

# Comprehensive Utilization for Neogene Lignite of the Zhaotong Basin, South China, and Its Environment Impacts

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## S Supporting Information

**ABSTRACT:** Neogene lignite is widely used for enterprise's electric power generation, local residents' warming and cooking, and crops' fertilizer in South China nowadays. But there is still no report about the element variations in Neogene lignite from the Zhaotong Basin, South China. Understanding the elemental concentration in lignite is of great importance to comprehensive utilization and to evaluation of environmental impacts of the Neogene lignite. We studied the variation patterns of 34 elements in lignite samples collected from the Neogene Zhaotong Formation at Zhaotong Basin, Yunnan Province, China. The arithmetic average of Cr, V, Ga, As, Cu, Rb, Co, Mo, and Cd in studied lignite samples is higher than those of China coals, while the content of Li and Bi are lower. Contents of As, Rb, La, Ni, Cd, Mo, Co, Ga, and V in northeastern Yunnan lignite are higher than the corresponding elements in common American Texas lignite, while contents of Li and Bi are lower. Elements are classified into four groups (Si–K–Zn–Rb–Ba–Pb, Co–Cd–Na–Al, Ni–Ti–Bi–Cr–Cu–In–Mn–Mg–Ga–Fe–Tl, and V–U–Cs–Sc–La–Sr–L–Se–Ca–As–Mo–S) based on their correlation coefficient with ash yield. Elements, including Al, K, Na, Si, Ti, Ba, Bi, Cd, Cr, Cu, Cs, Co, Ga, Ni, Sc, Zn, and Pb, decrease from bottom to top of the Neogene Zhaotong Formation, whereas Ca, Mg, As, Se, Mo, Fe, and S increase. In addition, in M2 and M3 coal-bearing beds, Ga has potential applications after recycling and Se could be reutilized as a kind of Se-containing fertilizer, and their reserves estimations are approximately  $98 \times 10^4$  (Ga) tons and  $7.8 \times 10^4$  tons (Se). Cr and Cd in Neogene lignite have potential risk for local natural environments and the health of human beings.

## 1. INTRODUCTION

Lignite, also known as brown coal,<sup>1</sup> is mined all around the world and is one of the most important fossil fuels.<sup>2</sup> China is the world's top lignite producer, which has 319.4 billion short tons of lignite reserves, amounting to 5.67% of the worldwide lignite reserves.<sup>3</sup> Neogene lignite in the Yunnan Province of South China is characterized by a stable occurrence at shallow depth and having giant reserves, accounting for 16.56% of the lignite reserves in China.<sup>4</sup>

Lignite is considered a low-rank coal due to its low heat content.<sup>1</sup> Its high moisture and ash content as well as susceptibility to spontaneous combustion can cause problems in storage and transportation.<sup>5</sup> For these reasons, lignite was not explored and utilized extensively for a long time. Since the 1960s, many countries have noted coal's multipurpose use, including its associated components (i.e., lignite and coal gangue), and tracked the corresponding measures.<sup>6–9</sup> After 2000, low rank coal-bed gas has been successfully explored and utilized in the Alberta basin of Canada<sup>10</sup> and in the Tuha basin of the USA.<sup>11</sup> Indeed, at present, the comprehensive utilization of coal (i.e., lignite) and its byproduct (i.e., gangue) have been paid more attention since it can be mined for germanium (Ge), lithium (Li), molybdenum (Mo), vanadium (V), gallium (Ga), rhenium (Re), uranium (U), selenium (Se), and rare earth elements,<sup>12–16</sup> and the low cost of lignite also makes it popular in China. Moreover, Neogene lignite in Yunnan Province is becoming the main source for electricity generation and fertilizer. Local residents also burn Neogene lignite for heating and cooking. In addition, in the Zhaotong county of Yunnan

Province, local residents are using the lignite to roast grain and tobacco leaves. But so far, there are still no reports about element variations in Neogene lignite from the Zhaotong basin.

In this study, elemental variation in Neogene lignite, in the Zhaotong basin, is systematically investigated, and the reserves of potentially valuable elements are also estimated. The health risk of lignite for local residents and the environment could be evaluated based on this study.

## 2. METHODS

**2.1. Sample Collection.** The Zhaotong Basin is situated in northeastern Yunnan Province, China<sup>17</sup> (Figure 1A). The main outcropping strata of the Zhaotong basin are the Lower Triassic Feixianguan Formation, Neogene Zhaotong Formation, and Quaternary Haizi Formation<sup>17,18</sup> (Figure 1B and C), and its coal-bearing strata belong to the Neogene Zhaotong Formation (Figure 1C and Table 1).

The Zhaotong Formation is mainly divided into three members in ascending order:<sup>18</sup> (1) **Member 1** ( $N_2^1$ )—ca. 210 m—is composed of gray arenaceous clay. (2) **Member 2** ( $N_2^2$ )—ca. 170 m—is characterized by lignite coal interbedded with gray arenaceous clay or brown carbonaceous clay. The M1 lignite coal-bearing seam (ca. 0.9 m) is located in the top section of Member 2. The M2 lignite coal-bearing seam (approximately 96 m) is situated in the mid to uppermost portion of Bed 2 ( $N_2^2$ ). The M3 lignite coal-bearing seam

