The volatilization of trace elements during oxidative pyrolysis of a coal from an endemic arsenosis area in southwest Guizhou, China

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ARTICLE INFO

ABSTRACT

Household coal combustion has caused endemic poisoning in southwest Guizhou Province of China. The mineralogy, geochemistry and mode of occurrence of trace elements (TEs) of coal from this area were examined, and oxidative pyrolysis experiments of the coal were conducted in a box resistance reactor at 300–1200 °C to evaluate the volatilization of trace elements. In coal, As, Sb, Pb, Zn, W, Mo, and Cr are highly enriched when compared to both the world coal and Chinese coal. Cadmium, Sr, and Ba are all slightly higher than the average value for Chinese coal. The volatility of trace elements exhibits a close correlation with the mode of element occurrence. The considerable volatilization of As, Sb, Pb, Zn, Cd and Cr below 450 °C is thought to be related to the organic form of these elements. In the temperature range of 450–1200 °C, the volatility of all trace elements except As increases slowly with temperature because these elements are highly associated with silicates. Among the hazardous trace elements, As is the most volatile, and Sb, Pb, Zn, Cd and Cr are moderately volatile. Arsenic exhibits a uniquely high release at 900–1000 °C, which could be attributed to the high proportion of As association with sulfide. Because TEs are primarily inorganically-associated, the volatilization of TEs is not comparable to the loss of coal weight during pyrolysis. At high temperatures, a significantly low coal weight loss can result in a significant volatility of TEs.

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1. Introduction

Coal is the second most important source of energy comprising 27.4% of the world's primary energy production [1]. The large abundance of coal makes it a reliable, long-term fuel source for both domestic and industrial applications. However, serious environmental concerns exist, as coal pyrolysis and utilization not only emit a large amount of solids into the environment but also a high content of potentially hazardous trace elements (TEs) [2,3]. For instance, TEs such as Hg, Pb, As, and Sb are known to be a serious public health concern.

In the southwest region of Guizhou Province in China, some coals have undergone mineralization, resulting in the enrichment of hazardous TEs such as As, Sb, Pb, and Zn. The mineralized coals are regularly burned in an unvented stove for domestic energy needs in rural households and have caused chronic poisoning of more than 3000 local residents [4]. Several studies have been conducted regarding the abundance, distribution and occurrence of As in the coal [5–9]. However, the behavior of hazardous elements during

the conversion of this coal has not been reported. Furthermore, although other hazardous elements such as Sb and Pb also exist at a high level [9], the geochemical distribution of these elements in the coal has not been studied in depth.

A number of studies addressed the transformation of TEs during coal conversion, and it has been concluded that the main factors that influence the volatilization of TEs include the reaction conditions (temperature, O_2, size of the coal, etc.) [10–13], the mode of occurrence of elements [14,15], and the interaction between these elements [16,17]. It should be noted that the mode of occurrence of elements varies significantly between coals from different regions and even between coals from the same seams [15], which can result in a different behavior of TEs for each coal. With respect to the coal in the endemic poisoning area in Guizhou Province, little information about the trace element transformation of this toxic coal is available. A particular concern is that Sb behavior in coal conversion is poorly understood, although Sb is commonly enriched in coals and fossil fuel combustion appears to be the largest single source of anthropogenic Sb to the global atmosphere [18]. Therefore, knowledge about the volatilization of TEs such as As, Sb, and Pb during the conversion of coal is crucially important.

The pyrolysis of coal, other than being an important process in itself, is the first essential step in the carbonization, gasification,

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and combustion of coal [19]. Most previous studies on the pyrolysis of coal are focused on inert conditions; however in practical applications, the thermal degradation of fuels often occurs in the presence of oxygen [20,21]. Hence, the pyrolysis of coal in oxidizing conditions has also been extensively reported in the literature [22–25]. In southwest Guizhou in China, the toxic coal is primarily used for domestic combustion in the atmosphere. Therefore, oxidative pyrolysis of the toxic coal in the atmosphere is performed in the present study to gain insight into the volatilization of TEs during coal conversion.

