

## Review Article

# Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization

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## ABSTRACT

China will continue to be one of the largest coal producers and users in the world. The high volume of coal use in China has focused attention on the amounts of toxic trace elements released from coal combustions and also the valuable trace elements extracted or potentially utilized from coal ash.

Compared to world coals, Chinese coals have normal background values for most trace elements, with the exception of higher Li (31.8 µg/g), Zr (89.5 µg/g), Nb (9.44 µg/g), Ta (0.62 µg/g), Hf (3.71 µg/g), Th (5.84 µg/g), and rare earth elements ( $\Sigma$  La–Lu + Y, 136 µg/g). This is not only due to the higher ash yields of Chinese coals but also to alkali volcanic ashes found in some southwestern coals. The background values of toxic elements of Hg (0.163 µg/g), As (3.79 µg/g), and F (130 µg/g) in Chinese coals are comparable to coals from most other countries. The genetic types for trace-element enrichment of Chinese coals include source-rock-controlled, marine-environment-controlled, hydrothermal-fluid-controlled (including magmatic-, low-temperature-hydrothermal-fluid-, and submarine-exhalation-controlled subtypes), groundwater-controlled, and volcanic-ash-controlled. The background values of trace elements were dominated by sediment source regions. Low-temperature hydrothermal fluid was one of the major factors for the local enrichment of trace elements in southwestern China. Serious human health problems caused by indoor combustion of coal in China include endemic fluorosis, arsenosis, selenosis, and lung cancer. Endemic fluorosis, mainly occurring in western Guizhou, was mostly attributed to the high fluorine in clay that was used as a briquette binder for fine coals, in addition to a small quantity of fluorine from coal. Fluorine in the coal from endemic-fluorosis areas of western Guizhou is within the usual range found in China and the world. Endemic arsenosis in southwestern Guizhou is attributed to indoor combustion of high-As coal. Endemic selenosis in Enshi of Hubei was due to high Se in carbonaceous siliceous rocks and carbonaceous shales. Fine particles of quartz, released into air during coal combustion, are hypothesized as a possible cause for the lung cancer epidemic in Xuanwei, Yunnan, China.

Valuable elements, including Ge, Ga, U, REE (rare earth element), Nb, Zr, and Re are concentrated to levels comparable to conventional economic deposits in several coals or coal-bearing strata in China. The Ge deposits at Lincang, Yunnan province and Wulantuga, Inner Mongolia have been exploited and industrially utilized. The enrichment of Ge in the two deposits was caused by hydrothermal fluids associated with adjacent granitoids. The Ga (Al) ore deposit in the Jungar Coalfield, Inner Mongolia, was derived from the neighboring weathered and oxidized bauxite of the Benxi Formation (Pennsylvanian). The Nb(Ta)–Zr(Hf)–REE–Ga deposits in the Late Permian coal-bearing strata of eastern Yunnan and Chongqing of southwestern China were attributed to ashes of the alkali volcanic eruptions.

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## 1. Introduction

At present, China is both the largest consumer and producer of coal in the world. According to the World Energy Council, as of 2009, China held an estimated 103.87 Gt of recoverable coal reserves, the third-largest in the world behind the United States and Russia and about 14% of the world's total reserves. In recent years, coal made up about 74% of China's total primary energy consumption and about 60% of the chemical materials are derived from coal products. From 1949 to 2009, coal production in China increased rapidly (Fig. 1). Coal production in China amounted to 2.96 Gt in 2009, accounting for 45.6% of the total production of the world; and the consumed coal in China in 2009 is up to 2.74 Gt, constituting 46.9% of the total global coal consumption (BP report; bp.com/statisticalreview).

From a genetic point of view, trace elements in coals provide geologic information about depositional conditions, coal-bearing sequence formation, and regional tectonic history (Ren, 1996), because their distributions resulted from the processes associated

with peat accumulation and rank advance, as well as interaction between the organic matter and basinal fluids, sediment diagenesis, and syndimentary volcanic inputs (Dai et al., 2003b, 2008b; Ren et al., 2006; Ward, 2002; Yudovich and Ketris, 2002;). Moreover, human health problems relevant to coal combustion, for example, endemic arsenosis, fluorosis, selenosis, and lung cancer, occur and are serious in some areas of China (Belkin et al., 1998, 1999a,b, 2008; Dai et al., 2004b, 2007a; Finkelman et al., 2002; Liu et al., 2002; Zheng et al., 1999). Trace elements in coal can provide useful information from an environmental point of view for possible pollution control of toxic trace elements during coal combustion and utilization (Dai et al., 2005b; Finkelman et al., 2002; Liu et al., 2005; Tang et al., 2009; Querol et al., 2001; Wang et al., 2006a,b, 2008b; Wu et al., 2008). Some valuable trace elements (e.g., Au, Ge, Ga, Nb, Zr, U, Re, rare earth elements, and platinum group elements) are enriched in some coals or coal-bearing strata, and, thus are being or can be potentially recovered from coal ashes (Dai et al., 2006a, 2010c; Hu et al., 2006, 2009; Huang et al., 2008; Qi et al., 2007a,b; Zhuang, et al., 2006).

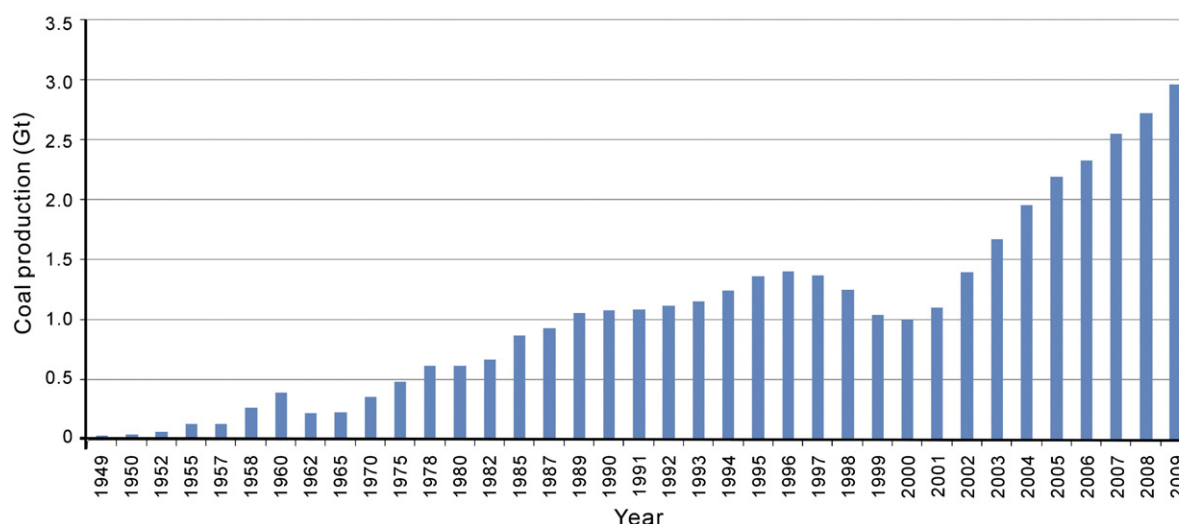


Fig. 1. China's coal productions from 1949 to 2009.

In this paper, based on published literature and combining our new data, some important aspects related to geochemistry of trace elements in coals from China are reviewed, including the background values, genetic types of enrichment, human health problems caused by domestic coal combustion, and possible recovery of valuable trace elements.

## 2. Main Coal-forming Periods and Coal-distribution Areas in China

Based on the characteristics of coal geology and the coalfield distribution in China, there are six major coal-forming periods: Late Carboniferous and Early Permian ( $C_2$ – $P_1$ ), Late Permian ( $P_2$ ), Late Triassic ( $T_3$ ), Early and Middle Jurassic ( $J_{1-2}$ ), Late Jurassic and Early Cretaceous ( $J_3$ – $K_1$ ), and Paleogene and Neogene (E–N) (Ren et al., 2006). Based on data from The Third National Prediction of Coal Resources of China (China Coal Geology Bureau, 1996a), the total recoverable coal reserves are made up of 38.1%  $C_2$ – $P_1$ , 7.5%  $P_2$ , 0.4%  $T_3$ , 39.6%  $J_{1-2}$ , 12.1%  $J_3$ – $K_1$ , and 2.3% E–N coals. In addition, there is a minor but significant amount of Early Carboniferous ( $C_1$ ) coal in southern China (Fig. 2).

In terms of geotectonic units and coal-forming periods, five coal-distribution areas can be outlined (Fig. 2): the Northern area (dominated by  $C_2$ – $P_1$  coals); the Southern area ( $P_2$ ,  $T_3$  and  $C_1$  coals);

the Northeastern area ( $J_3$ – $K_1$  and E–N coals); the Northwestern area ( $J_{1-2}$  coals); and the Tibet–western Yunnan area (E–N and  $T_3$  coals) (Fig. 2).

## 3. Abundances of Trace Elements in Chinese Coals

The mean abundances of elements in coal can provide an important scientific basis for many geochemical comparisons and studies (Ketris and Yudovich, 2009). For example, representative element concentrations are essential to better estimate not only the environmental and health effects associated with toxic element emissions from coal utilization (Ren et al., 2006), but also the possibility of valuable element utilization (Dai et al., 2008a; Seredin and Finkelman, 2008). Finkelman (1993) and Spears and Zheng (1999) reported concentrations of trace elements in coals from USA and UK, respectively. Swaine (1990) estimated the ranges of trace elements in most coals over the world. Bouška and Pešek (1999) reported the concentrations of trace elements in lignites of the world. Ketris and Yudovich (2009) estimated world averages for trace element contents in coals, including average content in hard coals and their ashes, average content in brown coals and their ashes, average content in all coals and their ashes, and coal affinity index.

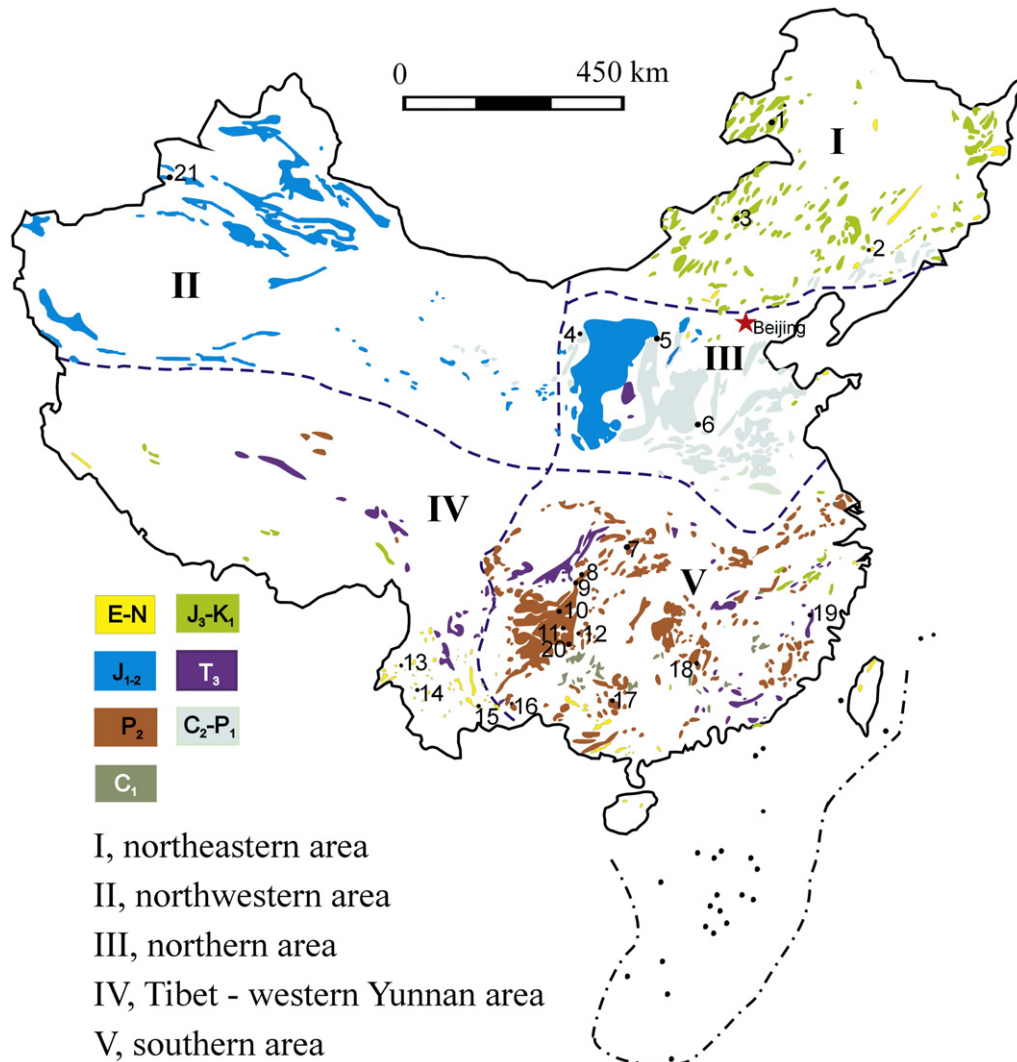


**Fig. 2.** Coal-distribution areas in China. 1, Yimin Coalfield; 2, Shenbei Coalfield; 3, Wulantuga; 4, Wuda Coalfield; 5, Jungar Coalfield; 6, Fengfeng–Hangdan Coalfield; 7, Enshi; 8, Nanchuan; 9, Songzao Coalfield; 10, Dafang Coalfield; 11, Zhijin Coalfield; 12, Guiding; 13, Tengchong; 14, Lincang; 15, Jianshui; 16, Yanshan; 17, Heshan; 18, Meitian Coalfield; 19, Jianou; 20, Ziyun; 21, Yili. Data compiled mainly from the Third National Prediction of Coal Resources of China, Hu and He (2008), Yuan (1999), Ren (1996), and Ren et al. (2006).

Some researchers evaluated the concentrations of elements in coals from China or in some coalfields in China (Bai et al., 2007; Dai et al., 2007b, 2008a; Luo et al., 2004; Sun et al., 2010a; Tang and Huang, 2004; Ren et al., 1999, 2006; Zhuang et al., 2000). Most trace element concentrations in coals were generally given as arithmetic or geometric means. However, the relative proportions of coal resources should be taken into account when average concentrations of trace elements in coals from a region are estimated to reflect their toxicity or their potential utilization (Dai and Ren, 2006); otherwise, the estimated concentrations of trace elements in coals cannot be representative for the region if coal samples were not evenly distributed either in space or in geologic ages (Dai and Ren, 2006; Ren et al., 2006). For example, Ren et al. (1999) estimated that the arithmetic mean of As in Chinese coals is as high as 277  $\mu\text{g/g}$ , based on 132 coal samples. It is unusually high, because the coal reserves are not taken into account. Some coal samples with superhigh-As content (32,000  $\mu\text{g/g}$ ) were included in the calculation but the reserves of such superhigh-As coal are extraordinary small and the coal seams are commercially unworkable. Thus, Ren et al. (1999) pointed out that “The high arithmetic mean of As, 277  $\mu\text{g/g}$ , is caused by a single sample with 3.2% As from southwestern China. Such superhigh-As coal is highly localized. Hence, the geometric mean of 4.26  $\mu\text{g/g}$  As should be a more representative value for Chinese coals.” Having considered the relative proportions of coal reserves, Ren et al. (2006) estimated an average arsenic concentration of coals in China as 3.9  $\mu\text{g/g}$ .

Taking the coal reserves into consideration, Ren et al. (2006) estimated 22 trace elements in Chinese coals and Bai et al. (2007) also estimated 31 trace elements in coal based on 1123 samples collected from 504 coal mines in 26 provinces (Table 1). Based on the work by Ren et al. (2006) and Dai et al. (2007b, 2008a) and new data obtained in past two years, the background values of elements in Chinese coals are estimated and listed in Table 1. The method of estimation has been described in detail by Dai and Ren (2006) and Ren et al. (2006).

Compared to US and world coals reported by Finkelman (1993) and Ketris and Yudovich (2009), concentrations of most trace elements in Chinese coals are similar. However, Chinese coals have higher content of Li (31.8  $\mu\text{g/g}$ ), Zr (89.5  $\mu\text{g/g}$ ), Nb (9.44  $\mu\text{g/g}$ ), Ta (0.62  $\mu\text{g/g}$ ), Hf (3.71  $\mu\text{g/g}$ ), Th (5.84  $\mu\text{g/g}$ ), and total REE ( $\sum \text{La-Lu} + \text{Y}$ , 136  $\mu\text{g/g}$ ) (Table 1). The higher concentration of these elements is not only attributed to the high ash yields, but also to intra-seam alkali tonsteins found in southwestern China, which led to enrichment of Zr, Nb, Hf, Ta, and REE (Dai et al., 2007b, 2011). Note that toxic elements, including Hg (0.163  $\mu\text{g/g}$ ), As (3.79  $\mu\text{g/g}$ ), and F (130  $\mu\text{g/g}$ ), in Chinese coals have been widely studied. Some coals from restricted areas, for example, Xingren, Guizhou (Belkin et al., 1998, 1999b; Dai et al., 2006b; Ding et al., 2001; Zhao et al., 1998; Zheng et al., 1999, 2005) and Laochang, Yunnan (Zhou and Ren, 1992), are significantly enriched in As and Hg. The world highest As (3.2–3.5%) in coal was found in Xingren, Guizhou (Belkin et al., 1999b; Zhao et al., 1998). However, the reserves of high-As coals in Xingren are extraordinary small, compared to abundant coal resources in western Guizhou (Dai et al., 2005b).

Although the overall features of elemental concentrations in Chinese coals have been determined, the collected coal samples are not evenly distributed either in space or in geological ages. Most coal samples are from  $\text{C}_2$ – $\text{P}_1$  coals in northern and  $\text{P}_2$  coals from southwestern areas, but samples from northeastern ( $\text{E-N}$  and  $\text{J}_3$ – $\text{K}_1$ ) and northwestern ( $\text{J}_{1-2}$ ) areas are not as well represented. More samples from the last two areas are needed for improving the representativeness of trace element abundances in Chinese coals.

#### 4. Genetic Types of Trace-element Enrichment in Chinese Coals

For different coal basins and coal-forming periods, there are always one or more particular geological factors that influence the

enrichment of trace elements in coals (Dai et al., 2003b). Bouška et al. (2000) classified the accumulation of elements in coal into two groups: (1) those accumulated by plants and partly by animals; and (2) those accumulated by geologic processes that occur in the peat stage and postpeatification stage (including coalification and later epigenetic processes). Ren et al. (1999) preliminarily proposed five genetic types of trace elements in Chinese coals: source-rock-controlled, sedimentation-environment-controlled, magmatic/hydrothermal-controlled, fault-controlled, and groundwater-controlled. Recent studies indicated that the processes of trace element enrichment in coal is rather complicated and additional genetic types, for example, submarine-exhalation-controlled and volcanic-ash-controlled, have been proposed (Dai et al. 2003b, 2008b; Ren et al., 2006). Overall, to date, enrichment of trace-elements in Chinese coals can be explained by the genetic types including source-rock-controlled, marine-environment-controlled, hydrothermal-fluid-controlled (including magmatic-, low-temperature-hydrothermal-fluid-, and submarine-exhalation-controlled subtypes), groundwater-controlled, and volcanic-ash-controlled.

##### 4.1. Source-rock-controlled Type

Generally, the nature of sediment-source region located on the margin of coal basin is the dominant factor for the background values of trace elements in the coal basin.