Received: July 8, 2018

Revised: August 28, 2018

Published: September 5, 2018

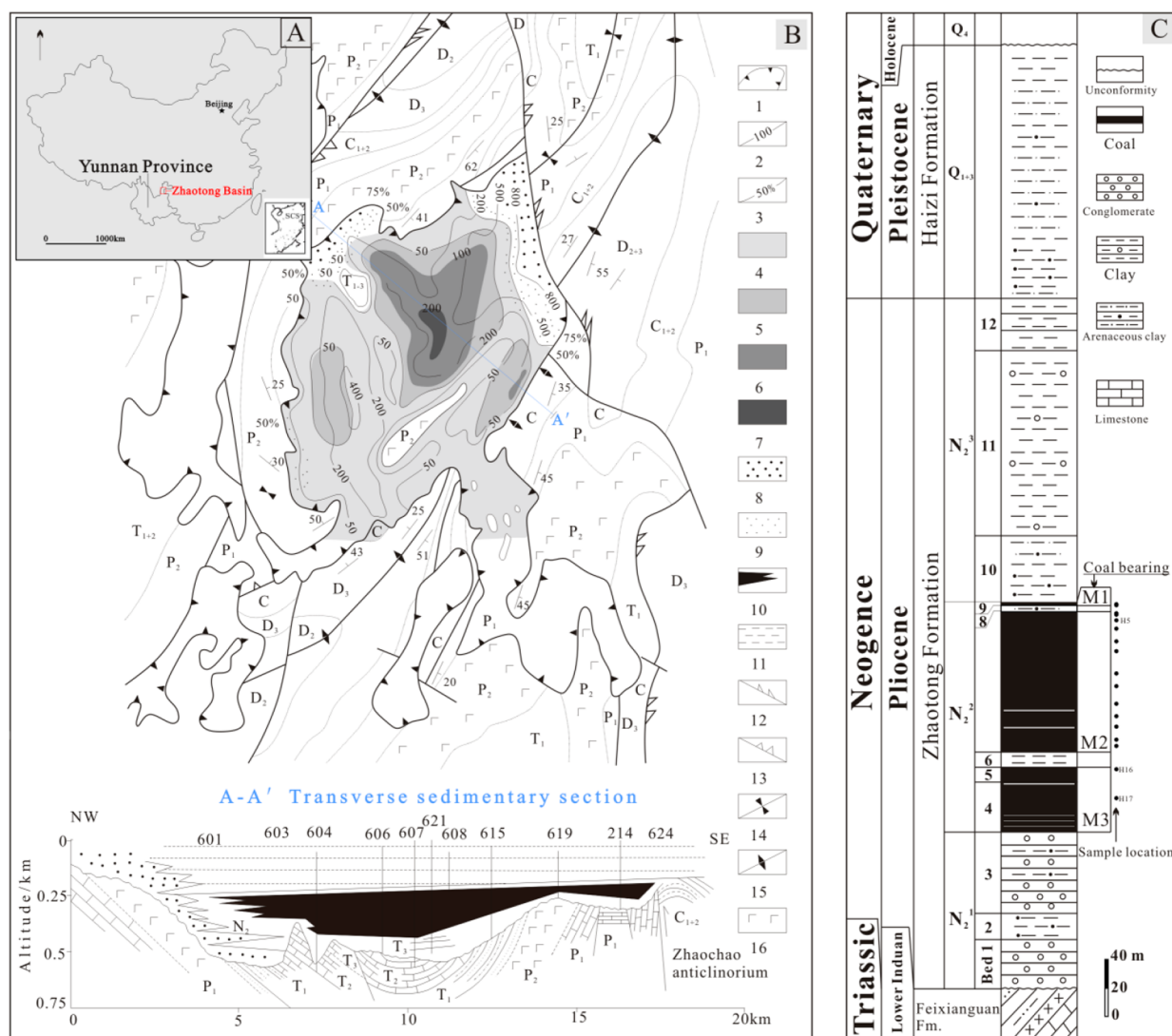


**Figure 1.** (A) Location of the Zhaotong Basin. SCS = South China Sea. (B) Relationship between basement tectonic framework and Neogene coal-accumulation age sedimentation in Zhaotong Basin, modified from ref 17. 1: Basin denudation boundary. 2: Stratigraphic thickness line. 3: sandstone percent isoline. 4: Coal sea thickness 0–50 m. 5: Coal seam thickness 50–100 m. 6: Coal seam thickness 100–200 m. 7: Coal seam thickness > 200m. 8: Near facies. 9: Distal facies. 10: Swamp facies. 11: Lacustrine facies. 12: Compress shear fault. 13: Compression fault. 14: Basement syncline. 15: Basement anticline. 16: Basement basalt. (C) Stratigraphy sequence of the Zhaotong Basin, Yunnan Province, China, modified from ref 18.

(ca. 55 m) is located in the lower Member 2. (3) **Member 3** ( $N_2^3$ )—ca. 120 m—is characterized by gray conglomeration rocks.

A detailed description of the Neogene Zhaotong Formation (Zhaotong Basin, northeastern Yunnan Province) is listed into Table 1, including the lithologic categories, locations, and thicknesses.

We collected coal samples from the M1, M2, and M3 coal-bearing seams of the Shansantang (Qiaojia County) and Hongni open-cast coal mine (Zhaotong County) at the Zhaotong basin from Yunnan Province, China. The position of these samples is shown in Figure 1C.

**2.2. Analytical Methods.** The fresh parts of the samples were crushed and ground into a fine powder that was less than 200 mesh size for the analyses. Fine powder (approximately 50 mg) was digested with a mixture of acids solution ( $HF + HNO_3 + HClO_4$ ),<sup>19</sup> and the major and trace element (excluding Se and As) compositions were analyzed using inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry. Analyses followed the China coal standards GBW11103J and GBW 11112 and China soil standard GBW 07403 (GSS3). The relative error was lower than 10%, and its detection limit was  $10^{-9}$ . A blank experiment, parallel samples, and repeated measurements were also

used. As and Se were texted using a hydride generation atomic fluorescence spectrometer. The procedures detailed for sample digestion have been documented by Ni et al.,<sup>20</sup> Li et al.,<sup>21,22</sup> and Long and Luo.<sup>23</sup>

All lignite coals were crushed and texted at the Lab Analytical and Testing Center in Institute of Geographic Sciences and Natural Resources Research, China Academy of Sciences (CAS).

### 3. RESULTS AND DISCUSSION

Maceral compositions of the Neogene lignite are vitrinite, together with some fusinite, exinite, and algae-like substances (Table 2). The  $R_{O,max}$  of vitrinite was between 0.515% and 0.515%, with the average  $R_v$  value of 0.315%,<sup>24</sup> indicating (1) the metamorphic degree of lignite in Zhaotong Basin is characterized by soft lignite under the immature stage, and (2) the coal bed gas is mainly derived from the biodegradation of organic matter under the primary stage of coal seam

**Table 1. Descriptions of 12th Bed of the Neogene Zhaotong Formation from Zhaotong Basin, Northeastern Yunnan Province, South China<sup>a</sup>**

| P                   | E        | Fm                 | M                           | bed | T (m) | Coal S | S No.         | description <sup>18</sup>                                                                                                                                                                                                                                                                                                                                                              |
|---------------------|----------|--------------------|-----------------------------|-----|-------|--------|---------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Quaternary Haizi Fm |          |                    |                             |     |       |        |               |                                                                                                                                                                                                                                                                                                                                                                                        |
| Neogene             | Pliocene | Zhaotong Formation | N <sub>2</sub> <sup>3</sup> | 12  | 31.3  |        |               | fine sandstone and medium sandstone conglomerate (lower part); <i>Cervus (Pseudasix) horlulorum</i> sp.                                                                                                                                                                                                                                                                                |
|                     |          |                    |                             | 11  | 117.3 |        |               | gray sand–clay                                                                                                                                                                                                                                                                                                                                                                         |
|                     |          |                    |                             | 10  | 53.5  |        |               | green to gray sand–clay contain lignite detritus and abundant snail fossils: <i>Viviparus tingi</i> Yen (sp. nov), <i>Tulotomoides kwangsiensis</i>                                                                                                                                                                                                                                    |
|                     |          |                    | N <sub>2</sub> <sup>2</sup> | 9   | 0.9   | M1     | <i>n</i> = 2  | green- gray, yellow-gray sand–clay interbedded with thin flow sand seam, contain ostracod, snail, and hydrophyte ( <i>Trapa</i> sp.) fossils                                                                                                                                                                                                                                           |
|                     |          |                    |                             | 8   | 3.9   |        |               | <b>M1 coal-bearing</b>                                                                                                                                                                                                                                                                                                                                                                 |
|                     |          |                    |                             | 7   | 95.6  | M2     | <i>n</i> = 13 | gray sand–clay and contain abundant plant fossils ( <i>Phyllites</i> sp.)                                                                                                                                                                                                                                                                                                              |
|                     |          |                    | N <sub>2</sub> <sup>1</sup> | 6   | 12.4  |        |               | <b>M2 coal-bearing</b> ; interbedded with several to 10 thin carbonaceous clay, clay-parting seam, and contain abundant plant ( <i>Pinus yunnanensis</i> Fr.) and animal fossils ( <i>Stegolophodon</i> sp., <i>Stegolophodon banguensis</i> , <i>Chilotherium</i> sp.?, <i>Zygodontodon</i> sp.?, <i>Stegodon zhaotongensis</i> , <i>Rhynchotherium huananensis</i> ; Chow and Chang) |
|                     |          |                    |                             | 5   | 11.9  | M3     | <i>n</i> = 1  | gray clay                                                                                                                                                                                                                                                                                                                                                                              |
|                     |          |                    |                             | 4   | 43.5  |        | <i>n</i> = 1  | <b>M3 coal-bearing</b>                                                                                                                                                                                                                                                                                                                                                                 |
|                     |          |                    |                             | 3   | 67.1  |        |               | lignite coal interbedded with clay, carbonaceous clay                                                                                                                                                                                                                                                                                                                                  |
|                     |          |                    |                             | 2   | 29.5  |        |               | green- gray sand–clay                                                                                                                                                                                                                                                                                                                                                                  |
|                     |          |                    |                             |     |       |        |               | gray sand–clay interbedded with coarse sandstone conglomerate made up of basalt                                                                                                                                                                                                                                                                                                        |
|                     |          |                    |                             | 1   | 40    |        |               | light green conglomerate -with coarse grained limestone                                                                                                                                                                                                                                                                                                                                |

