

# Geochemistry of arsenic and selenium in a Ge-poor coal from the Wulantuga coal-hosted Ge ore deposit, Inner Mongolia, North China

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**Abstract** This paper reports new data for arsenic (As) and selenium (Se) in a total of twelve bench samples of Ge-rich and Ge-poor coals in the No. 6 coal seam from the Wulantuga ore deposit, Inner Mongolia, Northeastern China. The Ge-poor coals are characterized by low-ash (with a weighted average ash yield 10.59 %). The coal samples were digested using an UltraClave microwave high pressure reactor (milestone) and trace elements were detected by inductively coupled plasma mass spectrometry—collision/reaction cell technology, a reliable method for As and Se determination in coal samples. The contents of As and Se in the Ge-poor (with a weighted average content of 9.14 and 0.30  $\mu\text{g/g}$ , respectively) and Ge-rich coal samples in the present study (varies from 16.88 to 17,776  $\mu\text{g/g}$  and from 0.26 to 14.39  $\mu\text{g/g}$ , respectively) are in a sharp contrast. The As in the Ge-poor coals is of both organic- and pyrite-associations, and its enrichment is attributed to the sediment source, and to a lesser extent, to hydrothermal fluids. Se is predominantly connected with organic matter in the Wulantuga Ge-poor coals.

**Keywords** Arsenic · Selenium · Wulantuga Ge ore deposit

## 1 Introduction

The interests and concerns on studying arsenic and selenium have been and are increasing worldwide (Vladimir and Karel 1977; Vladimir et al. 1977; Ren et al. 1999; Dai et al. 2003; Tang and Huang 2004; Shao et al. 2006), due to their high toxicity and hence the adverse effects on human health and environments. Particularly, the serious arsenic poisoning caused by in-door coal burning in the west of Guizhou Province (Dai et al. 2003, 2005) has attracted much attention. Being different from the Ge-rich coals in the Wulantuga ore deposit, the content of germanium in the present study is rather low. This paper reports the contents, modes of occurrence, and genetic origins of arsenic and selenium in the No. 6 coal seam from the Wulantuga ore

deposit, Inner Mongolia, North China, which, however, have never been reported previously. Additionally, the digestion method with an UltraClave microwave high pressure reactor (milestone) and the analytical procedures for arsenic and selenium contents by ICP–CCT–MS were also discussed in detail.

## 2 Geological background

The Wulantuga Coal Mine is located at the southwest of Shengli coalfield, with a total area around 342 km<sup>2</sup>, 45-km long and 7.6-km wide. Belonging to a trapped and wide syncline and in the elevation scope of 970–1,212 m, the Shengli coalfield with smooth layers is located in the Wunite depression in the west of Erlan Basin in north-eastern Inner Mongolia (Huang et al. 2007), covering the area between latitudes 43°54'15" and 44°13'52"N and longitudes 115°24'26" and 116°26'30"E. The distance between the Early Cretaceous Wulantuga high-Ge and the studied Ge-poor coals ore deposit is around 300 m.