For large-scale down-warped coal basins, it is difficult for the sediment-source region to influence trace-element enrichment in coal, not only because the trace elements derived from sediment-source region will be “diluted” over a wide area, but also because of long-distance transport from the sediment-source region to coal basin interior.

However, in some small-scale fault-controlled basins or coalfields, the sediment-source region can be a dominant factor in trace-element enrichment in coal. Because the source region is near the basin, detrital materials can be transported to the interior of coal basin. Hence, elements with high concentrations in the source rocks are commonly enriched in these coals. However, if the ash yield derived from the source rocks is very high, the trace element concentration of the coal could be relatively high on a whole-coal basis even if the trace element concentration of the source rocks is low.

##### 4.1.1. Large-scale Coal Basins

The North China Coal Basin (NCCB) covers the Northern area (Fig. 2) with 1,200,000  $\text{km}^2$  (Fig. 2), making it the largest down-warped coal basin in China. The coal resources in the North China Coal Basin account for about 62.1% of the total in China. The major coal-bearing strata are dominantly Permo-Carboniferous sedimentary sequences. The major sediment-source region situated to the north of the coal basin is the Yinshan Oldland made up of Archean and Proterozoic metamorphic rocks and middle Proterozoic–Ordovician sedimentary rocks.

With a few exceptions of coals from NCCB, for example, Fengfeng–Handan and Jungar, which were enriched in some trace elements due to specific geologic factors, as described below, the trace element concentrations in coals from NCCB are at normal levels (Dai et al., 2003c), similar to worldwide coals (Ketris and Yudovich, 2009). The background values of trace elements in this large coal basin are largely controlled by the Yinshan Oldland.

##### 4.1.2. Small-scale Coal Basins

Although the Southwest Coal Basin (SCB) is a fault-controlled coal basin, it covers a relatively wider area of western Guizhou, eastern Yunnan, southern Sichuan, and Chongqing; however, it is much smaller than NCCB. The sediment-source region is the Kangdian Oldland, which is situated to the west of the basin and is mostly made up of basaltic rocks. The coal bearing-strata are the Late Permian

**Table 1**

Content of elements in Chinese coals, as well as their comparisons with average U.S. and world coals (content in µg/g unless indicated as%).

| Elements                         | Elements in coals from China |               |                       |               |                   |               |                                                          |               | USA <sup>b</sup> |          |               | World <sup>c</sup> |
|----------------------------------|------------------------------|---------------|-----------------------|---------------|-------------------|---------------|----------------------------------------------------------|---------------|------------------|----------|---------------|--------------------|
|                                  | Bai et al. (2007)            |               | Tang and Huang (2004) |               | Ren et al. (2006) |               | Dai et al. (2007b, 2008a, unpublished data) <sup>a</sup> |               | Arithmetic       | Geometrc | Sample number |                    |
|                                  | Concentration                | Sample number | Concentration         | Sample number | Concentration     | Sample number | Concentration                                            | Sample number |                  |          |               | Content            |
| Al <sub>2</sub> O <sub>3</sub> % | Nd                           | nd            | nd                    | nd            | nd                | nd            | 5.98                                                     | 1322          | 2.8              | 2.1      | 7882          | nd                 |
| SiO <sub>2</sub> %               | Nd                           | nd            | nd                    | nd            | nd                | nd            | 8.47                                                     | 1322          | 5.8              | 4.1      | 7846          | nd                 |
| CaO%                             | Nd                           | nd            | nd                    | nd            | nd                | nd            | 1.23                                                     | 1322          | 0.64             | 0.32     | 7887          | nd                 |
| K <sub>2</sub> O%                | nd                           | nd            | nd                    | nd            | nd                | nd            | 0.19                                                     | 1322          | 0.22             | 0.12     | 7830          | nd                 |
| TiO <sub>2</sub> %               | nd                           | nd            | 0.063                 | 905           | nd                | nd            | 0.33                                                     | 1322          | 0.13             | 0.10     | 7653          | 0.133              |
| Fe <sub>2</sub> O <sub>3</sub> % | nd                           | nd            | Nd                    | nd            | nd                | nd            | 4.85                                                     | 1322          | 1.9              | 1.1      | 7882          | nd                 |
| MgO%                             | nd                           | nd            | Nd                    | nd            | nd                | nd            | 0.22                                                     | 1322          | 0.18             | 0.11     | 7887          | nd                 |
| Na <sub>2</sub> O%               | nd                           | nd            | Nd                    | nd            | nd                | nd            | 0.16                                                     | 1322          | 0.11             | 0.05     | 7784          | nd                 |
| MnO%                             | nd                           | nd            | 0.006                 | 1187          | 0.016             | 1269          | 0.015                                                    | 1322          | 0.006            | 0.002    | 7796          | 0.011              |
| P <sub>2</sub> O <sub>5</sub> %  | 0.049                        | 1123          | 0.047                 | 1770          | nd                | nd            | 0.092                                                    | 1322          | 0.098            | 0.005    | 5079          | 0.053              |
| Li                               | nd                           | nd            | 19                    | 395           | nd                | nd            | 31.8                                                     | 1274          | 16               | 9.2      | 7848          | 12                 |
| Be                               | 1.75                         | 1123          | 1.9                   | 1195          | 2.13              | 1198          | 2.11                                                     | 1249          | 2.2              | 1.3      | 7484          | 1.6                |
| B                                | nd                           | nd            | 65                    | 927           | nd                | nd            | 53                                                       | 1048          | 49               | 30       | 7874          | 52                 |
| F                                | 157                          | 1123          | 186                   | 1069          | 131.3             | 729           | 130                                                      | 1964          | 98               | 35       | 7376          | 88                 |
| Cl                               | 218                          | 1123          | 260                   | 311           | 264               | 721           | 255                                                      | 812           | 614              | 79       | 4171          | 180                |
| Sc                               | 4.4                          | 1123          | 4                     | 1339          | nd                | nd            | 4.38                                                     | 1919          | 4.2              | 3.0      | 7803          | 3.9                |
| V                                | 51.18                        | 1123          | 25                    | 1257          | 35.05             | 1266          | 35.1                                                     | 1324          | 22               | 17       | 7924          | 25                 |
| Cr                               | 16.94                        | 1123          | 16                    | 1614          | 15.35             | 1592          | 15.4                                                     | 1615          | 15               | 10       | 7847          | 16                 |
| Co                               | 10.62                        | 1123          | 7                     | 1572          | 7.05              | 1488          | 7.08                                                     | 1523          | 6.1              | 3.7      | 7800          | 5.1                |
| Ni                               | 14.44                        | 1123          | 15                    | 1424          | 13.71             | 1335          | 13.7                                                     | 1392          | 14               | 9.0      | 7900          | 13                 |
| Cu                               | 17.87                        | 1123          | 13                    | 1319          | 18.35             | 1296          | 17.5                                                     | 1362          | 16               | 12       | 7911          | 16                 |
| Zn                               | nd                           | nd            | 38                    | 1529          | 42.18             | 1394          | 41.4                                                     | 1458          | 53               | 13       | 7908          | 23                 |
| Ga                               | 6.84                         | 1123          | 9                     | 3407          | 6.52              | 2334          | 6.55                                                     | 2451          | 5.7              | 4.5      | 7565          | 5.8                |
| Ge                               | 2.43                         | 1123          | 4                     | 3289          | 2.97              | 3195          | 2.78                                                     | 3265          | 5.7              | 59       | 5689          | 2.2                |
| As                               | 4.09                         | 1123          | 5                     | 3193          | 3.8               | 3386          | 3.79                                                     | 3386          | 24               | 6.5      | 7676          | 8.3                |
| Se                               | 2.82                         | 1123          | 2                     | 1460          | 2.47              | 1536          | 2.47                                                     | 1537          | 2.8              | 1.8      | 7563          | 1.3                |
| Rb                               | nd                           | nd            | 8                     | 612           | nd                | nd            | 9.25                                                     | 1212          | 21               | 0.62     | 2648          | 14                 |
| Sr                               | 195                          | 1123          | 149                   | 693           | nd                | nd            | 140                                                      | 2075          | 130              | 90       | 7842          | 110                |
| Y                                | 9.07                         | 1123          | 9                     | 884           | nd                | nd            | 18.2                                                     | 888           | 8.5              | 6.6      | 7897          | 8.4                |
| Zr                               | 112                          | 1123          | 67                    | 526           | nd                | nd            | 89.5                                                     | 1335          | 27               | 19       | 7913          | 36                 |
| Nb                               | nd                           | nd            | 12                    | 138           | nd                | nd            | 9.44                                                     | 1025          | 2.9              | 1.0      | 6843          | 3.7                |
| Mo                               | 2.70                         | 1123          | 4                     | 405           | 3.11              | 679           | 3.08                                                     | 789           | 3.3              | 1.2      | 7107          | 2.2                |
| Cd                               | 0.81                         | 1123          | 0.3                   | 1307          | 0.24              | 1317          | 0.25                                                     | 1384          | 0.47             | 0.02     | 6150          | 0.22               |
| In                               | 0.74                         | 1123          | nd                    | nd            | nd                | nd            | 0.047                                                    | 85            | <0.3             | n.d      | n.d           | 0.031              |
| Sn                               | nd                           | nd            | 2                     | 178           | nd                | nd            | 2.11                                                     | 848           | 1.3              | 0.001    | 3004          | 1.1                |
| Sb                               | 0.71                         | 1123          | 1.3                   | 652           | 0.83              | 537           | 0.84                                                     | 596           | 1.2              | 0.61     | 7473          | 0.92               |
| Cs                               | 1.51                         | 1123          | 2.0                   | 512           | nd                | nd            | 1.13                                                     | 1208          | 1.1              | 0.70     | 4972          | 1.0                |
| Ba                               | 270                          | 1123          | 160                   | 851           | nd                | nd            | 159                                                      | 1205          | 170              | 93       | 7836          | 150                |
| La                               | nd                           | nd            | 18                    | 110           | nd                | nd            | 22.5                                                     | 392           | 12               | 3.9      | 6235          | 11                 |
| Ce                               | nd                           | nd            | 35                    | 110           | nd                | nd            | 46.7                                                     | 392           | 21               | 5.1      | 5525          | 23                 |
| Pr                               | nd                           | nd            | 3.8                   | 110           | nd                | nd            | 6.42                                                     | 392           | 2.4              | n.d      | 1533          | 3.5                |
| Nd                               | nd                           | nd            | 15                    | 110           | nd                | nd            | 22.3                                                     | 392           | 9.5              | n.d      | 4749          | 12                 |
| Sm                               | nd                           | nd            | 3                     | 110           | nd                | nd            | 4.07                                                     | 392           | 1.7              | 0.35     | 5151          | 2.0                |
| Eu                               | nd                           | nd            | 0.65                  | 110           | nd                | nd            | 0.84                                                     | 392           | 0.40             | 0.12     | 5268          | 0.47               |
| Gd                               | nd                           | nd            | 3.4                   | 110           | nd                | nd            | 4.65                                                     | 392           | 1.8              | n.d      | 2376          | 2.7                |
| Tb                               | nd                           | nd            | 0.52                  | 110           | nd                | nd            | 0.62                                                     | 392           | 0.30             | 0.09     | 5024          | 0.32               |
| Dy                               | nd                           | nd            | 3.1                   | 110           | nd                | nd            | 3.74                                                     | 392           | 1.9              | 0.008    | 1510          | 2.1                |
| Ho                               | nd                           | nd            | 0.73                  | 110           | nd                | nd            | 0.96                                                     | 392           | 0.35             | n.d      | 1130          | 0.54               |
| Er                               | nd                           | nd            | 2.1                   | 110           | nd                | nd            | 1.79                                                     | 392           | 1.0              | 0.002    | 1792          | 0.93               |
| Tm                               | nd                           | nd            | 0.34                  | 110           | nd                | nd            | 0.64                                                     | 392           | 0.15             | n.d      | 365           | 0.31               |
| Yb                               | 1.76                         | 1123          | 2                     | 110           | nd                | nd            | 2.08                                                     | 392           | 0.95             | n.d      | 7522          | 1.0                |
| Lu                               | nd                           | nd            | 0.32                  | 110           | nd                | nd            | 0.38                                                     | 392           | 0.14             | 0.06     | 5008          | 0.20               |
| Hf                               | nd                           | nd            | 3                     | 570           | nd                | nd            | 3.71                                                     | 1377          | 0.73             | 0.04     | 5120          | 1.2                |
| Ta                               | 0.40                         | 1123          | 0.8                   | 566           | nd                | nd            | 0.62                                                     | 1394          | 0.22             | 0.02     | 4622          | 0.28               |
| W                                | 1.05                         | 1123          | 1.8                   | 552           | nd                | nd            | 1.08                                                     | 1071          | 1.0              | 0.10     | 4714          | 1.1                |
| Hg                               | 0.154                        | 1123          | 0.1                   | 1458          | 0.19              | 1413          | 0.163                                                    | 1666          | 0.17             | 0.10     | 7649          | 0.10               |
| Tl                               | nd                           | nd            | 0.4                   | 809           | 0.48              | 1018          | 0.47                                                     | 1092          | 1.2              | 0.00004  | 1149          | 0.63               |
| Pb                               | 16.64                        | 1123          | 14                    | 1369          | 15.55             | 1387          | 15.1                                                     | 1446          | 11               | 5.0      | 7469          | 7.8                |
| Bi                               | nd                           | nd            | 0.9                   | 135           | nd                | nd            | 0.79                                                     | 856           | <1.0             | n.d      | 128           | 0.97               |
| Th                               | 5.88                         | 1123          | 6                     | 658           | 5.81              | 1011          | 5.84                                                     | 1052          | 3.2              | 1.7      | 6866          | 3.3                |
| U                                | 2.33                         | 1123          | 3                     | 1383          | 2.41              | 1317          | 2.43                                                     | 1383          | 2.1              | 1.1      | 6923          | 2.4                |

nd, no data.

<sup>a</sup> The content was evaluated based on the data from Dai et al. (2007b, 2008a) and Dai et al. (unpublished data).<sup>b</sup> From Finkelman (1993).<sup>c</sup> From Ketris and Yudovich (2009).

Xuanwei Formation (in eastern Yunnan and southern Sichuan) or Longtan Formation (in western Guizhou and southwestern Chongqing) or Wujiaping Formation (in southeastern Chongqing, middle and

eastern Guizhou, and southeastern Yunnan). Chronologically, the Xuanwei, Longtan, and Wujiaping Formations are parts of the same sedimentary sequence; however, they were, respectively, deposited in

a continental, continental-oceanic, and oceanic environment. The Late Permian coals from this coal basin are enriched in Ti, V, Co, Cr, Ni, Cu, and Zn, reflecting their derivation from the Kangdian Oldland (Dai et al., 2005b, 2008c; Ren et al., 2006; Zhang et al., 2002), which is high in these elements (Zhou et al., 2000). Moreover, the Late Permian coals from SCB are characteristically enriched in  $\text{SiO}_2$ . For example, the Si/Al ratio of the Xuanwei coals from eastern Yunnan ranges from 3.58 to 7.99, with an average of 5.89, much higher than that of ordinary Chinese coals (1.14; Dai et al., 2008a). Further studies by Large et al. (2009) confirmed the high quartz in the coal from Xuanwei. Quartz in coal was deposited from silica-containing solutions originated from weathering of basaltic rocks in the Kangdian Oldland (e.g., Ren, 1996). Large et al. (2009) built on this hypothesis to explain the high incidence of lung cancer in Xuanwei.

The Shenbei coalfield, a small intracontinental basin with an area of 384 km<sup>2</sup>, is located in Liaoning Province, northeastern China (Fig. 2). The Paleogene lignites in the coalfield have high contents of Cr and Ni, averaging 79 and 75 µg/g, respectively (Ren et al., 2004). The two elements are mainly associated with fulvic acid and/or coal organic macromolecular compounds, indicating an organic association. The high Cr and Ni are derived mainly from the olivine basalt (country rock of the coal basin) in the source region that consists of 52.7% plagioclase, 17.8% pyroxene, 14% olivine, and 15.5% Ti–Fe oxide minerals (Ren et al., 2004). These olivine basalts have high Cr (290 µg/g; 3 samples) and Ni (227 µg/g; 3 samples) contents (Xu, 1999).

The Upper Pennsylvanian No. 6 Coal in the Jungar Coalfield (with an area of 1700 km<sup>2</sup>) in Inner Mongolia, northern China (Fig. 2), is a low-sulfur coal ( $S_{t,d} = 0.73\%$ ,  $R_{o,ran} = 0.58\%$ ,  $V_{daf} = 33.5\%$ ) with an average thickness of 30 m. The coal is enriched in Ga (44.8 µg/g), Sr (423 µg/g), Zr (234 µg/g), Th (17.8 µg/g), and boehmite ( $\text{AlOOH}$ ; 6.1 vol.%). The high trace elements and boehmite (Fig. 3) were derived from the weathered and oxidized bauxite in the exposed crust of the older Benxi Formation (Mississippian) situated to the northeast of the coal basin. During peat accumulation, the Jungar Coalfield was in the lowlying area between the Yinshan Oldland to the N and W and the upwarped Benxi Formation to the N and E. The paleorivers ran dominantly in the N and E directions from these sediment-source regions to the Jungar Coalfield (Wang, 1996). The sediment-source region to the N and E was dominantly the Benxi Formation bauxite during peat accumulation.

The terrigenous supplies for most coals in the Songzao Coalfield (with an area of 235.5 km<sup>2</sup>; Fig. 2) from Chongqing were mainly derived from the Kangdian Oldland. However, in addition to the Kangdian Oldland, the mafic tuffs or the secondary uplifts composed of mafic tuffs in the coal basin may largely control the mineral and geochemical compositions of the Late Permian No. 12 Coal, which is characteristically high in pyrite ( $S_{p,d} = 8.83\%$ ). The No. 12 Coal was

deposited directly above the mafic tuff beds (China Coal Geology Bureau, 1996b). The uplifted mafic tuffs were the sediment-source for the low-lying peat swamp supplying kaolinite and boehmite. The high pyrite in the coal was related to sulfur from marine transgression over peat deposits and abundant Fe derived from the underlying mafic tuff bed. The coal has a low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (1.13) but a high  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  (80.1) value and is significantly enriched in trace elements including Sc (13.5 µg/g), V (121 µg/g), Cr (33.6 µg/g), Co (27.2 µg/g), Ni (83.5 µg/g), Cu (48.5 µg/g), Ga (17.3 µg/g), Y (68.3 µg/g), Zr (444 µg/g), Nb (23.8 µg/g), and total REE (392 µg/g on average), which were largely derived from the tuffs (Dai et al., 2010a).

#### 4.2. Marine-environment-controlled Type

The coals deposited in marine-influenced environment were generally enriched in some elements, e.g., B, V, Br, Rb, Sr, Mo, and U (Goodarzi and Swaine, 1994; Liu et al., 2004, 2006, 2007; Shao et al., 2003; Song et al., 2007; Zeng et al., 2005), not only because seawater contains higher content of these elements than freshwater, but also because plankton in marine water are enriched in these elements and can also change the pH, Eh, and  $\text{H}_2\text{S}$  content, leading to a favorable environment for enrichment of trace elements (Dai et al., 2003a; Gayer et al., 1999; Ren et al., 2006; Sun et al., 2007; Wang et al., 2007, 2008a).

