

Distribution and mode of occurrence of As, Hg and Se and Sulfur in coal Seam 3 of the Shanxi Formation, Yanzhou Coalfield, China

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Abstract

The Yanzhou mining area in the west Shandong Province, China contains coals of Permian and Carboniferous age. A total of 21 bench coal samples were collected from coal seam 3 of the Permian Shanxi Formation, Xinglongzhuang coal mine, Yanzhou Coalfield, China. Pyritic and organic sulfur generally account for the bulk of the sulfur in coal. In this paper, the distribution and concentration of sulfur in the Yanzhou mining district are analyzed, and the forms of sulfur are studied. Organic sulfur content was determined by subtraction and it is positively correlated to total and pyritic sulfur.

The vertical variation of Hg, As and Se and sulfur contents in coal seam 3 of the Shanxi Formation in the Xinglongzhuang mine show that all these trace elements are enriched in the roof and floor rocks of the coal bed and that the concentrations are also relatively high in the clay partings within the coal bed. In the studied samples, Hg and Se have an even higher concentration than that in the world coals. The concentrations of Hg and Se in the seam studied are greater than the global mean of these elements in coals. Se content in the studied coal is 5 times as high as the world coal value and Hg is about one to two orders of magnitude above World Clarke value. Hg is also more enriched compared to the average concentration in Chinese coals.

The pyritic sulfur is positively correlated with total sulfur, and both are enriched in the roof rock, floor rock and clay parting of the coal bed. The concentrations of the trace elements As, Hg and Se are closely related to sulfur. Hg correlates more with pyritic sulfur than organic sulfur. Se relates more to organic sulfur than to pyritic sulfur. As is almost equally related to organic sulfur and pyritic sulfur. Therefore three trace elements may be mainly associated with sulfides and other inorganic matter, also occur in organic forms, especially for Se, already said this.

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1. Introduction

A large coal resource occurs in the Yanzhou coalfield, Shandong Province, China. Currently, there are 18 working underground coal mines in the Yanzhou coalfield with a total annual production of 20 Mt. Most

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of the coal is used for power generation and a minor proportion is used for coke production. The location of the Yanzhou Coalfield and description of geologic formations has been previously reported by Liu et al. (1999b, 2004a) and shown on Fig. 1 and 1-1.

Geochemical studies of toxic trace elements in coal have intensified in recent years, due to a growing awareness of the potential effects of these elements on the environment, and the development of advanced analytical techniques. Despite this increase in research, knowledge of the distribution of most trace elements within the various host phases of the coal is limited. This is partly due to the paucity of trace element data for many coals, and partly due to the fact that the trace elements in coal are derived from a variety of host phases. A proportion of the trace elements in coal originated from the parent plant materials (Finkelman, 1980; Chen et al., 1987; Swaine, 1990; Zhou and Ren, 1992; Finkelman, 1993; Spears and Zheng, 1999; Liu et al., 1999b; Hower et al., 2000, 2005b,c; Yudovich and Ketris, 2005a,b, 2006; Shaver et al., 2006a,b), and these organically-associated trace elements may be redistributed during coalification. Another portion of the trace elements is hosted in various accessory minerals in coal,

these minerals having a variety of syngenetic to epigenetic origins (Fiene et al., 1979; Finkelman, 1980; Spears, 1987; Swaine, 1990; Finkelman, 1993, 1994; Palmer and Lyons, 1996; Ward and Gurba, 1998, 1999; Ward et al., 1999; Kolker et al., 2000a; Huggins et al., 2000; Ward et al., 2001; Huggins et al., 2002; Ward, 2002; Ruppert et al., 2005; Ward et al., 2005; Dai et al., 2006). It is normally assumed that chalcophile trace elements are associated with pyrite and other sulphides in coal, and lithophile elements with carbonates or clay minerals (Finkelman, 1980, 1989; Swaine, 1990; Finkelman, 1994, 1995; Liu et al., 1999b; Huggins et al., 2000, 2002; Liu et al., 2004a).

As, Se and Hg are potentially toxic trace elements in coal (Swaine, 1990, 1992; Finkelman et al., 1999; Zheng et al., 1999; Swaine, 2000; Liu et al., 2006, submitted for publication). Numerous studies have focused on the release of Hg, As and Se during coal combustion, the redistribution of trace elements in by-products of coal combustion and associated their environmental effects (Rong and Weng, 1990; Li and Tang, 1994; Helble, 1994; Wang et al., 1996a,b, 1997; Foner et al., 1999; Spears et al., 1999; Spears and Zheng, 1999; Vassilev and Colette, 1999; Yan et al., 1999; Qiu et al., 1999;