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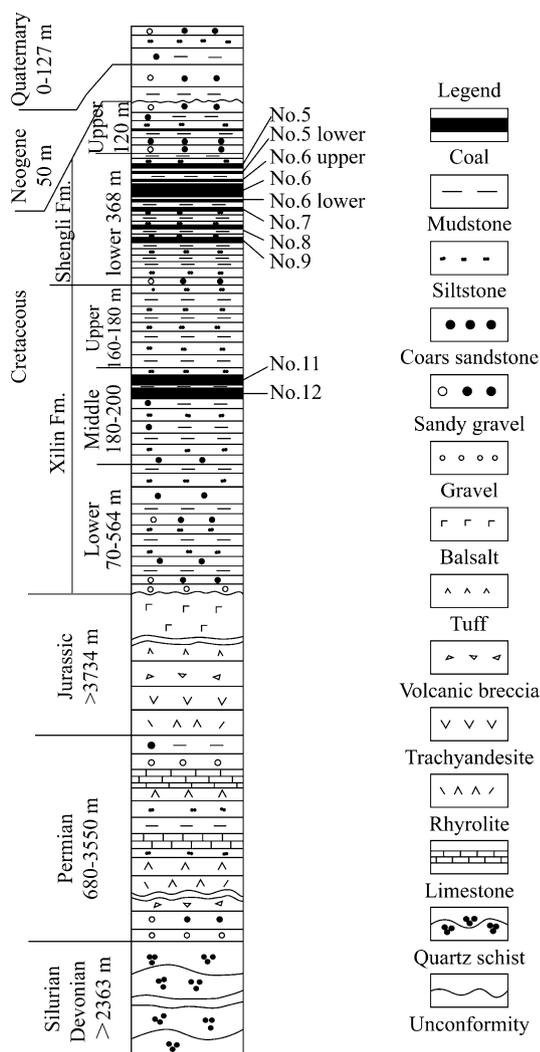
As illustrated in Fig. 1, the sedimentary strata in the Shengli coalfield contain Silurian, Devonian, Permian, Jurassic, Cretaceous, Neogene, and Quaternary sedimentary sequences (Dai et al. 2012a). The average thickness of the Silurian and Devonian sedimentary sequences is more than 2,363 m, including sericite–quartz schist, two-mica quartz schist, biotite–quartz schist, and quartzite. The thickness of the Permian strata varies from 680 to 3,550 m. From top to bottom, the upper strata are predominantly made up of conglomerate, sandy mudstone, limestone, and lenses of andesitic tuff. The siltstone was interlayered in the limestone horizons. Bioclastic rocks, limestone, marl, sandstone, and andesite make up the lower part. The Jurassic strata have a thickness >3,734 m and its compositions are characterized by mafic (such as basalts), intermediate-felsic (e.g., quartz trachyandesite and trachyandesite) and acid volcanic rocks (e.g., rhyolite). The Bayanhua Group contains three

formations, including the Aershan, Saihantala, and Hadatu Formations, which, however are absent in the study area (Sha 2007). The Aershan and Saihantala Formations are titled Xilin and Shengli Formations in this paper, respectively. The Nos. 11 (with an average thickness of 1.54 m) and 12 (2.3 m on average) coal beds occur in the upper part of the Xilin Formation. The lower portion of the Shengli Formation (368 m on average), the major coal-containing strata, primarily consists of coal beds, fine sandstone, siltstone, coarse sandstone, mudstone, and conglomerate. Eight coal beds are included in the Shengli Formation: Nos. 5, 5-lower, 6-upper, 6, 6-lower, 7, 8, and 9, and average thicknesses are 14.96, 2.98, unmineable, 16.1, 1.40, 4.57, 1.47 and 1.33 m, respectively. Furthermore, the currently-studied No. 6 coal seam (ranging from 0.8 to 36.2 m) is the major coal bed in the Wulantuga Ge ore deposit (Dai et al. 2012a).

### 3 Samples and analytical procedures

Twelve bench coal samples were collected from the mined face of the No. 6 coal seam at the Wulantuga Mine in the Shengli coalfield in Inner Mongolia, including six coal ply and one roof samples from the Ge-poor coal seam; two fusains, one fly ash, one slag and one pyrite samples from the Wulantuga Ge-rich ore deposit. Following the Chinese Standard Method GB/T 482-2008 (2008), each coal ply sample was cut over a volume of 10-cm deep and 10-cm wide and was put into a clean and uncontaminated plastic bag to prevent pollution and oxidation. From top to bottom, the six coal samples were identified as WLTG-1 to WLTG-6, and the thickness of each sample in No. 6 coal seam is 50 cm, except for the sample WLTG-3 (66 cm). The roof sample was numbered as WLTG-0-R. The two fusain samples were identified as WLTG-7-FU1 and WLTG-8-FU2, respectively. The fly ash sample was collected from baghouse filters and was numbered as WLTG-9-FA. The slag derived from Ge-rich coal and pyrite samples was identified as WLTG-10-SL and WLTG-11-PY, respectively.