2. Materials and experiment

2.1. Reagents

Deionized water (18.2 MΩ·cm) produced by a Milli-Q system (Millipore, Bedford, USA) was used throughout the sample preparation, digestion and determination. Prior to use, concentrated nitric acid (HNO$_3$, 69%), hydrochloric acid (HCl, 37%) and hydrofluoric acid (HF, 40%) were purified using a sub-boiling distillation system (Savillex DST-1000, Minnetonka, USA). Ultra-pure HNO$_3$ and HF were used for sample digestion. Ammonium acetate, hydrogen peroxide (H$_2$O$_2$) used for extraction of the mode of occurrence of TEs in coal were of analytical grade. Multi-element standard solutions (Accu-Trace ICP-MS Calibration Standard, 10 µg mL^{-1} each element) for ICP-MS analysis were purchased from AccuStandard Incorporation, New Haven, USA.

2.2. Site description and sample collection

Southwest Guizhou Province is an important region for coal production in China. In addition to coal, the study area is also enriched with many metallic and metalloid ore deposits, such as gold, antimony, arsenic and mercury (Fig. 1). Carlin-type gold deposits that are widely distributed in this area are also accompanied by As, Sb, Pb and Hg mineralization [4,5]. The distribution of toxic coal in this area was controlled by geological structures such as anticlines, faults, and sedimentary strata [5]. The As and Sb concentrations in the coal exist at up to 1000 µg g^{-1} and 600 µg g^{-1}, respectively [4].

As a result of the serious health problems caused by the utilization of coal in this area, the local government closed the coal mines several years ago. Consequently, coal samples can only be collected from several small coal mines. In August 2008, thirteen coal samples were collected at Haizi (HZ) (Fig. 1). Samples were air dried and then ground to smaller than 100 mesh (0.15 mm) prior to further processing.

2.3. Mineral, proximate analysis and major element concentrations

The mineralogical composition of the coal was determined by X-ray diffraction (Rigaku D/max2200, Japan). The reference intensity method was used to obtain a semi-quantitative estimation of the mineral composition in coal. Proximate analysis of the coal was performed following the ISO 17246-2010 recommendation. The major element concentrations of the coal were determined by chemical analysis. The total sulfur, Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, and P$_2$O$_5$ concentrations were determined using the barium sulfate gravimetric method, the acid–base titration method, the potassium dichromate capacity method, the hydrogen peroxide colorimetric method, and the phosphor molybdate blue colorimetric method, respectively. The concentrations of CaO, MgO, K$_2$O, Na$_2$O, and MnO$_2$ were analyzed by Flame Atomic Absorption Spectroscopy (FAAS) after the coals were digested by HF and HNO$_3$.
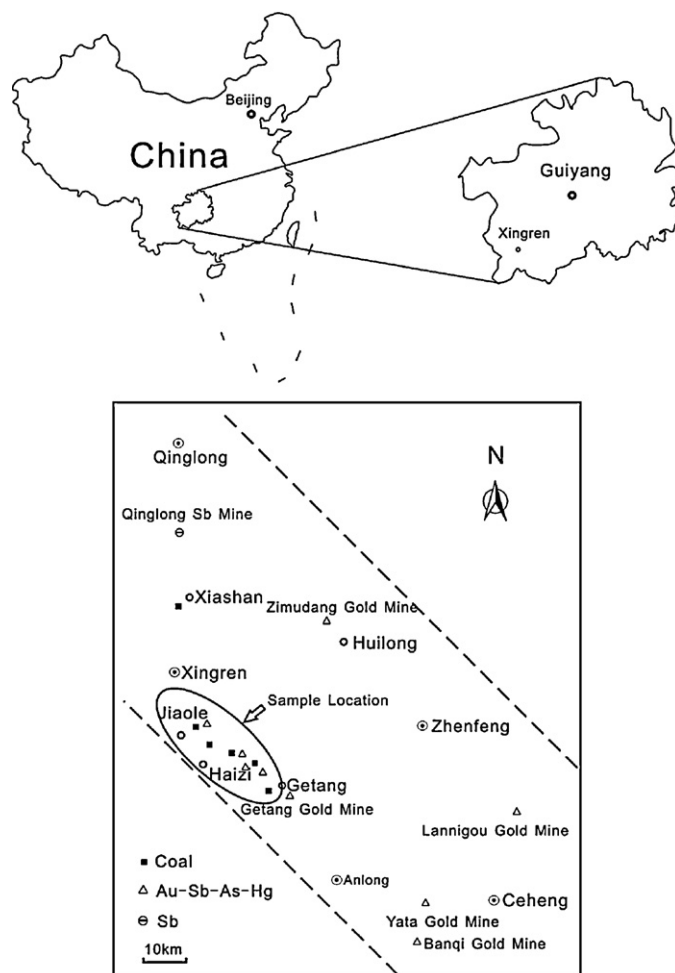

Fig. 1. Sketch map showing location of the study area.