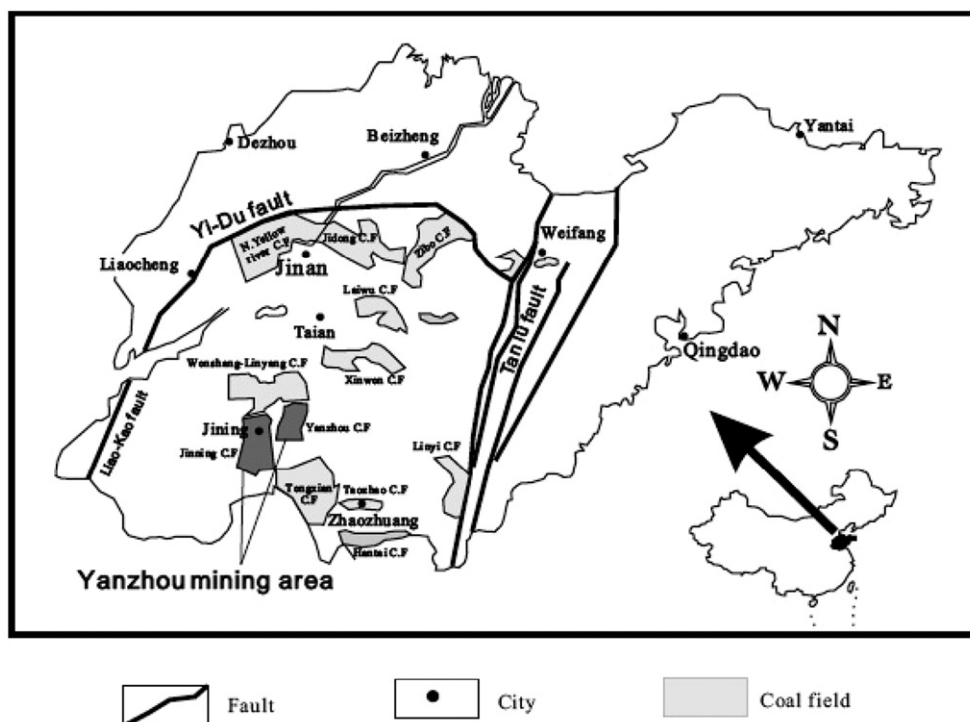


Fig. 1. Location of the Yanzhou mining district in Shandong Province, China. 1. Stratigraphic section of the Upper Carboniferous Taiyuan Formation and the Lower Permian Shanxi Formation in the Yanzhou coalfield. 2. The contents of total sulfur (St, %), pyritic sulfur (Sp, %), sulphide sulfur (Ss, %), organic sulfur (So, %).

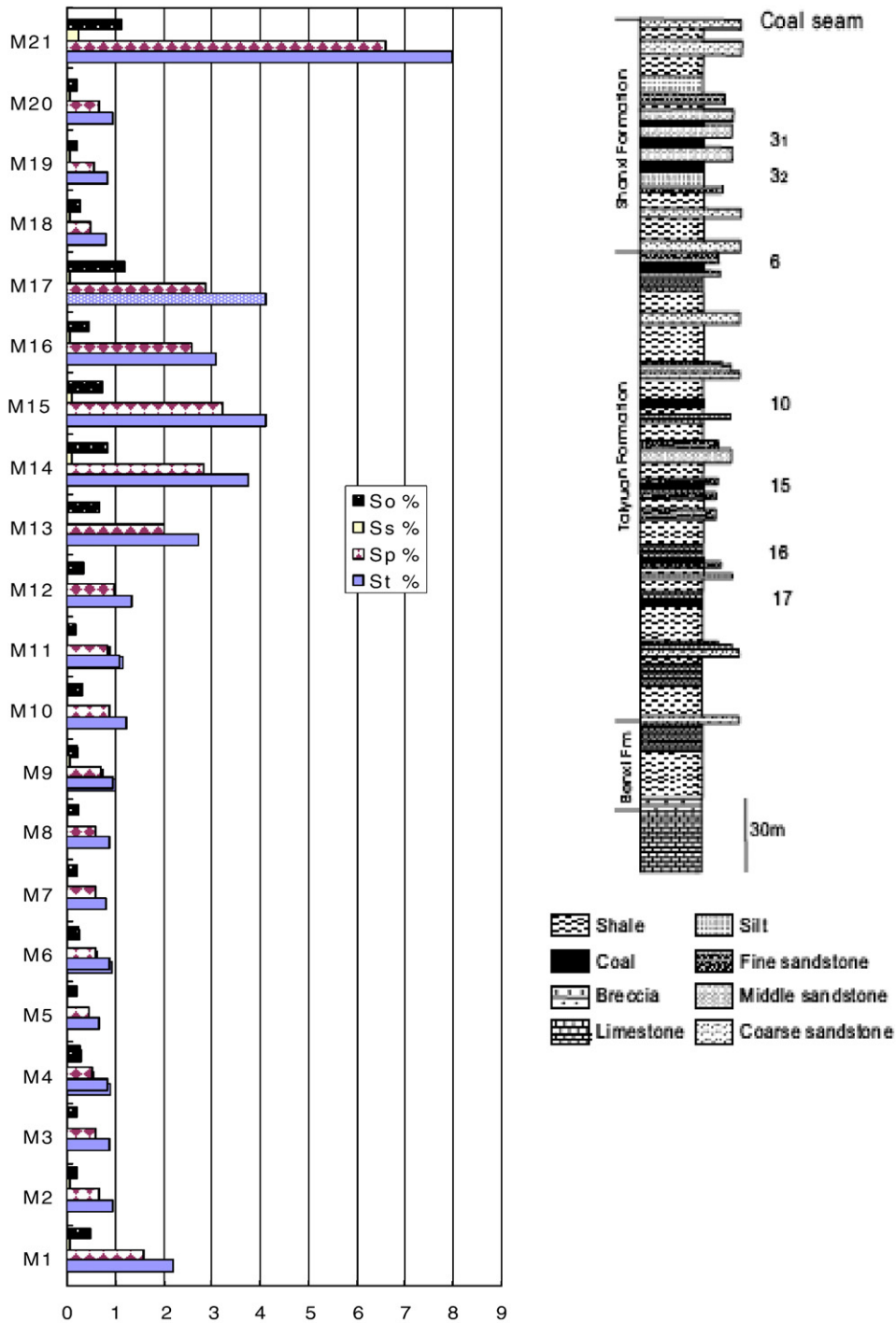


Fig. 1 (continued).

Furimsky, 2000; Swaine, 2000; Senior et al., 2000a,b; Zeng et al., 2001; Sugawara et al., 2002; Guo et al., 2002, 2003, 2004; Huang et al., 2004; Liu et al., 2004b; Mardon and Hower, 2004; Mastalerz et al., 2004;

Sakulpitakphon et al., 2004). Because of high toxicity of Hg, As, and Se and their compounds, it is desirable to reduce the Hg, Se, and As content of coals prior to combustion in power plants (Swaine, 2000; Swanson,

2001; Liu et al., 2002a). In order to reduce the pollution of Hg, Se, and As and to provide suitable processing methods, many studies have reported on the distribution and mode of occurrences of Hg, Se, and As in coal. The mode of occurrence of an element is an important factor in determining its toxicity and behavior during mining, processing, and utilization. Detailed knowledge on the mode of occurrence of an element is crucial to the understanding of its technological behavior, by-product potential, geological significance, and environmental impact (Finkelman, 1980, 1989; Swaine, 1990; Kolker et al., 2000b; Liu et al., 2002a; Kolker et al., 2005; Hower et al., 2005a; Yudovich and Ketris, 2005a,b, 2006; Zheng et al., submitted for publication).