Prior to geochemical analysis, the samples were crushed and ground to pass the 75- $\mu\text{m}$  sieve using SM-1 type vibration grinding instrument. The samples weighed 50-mg were put into closed thermally fused melamine (TFM) digestion vessels whose span is 10 mL. The further purified guaranteed-reagent (GR)  $\text{HNO}_3$  using a sub-boiling Duo-PUR acid purification system (Milestone) and the metal-oxide-semiconductors reagent HF were used for sample digestion (Li et al. 2014). Taking into consideration the strong dispelling capacity of HF, the reagents include 5-mL 40 % (V/V) HF and 2-mL 65 % (V/V)  $\text{HNO}_3$  for each non-coal sample materials, but for coal samples, the reagents were composed of 2-mL 40 % HF and 5-mL 65 %  $\text{HNO}_3$ . An UltraClave microwave high pressure reactor



**Fig. 1** Sedimentary sequence of the Wulantuga ore deposit (Dai et al. 2012a)

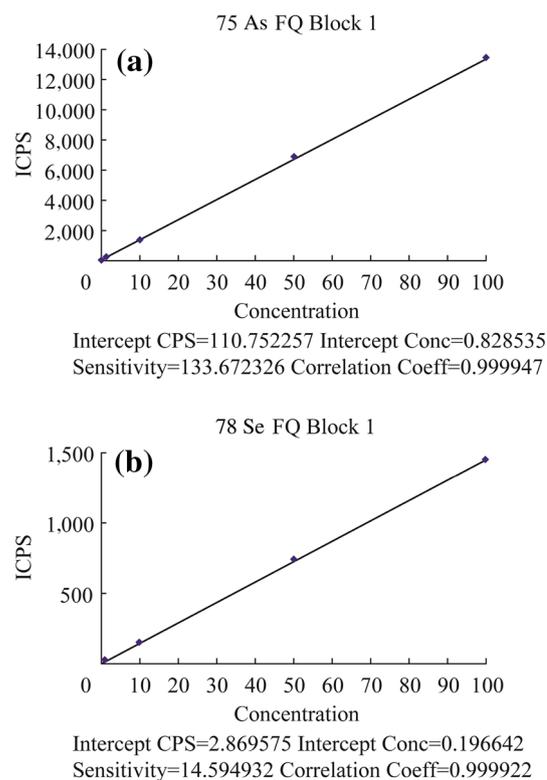
(milestone) was applied to digest samples prior to ICP–CCT–MS analysis. The basic load for the TFM tank of UltraClave reactor is composed of 2-mL 98 % H<sub>2</sub>SO<sub>4</sub> (GR reagent), 30-mL 30 % H<sub>2</sub>O<sub>2</sub> (MOS reagent), 330-mL Mili-Q H<sub>2</sub>O (Dai et al. 2011). The microwave digestion program contains five steps with the temperature rising from 60 to 240 °C, the pressure increasing from 100 bars to 160 bars, and 60 min are needed for cooling and decompression. The contents of arsenic and selenium in the samples were detected by inductively coupled plasma mass spectrometry (X seriesII, ICP/MS) plus collision cell technology (CCT), which could diminish the interferences of polyatomic ions (Li et al. 2014), and Ultra-pure and adequately mixed He (93.33 %) and H<sub>2</sub> (6.67 %) were used to be carriers of collision gases. NIST (National Institute of Standards and Technology) standard reference materials (e.g., NIST 2685b) were used for the calibration of arsenic and selenium contents obtained by ICP–CCT–MS. In order to avoid residues that can affect the precise content of trace elements, ultra-pure H<sub>2</sub>O and 2 % (V/V) HNO<sub>3</sub> (65 %) are used to flush pipeline in turn, for 5 and 10 min, respectively. The 1 µg/L tuning solution containing lithium, cobalt, indium and uranium and 10 µg/L internal standard solution containing single element rhodium are used to regulate the best state of ICP/MS before test beginning. A series of different content solutions diluted from standard solution 100 µg/mL (Inorganic Ventures, CCS4) were used to determine calibration curves of arsenic and selenium. All standard solutions mentioned above use 2 % (V/V) HNO<sub>3</sub> (65 %) as the substrate.

As listed in Fig. 2, Tables 1 and 2, the linearity of the calibration curves in the range 0–100 µg/L is considered as a satisfying parameter with a correlation coefficient  $r^2 > 0.9999$ . The % errors within 10 % of standard solutions showed in Table 1 are also assurances of the reliable contents of arsenic and selenium. The digestion method and the ICP/MS analysis technology for Ge determination in the samples were outlined by Dai et al. (2011).