2.4. Oxidative pyrolysis experiment

Powdered coal sample (0.3 g) was placed in a platinum crucible (mouth ID: 32 mm, bottom ID: 19 mm, height: 34 mm). The open crucible was placed in a box resistance furnace (dimension: 15 cm × 10 cm × 30 cm), and then heated under a static-air atmosphere. Pyrolysis was performed at a heating rate of 6 °C min^{-1} to a desired final temperature (300, 350, 400, 450, 500, 600, 700, 800, 900, 1000, 1100 and 1200 °C). The apparatus was maintained at the final temperature for 20 min. After cooling, the residue of the pyrolysis was weighed and then digested to determine the TEs.

2.5. Sample digestion

With regard to the determination of TEs in both the coal and char of pyrolysis, high pressure digestion has been proved efficient to accelerate the dissolution of organic matrix [26,27]. In this study, twenty milligrams of the powdered sample was placed in a polytetrafluorethylene (PTFE) crucible (ID: 30 mm, height: 55 mm). To each sample was added 1 mL of HNO$_3$ and 0.5 mL of HF. The crucible was sealed within a stainless steel bomb and heated typically at 170 °C (internal pressure: ca. 7.9 bar) for 12 h. In occasionally cases that samples were very refractory, the temperature was raised to 200 °C (internal pressure: ca. 15.6 bar). The digestion bomb was opened after cooling to avoid analyte loss by evaporation. The solution was heated until dry, and 1 mL of HNO$_3$ was added and evaporated until dry. When the residue was re-dissolved in 1 mL of

Table 1
Proximate analysis and mineralogy of HZ coals.

	HZ$_1$	HZ$_2$	HZ$_3$	HZ$_4$	HZ$_5$	HZ$_6$	HZ$_7$	HZ$_8$	HZ$_9$	HZ$_{10}$	HZ$_{11}$	HZ$_{12}$	HZ$_{13}$
Proximate analysis (wt.%)													
Moisture (total)	3.16	3.48	3.06	4.15	11.6	3.86	2.67	3.00	4.26	3.13	4.40	4.09	2.34
Ash	40.1	13.8	25.1	26.3	41.1	24.3	20.7	26.3	12.3	17.7	35.4	35.3	23.0
Volatile matter	8.86	5.49	6.93	8.84	22.6	9.81	6.36	7.98	16.7	8.50	13.7	16.4	7.93
Fixed carbon	47.9	77.2	64.9	60.7	24.7	62.1	70.3	62.7	66.7	70.7	46.5	44.3	66.7
Semi-quantitative mineral composition analysis (wt.% of ash)													
Quartz	54.7	73.1	81.6	85.4	90.1	82.5	91.1	69.5	85.1	89.4	81.8	64.0	85.0
Illite	3.2	5.3	2.2	7.3	2.8	3.0	3.0	11.2	2.7	1.0	8.1	2.9	3.2
Montmorillonite	3.2	4.6	3.0	1.2	3.6	2.7	0.9	5.9	3.3	1.4	0.9	6.3	4.4
Kaolinite	17.2	7.0	2.9	6.1	2.0	5.8		3.2	1.1	1.6	1.1	1.5	0.8
Pyrite	16.2		8.3					1.3	1.8			23.5	
Hornblende	1.1	4.2				2.1	0.7	2.0			2.3		1.7
Albite									Rare		1.6		0.5
K-feldspar	1.2	0.8				2.5	1.5	0.7		0.6		0.8	0.8
Anatase	3.2	1.4	1.5			0.4	1.4		2.7	2.2		0.3	2.7
Gibbsite		1.1	0.7				0.8						0.3
Barite		2.5							0.5				
Gypsum							0.6	2.4	1.9	1.1	2.1	Rare	
Ironmineral		Rare			Rare	1.1				1.8	1.9		0.7
Dolomite								3.9					
Pyrophyllite									1.0				
Calcite												0.8	
Boehmite					1.4					0.9			

HNO$_3$ and diluted into 100 mL, a transparent solution formed and was used for subsequent analysis.