In this study, samples were collected in coal seam 3 of the Shanxi Formation (Lower Permian). Coal rank in western Shandong is primarily high volatile bituminous, although medium volatile bituminous coal occurs in the deeper areas of the coalfield. Characterization of the samples was described in previous work (Liu et al., 1999a, b, 2004a). Results of these studies indicate that they are very similar to coals of the Jining and Zibao coalfields, which border the Yanzhou Coalfield (Liu et al., 2003, 2005).

In the current study, we determined the content of Hg, As, and Se in coal samples, with the objective of comparing their distribution and mode of occurrences in relation to sulfur. Our goal was to provide an increased understanding of the geochemistry of sulfur and concentration of potentially hazardous trace elements (As, Hg, and Se) in the coals of the study district, in addition to presenting information relevant to environmental protection during coal mining and utilization.

2. Sampling

In this study, coal seam 3, which is divided into two sub-seam, named 3₁ and 3₂, was sampled in the Yanzhou coalfield. A total of 21 samples of coal seam 3 and associated clay partings were collected from the Xinlongzhuang underground coal mine, which had a production of 5.0 Mt in 2005. The coal seams in the Yanzhou coalfield are numbered in ascending sequence from 17 to 1. The samples of seam 3 were analyzed to identify the vertical distribution of sulfur and selected trace elements. These samples are identified as M1 to M21 from bottom to top of the coal bed. Samples M14 and M15 represent clay partings in the coal bed, and M21 is roof of the bed (also coaly claystone). All samples were collected as channel samples from a fresh face of the coal bed. The individual sampling intervals were approximately 10-cm to 20-cm thick as they occur continuously, and the 10-cm thick clay parting in the coal bed was sampled separately.

3. Methods

Bulk coal samples were air-dried, ground and split until a representative 0.5-kg sample ground to pass a 0.250-mm sieve was obtained for mineralogical, proximate, and chemical analyses. Other splits were made at different size fractions for petrological studies. The methods used to obtain proximate and ultimate analysis, chemical and petrographic analysis and other parameters are reported in previous studies (Liu et al., 1999b, 2002b, 2004a). In this study, we determined Hg and Se in coal. Other parameters were reported in previous studies (Liu et al., 1999b, 2002b, 2004a).

For Hg and Se analysis, 0.1 g of coal samples was treated with 12 ml of an oxidizing mixture (HNO₃: HCl=3:1) and 3-ml HF in a Teflon crucible and placed in a microwave oven (600 W, 30 min; 1200 W, 25 min; 1200W, 30 min). After being cooled, the recovered samples were diluted to 25 ml with double-distilled deionized water.

Hg concentrations in solution were determined by a Flow Injection Mercury System (FIMS, PERKIN ELMER As90). Se and As concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The detection limit of this method is 0.05 ng/g. Quality control for Hg and Se was provided by parallel analysis of standard reference material from National Institute of Standards and Technology Certificate of Analysis (SRM 1632b). The precision are controlled in the limit of the standard quality. The measured value of Hg and Se are 63.4 ng/g and 85.1 ng/g, respectively.

The values of ash, total sulfur (St), pyritic sulfur (Sp), organic sulfur (So) and sulfate sulfur (Ss), As, Hg, and Se in coal are listed in Table 1.

4. Results and discussion

4.1. Distribution of sulfur

In the Yanzhou coalfield, it is well known that the sulfur contents in the Taiyuan coals are much higher than those in the Shanxi coals (Liu et al., 1999b, 2003, 2004a). The difference could be due to a marine influence on the depositional environment of the coal seams, as was pointed out in previous studies (Chou, 1990; Wu, 1990; Wu et al., 1995; Chou, 1999; Liu et al., 1999b, 2001, 2002b, 2004a). In these reports, the origin and formation of pyritic sulfur and organic sulfur in high-sulfur coals were studied. Results indicated that nearly all the iron in many coals in the study district was associated with pyrite and siderite. However, these results were preliminary and further research on sulfur is needed.

Table 1

Ash yield %, total sulfur (St, %), pyritic sulfur (Sp, %), sulphide sulfur (Ss, %), organic sulfur (So, %) and selected environmentally significant trace element concentrations (ppm), all presented on a dry whole coal basis, Shanxi Coal Seam 3

Samples	Ash	St	Sp	Ss	So	As	Hg	Se
	%	%	%	%	%	ppm	ppm	ppm
M1	19.81	2.31	1.69	0.09	0.53	3.78	0.58	6.72
M2	12.3	1.02	0.71	0.07	0.24	3.24	0.24	4.67
M3	10.7	0.92	0.64	0.05	0.23	1.25	0.21	4.43
M4	13.7	0.88	0.55	0.02	0.31	1.32	0.17	4.63
M5	9.65	0.72	0.48	0.01	0.23	1.05	0.16	3.15
M6	8.73	0.95	0.65	0.02	0.28	2.12	0.22	3.90
M7	11.25	0.86	0.62	0.02	0.22	1.96	0.18	2.93
M8	10.05	0.93	0.63	0.04	0.26	1.38	0.21	3.45
M9	9.45	1.02	0.74	0.07	0.21	1.62	0.27	2.61
M10	12.31	1.32	0.95	0.04	0.33	2.01	0.38	4.31
M11	11.72	1.15	0.91	0.05	0.19	2.17	0.37	2.25
M12	14.7	1.42	1.03	0.03	0.36	2.32	0.52	4.25
M13	24.7	2.87	2.11	0.05	0.71	3.21	0.71	7.36
M14	56.67	3.96	2.98	0.1	0.88	4.76	0.84	8.87
M15	59.96	4.32	3.41	0.12	0.79	4.54	1.07	8.12
M16	20.11	3.26	2.71	0.08	0.47	3.86	0.90	5.33
M17	17.2	4.35	3.02	0.06	1.27	2.97	0.97	9.84
M18	11.5	0.86	0.51	0.06	0.29	3.01	0.26	3.27
M19	12.3	0.91	0.59	0.08	0.24	2.31	0.20	2.73
M20	11.72	1.02	0.71	0.07	0.24	2.05	0.27	2.69
M21	60.81	8.42	6.96	0.26	1.20	3.63	1.76	6.42

4.1.1. Total sulfur

Table 1 shows the ash yield, sulfur forms, Hg, As, and Se concentrations, all presented on a dry, whole-coal basis, in channel samples from the Shanxi coal seam 3 from the Xinglongzhuang mine.