lower Triassic Feixianguan Fm

<sup>a</sup>Abbreviations: P = Period. E = Epoch. Fm = Formation. M = Member. T (m) = Thickness (meter). Coal S = Coal-bearing Seam. S No. = Sample number.**Table 2. Maceral Compositions of the Coal-Bearing Seam (Coal S) of the Neogene Zhaotong Formation from Zhaotong Basin, Northeastern Yunnan Province, South China (%; No Mineral-Free Basis)<sup>24</sup>**

| Coal S | sample no.     | vitrinite | fusinite | exinite | alginite | R <sub>O,ran</sub> |
|--------|----------------|-----------|----------|---------|----------|--------------------|
| M1     | <i>n</i> = 4   | 87.89     | 3.11     | 9       | 0        | 0.306              |
| M2     | <i>n</i> = 85  | 92.8      | 2.85     | 4.6     | 0.02     | 0.318              |
| M3     | <i>n</i> = 13  | 96.66     | 1.67     | 1.67    | 0        | 0.299              |
| total  | <i>n</i> = 102 | 93.27     | 2.47     | 4.24    | 0.02     | 0.315              |

evolution. The duration of gas generation is short and the amount of gas generated is small.

**3.1. Element Enrichment Patterns in Neogene Lignite.** Average contents of elements and the variations of the Neogene lignite from the Neogene Zhaotong Formation from Zhaotong Basin, northeastern Yunnan Province, China are listed in Table 3 and the Supporting Information as supplementary data. In order to evaluate the enrichment of elements, the concentration coefficients (CC) were calculated as the ratio between the elemental concentration in each sample and the average concentration of the upper continental crust,<sup>25</sup> China coals average,<sup>26</sup> world hard coals,<sup>27</sup> and Texas lignite (USA).<sup>9</sup> The elements with a CC are divided into five intervals:  $CC < 0.5$ ,  $0.5 < CC < 1$ ,  $1 < CC < 2$ ,  $2 < CC < 5$ ,  $CC > 5$ , which represent depletion, slight enrichment, strong enrichment, super enrichment, and anomalous enrichment of the corresponding elements, respectively.

Compared to the average concentrations of elements in the upper continental crust, the elemental enrichment characteristics of Zhaotong Neogene lignite are listed in descending order as Se > As > Mo > Cd > U > La > Ga > V > Cu > Bi > Pb > Cs > Co > Cr > Tl > Zn > Li > Ca > Fe > Ba > Ti > Sc > Ni > Si > Rb > P > Al > Sr > In > Mg > K > Na > Mn. Se is abnormally enriched, with a CC<sub>1</sub> of 33.20 (CC<sub>1</sub> = ratio between element concentration of studied samples vs the

upper continental crust), followed by As (CC<sub>1</sub> = 6.75), Mo (CC<sub>1</sub> = 5.89), and Cd (CC<sub>1</sub> = 3.07; Table 3 and Figure 2).

Compared to the average element contents in China coals, SiO<sub>2</sub> is enriched in Neogene lignite (average = 16.78%), followed with TiO<sub>2</sub> (average = 0.13%). Fe<sub>2</sub>O<sub>3</sub> in Neogene lignite (average = 3.78%) is close to the average Fe<sub>2</sub>O<sub>3</sub> content in China coals (4.85%; Table 3). The remaining major elements are higher than that in China coals (Table 3). The concentrations of Cr, V, Ga, As, Cu, Rb, Co, Mo, and Cd in Neogene lignite are 2.05–4.26 times more than those of China coals (Table 3). The CC<sub>2</sub> of Cs, Ni, Ca, La, U, Sc, Tl, Zn, Ba, Pb, Se, Sr, and In ( $0.5 < CC_2 < 2$ , CC<sub>2</sub> = concentration of elements from this study vs those of China coals) in Neogene lignite are close to those in China coals. Average content of Li and Bi in Neogene lignite are lower than in China coals (Table 3 and Figure 2).

As shown in Figure 2 and Table 3, V, La, Cr, Ga, Cu, Mo, Co, Cd, and U are slightly enriched ( $2 < CC_3 < 5$ , CC<sub>3</sub> = element concentration of studied samples vs those of world hard coals) in the Zhaotong Neogene lignite, while Ti, Ca, P, Al, and Bi are depleted ( $CC_3 < 0.5$ ). The remaining elements' average is closer to ( $0.5 < CC_3 < 2$ ) hard coals of the world.

Compared to average element contents in A1 bed Paleocene lignite (Calvert mine, Texas, USA), arsenic and P are significantly enriched in Zhaotong lignite, with a CC<sub>4</sub> of 20.24 and 12.50, respectively (CC<sub>4</sub> = investigated coals vs Texas lignite). Elements such as Zn, Cs, Fe, and Cr are strongly enriched ( $5 < CC_4 < 10$ ). Rb (CC<sub>4</sub> = 4.50), La (CC<sub>4</sub> = 4.48), Ni (CC<sub>4</sub> = 4.46), Cd (CC<sub>4</sub> = 3.54), Mo (CC<sub>4</sub> = 4.36), Co (CC<sub>4</sub> = 3.36), Ga (CC<sub>4</sub> = 3.32), and V (CC<sub>4</sub> = 2.51) are slightly enriched ( $2 < CC_4 < 5$ ). But, Bi, Mn, and Se are lower (CC<sub>4</sub> < 0.5). CC<sub>4</sub> of the remaining elements ( $0.5 < CC_4 < 2$ ) in Neogene lignite is close to the CC<sub>4</sub> in A1 bed lignite from Texas, USA (Table 3 and Figure 2).

**3.2. Geochemical Associations.** Clustered elements are categorized into four groups according to cluster analysis

**Table 3. Average Contents of Elements in Neogene Lignite from Zhaotong Basin (South China) and Other Basins of USA, Canada, and Turkey (mg/kg)<sup>a</sup>**