Coals deposited in the tidal flat environments of restricted carbonate platforms are highly enriched in B, V, Cr, Ni, Mo, and U (Dai et al., 2008b; Shao et al., 2003; Zeng et al., 2005). The typical coals formed in these kinds of sedimentary environments include the Late Permian coals from Guiding and Ziyun in Guizhou province, Heshan in Guangxi province, and Yanshan in Yunnan Province (Fig. 2; Table 2). These environments often had algae growing and a low Eh value, forming a strong reducing environment. Algae have a strong capacity to enrich some metal elements.

Another example of this type is the Pennsylvanian No. 15 Coal, deposited on a tidal flat, in the Jincheng Coalfield of Shanxi Province (Fig. 2). The peat swamp was strongly influenced by seawater and had a reducing environment; therefore, the contents of most of elements are higher than those in other coal seams in the Jincheng Coalfield. The top portion of this coal seam is a humosapropelic coal (the precursor of the coal is dominated by lower plants or/and plankton, followed by higher plants), with 8.4% alginites, 83.7% humosapropelic groundmass, and 4.7% pyrite (Ren et al., 1999). The contents of As, Se, Sr, and Mo in the humosapropelic coals are 22.3, 138, 427, and 16.3 µg/g, respectively, which are 47, 17, 8, and three times higher than those of vitrinites from the same coals (Wang, 1994). Obviously, algae played an important role in enrichment of some trace elements.

Pyrites in the No.9 Coal ( $S_{t,d} = 3.46\%$ ,  $R_{o,max} = 1.09\%$ ; Dai et al., 2003a) from the Wuda Coalfield, Inner Mongolia, northern China (Fig. 2) occur as bacteriogenic (Fig. 4A), framboidal, massive, cell-filling, fracture-filling, and nodular forms. Compared to other pyrite forms, bacteriogenic pyrites are enriched in Cu, Zn, and Ni, suggesting that bacteria probably play an important role in the enrichment of these metals during the formation of pyrite. Biogenic pyrites, for example, an assemblage of pyritized monosporophyte of red algae (Fig. 4B), pyritized *Pediastrum* (Fig. 4C), and pyritized *Desulfovibrio* (Fig. 4D) have been found in other marine-influenced coals of southwestern China.

#### 4.3. Volcanic-ash-controlled Type

Influences of volcanic ashes on trace elements in coal were mainly reported from southwestern China. There were two ways that volcanic ash affected trace element concentrations in coal: 1) Intra-seam tonsteins, widely distributed in the Late Permian coals of southwestern China, may be incorporated with mined coal products, and if not removed in the preparation plant, become part of the feed

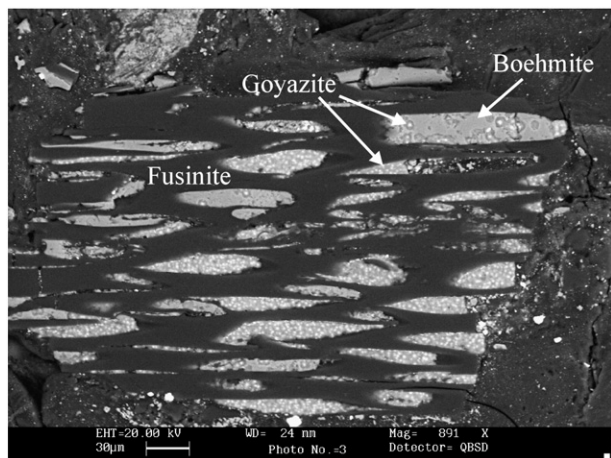


Fig. 3. Cell-filling boehmite in the No. 6 Coal from the Jungar Coalfield (Dai et al., 2006a).

**Table 2**Concentration of V, Cr, Rb, Mo, and U in coals preserved within marine carbonate successions ( $\mu\text{g/g}$ ; Dai et al., unpublished data).

| Area             | Coal mine       | Coal seam   | Thickness (cm) | $A_d\%$ | V    | Cr   | Rb   | Mo   | U    |
|------------------|-----------------|-------------|----------------|---------|------|------|------|------|------|
| Guiding, Guizhou | Guanchong       | No. 7       | 20             | 23.25   | 1153 | 461  | 26.3 | 472  | 288  |
|                  | Guanchong       | No. 8       | 101            | 23.84   | 1013 | 548  | 36.3 | 349  | 211  |
|                  | Heishentian     | No. 3       | 65             | 23.51   | 838  | 268  | 35.8 | 369  | 223  |
|                  | Laoheidong      | No. 2       | 20             | 16.94   | 835  | 246  | 20.3 | 419  | 229  |
| Heshan, Guangxi  | Zhongxu         | No. 3 Upper | 83             | 36.13   | 106  | 21.8 | 25.4 | 59.1 | 47.7 |
|                  | Zhongxu         | No. 3 Lower | 113            | 29.30   | 77.6 | 23.3 | 21.4 | 25.5 | 43.3 |
|                  | Shicun No.2Mine | No. 4 Upper | 227            | 34.01   | 119  | 43.4 | 9.79 | 12.1 | 21.4 |
|                  | Shicun No.2Mine | No. 4 Upper | 155            | 45.46   | 238  | 269  | 40.5 | 39   | 48.7 |
|                  | Shicun No.2Mine | No. 4 Lower | 106            | 41.65   | 150  | 93.9 | 46   | 49.1 | 31.6 |
| Yanshan, Yunnan  | Ganhe           | M9          | 191            | 27.51   | 567  | 329  | 23.4 | 204  | 153  |

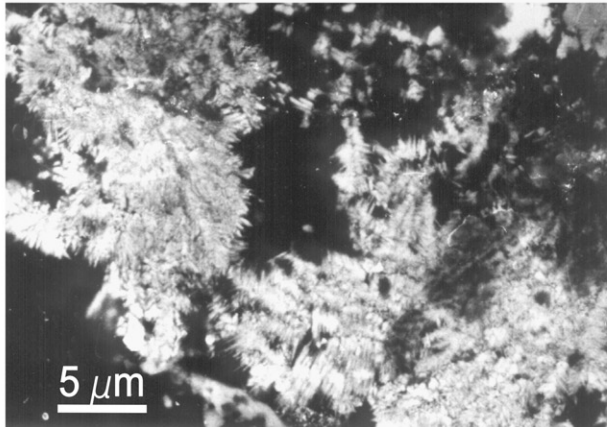
A, ash yield; d, dry basis.

coal (Ward, 2002); and 2) Similar volcanic ash that forms tonstein bands intimately dispersed in the peat, and during diagenesis the originally pyroclastic matter becomes part of the inherent mineral matter in the coal seam (Ward, 2002).

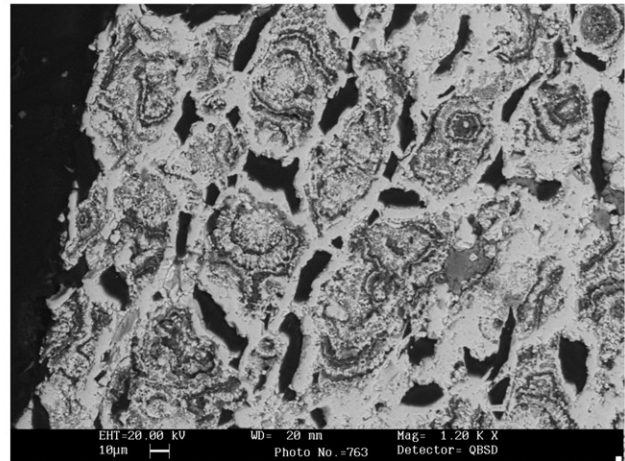
Mafic, silicic, and alkali intra-seam tonsteins in the Late Permian coals were identified in southwestern China, based on their lateral correlation over a large coalfield area and their similarity of mineralogical and chemical compositions (Dai et al., 2007b; Dai et al., 2011; Zhou et al., 1982, 2000). The mafic tonsteins are enriched in Sc, V, Cr, Co, and Ni, similar to the chemical composition of basalt of

the Kangdian Oldland, suggesting that it is the source of tonsteins. Alkali tonsteins were characterized by high contents of Nb, Ta, Zr, Hf, REEs, and Ga (Dai et al., 2011; Zhou, et al., 2000). Silicic tonsteins contain a relatively lower REE but have the higher fractionation between light REE and heavy REE. The  $\text{TiO}_2/\text{Al}_2\text{O}_3$  value can be used to classify the three kinds of tonstein:  $<0.02$  for silicic,  $0.02\text{--}0.08$  for alkali, and  $>0.10$  for mafic tonsteins (Fig. 6; Dai et al., 2011), indicating different magma sources. However, all their source magmas had an alkali-basalt composition and were similar to that of ocean island basalt (Dai et al., 2011). The alkali and silicic tonsteins were well

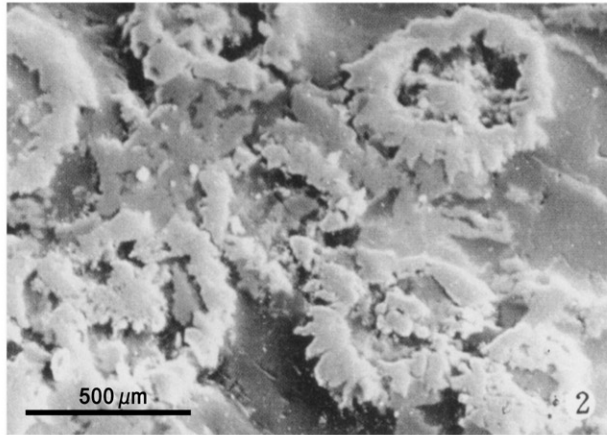
(A)



(B)



(C)



(D)

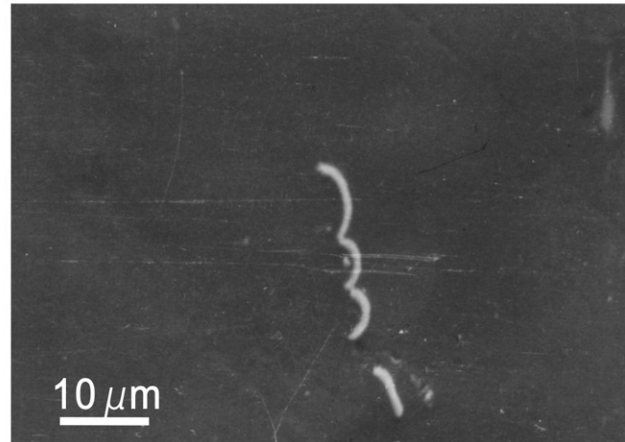


**Fig. 4.** Biogenetic pyrites in coals. (A) Pyritized rod-like bacteria (SEM, back-scattered electron image) (Dai et al., 2002), (B) Assemblage of pyritized monosporophyte of red algae (SEM, back-scattered electron image) (Dai and Chou, 2007), (C) Pyritized *Pediatrum* (SEM, secondary ion image) (Ren et al., 2006), and (D) Pyritized *Desulfovibrio* (SEM, secondary ion image) (Ren et al., 2006).

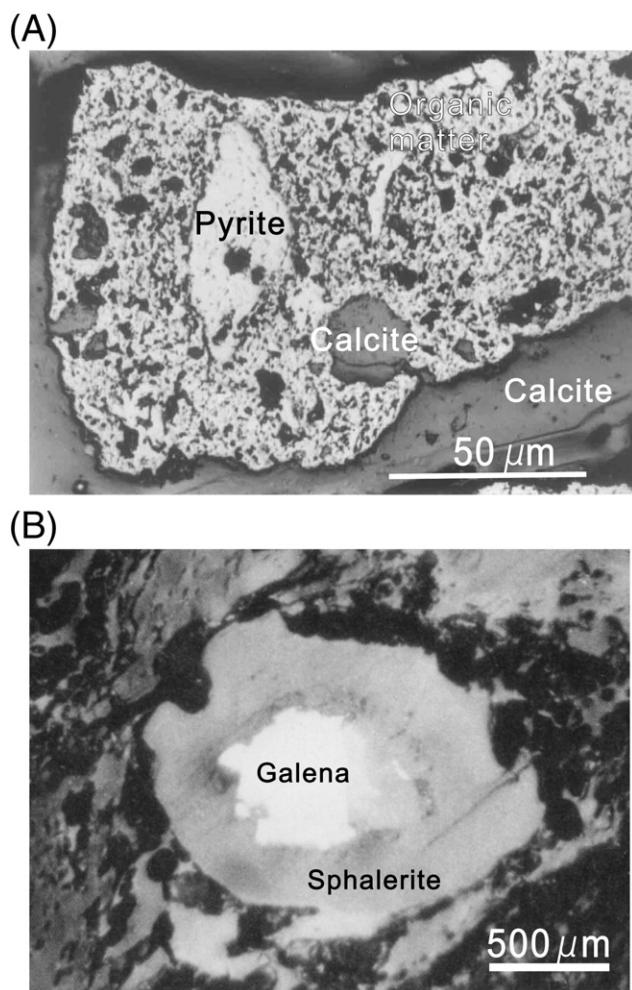


**Fig. 5.** Minerals derived from igneous hydrothermal fluids. (A) Pyrite and calcite occurring as vesicle and fracture fillings in the anthracite of the Fengfeng-Handan Coalfield, northern China (reflected light, oil immersion) (Dai and Ren, 2007). (B) Galena and sphalerite in the Late Triassic anthracite in the Jianou Coalfield, Fujian Province in southeastern China (reflected light, oil immersion) (Ren et al., 2006).

developed in the early and late stages of the Late Permian, respectively. However, mafic tonsteins were thoroughly distributed in the Late Permian coal-bearing stratigraphic section.

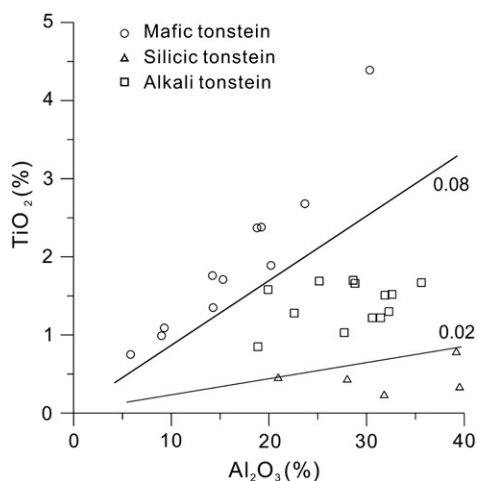


**Fig. 6.** Classification diagram of tonstein based on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> values (Dai et al., 2011).

The Late Permian No. 9 coal in the Zhijin Coalfield, Guizhou, southwestern China (Fig. 2), has a very high contents of Fe (4.34%), Cu (370 μg/g), U (49.6 μg/g), Mo (63.1 μg/g), and Zr (842 μg/g) (Dai et al., 2003b). The Fe and Cu do not occur as sulfides in this coal seam, in sharp contrast to many other coal seams in China. The geochemical and mineralogical anomalies of the coal seam are attributed to synsedimentary volcanic ash (Dai et al., 2003b; Ren et al., 2006). In addition to the common macerals and minerals in coal, they identified a volcanic-influenced material derived from volcanic ash, detrital material of terrigenous origin, and organic matter. The volcanic-influenced material is the main carrier of the above elements in this coal. Similar volcanic-influenced material was also found in the No. 6 Coal of the Qinglong Coalfield of western Guizhou (Li et al., 2008a,b). Bornite was observed under SEM-EDX and was considered as volcanic origin by Li et al. (2008a). The distance between the Zhijin Coalfield and Qinglong Coalfield was about 200 km. Although the volcanic-influenced material was found in the two coalfields of western Guizhou, it is uncertain if the material is common or widely distributed in the Late Permian coals in southwestern China, and if the No. 9 Coal in the Zhijin Coalfield and the No. 6 Coal in the Qinglong Coalfield are correlative.

The No.11 Coal in the Songzao Coalfield, Chongqing, southwestern China (Fig. 2), has high concentrations of Be (9.14 μg/g), Ti (9510 μg/g), Ga (32 μg/g), Zr (1300 μg/g), Nb (169 μg/g), Hf (32.7 μg/g), Ta (11.4 μg/g), W (24.8 μg/g), Th (24.1 μg/g), and total rare earth elements (510 μg/g). Besides pyrite, quartz, calcite, and kaolinite, trace minerals including albite, mixed-layer clay minerals of illite and smectite, monazite, apatite, and anatase, were found in the coal. The higher concentrations of trace elements and the trace mineral suite in the coal were believed to have been derived from alkali volcanic ashes that were deposited in the swamp during peat accumulation (Dai et al., 2007b).

#### 4.4. Hydrothermal-fluid-controlled Type

Hydrothermal-fluid-controlled type includes magmatic-, low-temperature-hydrothermal- fluid-, and submarine-exhalation-controlled subtypes. Hydrothermal fluids in coal basins can be classified as two types: deep circulating and igneous differentiated hydrothermal fluids (Yang et al., 1996). The former was derived from meteoric water that had circulated in the deep ground and then penetrated into coal seams along faults.

##### 4.4.1. Magmatic-controlled Subtype

Coal intruded by igneous rocks is not an uncommon occurrence (Finkelman et al., 1998). Igneous intrusions affect the safety, productivity, and economic viability of many coal mines (Golab and Carr, 2004). Frequent igneous activities in eastern China during Mesozoic and Cenozoic Eras led to a wide distribution of contact metamorphism of coal. Igneous intrusions not only affect organic matter, leading to elevated coal rank, but also lead to enrichment or depletion of trace elements in coal (Finkelman et al., 1998; Stewart et al., 2005; Dai and Ren, 2007; Sun et al., 2010b; Zheng et al., 2008). Although the mechanism of elements derived from igneous intrusion and then deposited in coal is not entirely clear, it seems that minerals from igneous hydrothermal fluids were major carriers of elevated trace element levels. However, some volatile elements inherent in coal were easily driven off by magmatic heat, leading to the depletion of these trace elements in coal.

The Early Cretaceous coal from the Fuxin Coalfield, Liaoning Province, northeastern China (Fig. 2) is a high quality coal with a low ash yield (4–18%) and low total sulfur content (0.3–0.8%) (Querol et al., 1997). The rank of the coal (mainly high volatile B bituminous coal) is clearly influenced by the diabase intrusion, which has induced the formation of natural coke. Both major and trace elements in the coal are at very low concentrations; only a high Mn concentration (up

to 8600 µg/g) was determined, which was attributed to the diabase intrusion (Querol et al., 1997).

The Fengfeng-Handan Coalfield is located in northern China (Fig. 2) and consists of coal-bearing strata of Pennsylvanian and Permian ages. The coal ranks are narrowly zoned, from high volatile A bituminous, through medium volatile bituminous, low volatile bituminous, semianthracite, and anthracite, to meta-anthracite. This situation can best be explained by diorite intrusions during the Yanshan Movement of the Cretaceous Period (Dai and Ren, 2007; Ren et al., 2006). The minerals derived from magmatic thermal alteration consist of pyrite, calcite, and ankerite, which mainly occur as fracture- or vesicle-fillings in the thermally altered high-rank coals (Fig. 5A). Elements including B (57.5–78.6 µg/g), F (101–886 µg/g), Cl (563–1220 µg/g), Br (70.6–113 µg/g), Hg (0.55–1.64 µg/g), As (18.4–48.4 µg/g), Co (14.6–33.7 µg/g), Cu (65.4–181 µg/g), Ni (20.8–74.6 µg/g), Pb (57.9–86.6 µg/g), Sr (590–2422 µg/g), MgO (0.98–1.41%), CaO (1.92–10.4%), MnO (0.1–0.2%), Zn (70.6–151 µg/g), and U (8.5–32.5 µg/g) were high in the altered coals and the magmatic inputs are the source of these elements (Dai and Ren, 2007).