Within the section of the Shanxi coal seam 3 analyzed in detail (Table 1), the total sulfur content of the coal samples varied from 0.72 (M5) to 4.35 (M17) wt.%. The average total sulfur content of the coal itself is 1.49 wt.%, excluding clay partings and roof rock samples (M14, M15 and M21). There is an increase in the total sulfur content for this seam section in both of the clay partings (3.96 wt.% (M14) and 4.32 wt.% (M15)) and the roof rock (8.42 wt.%, M21). However, in the middle of the seam, the total sulfur contents of samples M13 (2.87 wt.%) to M17 (4.35 wt.%) are unusually high, with an average value of 3.75 wt.%, because they are associated with banded pyrite lamellae.

4.1.2. Pyritic sulfur

Pyritic sulfur is the dominant form of sulfur. SEM and XRD indicate the presence of sulfur-bearing minerals in addition to pyrite, including marcasite, sphalerite, galena, and chalcopyrite. Pyrite occurs in several forms, most commonly as nodules and partings (e.g.

M15, M17). Disseminated pyrite, ranging in size from a few millimeters to less than 1 μm , is also present, as well as platy pyrite in cleats, pyrite veins, and pyrite in permineralized peat or coal balls, and studies of their coal samples (Chou, 1990; Swaine, 1994; Chou, 1999; Liu et al., 1999a,b; Liu and Yang, 2000; Liu et al., 2001).

The pyritic sulfur contents of the plies in the Xinglongzhuang coal mine seam section varied from 0.48 to 6.96 wt.%, with an average of 1.55 wt.% (Table 1). Excluding samples M14, M15 and M21 (clay partings and roof rock), the pyritic sulfur content of the seam varies from 0.48 to 3.02 wt.%, with an average of 1.07 wt.%. Pyritic sulfur is closely correlated with total sulfur in the coal bed (Fig. 1–2). There are several distinct forms of pyrite in M21. An early, syngenetic phase developed as framboids and isolated euhedral crystals. The second phase of pyrite occurs as an anastomosing array of veins, sub-parallel to the coal banding, which cross-cut the framboidal clusters. These veins are themselves cut by cleat-fill pyrite of a third phase.

From Table 1, it can be seen that the coal with a marine roof in the underground coal mine presents a more complex situation. Not only are the total sulfur and pyritic sulfur concentrated in the lower and upper plies of the seam, but also plies with higher sulfur content occur in the middle of the seam (M13–M17) (Fig. 1–2). The high levels of total sulfur in the basal and top plies could be explained by the development of peat mire in a transgressive marine setting and inundation of the peat surface by sulfate-rich sea water. The concomitant high pyritic sulfur levels would indicate the availability of ferrous iron in peat.

4.1.3. Organic sulfur

The organic sulfur in the Yanzhou coalfield has been reported and studied by previous studies (Chen et al., 1993; Liu et al., 1999b, 2001; Gao et al., submitted for publication). In these studies, macerals were separated from the coal seam by means of isopycnic density gradient centrifugation. Direct measurement of the organic sulfur content and its distribution in the coal macerals was made by transmission electron microscope (TEM) (Chen et al., 1993). In this study, organic sulfur in 21 samples was determined by subtraction. The organic sulfur ranges from 0.19 wt.% to 1.27 wt.%, with an average of 0.45 wt.% (Table 1). The organic sulfur levels show the correlation with the total sulfur (Fig. 1–2). According to the results of this study, the highest concentration of organic sulfur in the macerals of the coal seam is 1.27 wt.%. The range of organic sulfur contents in liptinite is much wider than that of other macerals. The individual macerals have various proportions of organic

sulfur (Ward and Gurba, 1998, 1999; Liu et al., 1999b). Inertinite in the seam has the lowest organic sulfur concentration. The organic sulfur concentration of vitrinite lies between the liptinite and the inertinite.

4.1.4. Sulfate sulfur

The coals contain minor amounts of sulfate sulfur. Sulfate minerals such as gypsum and barite are found in some study samples. The following iron sulfate minerals may be weathering products of pyrite: szomolnokite, rosenite, melanterite, coquimbite, etc. The sodium sulfate minerals, mirabilite and thenardite, found in coal refuse, are reaction products of iron sulfate with sodium associated with coal.

The proportions of sulfate sulfur in the samples are less than 0.1 wt.%, with the exception of samples M14, M15 and M21 (clay partings and roof rock). Average sulfate sulfur is 0.07 wt.%, which is much lower than the other sulfur forms.

4.2. The distribution and occurrences of As, Hg and Se

Trace elements are present in coals at different concentrations, depending on the various processes by which they have entered the coal at the different stages of coalification. Most elements are associated with the mineral matter in coal; however, certain elements may have an organic affinity (Finkelman, 1981, 1989; Swaine, 1990; Zhong, 1992; Finkelman, 1993, 1994; Liu et al., 2002b). The elements associated with mineral matter are variably affected by combustion, but are mostly concentrated in ash (Yang and Qian, 1983; Sun and Jervis, 1986; Finkelman, 1994; Swaine, 1994; Nerin et al., 1994; Lu et al., 1995, 1996; Xu and Zhai, 1997; Spears and Zheng, 1999; Yan et al., 1999; Zheng et al., 1999; Liu et al., 2002b; Ding et al., 2001; Liu et al., 2004c).

4.2.1. Arsenic

The concentration of As in 21 incremental channel samples from the Yanzhou Coalfield is presented in Table 1. The content of As ranges from 1.05 ppm (M5) to 4.76 ppm (M14), with an average value of 2.59 ppm. The average value of As is 2.31 ppm, excluding clay parting and roof rock (M14, M15 and M21), with the As content ranging from 1.05 ppm (M5) to 3.86 ppm (M16). The distribution of As in the channel samples is approximate to the distribution of the total sulfur. The highest As values are from a middle bench (M14 and M15), the samples also have relatively higher total sulfur contents ($St=4.32\%$ and 3.96%), with pyritic sulfur accounting for 3.41% and 2.98% . However, the highest sulfur is in the roof of coal (M21) (8.42%) with

highest pyritic sulfur 6.96% , and the content of As in the sample is 3.63 ppm, which is fifth highest in all samples.