| element | lignite (this study) |        |        | WHC   | UCC  | CC    | AC    | Bs   | Es    | Al B  | BB   | <i>a</i> | <i>b</i> | <i>c</i> |
|---------|----------------------|--------|--------|-------|------|-------|-------|------|-------|-------|------|----------|----------|----------|
|         | min                  | max    | avg    |       |      |       |       |      |       |       |      |          |          |          |
| Al (%)  | 0.28                 | 7.41   | 2.82   | 5.98  | 8.23 | 5.98  | 2.8   | 3    | 1.37  | 1.27  | 0.9  | -        | -        | -        |
| As      | 4.9                  | 28.44  | 12.14  | 8.3   | 1.8  | 3.79  | 24    | 11   | 0.5   | 0.6   | 57   | -        | 25.4     | 40       |
| Ba      | 20.98                | 267.18 | 136.05 | 150   | 425  | 159   | 170   | 196  | 970   | 136   | 8.4  | -        | -        | -        |
| Bi      | 0.01                 | 0.28   | 0.1    | 1.1   | 0.13 | 0.79  | 1     | 0.3  | -     | 0.3   | 0.7  | -        | -        | -        |
| Ca (%)  | 0.13                 | 4.05   | 1.75   | 6     | 4.15 | 1.23  | 0.64  | 3.2  | 1.62  | 1.07  | 1.6  | -        | -        | -        |
| Cd      | 0.1                  | 1.19   | 0.46   | 0.2   | 0.15 | 0.25  | 0.47  | 3.3  | -     | 0.13  | 0.4  | -        | 0.22     | 1        |
| Co      | 3.06                 | 22.73  | 10.07  | 6     | 25   | 7.08  | 6.1   | 6.6  | 1.4   | 3     | 3    | -        | 17.5     | 40       |
| Cr      | 5.26                 | 749.6  | 68.48  | 17    | 102  | 15.4  | 15    | 23.8 | 5.8   | 13    | 57   | -        | 65.2     | 300      |
| Cs      | 0.06                 | 5.66   | 2.02   | 1.1   | 3    | 1.13  | 1.1   | 0.88 | ND    | 0.32  | 1    | -        | -        | -        |
| Cu      | 16.48                | 78.78  | 40.24  | 16    | 60   | 17.5  | 16    | 70.5 | 6.9   | 24    | 9    | -        | 46       | 400      |
| Fe (%)  | 1.49                 | 7.17   | 3.35   | 4.85  | 5.63 | 4.85  | 1.9   | 2.4  | 0.38  | 0.42  | 2.3  | -        | -        | -        |
| Ga      | 6.88                 | 41.5   | 20.6   | 6     | 19   | 6.55  | 5.7   | 5    | -     | 6.2   | 2    | 30       | -        | -        |
| In      | 0                    | 0.09   | 0.02   | 0.04  | 0.25 | 0.05  | 0.03  | -    | -     | -     | -    | -        | -        | -        |
| K (%)   | 0.01                 | 0.57   | 0.14   | 0.19  | 2.09 | 0.19  | 0.22  | 0.31 | 0.13  | 0.1   | <0.1 | -        | -        | -        |
| La      | 8.93                 | 71.64  | 44.81  | 11    | 30   | 26    | 12    | 6.2  | 6.3   | 10    | 3    | -        | -        | -        |
| Li      | 0.03                 | 35.2   | 10.16  | 14    | 20   | 31.8  | 16    | -    | -     | 14.34 | 8.7  | 120      | -        | -        |
| Mg (%)  | 0.04                 | 0.57   | 0.18   | 0.22  | 2.23 | 0.22  | 0.18  | 0.44 | 0.25  | 0.18  | 0.3  | -        | -        | -        |
| Mn (%)  | 0                    | 0.1    | 0.02   | 0.015 | 2.33 | 0.015 | 0.006 | 0.15 | 0.013 | 0.13  | 0.07 | -        | -        | -        |
| Mo      | 2.44                 | 11.11  | 7.49   | 2.1   | 1.2  | 3.08  | 3.3   | 14.1 | 1.9   | 2.1   | 5    | -        | -        | -        |
| Na (%)  | 0.01                 | 0.15   | 0.08   | 0.16  | 2.36 | 0.16  | 0.11  | 0.48 | 0.82  | 0.05  | 0.14 | -        | -        | -        |
| Ni      | 4.08                 | 34.61  | 17.86  | 17    | 84   | 13.7  | 14    | 19.6 | 3.9   | 4     | 98   | -        | 42.5     | 200      |
| P (%)   | 0.01                 | 0.24   | 0.06   | 0.092 | 0.12 | 0.092 | 0.098 | 0.08 | -     | 0.002 | 0.16 | -        | -        | -        |
| Pb      | 1.38                 | 36.36  | 10.13  | 9     | 14   | 15.1  | 11    | 13.7 | 6.4   | 8     | 5    | -        | 40.6     | 500      |
| Rb      | 4.16                 | 60.08  | 18.45  | 18    | 90   | 9.25  | 21    | 13.7 | 5     | 4.1   | 5    | -        | -        | -        |
| Sc      | 0.28                 | 16.85  | 5.64   | 3.7   | 22   | 4.38  | 4.2   | 7.8  | 1.7   | 4.3   | 3    | -        | -        | -        |
| Se      | 0.45                 | 7.69   | 1.66   | 1.3   | 0.05 | 2.4   | 2.8   | -    | -     | 24.3  | -    | 10       | -        | -        |
| Si (%)  | 0.45                 | 34.44  | 13.5   | 8.47  | 28.2 | 8.47  | 5.8   | 5.62 | 5.43  | 3.78  | -    | -        | -        | -        |
| Sr      | 13.11                | 101.2  | 74.87  | 100   | 370  | 140   | 130   | 94.3 | 537.7 | 143   | 87   | -        | -        | -        |
| Ti (%)  | 0.012                | 0.36   | 0.13   | 0.33  | 0.41 | 0.33  | 0.13  | 0.13 | 0.06  | 0.18  | 0.1  | -        | -        | -        |
| Tl      | 0.13                 | 0.96   | 0.5    | 0.58  | 0.85 | 0.47  | 1.2   | 0.2  | -     | 0.3   | 0.6  | -        | -        | -        |
| U       | 1.54                 | 8.96   | 4.18   | 1.9   | 2.7  | 2.43  | 2.1   | 1.2  | 1.6   | 2.5   | 6    | 40       | -        | -        |
| V       | 26.94                | 198.6  | 103.02 | 28    | 120  | 35.1  | 22    | 31   | 9.1   | 41    | 47   | 7000     | -        | -        |
| Zn      | 2.12                 | 93.39  | 32.69  | 28    | 70   | 41.1  | 53    | 39.4 | 20    | 3.6   | 13   | -        | -        | -        |
| ash (%) | 4.54                 | 39.27  | 22.1   | 20.7  | -    | -     | -     | 18.3 | <20.0 | 15.8  | 19.2 | -        | 89.7     | 500      |

<sup>a</sup>“-” = no data. WHC = World Hard Coals. UCC = Upper Continental Crust. CC = China Coals average. AC = American Coals averages. Bs = Balsha seam from Bulgaria. Es = Estevan seam, Canada. Al B = A1 Bed Calvert mine from Texas, USA. BB = Beyrzari Basin, Turkey. *a* = industrial grade of DZT0203-2002.<sup>28</sup> *b* = soils content average from Yunnan Province.<sup>29</sup> *c* = environmental quality standards for soils, China (GB 15618–2008).<sup>30</sup>

(Figure 3). Silicon (Si), K, Rb, and Na are closely connected with ash yield (Figure 3, Group A), among which Si has the closest connection with ash yield.

In Group B, high positive correlation exists in cobalt (Co) and ash yield (Table 4). Co, Ni, and Cr are categorized into Group B.

There is relative high positive correlation coefficient between Ba and Zn with ash yield, while Cu, Ga, and Bi are lower (Table 4). Ba, Zn, Cu, Ga, and Bi are categorized into Group C (Figure 3, Group C).

In Group D are Cd, In, Ti, Pb, V, Mg, and Mn (Figure 3, Group D), and their correlation coefficients are between −0.31 and 0.67 (Table 4). The correlation between Mn and Mg is the highest (Figure 3), reaching 0.67.