The high rank ( $R_o, \text{ran} = 2\text{--}13\%$ ) of the Late Permian anthracite in the Meitian Coalfield, Hunan Province, southern China (Fig. 2), resulted from a granite intrusion (Wang et al., 1999). Elements including W (34.9 µg/g), Th (18 µg/g), and Ta (327 µg/g) are significantly enriched in the dike derived from magmatic hydrothermal fluids. The content of Ce, Cr, Eu, Hf, K, La, Lu, Na, Nd, Ni, Rb, Sc, Th, and U in coal decreases with increasing distance from the contact of coal with granite.

The Late Triassic anthracite coal in the Jianou Coalfield, Fujian Province in southeastern China (Fig. 2), has a much higher content of W (57.6 µg/g) than average Chinese (1.08 µg/g) and world coals (1.1 µg/g; Ketris and Yudovich, 2009). The coalfield was surrounded by granite intrusions resulting from the Yanshan Movement during the Cretaceous period. The SEM-EDX data indicated that W was mainly distributed in hydrothermal quartz veins. Finkelman et al. (1998) noted an extraordinary enrichment of W in the coke zone adjacent to an intrusion into a Colorado coal. In addition, sulfide minerals such as galena and sphalerite were observed in the Jianou coal (Fig. 5B), leading to the enrichment of Pb and Zn.

#### 4.4.2. Low-temperature-hydrothermal-controlled Subtype

As discussed above, the sediment-source region is the dominant factor for the background values of trace elements in coals from southwestern China. However, the epigenetic hydrothermal fluid was the major factor for local enrichments of trace elements in coal. The epigenetic minerals derived from hydrothermal fluids in coals of southwestern China include sulfides (pyrite, chalcopyrite, alabandite, sphalerite, galena, selenio-galena, getchellite, realgar, orpiment, cinnabar, and stibnite), carbonates (calcite, dolomite, ankerite, and strontianite), clays (kaolinite and chamosite), oxides (quartz), fluorides (fluorite) (Dai et al., 2004a, 2005a, 2006b; Dai and Chou, 2007; Zhang, 1999; Yang, 2006; Zhang et al., 1999, 2002, 2004) (Fig. 7A–F), which are the major carriers of some trace elements. Fluid inclusion studies show that the formation temperatures of calcic and siliceous veins, which host metals, are between 160 and 200 °C (Dai et al., 2004a; Guo et al., 1994; Zhang et al., 2002; Zhou and Ren, 1992).

Late Permian coals from western Guizhou Province and eastern Yunnan are enriched in many trace elements of epigenetic origin. For example, Zhang (1999) and Zhang et al. (1999) showed that pyrite-filled veins in the Late Permian coals in western Guizhou are enriched in As (up to 255 µg/g), Hg (up to 22.5 µg/g), Se (up to 242 µg/g), and Zn (up to 326 µg/g); and calcite-filled veins are strongly enriched in Hg (up to 11.9 µg/g) and Zn (up to 282 µg/g). The No. 30 Coal in the Zhijin Coalfield, Guizhou, is enriched in Cu (356 µg/g) and U (8 µg/g) because of alteration by a siliceous low-temperature hydrothermal fluid (Dai et al., 2004a).

In eastern Yunnan, the Neogene lignites, close to the deep faults, contain a high content of As (65.5–138.8 µg/g) (Zhou and Ren, 1992). The Late Permian anthracite in the Laochang Mine of eastern Yunnan (Fig. 2) has 152–1139 µg/g As. Epigenetic hydrothermal-fluid-derived minerals including fluorite, stibnite, and realgar were deposited in the disconformable contact between the Maokou Limestone (Early Permian) and Longtan Formation (Late Permian). The epigenetic hydrothermal fluid was the dominant factor for the enrichment of As in coal from eastern Yunnan (Zhou and Ren, 1992).

The siliceous and Fe-rich calcic low-temperature hydrothermal fluids significantly influenced the chemical compositions of the Late Permian No. 11 Coal (anthracite,  $R_o, \text{ran} = 2.85\%$ ) in the Dafang Coalfield in northwestern Guizhou Province, China (Fig. 2). The No. 11 Coal has high contents of vein ankerite (10.2 vol.%) and vein quartz (11.4 vol.%), with formation temperatures of 85 and 180 °C, respectively, indicating that vein ankerite and vein quartz were derived from low-temperature calcic and siliceous hydrothermal fluids in two epigenetic episodes (Dai et al., 2005a). There are epigenetic chalcopyrite, sphalerite, and Se-galena in the quartz vein (Fig. 7A). The vein ankerite and epigenetic sulfide minerals are the dominant sources of Mn, Cu, Ni, Pb, and Zn in the coal, and the contents of these five elements in the coal are as high as 0.09% and 74, 33.6, 185, and 289 µg/g, respectively.

Although hydrothermal fluids leading to local enrichment of trace elements in coal is common in southwestern China, occurrences are also found in some coals in southern and northern China (Li and Zhao, 2007). The origins of the hydrothermal fluids, e.g., derivation from mantle, crustal, surface water, rain water, or their mixture in Chinese coal basins, are not entirely clear and merit further study.

#### 4.4.3. Submarine-exhalation-controlled Subtype

The submarine-exhalation-controlled type was only reported from the Yanshan Coalfield of southeastern Yunnan. However, submarine-exhalation was one of the major hypotheses for the enrichment of V, U, Mo, Ni, and Co in the black shales including stone coals ( $A_d > 50\%$ ; calorific value = 3.5–10.5 MJ/kg) of Early Proterozoic and Early Paleozoic ages (Wu et al., 1999), which was mainly distributed in southern China.

The super-high-organic-sulfur coal of the Late Permian from the Yanshan Coalfield has a total sulfur content of 10.12%–11.3% and an organic sulfur content of 8.77%–10.3%. The minerals in the coal consist mainly of high-temperature quartz, sanidine, albite, muscovite, illite, pyrite, and trace amounts of kaolinite, plagioclase, akermanite, rutile, and dawsonite. The coal is highly enriched in F (841 µg/g), V (567 µg/g), Cr (329 µg/g), Ni (73.9 µg/g), Mo (204 µg/g), and U (153 µg/g). Occurrences of albite (Fig. 8) and dawsonite in the coal and strong enrichment of some elements, including F, S, V, Cr, Ni, Mo, and U, are attributed to the influence of submarine exhalation which invaded along with seawater into the anoxic peat swamp (Dai et al., 2008b). However, the sanidine and the high-temperature quartz in this coal are derived from silicic volcanic ashes (Fig. 8). Fig. 8 showed a well-developed albite crystal that fills in the interior of heavily-corroded sanidine, indicating that the former formed earlier than the latter.

Although it is pointed out that the numerous minerals derived from hydrothermal fluids are the major carriers of some trace elements in coal, interaction of the fluids with the organic matter is a significant factor for the enrichment of some elements, for example, enrichment of Ge and some other elements in the Wulantuga and Lincang coals, as discussed below, is the result of such process.

#### 4.5. Groundwater-controlled Type

There are fewer studies in the literature related to groundwater influence on the enrichment of trace elements in Chinese coals, compared to data from other countries (Chou, 1997; Goodarzi and Van der Flier Keller, 1990; Hower et al., 1999; Mukhopadhyay et al., 1998; Seredin, 2004; Seredin and Finkelman, 2008).

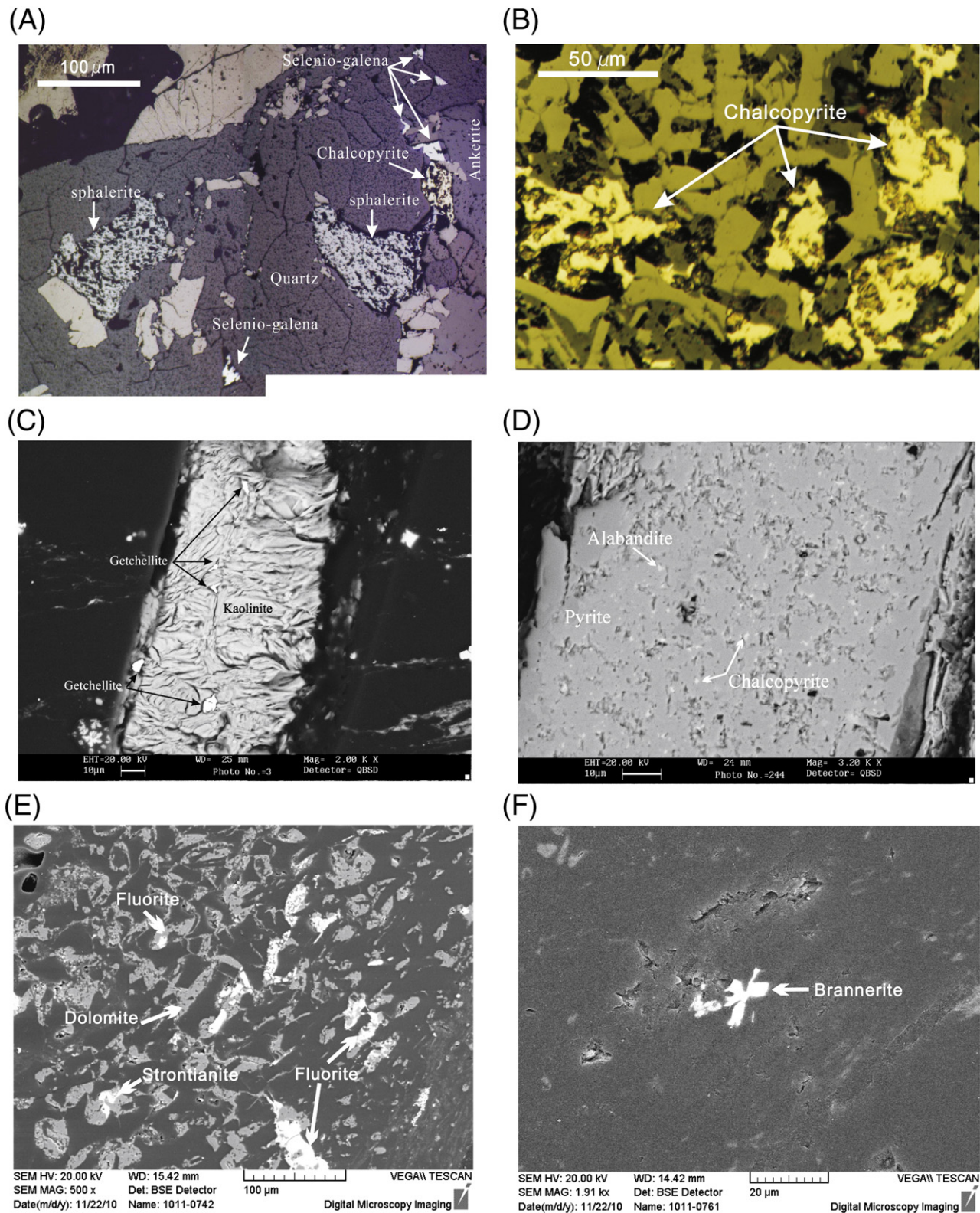


**Fig. 7.** Trace minerals derived from low-temperature hydrothermal fluid in the Late Permian coals from southern and southwestern China. (A) Chalcopyrite, sphalerite, selenio-galena in the coal from the Dafang Coalfield, western Guizhou (Reflected light); (B) Chalcopyrite in the coal from Muchuan, Sichuan (Reflected light) (Ren et al., 2006); (C) Getchellite and kaolinite in the coal from Xingren, southwestern Guizhou (SEM, back-scattered electron image) (Dai et al., 2006b); (D) Alabandite in the coal from the Sognzao Coalfield, Chongqing (SEM, back-scattered electron image) (Dai et al., 2007b); (E) Fluorite, strontianite, and dolomite in Heshan of Guangxi (SEM, back-scattered electron image) (Dai et al., unpublished data); and (F) Brannerite in the coal from Guiding of Guizhou (SEM, back-scattered electron image) (Dai et al., unpublished data).

Rare earth elements are enriched in the No. 6 Coal in the Heidaigou and Haerwusu Surface Mines of the Jungar Coalfield, northern China (Fig. 2), but they are very low in the intra-seam partings of the coal

(Dai et al., 2006a, 2008a). The lower REE abundances of the partings are attributed to leaching by groundwater during parting formation. When the REE-enriched leachate infiltrated the underlying coal

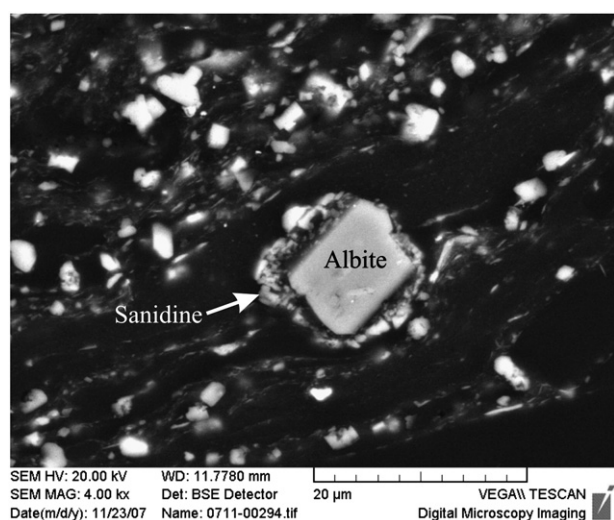


Fig. 8. Albite and sanidine in the Late Permian coal of Yanshan, eastern Yunnan (SEM, back-scattered electron image) (Dai et al., 2008b).

benches, three possible processes may have happened that fixed REEs in the coal: (1) Authigenic REE-rich minerals, such as cell-filling goyazite, were precipitated from the leachate, (2) Rare earth elements in the leachate were incorporated in aluminum hydrate minerals, and (3) Rare earth elements in the leachate were probably absorbed by the organic matter (Dai et al., 2008a).

The Late Triassic K8 Coal in the Changhe Mine of Sichuan Basin is enriched in REE ( $\Sigma$  La–Lu, 288  $\mu\text{g/g}$ ), Be (8.4  $\mu\text{g/g}$ ), Zr (302  $\mu\text{g/g}$ ), Nb (26  $\mu\text{g/g}$ ), Hf (9.7  $\mu\text{g/g}$ ), Th (18.8  $\mu\text{g/g}$ ), U (5.8  $\mu\text{g/g}$ ), and Ga (16.1  $\mu\text{g/g}$ ), probably due to the groundwater leaching process from the K8 roof. The K8 roof was composed of silicic volcanic ash (Wang, 2009). Authigenic rhabdophane and kaolinite in the K8 Coal are the main carriers of the elevated REEs (Wang, 2009).

## 5. Endemic Diseases Caused by Domestic Coal Combustion in China

Human health problems caused by indoor combustion of coal for heating and cooking in China are mostly confined to rural areas and are of great concern because millions of people have been affected by arsenic, selenium, fluorine, and nanoquartz poisoning (Belkin et al., 1998, 1999a,b; Dai et al., 2004b, 2005b, 2007a, 2008c; Finkelman et al., 2002; Tian 2005; Tian et al., 2008; Yang et al., 1981, 1983; Zhang and Cao, 1996; Zheng et al., 1999; Zheng and Huang, 1989). These endemic diseases caused by domestic coal combustion in China are nosogeographically special because they have rarely been reported in other countries.

### 5.1. Endemic Fluorosis

It was known that excessive fluoride ingestion predominantly comes from drinking water sources (Jacks et al., 2005; Kaseva, 2006; Ncube and Schutte, 2005; Subba, 2003). Brick tea is another source of fluorosis in some pastoral, semipastoral, and semiagricultural areas of China (Fung et al., 1999). However, endemic fluorosis attributed to indoor coal combustion has only been reported from China. Endemic fluorosis caused by indoor coal combustion, much more widespread than arsenic-poisoning, have been found in 199 counties of 13 provinces of China with more than 16 million people suffering from dental fluorosis and about 2 million people suffering from skeletal fluorosis as of 2008. Endemic fluorosis is most serious in western Guizhou Province where about 10 million suffer from dental fluorosis and 1 million people suffer from skeletal fluorosis (Dai et al., 2004b).

Some research has attributed the health problems to F released from indoor combustion of high-F coal (An et al., 1995; Ando, et al., 2001; Zhang and Cao, 1996; Zheng et al., 1999; Zheng and Huang, 1989). However, Dai et al. (2004b, 2007a) and Wu (2004) indicated that F in the coal from western Guizhou is within the usual range found in China (130  $\mu\text{g/g}$ ; Dai and Ren, 2006), USA (98  $\mu\text{g/g}$ ; Finkelman, 1993), and the world (88  $\mu\text{g/g}$ ; Ketris and Yudovich, 2009), and endemic fluorosis was due to the combustion of high-F clay used as a briquette binder for fine coal (Dai et al., 2004b). Later studies by Sun (2005) and Luo et al. (2007, 2010) further confirmed that the fluorosis is mainly caused by high-F clay in briquettes. The disease-causing scenario for fluorosis in western Guizhou is: (1) The local residents use furnaces without chimneys to dry corn and chilies, to cook, and to keep warm indoors. As a result, the food is polluted by F carried in ash particles released during the burning of the mixture of coal and high-F clay, and the residents who eat dried corn and chilies suffer from serious fluorosis. (2) Inhalation of indoor air polluted with volatilized fluorine is another pathway or exposure. The beds and stoves of the families in the endemic area are in the same room, and the distance between them is often within 1.5 m (Dai et al., 2007a).

Although the sources and pathways for endemic fluorosis have been revealed, new cases of fluorine poisoning still occur in the area. There are several ways to prevent endemic fluorosis in Guizhou:

- (1) Government-sponsored projects to replace the coal with other energy sources such as marsh gas, or to install chimneys for homes in the region to reduce indoor exposure. However, the residents cannot afford to pay for the repair if and when the chimneys and equipment for marsh gas are broken. Moreover, the fire from marsh gas and stoves with installed chimneys is not as good as the residents require, and most residents have abandoned them.
- (2) Improve health education, particularly, changing living habits, such as washing the corn and chilies before cooking and peeling the corn before pulverizing, can lead to a sharp decrease of the F pollution (Dai et al., 2007a). Moreover, it is better to store foods using boxes and bags, or seal foods in a storeroom far away from the coal fires.
- (3) Improve the living standards of the residents and to provide medical assistance. However, for medical assistance, the best way is disease prevention rather than the disease cure because it is very difficult to cure the fluorosis using present available medical methods or technology.
- (4) Adding limestone into the mixture of coal and clay (Sun, 2005) or replacing the high-F clay by a low-F clay to reduce the quantity of F released.

These protective measures must be comprehensively considered in order to be effective in fluorosis prevention.

### 5.2. Endemic Arsenosis

Endemic arsenosis caused by domestic arsenic-rich coal combustion is locally very severe in several villages in southwestern Guizhou, China (Fig. 2). More than 3000 patients in the mountainous region of southwestern Guizhou have been diagnosed with arsenosis (Ding et al., 2001) and 265 people died from the arsenosis from 1976 to 2003 (Yang, et al., 2006). The arsenic source of endemic arsenosis is high-arsenic coals, located in the Xingren, Xingyi, and Anlong counties of Guizhou (Belkin et al., 1999b; Ding et al., 2001; Ren et al., 1999; Wang et al., 2009). The high-arsenic coal occurs in the Late Permian Longtan Formation ( $P_2$ ), which is made up of alternating marine and terrestrial facies (Dai et al., 2006b). The highest arsenic (3.2–3.5%) in coal in the world was reported from this area (Belkin et al., 2008; Ren et al., 1999; Zhao et al., 1998).