The contents and distribution of trace elements in coals are clearly relevant to any aspects such as geological background, coal-forming plant, sedimentary environment and coalification. The category and distribution varies in different coalfields. Previous studies (Chen et al., 1985; Zhou, 1985; Chen and Yang, 1989; Zhou and Ren, 1992; Liu and Xu, 1992; Cui and Chen, 1998; Zhou, 1998; Liu et al., 1999a,b; Zhuang et al., 1999a,b; Ren et al., 1999; Zhang et al., 1999; Ding et al., 2001; Li et al., 2002; Lu, 2003; Liu et al., 2004a; Zhang et al., 2004a) indicated that the range of As is below detection limit to 10 ppm in most Chinese coalfields and the mean value is about 5 ppm. This value is lower than that of the average for World coals, and it is much lower than the mean value for coals in the United State (24 ppm) and Russia (25 ppm) (Swaine, 1990; Finkelman, 1993).

Compared other provincial coal from previous results (Liu et al., 1999a,b, submitted for publication), the average As content in the Yanzhou coal is higher by about 2 ppm than Inner Mongolia, Hebei, Jiangsu, Ningxia and Qinghai Provinces. However, the average value of As in the Yanzhou coal is much lower than the average value (18.16 ppm) of As in coals from the southwest China (Yunnan, Guizhou, Sichuan and Chongqing) (Chen et al., 1985; Chen and Yang, 1989; Cui and Chen, 1998). For example, Ding et al. (2001) analyzed 32 samples from Guizhou coals, and showed that the contents of 12 samples exceeded 1000 ppm with a maximum value of 35,000 ppm.

Many studies on modes of occurrences of As in coals have been conducted. Some work (Finkelman, 1981; Coleman and Bragg, 1990; Finkelman, 1994; Belkin et al., 1997; Hower et al., 1997; Swaine, 2000; Liu et al., 2001; Ruppert et al., 2005) reported that As-bearing sulfide, often associated with pyrite, was the most common form of inorganic As. Kolker et al. (2000b) concluded that arsenic is most often found in the minerals realgar (AsS), orpiment (As_2S_3), and arsenopyrite ($FeAsS$). As is also found in association with sulfides of copper, lead, and zinc and with the minerals pyrite, chalcopyrite, and sphalerite. Finkelman (1995) reported that 80% of As exists in these forms. The modes of occurrence of As in coal are quite complex, As is found mainly in the form of inorganic compounds, but As in association with organic matter was also been observed.

In China, many researchers (Zhang et al., 1992; Zhong, 1992; Wang et al., 1996a,b, 1997; Lu et al., 1997; Zhou, 1998; Zhao et al., 1998; Zhang et al., 1999;

Ding et al., 1999; Liu et al., 1999b; Huang et al., 2000; Wang, 2000; Zhang et al., 2000a; Guo et al., 2001; Chen et al., 2002; Liu et al., 2002b; Chen and Tang, 2002a; Ding et al., 2003; Zhao et al., 2003; Liu et al., 2004a; Zhang et al., 2004a,b; Liu et al., submitted for publication) indicated that As is associated with organic matter, but also associated with pyrite. Many factors impact the occurrences of As in coals and there are many occurrences of organic As.

Guo et al. (2001) conducted chemical sequential leaching on anthracite of Laiyang, lignites of Qianjiayin, and bituminous coals of Qingshan, and found that most As (73%–83%) occurred in sulfide minerals. Liu et al. (2002b) studied the relationship between the contents of trace elements and sulfur in coals of different density with float-sink test from Baodian of Shandong Province and found that: 1) As content was positively correlated with sulfides and sulfate; and 2) As content decreased with increasing coal density due to high mineral. Using neutron activation analysis, Huang et al. (2000) examined high-S coals of Paleozoic Taiyuan Formation from Zaozhuang of Shandong Province and reported As content up to 20 ppm in bright coals. Further analyses with SEM-EDX showed that As was mainly associated with pyrite and As up to 90 ppm was found in pyrite which contained high calcium. Zhou (1998) analyzed samples of Permian coals from Laochang mine in eastern Yunnan Province and found that: 1) As content increased with increasing sulfur content in coal beds with greater than 0.6% sulfur; and 2) pyrite was the main carrier of arsenic, containing more As than organic matter and clay minerals. Using sequential leaching and statistical analyses, Zhao et al. (2003) determined the modes of occurrence of As in the following order: sulfide As > organic As > arsenate > silicate As > soluble and exchangeable arsenic. Using neutron activation analysis, Chen et al. (2002) tested 147 samples of Chinese coals from different regions, ages, and ranks, and concluded that inorganic arsenic mostly occurred as isomorphic substitution of sulfur in pyrite. However, Zhou (1998) analyzed samples of Late Permian coals from Xingren and Xingyi of Guizhou Province using X-ray absorption fine structure spectroscopy and found that As existed as arsenate and arsenite, not sulfide, in high-As coals.

From Fig. 2(a,b,c), it can be shown that the As is correlated with sulfur, especially for pyritic sulfur and organic sulfur. When the pyritic sulfur exceeds 1%, the content of As is over 2 ppm. For example, pyritic sulfur concentrations in M1 (1.69%), M12 (1.03%), M13 (2.11%), M14 (2.98%), M15 (3.41%), M15 (2.71%), M16 (3.02%) and M21 (6.96%), have As in those

samples ranging from 2.32 ppm to 4.76 ppm. The form of As may mainly be associated with sulfide. In these samples, M2, M6, M18, M19 and M20, the pyritic sulfur contents are relatively low, as is the total sulfur. However, in these samples, the content of As is also over 2 ppm. The correlation coefficients of As to total sulfur, pyritic sulfur and organic sulfur are 0.671, 0.648 and 0.653, respectively. The organic sulfur is slightly higher than the association with pyritic sulfur. Based on these data, we conclude that the form of As may be associated with either inorganic or organic components in the samples.