The other two associations are La, Tl, Cs, Sc, Li, Sr, and Al (Figure 3, Group E) and their correlation coefficients with ash yield changes from 0.02 to 0.49. Fe, S, As, Se, Ca, U, and Mo (Figure 3, Group F) are produced into Group F, and these

elements' correlations range from −0.4 to 0.23. The correlation among Fe, S, As, and Se is very high (Figure 3).

**3.3. Element Affinity.** The relationship between concentration of element with ash yield of coal will provide initial information to their inorganic or organic affinity. Elements of this studied lignite samples are categorized into four groups, based on their relationship.

A relatively high positive correlation level existed into the first group (>0.61; Si, K, Zn, Rb, Ba and Pb; Table 4 and Figure 3) and suggests high inorganic affinity. The highest correlation coefficients is 0.95 ( $r_{\text{Ash-Si}}$ ), and it is probably caused by clastic silicate or veined quartz. Si, K, Zn, Rb, Ba, and Pb concentrations increase with an increase in ash yield content (Figure 3). Potassium (K), Rb, Ba, Zn, Pb, Cd, Co, Sc, Cr, Ti, and Bi also show aluminosilicate affinity ( $r_{\text{Al-Si}} > 0.47$ ; Table 4).

Elements including Co, Cd, Na, and Al from the second group (Table 4) are chartered by positive correlation



**Figure 2.** Enrichment patterns of major and trace elements in Neogene lignite from the Zhaotong Formation.

coefficients with ash yield (0.48–0.56; Table 4), which represent the prevailing inorganic affinity.

Correlation coefficients of elements in the third group range from 0.23 to 0.46: Ni (0.46), Ti (0.42), Bi (0.41), Cr (0.39), Cu (0.36), In (0.35), Mn (0.34), Mg (0.27), Ga (0.26), Fe (0.23), and Tl (0.23). There are no clear positive correlations existing at Fe and Ca+Mg, with ash yield (Figure 4). It is noticed that high ash yield is mainly correlated with alluminosilicate minerals, rather than Fe-containing and carbonate minerals (Figure 4).

As shown in the Table 3, correlation coefficients of elements in the fourth group are between  $-0.4$  and  $0.22$  and follow the order V (0.22), U (0.13), Cs (0.12), Sc (0.06), La (0.05), Sr (0.03), Li (0.02), Se ( $-0.18$ ), Ca ( $-0.28$ ), As ( $-0.32$ ), Mo ( $-0.32$ ), and S ( $-0.40$ ), indicating intermediate affinity. In addition, As and Se are characterized by sulfide affinity ( $r_{S-Fe} > 0.47$ ; Table 2), indicating that As and Se mainly occur in sulfide in Neogene lignite of the Zhaotong Basin.

Manganese (Mn), Fe, and Sr are also characterized by carbonate affinity (Table 3). It is probably due to the relatively high component of epigenetic veined ankerite in the M2 coal-bearing seam, for instance, that the contents of Fe and Mn of sample no. H12 are relative higher and reach 235 mg/kg and 2.20%, respectively.

**3.4. Element Distribution Patterns in Lignite from Neogene Zhaotong Formation.** Depending on the ash yield, the lignite thickness of Member 2 ( $N_2^2$ ) of the Zhaotong Formation can be divided into four separate parts (Figures 5 and 6): (1) top part, 0–10 m (ash yield average 11.74%); (2) upper part, 11–65 m (average coal ash 30.22%); (3) middle part, 66–105 m (average coal ash 14.96%), and (4) low part, 115–160 m (average coal ash 36.25%). The ash yield in the low and upper part is above 20%, while the ash yield in the middle and top part is below 20% (Figure 6). Elements

including Si, K, Zn, Rb, Ba, and Pb have a similar distribution pattern with the ash yield from bottom to top, due to the high positive correlation ( $r > 0.61$ ).

Elements that have obvious correlation ( $r = 0.23$  to  $0.46$ ) with ash content are characterized by two types of distribution patterns in ascending order. The first group includes Ti, Mn, Mg, Fe, and Tl, which have the highest concentrations in the upper part of the seam (Figures 5 and 6). The rest of the elements, including Ni, Bi, Cr, Cu, In, and Ga, have irregular distribution.

Elements that have no correlation ( $r = -0.4$  to  $0.22$ ) with the ash yield are also characterized by two types of distribution patterns. One type includes Se, Ca, As, and S ( $-0.40$ ), which have the highest concentrations in the upper part of the seam (Figure 6), and the element contents decrease from bottom to top of the Neogene Zhaotong Formation. The other, including V, U, Cs, Sc, La, Sr, Li, and Mo, has irregular distribution.

Overall, elements including Al, K, Ti, Si, Na, Ba, Bi, Co, Cd, Cs, Cu, Cr, Ga, Ni, Sc, Pb, and Zn decrease from the bottom to the top of the Neogene Zhaotong Formation, whereas Ca, Mg, As, Se, Mo, Fe, and S increase from the bottom to the top. The rest of the elements, including V, U, Tl, Sr, Sc, Rb, Li, La, In, P, and Mn, have irregular distribution.

### 3.5. Significance and Estimation of Enriched Element.

**3.5.1. Resource Utilization.** Lignite is a significant non-renewable and coal resource. Elements including Ga, Li, Se, U, V, and rare earth elements in coal are considered potentially valuable elements, as they are beneficial minerals to utilize.<sup>12,31</sup>

**Gallium (Ga) and Selenium (Se).** Ga and Se are considered dispersed elements. These two elements are very difficult to enrich and hard to be of commercial utilization.<sup>32</sup>

Ga is called the food of the electronics industry,<sup>32</sup> with a price of  $1.65 \times 10^8$  (¥) per ton in April 2018. But a coal-hosted ore deposit of aluminum-Ga was not discovered until 2006 in