However, the content of As in coals from this area is highly variable, from <1  $\mu\text{g/g}$  to 3.5% (Belkin et al., 2008; Dai et al., 2006b;

Ding et al., 2001; Ren et al., 1999; Zhang et al., 2002; Zhao et al., 1998). The arsenic content even varies greatly in the same coal bed at different mines in a restricted area (Dai et al., 2006b; Ding et al., 2001). Thus, the enrichment of As, as well as Hg, Sb, and Tl in coals from the southwestern Guizhou is not ubiquitous, but very local. Dai et al. (2005b) also indicated that high-As coals from Xingren County, southwestern Guizhou, are very restricted, and the high-As coal reserve of southwestern Guizhou is extraordinary small. It should be noted that almost all the coal geochemical studies from southwestern Guizhou were related to the local endemic arsenosis (Belkin et al., 1998, 1999b, 2008; Ding et al., 2001; Ren et al., 1999; Zhao et al., 1998), and, hence, researchers collected coals that had high arsenic contents and, therefore, these studies should not be considered as typical of the As content of coals in this area (Belkin et al., 2008; Dai et al., 2006b).

The pathway of As from coal to humans is similar to that of fluorine as described above. The arsenosis is the result of the ingestion of foodstuffs (chili peppers and corn) contaminated by As-containing smoke from domestic combustion of coal using open, unvented stoves. Although the ingestion of As-contaminated food is the primary factor, other As sources are also important (Liu et al., 2002), for example, air–dust, water, and direct skin contact. Note that arsenosis in Guizhou is often accompanied by fluorosis. The co-exposure of F and As, as well as Tl and Hg, may occur through the same pathway (coal–clay mixture burning and food contamination) in largely the same endemic areas of southwestern Guizhou.

A wide variety of As-bearing phases was observed in high-As coals from southwestern Guizhou, for examples: pyrite; arsenopyrite; getchellite; arsenic-bearing sulfide (realgar?); Fe–As oxide; K–Fe sulfate; scorodite; As-bearing sulfide composed of As, Pb, and S (probable sartorite or a related species?); and As-bearing clays (Belkin et al., 1998, 2008; Dai et al., 2006b; Ding et al., 2001; Tang and Huang, 2004; Zheng et al., 1999). Occurrences of organically associated As have also been reported in Guizhou coal (Ding et al., 2001; Zhao et al., 1998). Although both occurrence modes and content of As in coals greatly varies, almost all authors had a consensus that high As in coal was derived from epigenetic hydrothermal solutions (Belkin et al., 2008; Dai et al., 2006b; Ding et al., 2001). The area of high-arsenic coal distribution is within the sediment-hosted Au area of Southwest China, which is called “golden triangle” (He et al., 1993). Small Au deposits can be found near the high-As coals. No igneous rocks are exposed in the immediate vicinity of the study area. Carlin-type ore-forming fluids were the probable source responsible for the gold and enrichments in As, Sb, and Hg in the coal (Belkin et al., 2008; Dai et al., 2006b; Huang, 1993). The element assemblage characteristic in the Carlin-type gold deposits in this area is similar to that found enriched in the coal (Ashley et al., 1991; Belkin et al., 1998, 2008; Peters et al., 2007; Qian et al., 1995).

The ways to prevent endemic arsenosis in Guizhou are similar to those for fluorosis. In addition, coals with >100 µg/g As have been forbidden for mining in the endemic-arsenosis areas. The preventive effects for endemic arsenosis have been greatly improved especially from 2005. The results of arsenosis prevention are much better than endemic fluorosis.

### 5.3. Endemic Selenosis

Endemic selenosis was found during 1958–1963 in Enshi County of Hubei Province of southern China (Fig. 2). During the years of the highest prevalence, from 1961 to 1964, the morbidity was almost 50% in the 248 inhabitants of the five most heavily affected villages (Yang et al., 1983). As of 1987, 477 people (from 3- to 66-years old) had suffered from Se poisoning in Enshi and surrounding areas (Mao et al., 1990). Domestic animals, for example, chickens and pigs, also suffered from Se poisoning and only a few animals could survive once they developed the disease.

The major exposed sedimentary sequences in the endemic areas are Permian and Triassic strata. High Se occurs in the carbonaceous siliceous rocks and carbonaceous shales of the lower Permian Maokou Formation, known locally as “stone coal” and with a thickness of 13–16 m (Song, 1989). The selenium content varies from >10 µg/g to several thousand µg/g (Mao et al., 1990; Song, 1989; Yang et al., 1983; Zhu et al., 2004). The Se concentration in two stone coal samples collected by Song (1989) and Yang et al. (1981, 1983) was as high as 84,123 and 8290 µg/g, respectively.

The weathering of the “stone coal” and stone-coal ashes used as fertilizer are considered as the two sources for Se enrichment in soil. High Se in soil was available for uptake by crops. The selenium in “stone coal” may occur in pyrite, eskebornite, mandarinoite (Belkin et al., 2003; Zheng et al., 1992, 1993); in the form of adsorbed Se on organic matter (Song, 1989); or as native Se (Zhu and Zheng, 2001; Zhu et al., 2004).

Measures to prevent selenosis had been taken since 1960s and had achieved expected results. These measures include migration of residents, forest conservation, closing five kinds of small industrial factories (small steel, cement, farming machine, fertilizer factories, and coal mines), changing farming styles, and living habits. No selenosis cases have been reported since 1987.

### 5.4. Lung Cancer

Some miners from the Shenbei Coalfield, Liaoning Province of northeastern China (Fig. 2), have suffered serious lung disease caused by inhaling coal dust. Some lung autopsies of the miners from this mine contain higher Cr than those of common people (Ren et al., 2004). The Shenbei lignite is highly enriched in potentially hazardous trace elements such as Co (22 µg/g), Cr (79 µg/g), Cu (63 µg/g), Zn (93 µg/g), V (88 µg/g), and Ni (75 µg/g), which may be related to lung cancer.

The Xuanwei area in Yunnan Province, southwestern China (Fig. 2), has one of the highest female lung cancer mortality rates in China (Dai et al., 2008c; Large et al., 2009; Tian, 2005; Tian et al., 2008). Smoking was excluded as a cause of excessive cases of lung cancer because almost all women were non-smokers. As compared with Chinese coals, the composition of Xuanwei coal is high in SiO<sub>2</sub> (13.66–22.94%), Fe<sub>2</sub>O<sub>3</sub> (4.93–7.37%), TiO<sub>2</sub> (0.24–0.89%), CaO (2.92–6.84%), MnO (0.19–0.14%), V (27–166 µg/g), Co (24–31 µg/g), Ni (27–41 µg/g), Cu (24–168 µg/g), and Zn (45–158 µg/g) (Dai et al., 2008c). Elements Ti, Co, Ni, Cu, and Zn were derived from the basaltic rocks at the sediment source region (Dai et al., 2008c). However, there is no evidence to support the link between metals in coal and lung cancer in the area. Previous studies attributed the epidemic disease in the area to the polycyclic aromatic hydrocarbons (PAHs) released into domestic air from coal burning (Mumford et al., 1987). However, Tian (2005) failed to reproduce the link between PAHs and lung cancer in a geographical correlation study in Xuanwei. Tian (2005) and Tian et al. (2008) found nanometer-scale quartz in these coals, soot emissions, and lung cancer tissues. Abundant crystalline silica was found in certain types of coals, soot emissions, and lung cancer tissue samples and was, thus, hypothesized as a possible cause for the lung cancer epidemic in Xuanwei.

In these four endemic diseases, knowledge of the abundances, modes of occurrence, and origin of trace elements and minerals in coal was pivotal for a better understanding and mitigation of the diseases. For the situation concerning As and Se poisoning, the suspect coals have been identified and mining from these deposits has been curtailed. However, F has been a much more difficult problem for the local public health officials, not only because it is difficult to find a low-F, cheap, and easily-dug clay around the villages to replace the high-F clay, but also because of the extraordinary poor situation of the residents. Regional geochemical and mineralogical studies can help define low-F coal and clay deposits, suitable for domestic use.

## 6. Valuable Elements in Coals and Coal-bearing Strata of China

In some specific geological conditions, some rare and noble elements can be significantly enriched in coals, equal to or even higher than their concentrations in many conventional types of ores. Although coals with such high trace element concentrations are not common and generally small in volume, these metals could be useful economic by-products of coal cleaning or combustion residues (Finkelman and Brown, 1991; Seredin and Shpirt, 1995; Seredin, 2004; Sun et al., 2010a). For example, Ge from coals is currently being used by the industry as raw material (Seredin and Finkelman, 2008). REEs, Ga, Nb, Zr, Ag, Au, and PGE have the best chance for such use. However, it is unlikely that coal will be an important source of Cu, Zn, Pb, Co, Ni, Cr, As, and Sn in the foreseeable future not only in China but also in the world, as sufficient conventional ore deposits exist (Seredin and Finkelman, 2008).

In China, Ge from Lincang, Yunnan province, and Wulantuga, Inner Mongolia, has been studied in detail and is being used industrially. Extraction of Ga, as well as Al, is now under study for extraction from coal combustion residues. However, publications on Be-, PGE-, Ag-, and Au-rich coals in China are scarce.

### 6.1. Germanium

Germanium in Chinese coals has been studied since the late 1950s. The reported large Ge hosted coal deposits in China mainly occur in Lincang (Yunnan), Wulantuga (Inner Mongolia), and Yimin (Inner Mongolia) (Du et al., 2003; Hu et al., 2006, 2009; Li et al., 2011; Qin, 2001; Qi et al., 2004; 2007a,b; Wang, 1999; Zhuang et al., 2006).

The Early Cretaceous Wulantuga high-Ge coal deposit is located in the Shengli Coalfield, Inner Mongolia, northeastern China (Fig. 2). The Ge content in the coal ranges from 32 to 820 µg/g, with a mean value of 137 µg/g (on a whole coal basis, mean of 939 coal samples from 75 boreholes in an area of 2.2 km<sup>2</sup>) (Du et al., 2009). It was estimated that there was 1700 t of metallic Ge extractable from coal with Ge content >100 µg/g (Du et al., 2009). There is a negative correlation between the mean Ge content and the thickness of the coal seam and the lower, upper, and middle parts of the coal seams are high in Ge (Du et al., 2009). A major organic affinity of Ge was determined (Du et al., 2009; Qi et al., 2007a). Fine-grained Ge-minerals (oxides or oxalates) were also found in the coal of the deposit (Zhuang et al., 2006).

The Wulantuga Ge-rich coal is also enriched in Au and PGEs (Seredin et al., unpublished data; Zhuang et al., 2006). The noble metal contents in the coal of the lower part of Ge-bearing seam are anomalously high and their concentrations are nine (Pd) and 25 (Au, Pt) times, respectively, that in the Upper Continental Crust (Seredin et al., unpublished data).

The Lincang Neogene Ge-deposit is located in western Yunnan province (Fig. 2) and was discovered in the 1950s during prospecting for U. The Ge coal deposit is in the Miocene Bangmai Formation, deposited on top of a granitic batholith. The mineralized area in the major orebody, Dazhai, is 600-m long and 400-m wide, with an area of 0.25 km<sup>2</sup>. The proven Ge reserves are 1000 t in the Dazhai (800 t) and Zhongzhai (200 t) ore fields of the Lincang Ge deposit (Hu et al., 2009; Qi et al., 2007a). The concentration of Ge in the deposit is a few tens of µg/g to about 2500 µg/g, with an average of about 850 µg/g (Qi et al., 2004).

The Ge-rich coal seams are inter-layered with siliceous rocks and siliceous limestones in the basal coal-bearing unit (Hu et al., 2009; Qi et al., 2004; Zhuang et al., 1998). These rocks contain abnormal high Ge content (78 and 67 µg/g on average, respectively) and are considered as analogues of a hot-spring siliceous sinters or hydrothermal travertines (Hu et al., 2009; Qi et al., 2004). However, the coal seams in the coal basin that are not interbedded with siliceous rocks and siliceous limestones are barren of Ge (Hu et al., 2009). Germanium is concentrated at the top and bottom benches of the coal seams, and the

former is in contact with the layered siliceous rocks or siliceous limestones. Germanium in the mineralized coal seams is mainly associated with organic matter (Li et al., 2011). Ge-rich coals are also rich in Be, Cs, As, Sb, Hg, Nb, W, and U (Table 3). The Ge-rich coal mined primarily is also as a U deposit.

Ge-bearing coals both in the Wulantuga and Lincang deposits are enriched in other trace elements. In spite of sharp distinctions of a geological structure of these deposits, coal ages and compositions, as well as considerable distance between these deposits (thousands km), the list of elements accumulated in the Ge-rich coals is very similar (Table 3). Coals in both deposits contain high concentrations of lithophile elements (Wulantuga: W, Be, U, and Cs; Lincang: W, Be, U, Cs, and Nb; they are typical compositions of felsic rocks) and high-volatile elements that are members of the epithermal or volcanogenic group (Wulantuga—Sb, As, Hg, and Tl; Lincang—Sb and As) (Table 3). The latter indicates that the hydrothermal fluids may have been responsible for deposit formation. The assemblage of epithermal and lithophile trace elements in Ge-bearing coals may be the result of leaching granite basement rocks by ascending volcanogenic fluids (Seredin, 2004).

A similar geochemical assemblage (Sb, W, Be, Cs, and As) is typical of the Spetzugli Ge-bearing coal deposit (Russian Far East), the third largest Ge deposit in the world that is being mined now (Seredin, 2003a,b; Seredin and Finkelman, 2008). It obviously indicates a similarity of the ore-forming processes in all large coal-hosted Ge deposits.

The largest Ge-bearing coal deposit, not only in China but also in the world, is probably in the Yimin Coalfield of Inner Mongolia, with an estimated resource of 4 Kt Ge (Wu et al., 2002). The coal-bearing strata are in the Damoguaihe and Yimin Formations (Early Cretaceous) and the Ge enrichment occurred in coals and partings from the former Formation. The concentration of Ge in the mineralized coals and partings is up to 470 µg/g. Unfortunately, only limited information is available to date about this unique deposit (Wu et al., 2002).

The main Ge anomaly in the above ore deposits occurred in low-rank coals and was attributed to hydrothermal fluids circulating through the fault systems, probably from the adjacent granitoids. The Ge-rich hydrothermal fluids entered the buried peat and Ge was adsorbed by the organic matter during early diagenetic stage (Du et al., 2009; Hu et al., 2006, 2009; Qi et al. 2004; Zhuang et al., 2006).

It should be noted that some elements (including Sb, As, Hg, Tl, U, and Be) enriched in Ge-bearing coals have high toxicity. However, their negative influences on human health have rarely been studied. The health of workers in power plants and Ge-recovery factories is

**Table 3**

Trace element contents (µg/g) with concentration coefficient (CC) ≥ 5 relatively to Chinese coals in Ge-bearing coals of the Wulantuga and Lincang deposits.

| Element | Wulantuga |      |      |         |    | Lincang |      |      |         |    |
|---------|-----------|------|------|---------|----|---------|------|------|---------|----|
|         | CC        | Min  | Max  | Average | N  | CC      | Min  | Max  | Average | N  |
| W       | 230       | 31   | 911  | 248     | 63 | 350     | 109  | 975  | 378     | 52 |
| Sb      | 228       | 1.8  | 2382 | 191.2   | 63 | 39      | 0.8  | 347  | 32.8    | 52 |
| As      | 127       | 9    | 1321 | 482.9   | 31 | 13      | 0.8  | 410  | 47.6    | 52 |
| Ge      | 124       | 22   | 1894 | 344.6   | 63 | 306     | 25.5 | 2523 | 852     | 52 |
| U       | 8         | 0.2  | 115  | 20.3    | 33 | 23      | 1.1  | 640  | 56      | 52 |
| Cs      | 6         | 1    | 43   | 6.6     | 63 | 20      | 3.7  | 75.1 | 22.7    | 52 |
| Be      | 16        | 2    | 111  | 33.4    | 63 | 94      |      |      | 198     | 1  |
| Tl      | 12        | 0.1  | 31.7 | 5.7     | 58 |         |      |      |         |    |
| Hg      | 41        | 0.03 | 36   | 6.7     | 22 |         |      |      |         |    |
| Nb      |           |      |      |         |    | 5       | 0.5  | 315  | 46.8    | 52 |

Note: The table is based on data from Du et al. (2009), and Hu et al. (2009), Qi et al. (2007a), Zhuang et al. (2006), and Li et al. (2011). N, number of samples. CC Coal/Chinese coal average (this work).

under a high threat of these toxic elements due to the following two conditions:

1. The toxic elements listed above highly concentrate in fly ash together with Ge, because of the high volatility of Sb, As, Hg, and Tl under high-temperature conditions, and the organic modes of occurrences of U and Be in Ge-rich coals in Wulantuga and Lincang deposits (Li et al., 2011). The contents of Tl, Hg, Sb, and As in a fly-ash sample collected by baghouse filter from the Wulantuga Ge recovery factory are as high as 58, 67.5, 5160, and 9215 µg/g, respectively (Dai et al., unpublished data).
2. Such fine-graded material as fly ash with high concentrations of toxic trace elements represents a special danger, because they can penetrate into the lungs of people in contact with the fly ash in the course of industrial activity.

Thus, the impact of these toxic trace elements in Ge-rich coals and in fly ashes on human health merits further studies (Seredin, 2003a, 2004).

### 6.2. Gallium

The content of Ga could be up to 50–100 µg/g in coal and can be as high as several hundred µg/g or even a few kilograms per ton in coal fly ash, making Ga-rich coals a potential resource for Ga recovery as a by-product of coal combustion (Seredin and Finkelman, 2008). However, Ga is typically a dispersed element and it is relatively rare to form a Ga ore deposit (Dai et al., 2008a; Zhou and Ren, 1981). The Ga content in Chinese coals and world coals is 6.55 µg/g (this study) and 5.8 µg/g (Ketris and Yudovich, 2009), respectively. According to the Chinese standard, the industrial grade of Ga content in coal is 30 µg/g. Only a few Chinese coals contain >30 µg/g Ga (Tang and Huang, 2004; Zhuang et al., 2003, 2007; Zhao et al., 2009; Zhou et al., 2010). The Ga coal deposit was found in the Heidaigou Surface Mine of Jungar Coalfield, Inner Mongolia, northern China (Fig. 2).

As discussed above, the Pennsylvanian No. 6 Coal (30-m average thickness) in the Heidaigou Surface Mine is enriched in Ga, with a weighted average of 45 µg/g Ga, much higher the industry grade of 30 µg/g. In addition, Al<sub>2</sub>O<sub>3</sub> in the coal is also high and the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is 0.34–0.58 in the Ga-rich coal benches, much lower than that of Chinese coals (1.42). Note that the fly ash from the Jungar Power Plant is unique because it is high in alumina (Al<sub>2</sub>O<sub>3</sub>>50%) (Dai et al., 2010b), which was attributed to high boehmite in the feed coal (Dai et al., 2006a, 2008a; Wang et al., 2011).