Previous studies showed that organic As exists in coal, but the exact organic form was still unclear. Finkelman (1981) reported that for coals having less than 5 ppm As, most As is associated with organic matter. Liu et al. (1999b) analyzed coal samples from the Baodian deposit of Shandong Province and also found As to be associated with organic matter in low density coal, in addition to its association with sulfides. Based on sequential leaching of anthracite of Laiyang, lignite of Qianjiayin, and bituminous coal of Qingshan, Guo et al. (2001) found that 8% of the As was organically associated. Zhao et al. (1998, 1999, 2003) analyzed Late Permian anthracite from Xingren and Xingyi of Guizhou Province using XRD, TEM-EDX-SAD, and EMPA, and found that As occurred in organic association, instead of in the form of elemental As or As-containing minerals.

Knowledge of modes of occurrence of an element is crucial to the assessment of the feasibility of its recycling and utilization and to the understanding of pathways by which it is introduced into the environment. Study of the mode of occurrence is complicated by the fact that variable modes of occurrence could occur for an element in the same sample, and multiple elements could co-exist in a single mode. Modes of occurrence of trace elements in coal have been determined mostly indirectly, and to a lesser extent directly, because of limitations in direct methods. More research is needed to fully understand the modes of occurrence of arsenic in coal, particularly the organically associated form (Zhang et al., 2000a,b).

4.2.2. Mercury

The concentration of Hg in 21 incremental channel samples of seam 3 from the Yanzhou Coalfield is presented in Table 1. Including clay partings and roof rock, the content of Hg ranges from 0.16 ppm (M5) to 1.76 ppm (M21), with an average value of 0.50 ppm. The average value of Hg is 0.37 ppm, excluding clay partings and roof rock (M14, M15 and M21), with the Hg content ranging from 0.16 ppm (M5) to 0.97 ppm (M17).

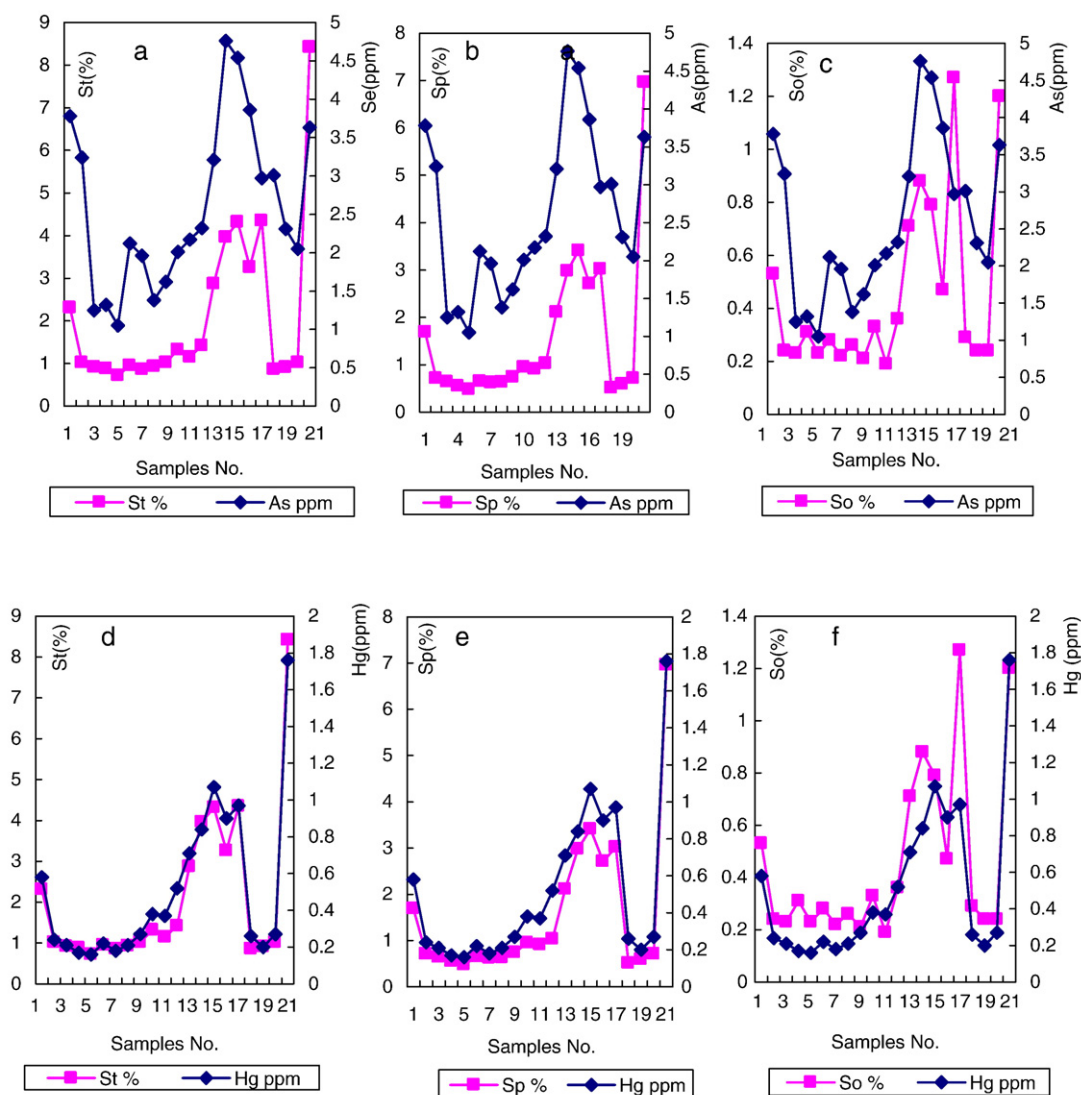


Fig. 2. The relationship between different forms of sulfur and trace elements (Hg and As).

The highest Hg value was from the roof bench sample, which also had the highest sulfur content (St=8.42%), and highest pyritic sulfur content (6.96%). However, some high Hg values were from middle benches (M13–M17), with Hg value ranging from 0.71 ppm to 1.07 ppm. The total sulfur in the middle benches ranges from 2.87% to 4.35%, and pyritic sulfur ranges from 2.11% to 4.35%. The third highest Hg value was from a bottom seam bench (M1), which also had a high sulfur content (2.31%).