## 4 Results and discussion

Under the guidance of optimized experimental conditions above, both the observed contents and the certified values of arsenic and selenium in NIST 2685b determined by ICP–CCT–MS are listed in Table 3.

As presented in Table 3, the relative errors of arsenic (6.33 %) and selenium (0.53 %) between the observed and certified values are within 10 %, suggesting the high reliability for both the digestion method by UltraClave microwave high pressure reactor and the ICP–CCT–MS technology for the determination of arsenic and selenium in the samples.



**Fig. 2** Calibration curves of arsenic and selenium conducted by ICP/MS

Table 4 summarizes the results of the thickness, the ash yield, and the observed content of arsenic, selenium and Ge in the studied samples from the Wulantuga ore deposit, as well as their comparisons with average values for Chinese and world low-rank coals.

Compared to the coals (the content of Ge is as high as 274 µg/g) from the Wulantuga Ge ore deposit, the present Ge-poor coal samples display lower Ge content (with a weighted average concentration of 3.42 µg/g). It is a low-ash coal, according to Chinese Standard GB/T 15224.1-2010 (2010); coals with ash yield between 10.01 % and 20 % are low-ash coals. The average ash yield (10.59 %) presented in Ge-poor coals is higher than that in high-Ge coals (8.77 %) reported by Dai et al. (2012a).

### 4.1 Arsenic

Arsenic is one of the most environmentally-sensitive elements in coal and is easily released into the atmosphere in the form of gas during coal combustion. A number of cases concerning the damage and carcinogenicity of arsenic on human health have been reported not only in China but in several other countries (Vladimir and Karel 1977; Vladimir et al. 1977; Finkelman 1999; Zheng et al. 1999). Hence, the abundance and occurrence modes of arsenic in coal have previously been described in a greater detail.

**Table 1** Calibration curves and method detection limit (MDL) of arsenic and selenium

Elements	Isotopes	Linearity ( $\mu\text{g/L}$ )	Determination coefficient	MDL ( $\mu\text{g/L}$ )	RSD (%)
Arsenic	75	1–100	0.999947	0.057	1.603
Selenium	78	1–100	0.999922	0.216	4.282

**Table 2** Defined and measured contents of arsenic and selenium ( $\mu\text{g/L}$ ) in standard solutions conducted by ICP/MS, % error = (measured – defined)  $\times$  100/defined

Sample	Defined	Measured	Mean CPS	Error	% Error
(a) Defined and measured contents of arsenic					
Blank	0	0	111	0	0.00
CCS4–1PPB	1.000	1.070	254	0.070	7.04
CCS4–10PPB	10.000	10.461	1,509	0.461	4.61
CCS4–50PPB	50.000	50.792	6,900	0.792	1.58
CCS4–100PPB	100.000	99.557	13,419	–0.443	–0.44
(b) Defined and measured contents of selenium					
Blank	0	0	3	0	0
CCS4–1PPB	1.000	1.083	19	0.083	8.33
CCS4–10PPB	10.000	10.391	155	0.391	3.91
CCS4–50PPB	50.000	50.995	747	0.995	1.99
CCS4–100PPB	100.000	99.462	1,455	–0.538	–0.54

**Table 3** Observed (Obs) and Certified (Cer) values of arsenic and selenium ( $\mu\text{g/g}$ ) in NIST standard reference coal, as well as relative errors (RE, %) and internal solution recovery (Rec, %) of the ICP–CCT–MS analysis RE (%) =  $10\text{Obs} - \text{Cer}100/\text{Cer}$ 

Element	NIST 2685b			
	Cer	Obs	RE	Rec
Arsenic	12	11.24	6.33	97.59
Selenium	1.9	1.89	0.53	97.59

The average arsenic concentrations of common Chinese and world low-rank coals are reported to be 3.79 (Dai et al. 2012b) and 7.6  $\mu\text{g/g}$  (Ketris and Yudovich 2009), respectively.