The proven reserves of Ga in the No. 6 Coal of Heidaigou Surface Mine are estimated to be 54 Kt (new data of this study), making it a super-large Ga ore deposit. Because of the discovery of high Al<sub>2</sub>O<sub>3</sub> and Ga in both coal and fly ash, the management of the Heidaigou Surface Mine, which is owned by Shenhua Group Jungar Energy Corporation Ltd., has built a pilot plant to develop technologies to extract the metals from combustion residues.

### 6.3. Uranium

The largest uranium deposit in coal probably occurs in Middle Asia (Seredin and Finkelman, 2008). In addition to U-rich coals in the Yili coal basin of Xinjiang province (Fig. 2), which are closely situated to the large U deposits in Middle Asia, some smaller deposits of U-rich coals, including Tengchong, Yanshan, Jianshui, and Lincang of Yunnan province; Guiding of Guizhou province; and Heshan of Guangxi province, have been found in southern China. Uranium in the Tengchong coals of Yunnan province had been industrially used a few decades before.

The Yili Basin is a Mesozoic–Cenozoic continental basin, derived from the Paleozoic interarc taphrogenic trough. The sediment-source region mainly consists of Hercynian granite, pre-Triassic igneous rocks, and pyroclastic rocks interbedded with carbonate layers. The

latter also makes up the base of coal basin. The U-bearing strata are located in the lower Jurassic coal-bearing sedimentary sequences and include in situ leaching sandstone type as well as lignites. Data from three drill cores (Well nos. ZK0161, ZK0407, and ZK0177; Table 4) showed that U in coal is high and greatly variable (from 76 to 1835 µg/g). Compared to the ordinary world lignites (Ketris and Yudovich, 2009), these coals also contain high contents of Mo and Re. The highest concentrations are found in the upper zones at the contacts with the oxidized host sandstone, for example, the top bench (20 cm) of the No. 11 Coal of the ZK0177 Well contains 7207 µg/g U. This U-rich coal deposit is of epigenetic origin and is a bed-infiltration type deposit originating from confined water, whose geochemical features are similar to those described by Seredin and Finkelman (2008).

Coals preserved within marine carbonate successions, for example, Heshan of Guangxi Province; Guiding and Ziyun of Guizhou Province; and Yanshan of Yunnan Province in southern China, usually contain a high U content (71.7–153 µg/g; Table 2). These coals also usually have a high content of organic sulfur, from 4 to 13%, mostly 8–11%. Uranium in these coals usually occurs in the organic matter but rare U-bearing minerals, brannerite (UTi<sub>2</sub>O<sub>6</sub>) (Fig. 7F) and pitchblende (UO<sub>2</sub>), have been found in the Guiding coals. The fracture-filling modes of occurrence indicated that the two U-bearing minerals are of epigenetic origin. The EDX data showed that brannerite contains 49.93% UO<sub>3</sub> and 35.19% TiO<sub>2</sub> and the pitchblend contains 43.35–70.77% U (Dai et al., unpublished data). Elements including Mo, V, Cr, and Co normally accompany uranium in these high-S<sub>org</sub> coals. The high U content in the organic matter was of a syngenetic origin (Shao et al., 2003; Zeng et al., 2005) and attributed to seawater influences; however, as described above, Dai et al. (2008b) attributed the high U in the Yanshan coals to submarine exhalation.

### 6.4. Nb(Ta)–Zr(Hf)–REE–Ga Rare Metal Deposits in Coal-bearing Strata

High concentrations of Nb, Ta, Zr, Hf, and REEs in coal or coal-bearing strata can occur but are not common (Eskenazy, 1987, 1990; Seredin, 1994; Seredin and Finkelman, 2008; Tang and Huang, 2004). The assemblage of high Nb–Ta–Zr–Hf–REE–Ga in coal was mostly attributed to tuffs or alkali tonsteins (Dai et al., 2007b, 2011; Seredin, 2004; Seredin and Finkelman, 2008).

The enrichment of these elements in the No. 11 Coal in the Songzao Coalfield was attributed to the intra-seam alkali tonstein (Dai et al., 2007b). The Nb concentration in the high temperature ash of the No. 11 Coal is 275 µg/g, and is potentially a valuable by-product of coal combustion (Dai et al., 2007b).

Dai et al. (2010c) describes a new type of Nb(Ta)–Zr(Hf)–REE–Ga rare-metal deposit of volcanic origin in the Late Permian coal-bearing strata of eastern Yunnan, southwestern China. Well logging data (especially natural gamma-ray), geochemical data (high concentrations of Nb, Ta, Zr, Hf, REE, and Ga), and mineralogical compositions (Nb(Ta)–, Zr(Hf)–, or REE-bearing minerals rarely observed), together with the volcanic lithological characteristics indicate that there are thick (1–10-m, mostly 2–5-m) ore beds in the lower Xuanwei Formation (Late Permian). The ore beds are highly enriched in (Nb, Ta)<sub>2</sub>O<sub>5</sub> (302–627 µg/g), (Zr,Hf)O<sub>2</sub> (3805–8468 µg/g), REO (trioxides

**Table 4**

Selected metal concentrations in the U-bearing lignite seam from the Yili Basin, Xinjiang province (Elemental content in µg/g; On a dry basis; Dai et al., unpublished data).

| Well number | Coal seam | Thickness (m) | A <sub>d</sub> (%) | U    | Mo   | Re    |
|-------------|-----------|---------------|--------------------|------|------|-------|
| ZK0161      | 11        | 1.00          | 24.96              | 90   | 36   | 0.007 |
|             | 12        | 2.20          | 13.74              | 714  | 239  | 0.667 |
| ZK0407      | 10        | 1.08          | 43.84              | 275  | 46.3 | 0.96  |
|             | 11        | 2.15          | 34.57              | 76   | 27.9 | 0.245 |
| ZK0177      | 12        | 0.40          | 41.96              | 129  | 126  | 0.01  |
|             | 12        | 1.20          | 29.01              | 1835 | 684  | 5.808 |

A, ash; d, on a dry basis.

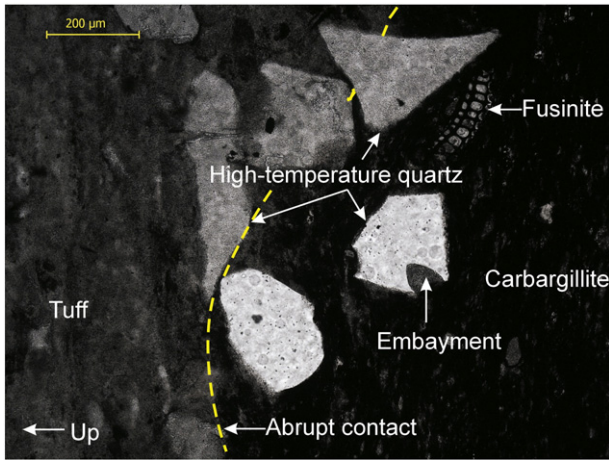


Fig. 9. High temperature quartz in the Nb-Ta-Zr-Hf-REE rare-metal ore deposit in Xuanwei, eastern Yunnan (Single-polarized optical microscope) (Dai et al., 2010c).

of La–Lu + Y) (1216–1358  $\mu\text{g/g}$ ), and Ga (52.4–81.3  $\mu\text{g/g}$ ). Preliminary studies suggest that the high concentrations of otherwise rare metals were mainly derived from the alkalic pyroclastic rocks (Fig. 9) (Dai et al., 2010c).

A similar ore deposit occurs in the Nanchuan coalfield of Chongqing, southwestern China. The ore deposit of tuff, with an average thickness of 3.05 m and identified as volcanic origin, is located in the lowermost of the Late Permian coal-bearing strata. The drill core samples (CK6 well, from top to bottom is numbered CK6-1 to CK6-12) contain 146–388  $\mu\text{g/g}$  (Nb,Ta)<sub>2</sub>O<sub>5</sub>, 763–1785  $\mu\text{g/g}$  (Zr,Hf)O<sub>2</sub>, 260–961  $\mu\text{g/g}$  REE (trioxides of La–Lu + Y), and 40–96  $\mu\text{g/g}$  Ga (Table 5). The ore deposit is widely distributed in southern Sichuan, Chongqing, and western Guizhou.

Compared to the normal sedimentary rocks in the sequences, natural gamma-ray data of the ore beds show a significant positive anomaly in well logging (Fig. 10). Based on the well logging analysis of more than 300 wells, if the value of natural gamma-ray is >250 API, it can be considered as a significant positive anomaly and the corresponding layers are expected to contain higher Nb, Ta, Zr, Hf, REE, and Ga. However, other sedimentary rocks generally have natural gamma-ray values less than 100 API. Thus, such positive anomaly of natural gamma-ray may be considered as a geophysical indicator of

Nb–Ta–Zr–Hf–REE–Ga in ore prospecting. Note that natural gamma-ray of intra-seam alkali tonstein of coal also showed positive anomalies (Dai et al., 2007b), the peak width of natural gamma-ray log, however, is very narrow because of the thin thickness of tonstein (3–7 cm).

The new type of Nb(Ta)–Zr(Hf)–REE–Ga rare metal deposit found in eastern Yunnan and Chongqing of southwestern China not only has a potential economic value, but also can be used in stratigraphic correlation. The similar macrostructures, chemical compositions, and geophysical features indicated that the two Nb(Ta)–Zr(Hf)–REE–Ga deposits are derived from the alkali volcanic ashes erupted at the same geologic period.

## 7. Conclusions

Based on studies of the past several decades, the overall features of elemental concentrations in Chinese coals has become clear, although some technical problems still exist, for example, area distribution of samples and elemental determination methods need improvement. More attention should be focused on coals in western China, including northwestern China and the Tibet–western Yunnan coal-distribution areas, since fewer samples have been taken from there.

Overall, Chinese coals have normal background values for most trace elements. Note that the average concentration of the three trace elements, Hg, As, and F in Chinese coals that have attracted considerable attention by geochemists for their exceptionally high concentrations in parts of Guizhou Province are at the same level as most coals in the world. The coal reserves should be taken into account when calculating the average concentration of trace elements in coal; otherwise, results may be biased by anomalous samples. Some researchers collected coals that may have high contents of toxic and valuable trace elements and these samples should not be considered as typical or representative because of trivial reserves.

Because the huge Chinese coal reserves are widely distributed in China and coals are deposited in various coal-forming periods under complex coal-forming environments, as well as epigenetic evolution, the trace element abundances in Chinese coals may be interpreted by a number of genetic types. The genetic types of trace element enrichment in Chinese coals include source-rock- controlled, marine-environment-controlled, hydrothermal-fluid-controlled (including magmatic-, low- temperature-hydrothermal-fluid-, and submarine-exhalation- controlled subtypes), groundwater-controlled, and volcanic-ash-controlled. The background values of trace elements in

Table 5

Rare metals in the tuffs of drill core (No. CK6) in the Nanchuan Coalfield, Chongqing, southwestern China ( $\mu\text{g/g}$ , on as-received basis; Dai et al., unpublished data).

| Sample No. | Thickness (cm)   | LOI   | Ga   | Nb   | Ta   | Zr   | Hf   | La   | Ce  | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm    | Yb   | Lu    | Y    | Sum (%) |
|------------|------------------|-------|------|------|------|------|------|------|-----|------|------|------|------|------|------|------|------|------|-------|------|-------|------|---------|
| CK6-1      | 22               | 16    | 94.2 | 258  | 15.1 | 1740 | 45.3 | 79.9 | 228 | 19.1 | 70.8 | 13.9 | 1.84 | 11.1 | 2.13 | 12.2 | 2.17 | 6.69 | 1.05  | 6.94 | 0.98  | 42.6 | 0.27    |
| CK6-2      | 12               | 15.71 | 88   | 213  | 13.1 | 1531 | 37.6 | 105  | 301 | 23.3 | 86.6 | 16   | 2.22 | 12.7 | 2.33 | 12.4 | 2.13 | 6.33 | 1.04  | 6.56 | 0.91  | 46.6 | 0.25    |
| CK6-3      | 18               | 14.67 | 96   | 234  | 14.6 | 1675 | 43.3 | 123  | 400 | 29.7 | 117  | 21.4 | 2.92 | 16.4 | 2.9  | 16.1 | 2.63 | 8.11 | 1.26  | 7.94 | 1.12  | 60.5 | 0.29    |
| CK6-4      | 29               | 17.69 | 68.8 | 192  | 12.2 | 1366 | 33.9 | 120  | 404 | 29.3 | 115  | 22.2 | 2.92 | 17.3 | 3.13 | 17   | 3.05 | 9.5  | 1.35  | 8.73 | 1.25  | 61.7 | 0.25    |
| CK6-5      | 21               | 16.58 | 60   | 203  | 13.4 | 1445 | 36.6 | 104  | 363 | 22.1 | 84.3 | 17.4 | 2.76 | 14.8 | 2.85 | 16.1 | 2.86 | 8.77 | 1.26  | 8.36 | 1.18  | 65.8 | 0.25    |
| CK6-6      | 18               | 17.15 | 55.3 | 189  | 12.1 | 1350 | 32.8 | 56.8 | 312 | 15.4 | 61.9 | 12.9 | 2.22 | 12   | 2.19 | 11.9 | 2.09 | 6.46 | 0.98  | 6.2  | 0.93  | 50.6 | 0.22    |
| CK6-7      | 25               | 14.74 | 61.1 | 133  | 8.5  | 1005 | 23.6 | 47.4 | 191 | 5.68 | 18.2 | 3.94 | 0.96 | 4.77 | 0.9  | 5.26 | 0.98 | 3.23 | 0.5   | 3.48 | 0.52  | 25.2 | 0.15    |
| CK6-8      | 23               | 16.7  | 55.9 | 134  | 8.11 | 981  | 23   | 101  | 295 | 12   | 36.1 | 4.81 | 1.14 | 6.11 | 0.98 | 5.25 | 0.98 | 3.24 | 0.5   | 3.32 | 0.51  | 25.3 | 0.17    |
| CK6-9      | 18               | 18.01 | 55   | 130  | 7.86 | 974  | 23.3 | 68.8 | 197 | 9.77 | 32.6 | 5.88 | 1.55 | 6.18 | 1.14 | 6.45 | 1.14 | 3.73 | 0.56  | 3.84 | 0.52  | 28.8 | 0.16    |
| CK6-10a    | 21               | 17.84 | 47.7 | 103  | 6.51 | 824  | 19.2 | 28.5 | 126 | 4.46 | 16.5 | 3.53 | 0.97 | 4.47 | 0.88 | 4.73 | 0.94 | 2.96 | 0.46  | 3.1  | 0.48  | 22.7 | 0.12    |
| CK6-10b    | 25               | 21.65 | 40   | 96.8 | 6.04 | 746  | 16.7 | 27.5 | 168 | 7.25 | 30.9 | 6.2  | 1.21 | 5.76 | 1    | 5.26 | 0.96 | 2.93 | 0.42  | 3    | 0.47  | 23   | 0.12    |
| CK6-11     | 25               | 18.6  | 49.2 | 127  | 8.05 | 949  | 21.7 | 94.3 | 257 | 13.5 | 45.5 | 7.58 | 1.68 | 7.31 | 1.27 | 7.2  | 1.26 | 3.94 | 0.615 | 3.99 | 0.61  | 30.5 | 0.16    |
| CK6-12a    | 25               | 20.84 | 46   | 126  | 8.18 | 960  | 22.6 | 34.3 | 188 | 10.1 | 45   | 9.85 | 2.03 | 8.37 | 1.58 | 8.58 | 1.52 | 4.71 | 0.722 | 4.55 | 0.64  | 34.5 | 0.15    |
| CK6-12b    | 23               | 21.57 | 43.3 | 117  | 7.12 | 866  | 20.1 | 51.1 | 256 | 18.1 | 82.4 | 16.6 | 2.94 | 12.5 | 2.06 | 10.4 | 1.76 | 5.37 | 0.79  | 4.83 | 0.709 | 39.1 | 0.16    |
| WA.        | 305 <sup>a</sup> | 17.9  | 60   | 158  | 9.8  | 1147 | 27.9 | 73.2 | 262 | 15.4 | 59.2 | 11.4 | 1.9  | 9.9  | 1.8  | 9.8  | 1.7  | 5.4  | 0.8   | 5.3  | 0.8   | 39.3 | 0.19    |

LOI, loss of ignition. WA., weighted average. <sup>a</sup>, the total thickness of the ore bed.

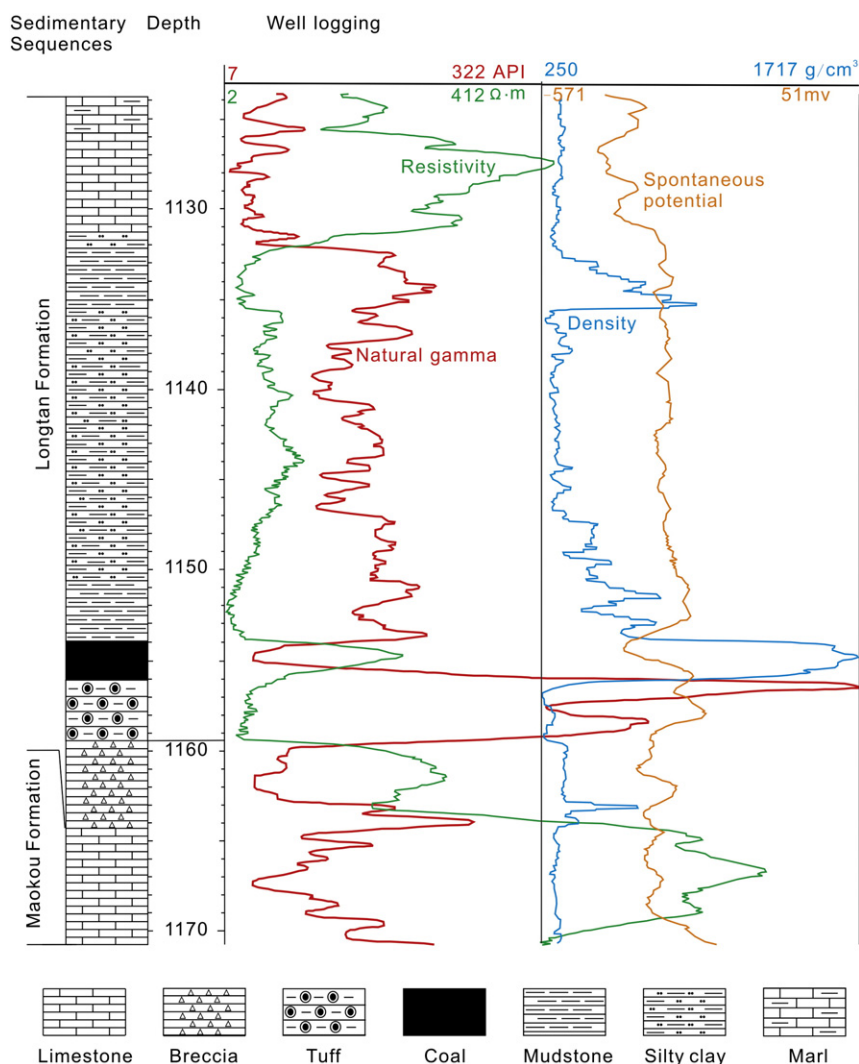


Fig. 10. Sedimentary sequences and well logging data including natural gamma-ray, density, spontaneous potential, and resistivity in Nanchuan, Chongqing.

Chinese coals were dominantly influenced by sediment source region in southwestern and northern China.