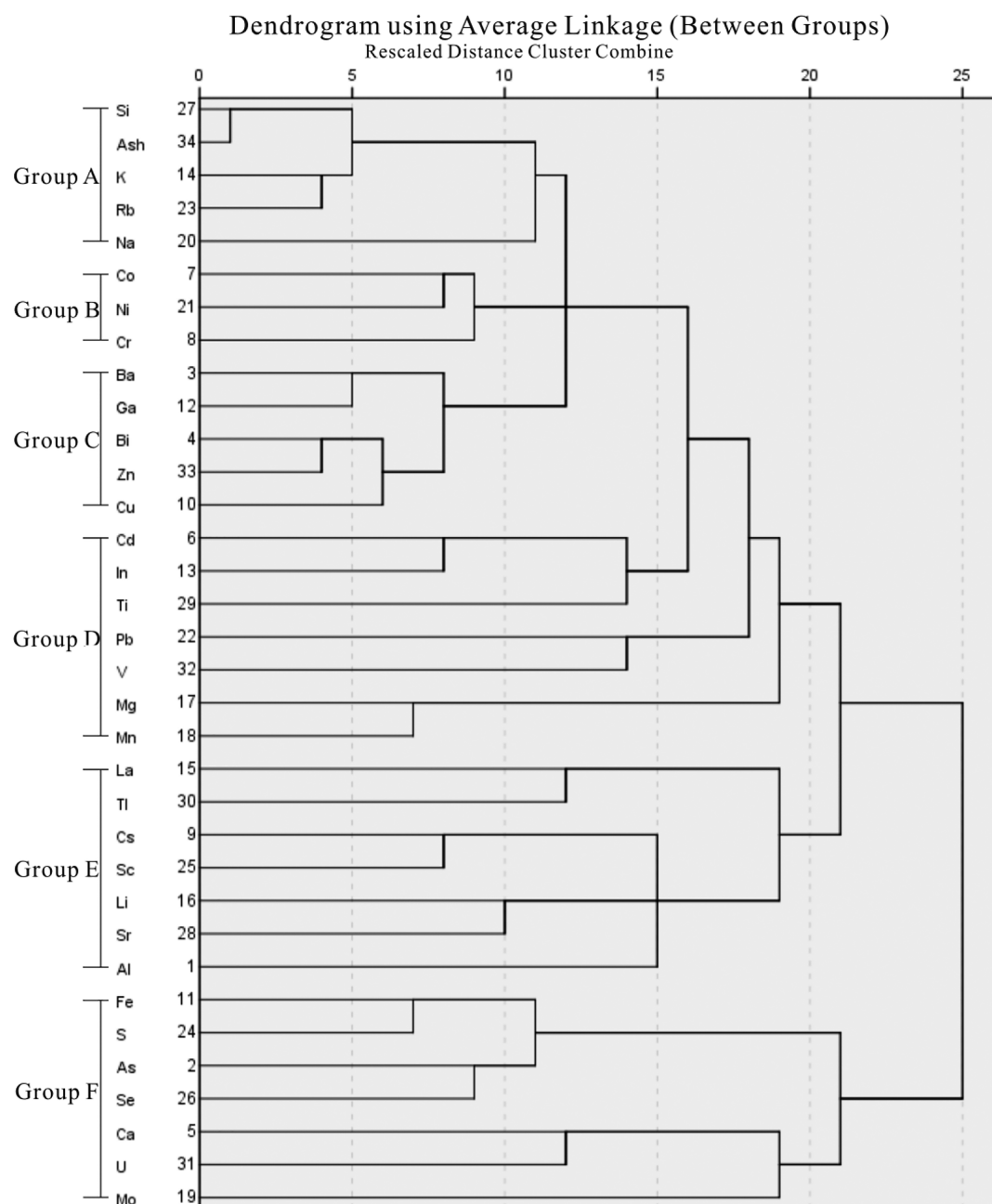


**Figure 3.** Cluster analysis of elements from the studied samples,  $r_0 = \pm 0.20$ .

China.<sup>33</sup> The arithmetic average of Ga in Neogene lignite from the Zhaotong Basin (Yunnan Province, China) is 20.6 mg/kg (6.88 to 41.5 mg/kg), and it is 1.08, 3.14, 3.43, and 3.33 times higher than in the upper continental crust, China coal, world hard coal, and Texas lignite, respectively. Ga contents of four lignite samples from the M2 and M3 coal-bearing seam are 33.72, 41.50, 41.08, and 31.9 mg/kg, respectively, which approach the average concentration of Ga in coals from the Heidaigou Mine of China (44.8 mg/kg)<sup>33</sup> and are higher than the boundary grade of exploration and utilization of Ga<sup>28</sup> (>30 mg/kg; Table 3). Ga in Neogene lignite from the Zhaotong Basin could be considered as an associated and useful mineral.

Se content in Neogene lignite from the Zhaotong Basin varies from 0.45 to 7.69 mg/kg, with the arithmetic average of 1.66 mg/kg, which is 33.2, 0.69, 1.27, and 0.07 times higher than in the upper continental crust, China coal, world hard

coal, and Texas lignite, respectively. Se content of only one lignite sample (no. H3) from the top part of the M2 coal-bearing seam reaches 7.69 mg/kg, which is close to the lowest Se industrial grade (10 mg/kg).<sup>28,29</sup> It is worth noticing that lignite is directly utilized as soil fertilizer in Zhaotong county. The average Se content (1.66 mg/kg) in Neogene lignite from the Zhaotong Basin is 5.72 and 4.15 times higher than that in Chinese soil (0.29 mg/kg)<sup>34</sup> and the world soil average (0.4 mg/kg).<sup>35</sup> Neogene lignite from Zhaotong Basin could be utilized as Se-containing fertilizer.

**Uranium (U).** Utilization of U from coal brought the first example of human extracted industrial metal from a coal-hosted ore deposit. The industrial index for the recovery and utilization of uranium content in raw coal is least 40 mg/kg.<sup>36</sup> The arithmetic average of U in Neogene lignite from Zhaotong

**Table 4. Element Affinities of Element Contents between Neogene Lignite and Ash Yield According to Pearson's Correlation Coefficients**

## correlation with ash content

Group 1:  $r_{\text{ash}} = 0.61-1.0$ , Si (0.95), K (0.81), Zn (0.74), Rb (0.73), Ba (0.63), Pb (0.61)

Group 2:  $r_{\text{ash}} = 0.47-0.60$ , Co (0.56), Cd (0.51), Na (0.49), Al (0.48)

Group 3:  $r_{\text{ash}} = 0.23-0.46$ , Ni (0.46), Ti (0.42), Bi (0.41), Cr (0.39), Cu (0.36), In (0.35), Mn (0.34), Mg (0.27), Ga (0.26), Fe (0.23), Tl (0.23)

Group 4:  $r_{\text{ash}} = -0.4$  to  $+0.22$ , V (0.22), U (0.13), Cs (0.12), Sc (0.06), La (0.05), Sr (0.03), Li (0.02), Se (-0.18), Ca (-0.28), As (-0.32), Mo (-0.32), S (-0.40)