The concentration of As in Ge-poor coals varies from 3.15 to 21.55  $\mu\text{g/g}$ , with a weighted average content of 9.14  $\mu\text{g/g}$ , much lower than that in the Ge-rich coals (499  $\mu\text{g/g}$ ) in the Wulantuga Ge ore deposit as reported by Dai et al. (2012a). However, as indicated in Table 4, the concentrations of arsenic in the six coal ply samples are higher than the average values for Chinese and world low-rank coals, except for sample WLTG-6 (slightly lower than the average value for Chinese coals) and WLTG-1 (slightly lower than the average value for world low-rank coals). Arsenic is enriched in the roof of the No. 6 coal seam (21.55  $\mu\text{g/g}$ ), relative to that in the middle and bottom

**Table 4** The thickness, ash yield, As, Se, and Ge in the coal benches of the No. 6 coal from Wulantuga ore deposit, Inner Mongolia (elements in  $\mu\text{g/g}$ ; thickness in cm; ash in %)

Sample	Thickness	Ash	As	Se	Ge
WLTG-0-R	>50		21.55	0.21	1.31
WLTG-1	50	18.84	6.16	1.39	14.24
WLTG-2	50	9.65	8.94	0.20	4.23
WLTG-3	66	9.96	12.12	bdl	0.07
WLTG-4	50	7.45	12.48	0.05	0.04
WLTG-5	50	5.88	11.05	0.09	bdl
WLTG-6	50	11.98	3.15	0.16	3.02
WLTG-7-FU1		51.23	16.88	0.44	0.13
WLTG-8-FU2		7.57	815	0.76	168
WLTG-9-FA			17,776	14.39	8,582
WLTG-10-SL			207	0.80	596
WLTG-11-PY			2,472	0.26	17.66
Av. Coal	316*	10.59	9.14	0.30	3.42
China <sup>a</sup>			3.79	2.47	2.78
World <sup>b</sup>			7.6	1	2

bdl below detection limit, Av weighted average (weighted by thickness of sample interval)

<sup>a</sup> Average contents of elements in the common Chinese coals (Dai et al. 2012b)

<sup>b</sup> Average concentration of elements in the world low-rank coals (Ketris and Yudovich 2009); Ash on a dry basis

\* Total thickness of coal benches

portions of the seam section. The contents of arsenic in the fly ash and slag samples derived from high-Ge rich coals are as high as 1.7 % and 207  $\mu\text{g/g}$ , respectively. The average content of arsenic in the two fusain samples is 415  $\mu\text{g/g}$ , 109 and 55 times higher than that in Chinese and world low-rank coals, respectively.

Previous studies showed that arsenic in coal generally occur in the sulfide, especially in the pyrite with the replacement of sulfur in the lattice (Finkelman 1999; Huggins and Haffman 1996; Chen et al. 2002), these including orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ) and arsenopyrite ( $\text{FeAsS}$ ) (Kolker et al. 2000; Ding et al. 2001). Arsenic is also associated with the oxidation minerals composed of Fe and arsenic, e.g., scorodite (Chen et al. 2002), getchellite (Dai et al. 2006), clay minerals (Swaine 1990), and phosphate minerals. Additionally, organic-association of arsenic in coal has also been reported (Huggins et al. 1993; Huggins and Haffman 1996; Zhao et al. 1998, 1999). Similar to the Ge-rich coals from the Wulantuga ore deposit previously described by Dai et al. (2012a), the low correlation coefficient of As-ash ( $-0.20$ ), as well as the high contents of arsenic in the two fusain samples, indicates that a large proportion of arsenic in the Wulantuga samples is associated with organic matters. Whereas the high content of arsenic in the WL TG-11-PY sample (2,472  $\mu\text{g/g}$ ) suggests that arsenic also occurs in pyrite, in accordance with previous investigations (Dai et al. 2012a). The arsenic in the fly ash sample probably distributes in the secondary (Ge-bearing complex oxides) and primary (sulfides) minerals (Dai et al. 2014).