The serious human health problems caused by indoor combustion of coal in China include endemic fluorosis, arsenosis, selenosis, and lung cancer. Preventive measures for arsenosis and selenosis have achieved desired results. Abundances, modes of occurrence, and behavior of trace elements and minerals during coal combustion can help prevent fluorosis in western Guizhou and lung cancer in Xuanwei of eastern Yunnan. The postulated cause of lung cancer by fine particles of quartz in coal is currently a working hypothesis and further study is needed for establishing a causal relationship.

Some Chinese coals or coal-bearing strata potentially contain valuable metals, at levels comparable to conventional economic ores. The effective utilization of these coals, in conjunction with the recovery of valuable metals as by-products, may greatly increase the resource values of Chinese coals. The discovery of these valuable metals in Chinese coals can effectively increase the reserves of such critical materials for industrial use. However, still little information is available on some metals, for example, Au, Ag, PGEs, and Cs, Re, and W in Chinese coals.

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## References

- An, D., He, G.Y., Wang, Q.D., Hu, X.Q., 1995. Indoor pollution by coal smoke containing sulfur, arsenic and fluorine and their influence on human's health. *Journal of Environment & Health* 12, 167–169 (in Chinese with English abstract).
- Ando, M., Tadano, T., Yamamoto, S., Tamura, T., Asanuma, S., Watanabe, T., Kondo, T., Sakurai, S., Ji, R., Liang, C., Chen, X., Hong, Z., Cao, S., 2001. Health effects of fluoride pollution caused by coal burning. *The Science of the Total Environment* 271, 107–116.
- Ashley, R.P., Cunningham, C.G., Bostick, N.H., Dean, W.E., Chou, I.-M., 1991. Geology and geochemistry of three sedimentary-rock-hosted disseminated gold deposits in Guizhou Province, People's Republic of China. *Ore Geology Reviews* 6, 133–151.
- Bai, X., Li, W., Chen, Y., Jiang, Y., 2007. The general distributions of trace elements in Chinese coals. *Coal Quality Technology* 1, 1–4 (in Chinese with English abstract).
- Belkin, H.E., Finkelman, R.B., Zheng, B., Zhou, D., 1998. Human health effects of domestic combustion of coal: a causal factor for arsenosis and fluorosis in rural China. *Proceedings of the Air Quality Conference*, McLean VA, Energy and Environmental Research Center, University of North Dakota (unpaginated).
- Belkin, H.E., Finkelman, R.B., Zheng, B., 1999a. Geochemistry of fluoride-rich coal related to endemic fluorosis in Guizhou Province, China. *Pan-Asia Pacific Conference on Fluoride and Arsenic Research*, Abstract 45, 47.
- Belkin, H.E., Finkelman, R.B., Zheng, B., 1999b. Human health effects of domestic combustion of coal: a causal factor for arsenic poisoning and fluorosis in rural China. *EOS. Transactions of the American Geophysical Union* 80 (17), 377–378.
- Belkin, H.E., Zheng, B., Zhu, J., 2003. First occurrence of mandarinoite in China. *Acta Geologica Sinica* 77, 169–172.
- Belkin, H.E., Zheng, B., Zhou, D., Finkelman, R.B., 2008. Chronic arsenic poisoning from domestic combustion of coal in rural China: a case study of the relationship between

- earth materials and human health. *Environmental Geochemistry* 401–420. doi:10.1016/B978-0-444-53159-9.00017-6.
- Bouška, V., Pešek, J., 1999. Quality parameters of lignite of the north Bohemian Basin in the Czech Republic in comparison with the world average lignite. *International Journal of Coal Geology* 40, 211–235.
- Bouška, V., Pešek, J., Sýkorová, I., 2000. Probable modes of occurrence of chemical elements in coal. *Acta Montana. Serie B, Fuel, Carbon, Mineral Processing, Praha* 10 (117), 53–90.
- China Coal Geology Bureau, 1996a. Atlas of coal resources in major coal mines of China. Internal Data of China Coal Geology Bureau (unpaginated).
- China Coal Geology Bureau, 1996b. Sedimentary Environments and Coal Accumulation of Late Permian Coal Formation in Western Guizhou, Southern Sichuan, and Eastern Yunnan, China. Chongqing University Press, Chongqing, pp. 156–216 (in Chinese with English abstract).
- Chou, C.-L., 1997. Abundances of sulfur, chlorine, and trace elements in Illinois Basin coals, USA. Proceedings of the 14th Annual International Pittsburgh Coal Conference, Taiyuan, Shanxi, China, September 23–27, pp. 76–87. Paper S1.
- Dai, S., Chou, C.-L., 2007. Occurrence and origin of minerals in a chamosite-bearing coal of Late Permian age, Zhaotong, Yunnan, China. *American Mineralogist* 92, 1253–1261.
- Dai, S., Ren, D., 2006. Fluorine concentration of coals in China—an estimation considering coal reserves. *Fuel* 85, 929–935.
- Dai, S., Ren, D., 2007. Effects of magmatic intrusion on mineralogy and geochemistry of coals from the Fengfeng-Handan Coalfield, Hebei, China. *Energy and Fuels* 21, 1663–1673.
- Dai, S., Ren, D., Tang, Y., Shao, L., Li, S., 2002. Distribution, isotopic variation and origin of sulfur in coals in the Wuda coalfield, Inner Mongolia, China. *International Journal of Coal Geology* 51, 237–250.
- Dai, S., Hou, X., Ren, D., Tang, Y., 2003a. Surface analysis of pyrite in the No. 9 coal seam, Wuda Coalfield, Inner Mongolia, China, using high-resolution time-of-flight secondary ion mass-spectrometry. *International Journal of Coal Geology* 55, 139–150.
- Dai, S., Ren, D., Hou, X., Shao, L., 2003b. Geochemical and mineralogical anomalies of the late Permian coal in the Zhijin coalfield of southwest China and their volcanic origin. *International Journal of Coal Geology* 55, 117–138.
- Dai, S., Ren, D., Li, S., Song, J., Wu, Z., 2003c. Concentrations of minor elements and regional distribution of arsenic in late Paleozoic coals from North China Platform. *Journal of China University of Mining & Technology* 32, 111–114 (in Chinese with English abstract).
- Dai, S., Li, D., Ren, D., Tang, Y., Shao, L., Song, H., 2004a. Geochemistry of the late Permian No. 30 coal seam, Zhijin Coalfield of Southwest China: influence of a siliceous low temperature hydrothermal fluid. *Applied Geochemistry* 19, 1315–1330.
- Dai, S., Ren, D., Ma, S., 2004b. The cause of endemic fluorosis in western Guizhou Province, Southwest China. *Fuel* 83, 2095–2098.
- Dai, S., Chou, C.-L., Yue, M., Luo, K., Ren, D., 2005a. Mineralogy and geochemistry of a Late Permian coal in the Dafang Coalfield, Guizhou, China: influence from siliceous and iron-rich calcic hydrothermal fluids. *International Journal of Coal Geology* 61, 241–258.
- Dai, S., Ren, D., Tang, Y., Yue, M., Hao, L., 2005b. Concentration and distribution of elements in Late Permian coals from western Guizhou Province, China. *International Journal of Coal Geology* 61, 119–137.
- Dai, S., Ren, D., Chou, C.-L., Li, S., Jiang, Y., 2006a. Mineralogy and geochemistry of the No. 6 coal (Pennsylvanian) in the Jungar Coalfield, Ordos Basin, China. *International Journal of Coal Geology* 66, 253–270.
- Dai, S., Zeng, R., Sun, Y., 2006b. Enrichment of arsenic, antimony, mercury, and thallium in a Late Permian anthracite from Xingren, Guizhou, Southwest China. *International Journal of Coal Geology* 66, 217–226.
- Dai, S., Li, W., Tang, Y., Zhang, Y., Feng, P., 2007a. The sources, pathway, and preventive measures for fluorosis in Zhijin County, Guizhou, China. *Applied Geochemistry* 22, 1017–1024.
- Dai, S., Zhou, Y., Ren, D., Wang, X., Li, D., Zhao, L., 2007b. Geochemistry and mineralogy of the Late Permian coals from the Songzao Coalfield, Chongqing, southwestern China. *Science in China Series D: Earth Science* 50, 678–688.
- Dai, S., Li, D., Chou, C.-L., Zhao, L., Zhang, Y., Ren, D., Ma, Y., Sun, Y., 2008a. Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. *International Journal of Coal Geology* 74, 185–202.
- Dai, S., Ren, D., Zhou, Y., Chou, C.-L., Wang, X., Zhao, L., Zhu, X., 2008b. Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: evidence for a volcanic ash component and influence by submarine exhalation. *Chemical Geology* 255, 182–194.
- Dai, S., Tian, L., Chou, C.-L., Zhou, Y., Zhang, M., Zhao, L., Wang, J., Yang, Z., Cao, H., Ren, D., 2008c. Mineralogical and compositional characteristics of Late Permian coals from an area of high lung cancer rate in Xuan Wei, Yunnan, China: occurrence and origin of quartz and chamosite. *International Journal of Coal Geology* 76, 318–327.
- Dai, S., Wang, X., Chen, W., Li, D., Chou, C.-L., Zhou, Y., Zhu, C., Li, H., Zhu, X., Xing, Y., Zhang, W., Zou, J., 2010a. A high-pyrite semianthracite of Late Permian age in the Songzao Coalfield, southwestern China: mineralogical and geochemical relations with underlying mafic tuffs. *International Journal of Coal Geology* 83, 430–445.
- Dai, S., Zhao, L., Peng, S., Chou, C.-L., Wang, X., Zhang, Y., Li, D., Sun, Y., 2010b. Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. *International Journal of Coal Geology* 81, 320–332.
- Dai, S., Zhou, Y., Zhang, M., Wang, X., Wang, J., Song, X., Jiang, Y., Luo, Y., Song, Z., Yang, Z., Ren, D., 2010c. A new type of Nb (Ta)–Zr(Hf)–REE–Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: possible economic significance and genetic implications. *International Journal of Coal Geology* 83, 55–63.
- Dai, S., Wang, X., Zhou, Y., Hower, J.C., Li, D., Chen, W., Zhu, X., 2011. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. *Chemical Geology* 282, 29–44.
- Ding, Z., Zheng, B., Zhang, J., Long, J., Belkin, H.E., Finkelman, R.B., Zhao, F., Chen, C., Zhou, D., Zhou, Y., 2001. Geological and geochemical characteristics of high arsenic coals from endemic arsenosis areas in southwestern Guizhou Province, China. *Applied Geochemistry* 16, 1353–1360.
- Du, G., Tang, D.Z., Wu, W., Sun, P.C., Bai, Y.L., Xuan, Y.Q., Huang, G.J., 2003. Preliminary discussion on genetic geochemistry of paragenetic germanium deposit in Shenli Coalfield, Inner Mongolia. *Geoscience* 17, 453–458 (in Chinese with English abstract).
- Du, G., Zhuang, X., Querol, X., Izquierdo, M., Alastuey, A., Moreno, T., Font, O., 2009. Ge distribution in the Wulantuga high-germanium coal deposit in the Shengli coalfield, Inner Mongolia, northeastern China. *International Journal of Coal Geology* 78, 16–26.
- Eskenazy, G.M., 1987. Zirconium and hafnium in Bulgarian coals. *Fuel* 66, 1652–1657.
- Eskenazy, G.M., 1990. Geochemistry of tantalum in Bulgarian coals. *International Journal of Coal Geology* 15, 137–149.
- Finkelman, R.B., 1993. Trace and minor elements in coal. In: Engel, M.H., Macko, S. (Eds.), *Organic Geochemistry*. Plenum, New York, pp. 593–607.
- Finkelman, R.B., Brown Jr., R.D., 1991. Coal as host and as an indicator of mineral resources. In: Peters, D.C. (Ed.), *Geology in Coal Resource Utilization*. Fairfax, Techbooks, Virginia, pp. 471–481.
- Finkelman, R.B., Bostick, N.H., Dulong, F.T., Senftle, F.E., Thorpe, A.N., 1998. Influence of an igneous intrusion on the inorganic geochemistry of a bituminous coal from Pitkin County, Colorado. *International Journal of Coal Geology* 36, 223–241.
- Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E., Zheng, B., Lerch, H.E., Maharaj, S.V., Bates, A.L., 2002. Health impacts of coal and coal use: possible solutions. *International Journal of Coal Geology* 50, 425–443.
- Fung, K.F., Zhang, Z.Q., Wong, J.W.C., Wong, M.H., 1999. Fluoride contents in tea and soil from tea plantations and the release of fluoride into tea liquor during infusion. *Environmental Pollution* 104, 197–205.
- Gayer, R.A., Rose, M., Dehmer, J., Shao, L., 1999. Impact of sulphur and trace element geochemistry on the utilization of a marine-influenced coal—case study from the South Wales Variscan foreland basin. *International Journal of Coal Geology* 40, 151–174.
- Golab, A.N., Carr, P.F., 2004. Changes in geochemistry and mineralogy of thermally altered coal, Upper Hunter Valley, Australia. *International Journal of Coal Geology* 57, 197–210.
- Goodarzi, F., Swaine, D.J., 1994. Paleoenvironmental and environmental implications of the boron content of coals. *Geological Survey of Canada Bulletin* 471, 1–46.
- Goodarzi, F., Van der Flier Keller, E., 1990. Variation of elements in the southern intermontane coals of British Columbia, Canada. *Journal of Coal Quality* 9, 62–65.
- Guo, Y., Hou, H., Li, J., 1994. The losing regulations of As, F, Hg, Pb and Cd in the course of ashing in coals. *China Coal Geology* 6, 54–56 (in Chinese with English abstract).
- He, L.X., Zeng, R.L., Lin, J., 1993. *Gold Ore in Guizhou*. Geological Press, Beijing. 156 pp. (in Chinese).
- Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, yttrium, and zirconium anomalies in the fire Clay coal bed, Eastern Kentucky. *International Journal of Coal Geology* 39, 141–153.
- (Editors-in-Chief) Hu, W., He, M. (Eds.), 2008. *Advances in Deep Coal Resources and Conditions of Exploration Geology in China*. Coal Industry Press, Beijing. 388 pp. (in Chinese).
- Hu, R., Qi, H., Bi, X., Su, W., Peng, J., 2006. Geology and geochemistry of the Lincang superlarge Germanium deposit hosted in coal seams, Yunnan, China. *Geochimica et Cosmochimica Acta* 70 (Suppl.), A269.
- Hu, R., Qi, H., Zhou, M., Su, W., Bi, X., Peng, J., Zhong, H., 2009. Geological and geochemical constraints on the origin of the giant Lincang coal seam-hosted germanium deposit, Yunnan, SW China: A review. *Ore Geology Reviews* 36, 221–234.
- Huang, Y., 1993. A possible relation between the disseminated gold mineralization and the Late Permian zonation of coal metamorphism in Western Guizhou. *Guizhou Geology* 10, 300–307 (in Chinese with English abstract).
- Huang, W., Wan, H., Du, G., Sun, L., Ma, Y., Tang, X., Wu, W., Qin, S., 2008. Research on element geochemical characteristics of coal-Ge deposit in Shengli Coalfield, Inner Mongolia, China. *Earth Science Frontiers* 15, 56–64.
- Jacks, G., Bhattacharya, P., Chaudhary, V., Singh, K.P., 2005. Controls on the genesis of some high-fluoride groundwaters in India. *Applied Geochemistry* 20, 221–228.
- Kaseva, M.E., 2006. Contribution of trona (magadi) into excessive fluorosis—a case study in Maji ya Chai ward, northern Tanzania. *The Science of the Total Environment* 366, 92–100.
- Ketris, M.P., Yudovich, Y.E., 2009. Estimations of Clarkes for carbonaceous biolithes: world average for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, 135–148.
- Large, D.J., Kelly, S., Spiro, B., Tian, L., Shao, L., Finkelman, R., Zhang, M., Somerfield, C., Plint, S., Ali, Y., Zhou, Y., 2009. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. *Environmental Science & Technology* 43, 9016–9021.
- Li, S., Zhao, L., 2007. Geochemistry and origin of lead and selenium in the No. 6 Coal from the Jungar Coalfield, North China. *Energy Exploration & Exploitation* 25, 175–184.
- Li, D., Tang, Y., Deng, T., Chen, K., Liu, D., Cheng, F., 2008a. Mineralogy of the No. 6 Coal from the Qinglong Coalfield, Guizhou Province, China. *Energy Exploration & Exploitation* 26, 347–353.