## Aluminosilicate affinity

$r_{\text{Al-Si}} > 0.61$ ; Zn, K, Rb, Ba, Pb

$r_{\text{Al-Si}} = 0.47-0.60$ , Cd, Co, Sc, Cr, Ti, Bi

$r_{\text{Al-Si}} = 0.23-0.46$ ; In, Ni, Na, Cu, Ga, Tl, Mg, Mn, V, Li

## Sulfur affinity

$r_{\text{S-Fe}} > 0.47-0.60$ ; Se, As

$r_{\text{S-Fe}} = 0.23-0.46$ ; Rb, Na, Mn, Ca, Na

## Carbonate affinity

$r_{\text{Ca-Mg}} > 0.7$ ; Mn

$r_{\text{Ca-Mg}} = 0.47-0.60$ ; K, U, Sr

$r_{\text{Ca-Mg}} = 0.23-0.46$ ; Ba, Na, Mo, Rb, Bi, Ca, S, Al, Cu, Ni, Se

## Correlation coefficients between selected major elements

Si-Al = 0.23; Fe-S = 0.69; Ca-Mg = 0.30; Ca-Fe = 0.20; Mg-Fe = 0.09

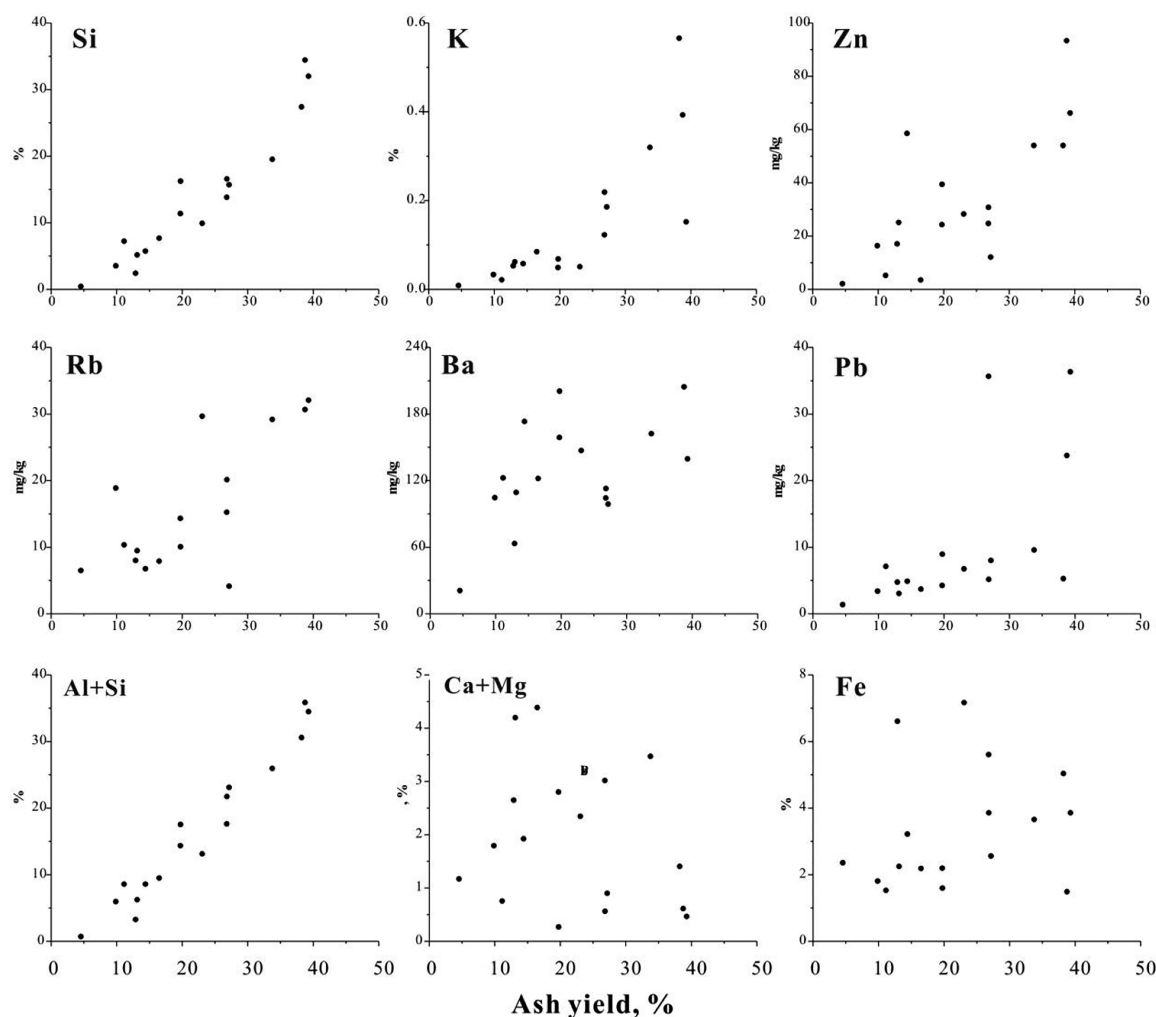
Basin is 1.66 mg/kg (1.54–8.96 mg/kg), which is below the industrial index for U recovery and utilization.

**Vanadium(V).** The arithmetic average of V content in Neogene lignite is 103.20 mg/kg (26.94–198.6 mg/kg), which is 0.86, 2.93, 3.68, and 1.67 times higher than in the upper continental crust, China coal, world hard coal, and Texas lignite, respectively. However, the V content in Neogene lignite is far below the boundary grade of V exploration and utilization (0.5%), minimum industrial grade (0.7%), and associated useful components (0.2–0.5%).<sup>29</sup>

**Lithium (Li).** Li content in China coal average, world hard coal, and Texas lignite is 31.8, 14, 14.34 mg/kg, respectively. The industrial grade for Li exploration and utilization from coal-bearing strata is above 120 mg/kg.<sup>14</sup> Average Li content in this study area is 10.16 mg/kg (0.03 to 35.20 mg/kg), and it is below the industrial index for Li recovery and utilization.

**3.5.2. Environment Impacts.** Under the influence of the weathering and leaching process, the content of trace elements in coal will decrease continuously.<sup>31</sup> One part of the trace elements will enter the atmosphere as gas or dust; the other part will infiltrate into the soil and aquifer, which could pollute soil and impair water.<sup>37</sup>

Average As content in Neogene lignite samples from Zhaotong Basin is 12.17 mg/kg (4.9–28.44 mg/kg), and it is 6.74, 3.20, 1.46, and 20.27 times higher than that in the

**Figure 4.** Correlation between elements including Si, K, Zn, Rb, Ba, Pb, Ca, Mg, Fe, and ash yield (both x-axes are ash yield).

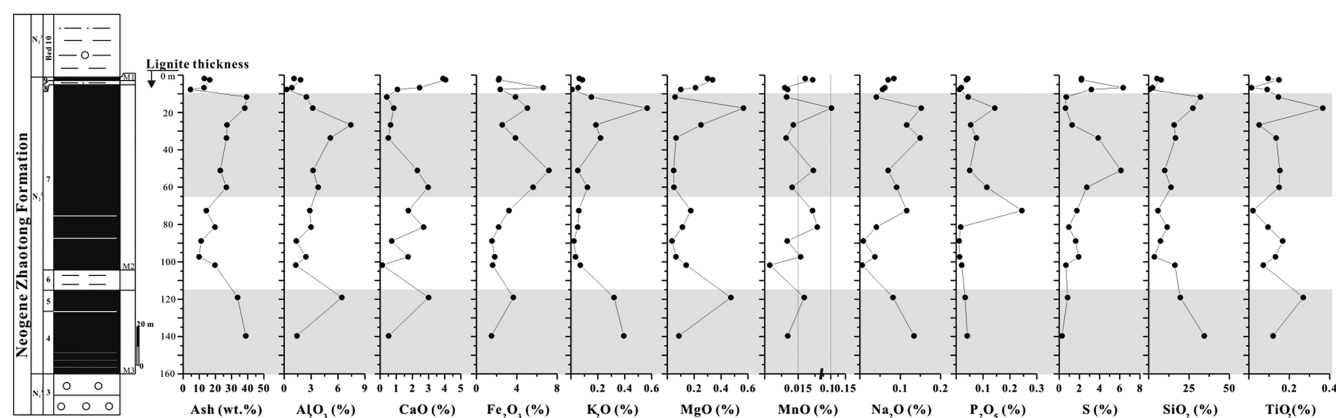


Figure 5. Distribution of ash and major elements in lignite from Member 2 ( $N_2^2$ ) of the Neogene Zhaotong Formation.