The average of Hg content in these 21 coal samples (including clay partings and roof rock) is higher than coals from other areas, as indicated by a comparison with those of Carboniferous–Permian coals of northern China (0.01 ppm to 5 ppm, average value of 0.17 ppm)

(Tang and Huang, 2004), Chinese coal (0.01 ppm to 5 ppm, average value of 0.1 ppm) (Tang and Huang, 2002, 2004), U.S. coal (average value of 0.17 ppm) (Finkelman, 1993), and the mercury Clarke value for world coal (0.1 ppm) (Yudovich and Ketris, 2005b). The mean Hg values for the Yanzhou coalfield are three times as high as those in World Clarke value. The highest levels of Hg in the Yanzhou coalfield exceed the range of Carboniferous–Permian coals of northern China and the Chinese coals (0.5 ppm) reported by Tang and Huang (2004). In comparison with the mercury Clarke value for world coal (Yudovich and Ketris, 2005b), Hg in the coals from the Yanzhou coalfield is much higher. However, most samples (11 samples are below 0.3 ppm)

in this study do not have particularly high levels of Hg, ranging from 0.16 ppm to 0.3 ppm.

The occurrence of Hg in coal in solid solution in pyrite has been reported by many authors, primarily based on the correlation of sulfur with Hg contents, particularly in coals extremely enriched in mercury (Ding et al., 2001; Diehl et al., 2004; Zheng et al., submitted for publication).

We can see from Fig. 2(d, e and f) that the Hg content is closely related to total sulfur and pyritic sulfur. The relationship is very close to pyritic sulfur and organic sulfur. The correlation coefficients of Hg to total sulfur, pyritic sulfur and organic sulfur are 0.985, 0.984 and 0.886, respectively. In the samples, Hg association with sulfides may be dominant, and organic Hg appears to be secondary.

Hg offers many challenges in determining its modes of occurrence. Because of relatively low concentrations and high volatility, there are little data on the behavior and Hg occurrence in coal. Finkelman (1980, 1981) carried out laboratory float–sink and analysis of minerals separated from coal. In these studies, he suggested that Hg is clearly associated with pyrite, especially late-stage (epigenetic) pyrite. He concluded that the level of confidence estimated of the Hg occurrence in coal is 6 out of 10 (Finkelman, 1994). In another study, Feng et al. (1998) and Feng and Hong (1999) indirectly proved that in the high-Hg coals of Guizhou, the sulfide form of Hg dominates.

During the last decade, many researchers have determined that Hg occurs in the form of pyrite. However, previous studies also suggest Hg may be associated with organic components in coal (Ruch et al., 1971; Fiene et al., 1979; Belyaev et al., 1989; Lyons et al., 1989; Palmer et al., 1993, 2000; Khrustaleva et al., 2001; Dronen et al., 2004; Brownfield et al., 2005). For example, Zheng et al. (submitted for publication) carried out the sequential extraction tests with 29 coal samples from Huaibei coalfield. The results showed that the correlation between Hg and the total sulfur contents in the Huaibei coal samples is only 0.17 ($n=29$). Interestingly, when they studied this relationship on coal seam 3, 4, and 10 coal samples in the Huaibei coalfield, a very high positive correlation coefficient between Hg and the total sulfur contents ($R=0.64$) was found. The results show that magmatic intrusions not only influenced the concentration and distribution of Hg in coals, but also the modes of occurrence. In No. 3, 4, and 10 coals of the Huaibei Coalfield, the sulfide and organic sulfur-bound forms of Hg may dominate, but in No. 5 and 7 coals, Hg may occur in organic modes. Palmer et al. (1993, 2000) concluded that organic Hg occurs in a subbituminous coal from the Powder River

basin. Organic Hg in coal has a wide range, from 0 to 100%. For example, Filby et al. (1977) concluded that over 78% of Hg in a Kentucky bituminous coal is associated with organics. Fiene et al. (1979) studied the Herrin No. 6 (Illinois), Blue Greek (Alabama), Pittsburgh No. 8, and Rosebud (Montana) coal, which results demonstrated organic Hg was that 100% in Herrin No. 6 and Blue Greek, and 47% and 3% in the Pittsburgh No. 8 and Rosebud coal, respectively.

4.2.3. Selenium

Se is a necessary trace element for plants, animals and humans. Selenium is present as Se^0 , Se^{2-} , Se^{4+} , Se^{6+} in natural waters. Although selenium metal has little toxicity, the selenide, selenite, and other selenium compounds such as selenium fluoride, have a high toxicity. During coal combustion and pyrolysis, Se is oxidized into SeO_2 and other forms, which can easily dissolve in water and transform into selenite or be distributed into atmosphere (Sun and Jervis, 1986; Nriagu and Pacyna, 1988; Finkelman et al., 1990; Clarke and Sloss, 1992; Liu et al., 2004c; Zhu and Zheng, 2004; Zhu et al., 2004).

Table 1 shows the Se content of the Shanxi seam 3 samples varied from 2.25 ppm (M11) to 9.84 ppm (M17). The average value is 5.23 ppm. Excluding clay parting and roof rock (M14, M15 and M17), the average value of Se is 4.35 ppm.

In the study area, the average value is much lower than that in Huainan coalfield, which is located south of the Yanzhou coalfield (Chen and Tang, 2002b). According to Ren et al. (1999) the geometric mean for 118 Chinese coals, is 3.6 ppm, and ranges from 0.12 ppm to 56.9 ppm, and the average value is lower than that in Yanzhou. However, the average Se content of Guizhou coal is 5.47 ppm (Feng et al., 1998), and is almost equal to the average Se content in Yanzhou coalfield. Some reports (Ren et al., 1999; Zhuang et al., 1999a,b; Chen and Tang, 2002b; Bai et al., 2003; Zhu and Zheng, 2004; Zhu et al., 2004; Li et al., 2006) showed the average value of Se from 129 samples in Yutangba coal is about 143 ppm, which is highest for any province.

The world average Se content in coals (coal Clarke of Se) for hard coals and brown coal are 1.6 ppm and 1.0 ppm, respectively (Yudovich and Ketris, 2006). The average Se content in the Yanzhou is five times as high as the world coal value, and higher than most published country averages. In Australian lignites, Se ranges from 0.2 ppm to 1.2 ppm (Swaine, 1990). In US coal, the average value of Se is 1.8 ppm for 7563 samples (Coleman et al., 1993).