- Li, D., Tang, Y., Deng, T., Chen, K., Liu, D., 2008b. Geochemistry of rare earth elements in coal—a case study from Chongqing, southwestern China. *Energy Exploration & Exploitation* 26, 355–362.
- Li, J., Zhuang, X., Querol, X., 2011. Trace element affinities in two high-Ge coals from China. *Fuel* 90, 240–247.
- Liu, J., Zheng, B., Aposhian, H.V., Zhou, Y., Chen, M., Zhang, A., Waalkes, M.P., 2002. Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China. *Environmental Health Perspectives* 110, 119–122.
- Liu, G., Yang, P., Peng, Z., Chou, C.-L., 2004. Petrographic and geochemical contrasts and environmentally significant trace elements in marine-influenced coal seams, Yanzhou mining area, China. *Journal of Asian Earth Sciences* 23, 491–506.
- Liu, G., Vassilev, S.V., Gao, L., Zheng, L., Peng, Z., 2005. Mineral and chemical composition and some trace element contents in coals and coal ashes from Huaibei coal field, China. *Energy Conversion and Management* 46, 2001–2009.
- Liu, G., Zheng, L., Wu, E., Peng, Z., 2006. Depositional and chemical characterization of coal from Yayu Coal Field. *Energy Exploration & Exploitation* 24, 417–437.
- Liu, G., Zheng, L., Zhang, Y., Qi, C., Chen, Y., Peng, Z., 2007. Distribution and mode of occurrence of As, Hg and Se and Sulfur in coal Seam 3 of the Shanxi Formation, Yanzhou Coalfield, China. *International Journal of Coal Geology* 71, 371–385.
- Luo, K., Ren, D., Xu, L., Dai, S., Cao, D., Feng, F., Tan, J., 2004. Fluorine content and distribution pattern in Chinese coals. *International Journal of Coal Geology* 57, 143–149.
- Luo, K., Li, H., Feng, F., Chen, D., Xiong, M., Wang, W., Liao, X., Li, W., Wang, L., 2007. Content and distribution of fluorine in rock, clay and water in fluorosis area Zhaotong, Yunnan Province. *Journal of China Coal Society* 32, 363–368 (in Chinese with English abstract).
- Luo, K., Li, H., Niu, C., 2010. Fluorine and arsenic pollution route of grain in Yunnan-Guizhou coal-burning endemic fluorosis area. *Geological Review* 56, 289–298 (in Chinese with English abstract).
- Mao, D., Su, H., Yan, L., Wang, Y., Yu, X., 1990. Investigation and analysis of endemic selenosis in Exi Autonomous Prefecture of Hunbei province. *Chinese Journal of Endemiology* 9, 311–314 (in Chinese).
- Mukhopadhyay, P.K., Goodarzi, F., Crandlemire, A.L., Gillis, K.S., MacNeil, D.J., Smith, W.D., 1998. Comparison of coal composition and elemental distribution in selected seams of the Sydney and Stellarton Basins, Nova Scotia, Eastern Canada. *International Journal of Coal Geology* 37, 113–141.
- Mumford, J.L., He, X.Z., Chapman, R.S., Cao, S.R., Harris, D.B., Li, X.M., Xian, Y.L., Jiang, W.Z., Xu, C.W., Chuang, J.C., Wilson, W.E., Cooke, M., 1987. Lung cancer and indoor air pollution in Xuan Wei, China. *Science* 235, 217–220.
- Ncube, E.J., Schutte, C.F., 2005. The occurrence of fluoride in South African groundwater: a water quality and health problem. *Water SA* 31, 35–40.
- Peters, S.G., Huang, J., Li, Z., Jing, C., 2007. Sedimentary rock-hosted Au deposits of the Dian-Qian-Gui area, Guizhou, and Yunnan Provinces, and Guangxi District, China. *Ore Geology Reviews* 31, 170–204.
- Qi, H., Hu, R., Su, W., Qi, L., Feng, J., 2004. Continental hydrothermal sedimentary siliceous coal and genesis of superlarge germanium (Ge) deposit hosted in coal: a study from the Lincang Ge deposit, Yunnan, China. *Sciences in China Series D: Earth Sciences* 47, 973–984.
- Qi, H., Hu, R., Zhang, Q., 2007a. Concentration and distribution of trace elements in lignite from the Shengli Coalfield, Inner Mongolia, China: implications on origin of the associated Wulantuga Germanium Deposit. *International Journal of Coal Geology* 71, 129–152.
- Qi, H., Hu, R., Zhang, Q., 2007b. REE Geochemistry of the Cretaceous lignite from Wulantuga Germanium Deposit, Inner Mongolia, Northeastern China. *International Journal of Coal Geology* 71, 329–344.
- Qian, H., Chen, W., Hu, Y., 1995. Features of As, Sb, Hg, Tl and their mineral assemblages of some disseminated gold deposits in Guizhou and Guangxi Provinces. *Geological Journal of China Universities* 1, 45–52 (in Chinese with English abstract).
- Qin, S.L., 2001. Preservative principals of germanium deposit in Shengli Coal-field of Inner Mongolia and prospecting direction. *Coal Geology of China* 13 (3), 18–19 (in Chinese with English abstract).
- Querol, X., Alastuey, A., Lopez-Soler, A., Plana, F., Fernandez-Turiel, J.L., Zeng, R., Xu, W., Zhuang, X., Spiro, B., 1997. Geological controls on the mineral matter and trace elements of coals from the Fuxin basin, Liaoning Province, northeast China. *International Journal of Coal Geology* 34, 89–109.
- Querol, X., Alastuey, A., Zhuang, X., Hower, J.C., Lopez-Soler, A., Plana, F., Zeng, R., 2001. Petrology, mineralogy and geochemistry of the Permian and Triassic coals in the Leping area, Jiangxi Province, southeast China. *International Journal of Coal Geology* 48, 23–45.
- Ren, D.Y., 1996. Mineral matters in coal. In: Han, D.X. (Ed.), *Coal Petrology of China*. Xuzhou, Publishing House of China University of Mining and Technology, pp. 67–77.
- Ren, D., Zhao, F., Wang, Y., Yang, S., 1999. Distribution of minor and trace elements in Chinese coals. *International Journal of Coal Geology* 40, 109–118.
- Ren, D., Xu, D., Zhao, F., 2004. A preliminary study on the enrichment mechanism and occurrence of hazardous trace elements in the Tertiary lignite from the Shenbei coalfield, China. *International Journal of Coal Geology* 57, 187–196.
- Ren, D., Zhao, F., Dai, S., Zhang, J., Luo, K., 2006. Geochemistry of Trace Elements in Coal. Science Press, Beijing. 556 pp. (in Chinese with English abstract).
- Seredin, V.V., 1994. The first data on abnormal niobium content in Russian coals. *Dokl. Russian Akad. Nauk* 335, 634–636.
- Seredin, V.V., 2003a. Anomalous concentrations of trace elements in the Spetsugli Germanium deposits (Pavlovsk brown coal deposit, Primorye): communication 1. *Antimony. Lithology and Mineral Resource* 38, 154–161.
- Seredin, V.V., 2003b. Anomalous concentrations of trace elements in the Spetsugli Germanium deposits (Pavlovsk brown coal deposit, Primorye): communication 2. *Rubidium and Cesium. Lithology and Mineral Resources* 38, 233–241.
- Seredin, V.V., 2004. Metalliferous coals: formation conditions and outlooks for development. : Coal Resources of Russia, vol. VI. Geoinformmark, Moscow, pp. 452–519 (in Russian).
- Seredin, V., Finkelman, R.B., 2008. Metalliferous coals: a review of the main genetic and geochemical types. *International Journal of Coal Geology* 76, 253–289.
- Seredin, V.V., Shpirt, M.Y., 1995. Metalliferous coals: a new potential source of valuable trace elements as by-products. *Coal Science (Proceedings ICCS '95)*, Pajares, Tascon. Elsevier Science B. V, pp. 1649–1652. II.
- Shao, L., Jones, T., Gayer, R., Dai, S., Li, S., Jiang, Y., Zhang, P., 2003. Petrology and geochemistry of the high-sulphur coals from the Upper Permian carbonate coal measures in the Heshan Coalfield, southern China. *International Journal of Coal Geology* 55, 1–26.
- Song, C., 1989. A brief description of the Yutangba sedimentary type Se mineralized area in southwestern Hubei. *Mineral Deposits* 8, 83–88 (in Chinese with English abstract).
- Song, D., Qin, Y., Zhang, J., Wang, W., Zheng, C., 2007. Concentration and distribution of trace elements in some coals from Northern China. *International Journal of Coal Geology* 69, 179–191.
- Spears, D.A., Zheng, Y., 1999. Geochemistry and origin of elements in some UK coals. *International Journal of Coal Geology* 38, 161–179.
- Stewart, A.K., Massey, M., Padgett, P.L., Rimmer, S.M., Hower, J.C., 2005. Influence of a basic intrusion on the vitrinite reflectance and chemistry of the Springfield (No. 5) coal, Harrisburg, Illinois. *International Journal of Coal Geology* 63, 58–67.
- Subba, R.N., 2003. Groundwater quality: focus on fluoride concentration in rural parts of Guntur district, Andhra Pradesh, India. *Hydrological Sciences Journal* 48, 835–847.
- Sun, Y., 2005. Geochemical study advance about fluorine in coal and “coal-buring” endemic fluorosis from western Guizhou. *Bulletin of Mineralogy, Petrology, and Geochemistry* 24, 350–356 (in Chinese with English abstract).
- Sun, Y., Lin, M., Qin, P., Zhao, C., Jin, K., 2007. Geochemistry of the barkinite liptobolite (Late Permian) from the Jinshan Mine, Anhui Province, China. *Environmental Geochemistry and Health* 29, 33–44.
- Sun, Y., Li, Y., Zhao, C., Lin, M., Wang, J., Qin, S., 2010a. Concentrations of lithium in Chinese coals. *Energy Exploration & Exploitation* 28, 97–140.
- Sun, R., Liu, G., Zheng, L., Chou, C.-L., 2010b. Geochemistry of trace elements in coals from the Zhuji Mine, Huainan Coalfield, Anhui, China. *International Journal of Coal Geology* 81, 81–96.
- Swaine, D.J., 1990. Trace Elements in Coal. Butterworths, London.
- Tang, X., Huang, W., 2004. Trace Elements in Chinese coals. The Commercial Press, Beijing, pp. 6–11. 24–25 (in Chinese).
- Tang, Y., Chang, C., Zhang, Y., Li, W., 2009. Migration and distribution of fifteen toxic trace elements during the coal washing of the Kailuan Coalfield, Hebei Province, China. *Energy Exploration & Exploitation* 27, 143–152.
- Tian, L., 2005. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China. Ph.D. thesis, University of California, Berkeley.
- Tian, L., Dai, S., Wang, J., Huang, Y., Ho, S.C., Zhou, Y., Lucas, D., Koshland, C.P., 2008. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: a retrospective cohort study. *BMC Public Health* 8, 398.
- Wang, Y., 1994. Study on occurrence and distribution of minor and trace elements in coal and its combustion products. Ph.D. Thesis, Beijing Graduate School, China University of Mining and Technology, 88 pp. (in Chinese with English abstract).
- Wang, S. (Editor in Chief), 1996. Coal Accumulation and Coal Resources Evaluation of Ordos Basin, China. China Coal Industry Publishing House, Beijing, p. 437 (in Chinese with English abstract).
- Wang, L.M., 1999. Introduction of the geological feature and exploring of Wulantuga germanium deposit in Xilinguole League, Inner Mongolia. *Geology of Inner Mongolia* 3, 15–20 (in Chinese with English abstract).
- Wang, X., 2009. Geochemistry of Late Triassic coals in the Changhe Mine, Sichuan Basin, southwestern China: evidence for authigenic lanthanide enrichment. *International Journal of Coal Geology* 80, 167–174.
- Wang, Y., Mo, J., Ren, D., 1999. Distribution of minor and trace elements in magmatic hydrothermal metamorphic coal of Meitian Coal Mine, Hunan Province. *Geochimica* 28, 289–296 (in Chinese with English abstract).
- Wang, W., Qin, Y., Sang, S., Jiang, B., Guo, Y., Zhu, Y., Fu, X., 2006a. Partitioning of minerals and elements during preparation of Taixi coal, China. *Fuel* 85, 57–67.
- Wang, W., Qin, Y., Wei, C., Li, Z., Guo, Y., Zhu, Y., 2006b. Partitioning of elements and macerals during preparation of Antaibao coal. *International Journal of Coal Geology* 68, 223–232.
- Wang, W., Qin, Y., Sang, S., Jiang, B., Zhu, Y., Guo, Y., 2007. Sulfur variability and element geochemistry of the No. 11 coal seam from the Antaibao mining district, China. *Fuel* 86, 777–784.
- Wang, W., Qin, Y., Sang, S., Zhu, Y., Wang, C., Weiss, D.J., 2008a. Geochemistry of rare earth elements in a marine influenced coal and its organic solvent extracts from the Antaibao mining district, Shanxi, China. *International Journal of Coal Geology* 76, 309–317.
- Wang, W., Qin, Y., Song, D., Wang, K., 2008b. Column leaching of coal and its combustion residues, Shizuishan, China. *International Journal of Coal Geology* 75, 81–87.
- Wang, J.P., Maddalena, R., Zheng, B., Zai, C., Liu, F., Ng, J.C., 2009. Arsenicosis status and urinary malondialdehyde (MDA) in people exposed to arsenic contaminated-coal in China. *Environment International* 35, 502–506.
- Wang, X., Dai, S., Sun, Y., Li, D., Zhang, W., Zhang, Y., Luo, Y., 2011. Modes of occurrence of fluorine in the Late Paleozoic No. 6 coal from the Haerwusu Surface Mine, Inner Mongolia, China. *Fuel* 90, 248–254.
- Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, 135–168.

- Wu, D.S., 2004. Study on Environmental Geochemistry of Fluorine in Chinese Coals. Ph.D. Thesis. Guiyang Institute of Geochemistry, Chinese Academy Sciences, 12–23, 49–50 (in Chinese with English abstract).
- Wu, C., Chen, C., Chen, Q., 1999. The origin and geochemical characteristics of Upper Sinian–Lower Cambrian black shales in western Hunan. *Acta Petrologica et Mineralogica* 18 (1), 26–39 (in Chinese with English abstract).
- Wu, W., Mo, R., Wang, Z., 2002. Occurrence features and geological work of germanium resource in Yimin coal field, Inner Mongolia. *Inner Mongolia Geology* 1, 27–30 (in Chinese).
- Wu, D., Deng, H., Zheng, B., Wang, W., Tang, X., Xiao, H., 2008. Iodine in Chinese coals and its geochemistry during coalification. *Applied Geochemistry* 23, 2082–2090.
- Xu, D., 1999. The study on the distribution, occurrence and environment influence of chromium, nickel and other hazardous trace elements in coal from Shenbei Coalfield. Master Thesis, China University of Mining & Technology, Beijing, 44–45 (in Chinese with English abstract).
- Yang, J., 2006. Concentrations and modes of occurrence of trace elements in the Late Permian coals from the Puan Coalfield, southwestern Guizhou, China. *Environmental Geochemistry and Health* 28, 567–576.
- Yang, G., Zhou, R., Sun, S., Wang, S., 1981. Research on the etiology of an endemic disease characterized by loss of nails and hair in Enshi county. *Journal of the Chinese Academy Medicine* 3 (Suppl. 2), 1–6 (in Chinese).
- Yang, G., Wang, S., Zhou, R., Sun, S., 1983. Endemic selenium intoxication of humans in China. *The American Journal of Clinical Nutrition* 37, 872–881.
- Yang, Q., Wu, C., Tang, D., Kang, X., Liu, D., Pan, Z., Chen, J., Su, Y., Zhou, C., Liu, G., Luo, Y., 1996. *The Coal Metamorphism in China*. China Coal Industry Publishing House, Beijing. 212 pp. (in Chinese with English abstract).
- Yang, Z., Zheng, X., Yi, Y., 2006. Investigation of death reason and prevention about arsenic poisoning caused by coal in Xingren, Guizhou. *Guandong Trace Elements Science* 13 (12), 18–24 (in Chinese).
- Yuan, S., 1999. Review of Coal Quality in China. Coal Industry Press, Beijing, pp. 92–138 (in Chinese).
- Yudovich, Ya.E., Ketris, M.P., 2002. Inorganic Matter of Coal. Urals Branch of RAS, Ekaterinburg. 422 p.
- Zeng, R., Zhuang, X., Koukouzas, N., Xu, W., 2005. Characterization of trace elements in sulphur-rich Late Permian coals in the Heshan coal field, Guangxi, South China. *International Journal of Coal Geology* 61, 87–95.
- Zhang, J., 1999. Enrichment mechanism and pollution restraining of potentially hazardous trace elements in coal. Ph.D. Thesis. China University of Mining and Technology, Beijing (in Chinese with English abstract).
- Zhang, Y., Cao, S.R., 1996. Coal burning induced endemic fluorosis in China. *Fluoride* 29, 207–211.
- Zhang, J., Ren, D., Xu, D., Liu, J., Dong, B., 1999. The distribution of mercury in major associated minerals from coal beds in southwestern Guizhou. *Geological Review* 45, 539–542 (in Chinese with English abstract).
- Zhang, J., Ren, D., Zheng, C., Zeng, R., Chou, C.-L., Liu, J., 2002. Trace element abundances in major minerals of Late Permian coals from southwestern Guizhou Province, China. *International Journal of Coal Geology* 53, 55–64.
- Zhang, J., Ren, D., Zhu, Y., Chou, C.-L., Zeng, R., Zheng, B., 2004. Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in southwestern Guizhou, China. *International Journal of Coal Geology* 57, 49–61.
- Zhao, F., Ren, D., Zheng, B., Hu, T., Liu, T., 1998. Modes of occurrence of arsenic in high-arsenic coal by extended X-ray absorption fine structure spectroscopy. *Chinese Science Bulletin* 43, 1660–1663.
- Zhao, C., Qin, S., Yang, Y., Li, Y., Lin, M., 2009. Concentration of gallium in the Permo-Carboniferous coals of China. *Energy Exploration & Exploitation* 27, 333–343.
- Zheng, B., Huang, R., 1989. Human fluorosis and environmental geochemistry in southwest China. Developments in Geoscience, Contributions to 28th International Geologic Congress, Washington. DC. Science Press, Beijing. p. 171–176.
- Zheng, B., Hong, Y., Zhao, W., Zhou, H., Xia, W., 1992. Se-rich carbonaceous-siliceous rocks of West Hubei and local Se poisoning. *Chinese Science Bulletin* 37, 1027–1029.
- Zheng, B., Yan, L., Mao, D., Thornton, I., 1993. The Se resource in southwestern Hubei province, China, and its exploitation strategy. *Journal of Natural Resources* 8, 204–212 (in Chinese).
- Zheng, B., Ding, Z., Huang, R., Zhu, J., Yu, X., Wang, A., Zhou, D., Mao, D., Su, H., 1999. Issues of health and disease relating to coal use in southwest China. *International Journal of Coal Geology* 40, 119–132.
- Zheng, B., Wang, B., Ding, Z., Zhou, D., Zhou, Y., Zhou, C., Chen, C., Finkelman, R.B., 2005. Endemic arsenosis caused by indoor combustion of high-As coal in Guizhou Province, P.R. China. *Environmental Geochemistry and Health* 27, 521–528.
- Zheng, L., Liu, G., Chou, C.-L., 2008. Abundance and modes of occurrence of mercury in some low-sulfur coals from China. *International Journal of Coal Geology* 73, 19–26.
- Zhou, Y., Ren, Y., 1981. Gallium distribution in coal of late permian coal fields, southwestern China, and its geochemical characteristics in the oxidized zone of coal seams. *International Journal of Coal Geology* 1, 235–260.
- Zhou, R., Ren, Y., 1992. Distribution of arsenic in coals of Yunnan Province, China, and its controlling factors. *International Journal of Coal Geology* 20, 85–98.
- Zhou, Y., Ren, Y., Bohor, B.F., 1982. Origin and distribution of tonsteins in late Permian coal seams of southwestern China. *International Journal of Coal Geology* 2, 49–77.
- Zhou, Y., Bohor, B.F., Ren, Y., 2000. Trace element geochemistry of altered volcanic ash layers (tonsteins) in Late Permian coal-bearing formations of eastern Yunnan and western Guizhou Province, China. *International Journal of Coal Geology* 44, 305–324.
- Zhou, J., Zhuang, X., Alastuey, A., Querol, X., Li, H., 2010. Geochemistry and mineralogy of coal in the recently explored Zhundong large coal field in the Junggar basin, Xinjiang province, China. *International Journal of Coal Geology* 82, 51–67.
- Zhu, J., Zheng, B., 2001. Distribution of selenium in a mini-landscape of Yutangba, Enshi, Hubei Province, China. *Applied Geochemistry* 16, 1333–1344.
- Zhu, J., Zuo, W., Liang, X., Li, S., Zheng, B., 2004. Occurrence of native selenium in Yutangba and its environmental implications. *Applied Geochemistry* 19, 461–467.
- Zhuang, H., Lu, J., Fu, J., Liu, J., 1998. Lincang superlarge germanium deposit in Yunnan province, China: sedimentation, diagenesis, hydrothermal process and mineralization. *Journal of the China University of Geosciences* 9, 129–136.
- Zhuang, X., Querol, X., Zeng, R., Xu, W., Alastuey, A., Lopez-Soler, A., Plana, F., 2000. Mineralogy and geochemistry of coal from the Liupanshui mining district, Guizhou, south China. *International Journal of Coal Geology* 45, 21–37.
- Zhuang, X., Querol, X., Plana, F., Alastuey, A., Lopez-Soler, A., Wang, H., 2003. Determination of elemental affinities by density fractionation of bulk coal samples from the Chongqing coal district, Southwestern China. *International Journal of Coal Geology* 55, 103–115.
- Zhuang, X., Querol, X., Alastuey, A., Juan, R., Plana, F., Lopez-Soler, A., Du, G., Martynov, V.V., 2006. Geochemistry and mineralogy of the Cretaceous Wulantuga high-germanium coal deposit in Shengli coal field, Inner Mongolia, Northeastern China. *International Journal of Coal Geology* 66, 119–136.
- Zhuang, X., Querol, X., Alastuey, A., Plana, F., Moreno, N., Andrés, J.M., Wang, J., 2007. Mineralogy and geochemistry of the coals from the Chongqing and Southeast Hubei coal mining districts, South China. *International Journal of Coal Geology* 71, 263–275.