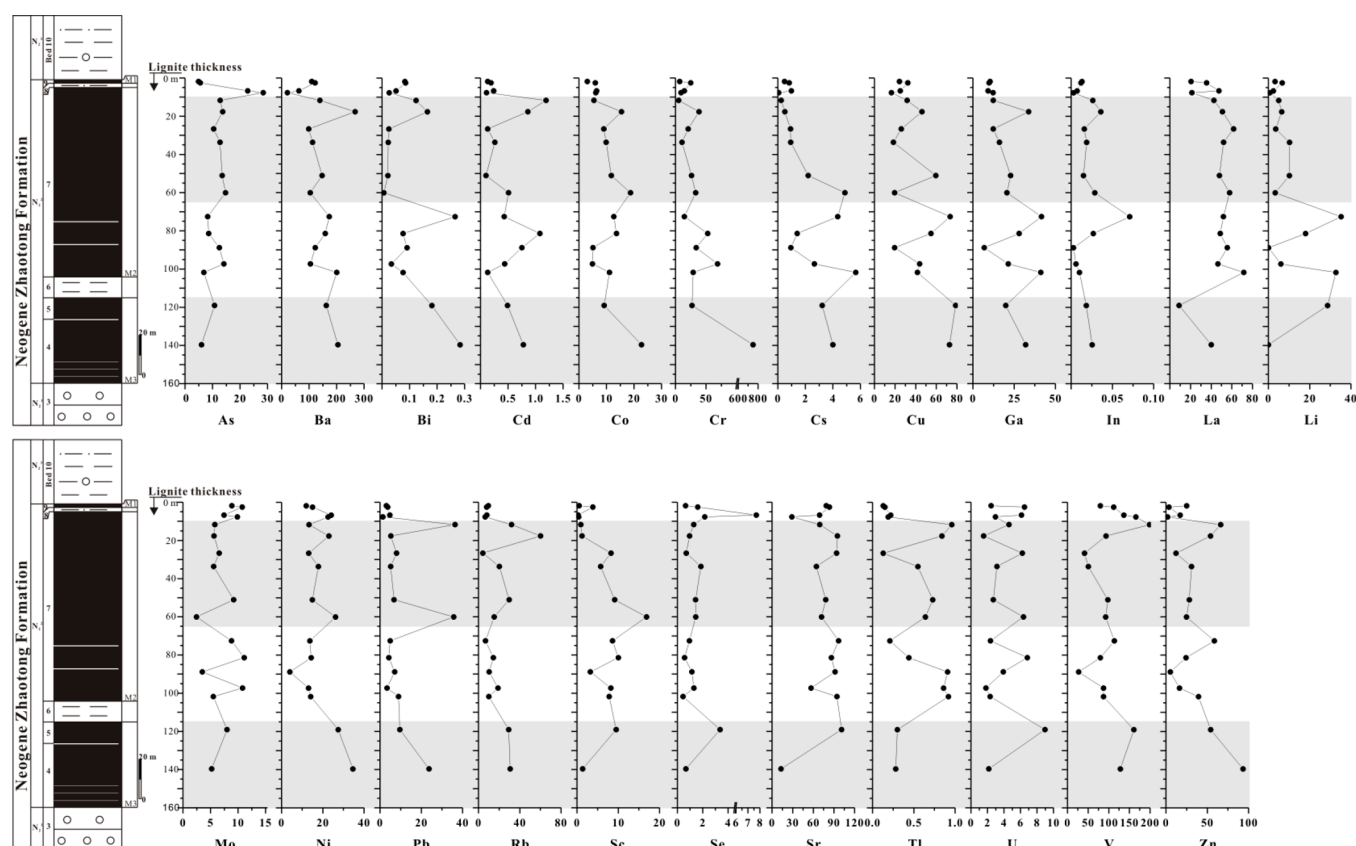


Figure 6. Distribution of trace element in lignite from Member 2 ( $N_2^2$ ) of the Neogene Zhaotong Formation (mg/kg).

upper continental crust, China coal, world hard coal, and Texas lignite, respectively. As contents in Neogene lignite are still lower than those in soil from Yunnan Province (25.4 mg/kg)<sup>34</sup> and the safety threshold of environmental quality standards for soils in China (40 mg/kg).<sup>30</sup> In addition, the average contents of Pb (1.38–36.36 mg/kg), Co (3.06–22.7 mg/kg), Ni (4.08–34.61 mg/kg), and Zn (2.12–93.39 mg/kg) in Neogene lignite are 10.13 mg/kg, 10.07 mg/kg, 34.6 mg/kg, and 32.69 mg/kg, respectively. Pb, Co, and Ni contents in Neogene lignite are lower than those in soil from Yunnan Province and the safety threshold of environmental quality standards for soils, China<sup>30</sup> (Table 3).

The average contents of Cr (5.26–749.6 mg/kg) and Cu (16.48–78.78 mg/kg) are 68.48 and 40.24 mg/kg, respec-

tively, which (1) are lower than that in upper continental crust but (2) are 1.7–5.3 times more than those of China coals, Texas lignite and World hard coal; (3) approach the average concentrations of these two elements in the soil of Yunnan Province;<sup>34</sup> and (4) are far below the safety threshold.<sup>30</sup> However, it is worth noticing that the Cr content of Neogene lignite samples (No. H17) from the middle part of the M3 coal-bearing seam is 749.60 mg/kg, which might cause environmental damage and adverse health impacts.

The arithmetic average of Cd is 0.46 mg/kg that changes from 0.1 to 1.19 mg/kg, and it is 3.01, 1.84, 2.3, and 3.54 times higher than that in upper continental crust, China coal, world hard coal, and Texas lignite, respectively. Also, Cd content in two samples (No. H5 and, H12) from the M2 coal-bearing

seam are 1.19 and 1.08 mg/kg and above the safety threshold.<sup>30</sup>

Therefore, Ga and Se elements in the Neogene lignite from the Zhaotong Basin of Yunnan Province should be taken as a potential comprehensive utilization. The reserves estimation of Ga and Se are 976 383 tons and 78 084 million tons, respectively, according to total estimation results of the M2 and M3 coal-bearing seam of Neogene lignite and their thickness in the Zhaotong Basin.<sup>4</sup> The relatively high Cr and Cd in these lignites may be hazardous to the health of humans and local natural environments, which should be of further concern.

## 4. CONCLUSIONS

Arithmetic average concentrations of Se, As, Mo, and Cd in Neogene lignite from Zhaotong Basin, northeastern Yunnan Province, China are higher than those of upper continental crust. Meanwhile, contents of Zn, Fe, Co, Ti, Ba, Ca, Sc, Si, Ni, P, Rb, Sr, Al, In, Mg, K, Na, and Mn in Neogene lignite are lower than those of the upper continental crust. Contents of Cr, V, Ga, As, Cu, Rb, Co, Mo, and Cd in northeastern Yunnan lignite are over those of China coals, while concentrations of Li and Bi are lower. As, P, Rb, La, Ni, Cd, Mo, Co, Ga, and V are enriched in the northeastern Yunnan lignite, compared to the American Texas lignite, while Bi, Mn, and Se are depleted.

Four groups of elements from the studied samples can be divided: Si–K–Zn–Rb–Ba–Pb, Co–Cd–Na–Al, Ni–Ti–Bi–Cr–Cu–In–Mn–Mg–Ga–Fe–Tl, and V–U–Cs–Sc–La–Sr–L–Se–Ca–As–Mo–S. It showed coefficients between the concentrations of elements from first and second groups, and its ash yield was positive. There exist no negative or lower positive correlation coefficients of those in the third and fourth groups.

Three types of element distribution patterns in ascending order of the Zhaotong coal-bearing bed are recognized: (1) elements including Al, K, Na, Si, Ti, Ba, Bi, Cr, Cd, Co, Cu, Cs, Ga, Ni, Sc, Pb, and Zn decrease from bottom to top, (2) whereas Ca, Mg, As, Se, Mo, Fe, and S increase from bottom to top; (3) the rest of the elements, including V, U, Tl, Sr, Sc, Rb, Li, La, In, P, and Mn, have irregular distribution patterns.

Contents of Ga and Se in Neogene lignite from Zhaotong Basin reach the industrial index and could be utilized, with crude reserves estimations of 976 383 tons and 78 084 tons, respectively. Contents of Cr and Cd in Neogene lignite are slightly higher than the safety threshold recovery and could cause damage to the environment and human health, which calls for further pollution management.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b02354.

Supplementary data (XLS)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported by the “973 program” of China (2014CB238906), the National Natural Sciences Foundation of China (41472322 and 41877229), and Strategic Priority Research Program (XDA19040301). Thanks to the editor and anonymous reviewers’ comments and suggestions.

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