The Se contents from M1 to M4, and M12 to M17, are relatively higher, particularly for the parting samples

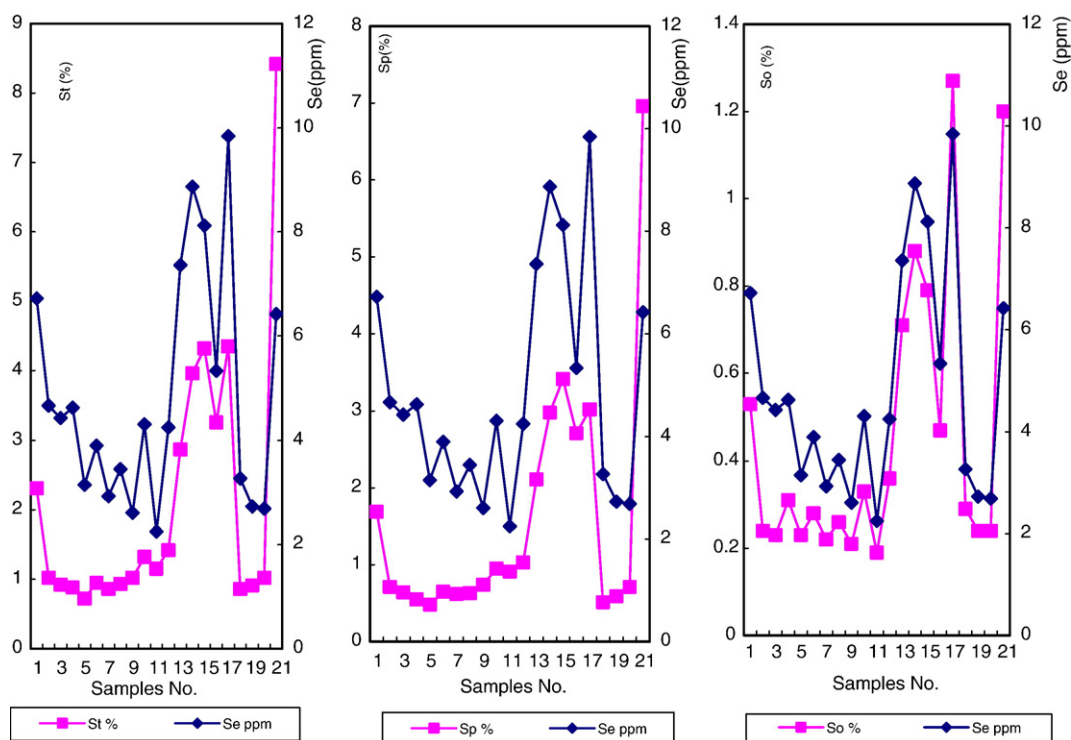


Fig. 3. The relationship between different forms of sulfur and Se.

(Fig. 3). The roof and floor rocks of the coal bed also have higher Se values. It can also be shown that Se content increases with increasing total sulfur, however, it is clear that the Se content is closely associated with organic sulfur (Fig. 3). The relationship of Se to organic sulfur is stronger than the relationship to total sulfur or pyritic sulfur. The correlation coefficient of Se to total sulfur, pyritic sulfur and organic sulfur is 0.707, 0.662 and 0.882, respectively. Hence, organic Se may dominate, but pyritic Se may be present in some samples.

Organic forms of Se in coals have been reported in previous studies (Finkelman, 1980, 1981; Minkin et al., 1984; Finkelman, 1985; Swaine, 1990; Dreher and Finkelman, 1992; Finkelman, 1994; Finkelman et al., 1999; Troshin et al., 2001; Dai et al., 2003; Zhu and Zheng, 2004; Zhu et al., 2004; Wen et al., 2006; Yudovich and Ketris, 2006). For example, Troshin et al. (2001) concluded that a strong correlation of Se and organic carbon ($R=+0.79$ for 29 samples) indicates Se bonding with coal organic matter. In order to study the occurrence of Se in coal, Finkelman et al. (1999) performed the semi-quantitative estimation of Se modes of occurrence in 25 coals by means of selective leaching, microprobe, and SEM-EDS analyses. The experiments concluded that organic Se contribution makes up no less than 50% with most of the remaining Se associated with pyrite.

According to the results of this study, we can see from Fig. 3, Se content is positive correlated to pyritic sulfur, but more closely tied to organic sulfur. Se can substitute readily for sulfur in many sulfide minerals. Several reports cite the occurrence of Se in pyrite extracted from coal (Minkin et al., 1984). Se also occurs in micrometer size crystals of clausthalite, a ubiquitous accessory phase in many coals (Finkelman, 1985; Hower and Robertson, 2003). Se has been detected in several other sulfide minerals (including galena) in coal (Finkelman, 1981) and in several other mineral forms (Swaine, 1990). In the studied samples, it can be concluded that the organic Se and pyritic Se are dominant forms.

5. Conclusions

- (1) In the Shanxi coal seam 3, the total sulfur and pyritic sulfur contents are both relatively high in the roof and floor rocks and in the upper clay parting ply of the coal seam. Organic sulfur content is positively correlated to total and pyritic sulfur. The origin of the sulfur enrichment in roof and floor rocks, and in the clay parting of the seam, is thought to be from sulphate ions carried into the palaeoenvironments during the peat forming process.

- (2) Hg, Se and As are more highly concentrated in the top and bottom of the seam. There are general similarities in the vertical variations. However, in the upper clay parting of the seam, all of the selected trace elements have an even higher concentration. The concentrations of Hg and Se in the seam studied are greater than the global mean of these elements in coals. Se content in the studied coal is five times as high as the world coal value and Hg is about three times as high as that in World Clarke value. Hg is more enriched compared with the average concentration in Chinese coals.
- (3) Hg, Se and As in studied samples are closely associated with sulfur. Hg is slightly more associated with pyritic sulfur than to organic sulfur. Se is much closer to organic sulfur than to pyritic sulfur. As is almost equally related to organic sulfur and pyritic sulfur.
- (4) In the studied samples, the three trace elements may be mainly associated with sulfide and other inorganic matter, however, they also occur in organic forms. Se shows most dependence for organic modes of occurrence followed by As and last Hg.

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