The enrichment of arsenic in the coals has generally been attributed to two genetic types: (1) terrigenous sediment region; (2) epigenetic mineralization, such as arsenic-rich hydrothermal fluids and sea water (Chen et al. 2002). The origin of the arsenic from the high-Ge coals is mostly related to the hydrothermal fluids (Dai et al. 2012a); however, arsenic in the Wulantuga Ge-poor coals is associated with sedimentary source region, and to a lesser extent, with hydrothermal fluids.

## 4.2 Selenium

The high concentration of selenium in some Chinese coals (especially “stone coal”) had caused a great deal of diseases (Nriagu and Pacyna 1988; Su et al. 1990; Tan and Huang 1991). The improper use of “stone coal” containing high selenium had triggered serious endemic diseases in Hubei province, South China (Chen et al. 2002).

The weighted average content of selenium in seven bench samples from Wulantuga is 0.30  $\mu\text{g/g}$ , much lower than that in Chinese (2.47  $\mu\text{g/g}$ ) and world low-rank coals (1  $\mu\text{g/g}$ ) (Dai et al. 2012b; Ketris and Yudovich 2009), but similar to that in Ge-rich coals (0.49  $\mu\text{g/g}$ ) in the

Wulantuga Ge ore deposit (Dai et al. 2012a). As a consequence of the high volatility of selenium, the concentration of selenium in the fly ash sample is as high as 14.39  $\mu\text{g/g}$ . Both the low content of Se in the slag (0.80  $\mu\text{g/g}$ ) and the high content in the fly ash sample show that the mode of occurrence of selenium in coals is partly associated with organic matter. A number of experiments showed that selenium in coals occurs in pyrite in some cases (Minkin et al. 1984; White et al. 1989; Palmer and Lyons 1996), which can be evidenced by the high correlation coefficient (0.91) between the Se contents and the ash yields in the study areas. However, the concentration of Se in WL TG-11-PY (0.26  $\mu\text{g/g}$ ) sample is lower than that in Chinese (2.47  $\mu\text{g/g}$ ; Dai et al. 2012b) and world low-rank coals (1  $\mu\text{g/g}$ ; Ketris and Yudovich 2009). Furthermore, selenium has also been reported to occur in clay minerals, ferroselite, clauthalite (Finkelman 1999), marcasite (White et al. 1989), galena (Chen et al. 2002) and selenium galena (Dai et al. 2006).

The factors affecting abundance of selenium in coals include coal-forming plants, environments, epigenetic hydrothermal activities, underground water, and coalification advancement. Selenium in coal may adhere to the surface of fine-grained fly ash or in gas and aerosol states during coal combustion, and then was emitted to the atmosphere directly, causing series adverse effects on environments. Besides, the leaching effects of selenium from fly ash are a great concern to soil and underground water (Zhang et al. 2007). All information above suggests that Se in coal needs a great attention for environment concern.

## 5 Conclusions

- (1) The comparison of content of arsenic and selenium of observed values in the present study and the certified values of NIST standard reference samples further demonstrates the digestion method using closed-vessel digestion plus collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP/MS) for content determination of arsenic and selenium in coal and coal combustion products were effective and reliable methods.
- (2) The Wulantuga Ge-poor coal is characterized by its low-ash yield. The weighted average content of Ge in the present study is 3.42  $\mu\text{g/g}$ , much lower than that in the Ge-rich coals (273  $\mu\text{g/g}$ ) in the Wulantuga ore deposit previously reported by Dai et al. (2012a).
- (3) The arsenic content in the samples of the present study varies from 3.15 to 21.55  $\mu\text{g/g}$ , with a weighted average content of 9.14  $\mu\text{g/g}$ , lower than that in the Ge-rich coals (499  $\mu\text{g/g}$ ) in the Wulantuga

ore deposit. Similar to the Ge-rich samples of the No. 6 coal seam in the Wulantuga ore deposit, arsenic in the Ge-poor coals is not only organically associated but also occurs in pyrite. Arsenic in the Wulantuga Ge-poor coals was derived from sedimentary source region, and to a lesser extent, from hydrothermal fluids, in contrary to that in the Ge-rich coals.

- (4) The content of selenium in the Ge-poor coals is as low as that in the Ge-rich coals from the Wulantuga ore deposit. Selenium is partly connected with organic matters in the Wulantuga ore deposit.

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