MgO+CaO}{SiO_2+Al_2O_3+Fe_2O_3}$, $C-\text{value} = \frac{Fe+Mn+Cr+Ni+V+Co}{Ca+Mg+Sr+Ba+K+Na}$

## Conclusions

1. The average concentrations of Si, K, Se, Cd, Sn, Sb, and W in No. 8 coal seam of Zhuji coal mine are higher, and Zn, As, and Lu are lower than corresponding elements in Chinese, the US, and world coals. The EF shows that Be, Se, Cd, Sn, Sb, W, and Bi are concentrated in coal. The enrichment of Se and Cd is likely attributed to the large amount of TOC in coal. Most trace elements in No. 8 coal seam of Zhuji are concentrated in the upper and lower sections of the coal seam. The correlation analysis of elements with ash yield reveals a periodic change of elemental behavior in coal along with the metallic activity.
2. Silicon the studied coals is considered to mainly disperse in organic matrix. Iron is in siderite and other iron-bearing minerals. Calcium presents in calcite and has association with clay minerals. Titanium shows apparent organic association. Three groups are

classified in dendrogram on the basis of the distance of different elements to TOC and ash yield.

3. REE distribution patterns and Eu and Ce anomalies suggest that REE was mainly supplied by terrestrial clastics from North China basin margin.. The differentiation of LREE and HREE is due to their differentiated physicochemical properties and specific paleo-sedimentary environment.
4. Various indexes and the existence of certain minerals indicate that No. 8 coal seam was deposited in a reducing and anoxic mire that were slightly influenced by seawater and with a steady supply of terrigenous detrital materials in a moist climate.

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