2.6. Sequential extraction

The mode of occurrence of TEs in the coal was identified through the sequential extraction. Five modes of occurrence of TEs in the coal, i.e., exchangeable, carbonate, organic, sulfide and residue fractions, were extracted according to the following methods. (i) Water soluble and ion exchangeable form: powdered sample (1 g) was extracted with 10 mL of 1 M ammonium acetate with continuous agitation. (ii) Carbonate form: the residue from (i) was extracted with 10 mL of 1 M HCl with continuous agitation. (iii) Organic form: the residue from (ii) was separated by 1.47 g cm^{-3} chloroform, and then the floater was digested with HNO$_3$ and H$_2$O$_2$ in a high-pressure manner the same as the whole sample digestion described above. (iv) Sulfide form: the subsider from (iii) was extracted with 10 mL of 2 M HNO$_3$ at 85 °C, with occasional agitation. (v) Residue form: the residue from (iv) was transferred to a PTFE crucible and digested with HNO$_3$ and HF under the high temperature and pressure described above.

2.7. Sample analysis and quality control

Trace element determination was conducted by Inductively-Coupled Plasma Mass Spectrometry (Platform ICP, Micromass Instruments Corporation, Manchester, UK). Method blanks for sample digestion were measured to meet the quality control. One certified reference material of soil (GBW07404-GSS-4, China National Research Center of CRM's, Beijing, China) was also digested to determine the accuracy of the analytical and digestion methods. The precision of the determination of elements is typically better than 5%.

3. Results and discussion

3.1. Proximate analysis and mineralogy of coal

The results of the proximate analysis and mineralogy of HZ coal are shown in Table 1. The moisture of most HZ coal is at a low level of 2.34–4.40%; however, the moisture of HZ$_5$ is at a medium level of 11.6%. The ash range of HZ coal is 12.3–41.1%, which is a medium or medium-high ash level. The volatile matter of HZ coal typically exists at a low level of 5.49–16.7%, whereas HZ$_5$ exhibits a medium volatile matter level of 22.6%. Most of the HZ coal contains a high sulfur content of more than 3% (Table 2), whereas only three samples contain a medium sulfur content of 1.75–2.65%. In summary, HZ coal is characterized by low moisture, medium ash yield, low volatile matter, and high sulfur content.

X-ray diffraction is often used to semi-quantitatively determine the fraction of constituents. By comparing the integrated intensities of the diffraction peaks from each of the known phases, their fraction can be identified. The results in Table 1 represent the semi-quantitative estimation of the mineral composition in coal and that quartz and clay minerals (illite, montmorillonite, kaolinite) are the major crystalline mineral constituents of HZ coal. The content of pyrite in coal is highly variable. In some coal, no crystalline pyrite can be observed; however in some other coal the content of pyrite can be up to 23.5%. Two types of coal, HZ$_1$ and HZ$_2$, have the highest content of pyrite at 16.2% and 23.5%, respectively. Both HZ$_1$ and HZ$_2$ also have a high level of sulfur at 6.27% and 7.26%, respectively. This result indicates a close association of sulfur with pyrite and suggests that a large portion of the sulfur in HZ coal is bound in pyrite. In addition to the major minerals, hornblende, potassium-feldspar, and anatase are also prevalent at low levels; minor albite, gibbsite, barite, gypsum, iron-mineral, dolomite, pyrophyllite, calcite, and boehmite are occasionally found in some HZ coal.

3.2. Major and trace elements in coal

In comparison to the average values of Chinese coal, HZ coal exhibits a higher concentration of SiO$_2$, MgO, K$_2$O, and Na$_2$O and a lower concentration of Al$_2$O$_3$, Fe$_2$O$_3$, CaO, MnO, TiO$_2$, and P$_2$O$_5$ (Table 2).

When compared with Chinese coal and other coal deposits located around the world, As, Sb, Pb, Zn, W, Mo, and Cr in HZ coal is significantly enriched, and Cd, Sr, and Ba is slightly enriched (Table 3). In addition, the average concentration of Rb in HZ coals is noticeably higher than the average value for Chinese coal; however it is slightly lower than the average value for coal deposits around the world. The average enrichment factors of As, Sb, Pb, Zn, W, Mo, and Cr relative to the average value of coal deposits around the

Table 2
Major element composition in HZ coals (%).

	HZ$_1$	HZ$_2$	HZ$_3$	HZ$_4$	HZ$_5$	HZ$_6$	HZ$_7$	HZ$_8$	HZ$_9$	HZ$_{10}$	HZ$_{11}$	HZ$_{12}$	HZ$_{13}$	HZ average	China average [41]
S (Total)	6.27	3.64	5.05	4.01	1.81	4.14	3.60	3.51	2.65	3.74	3.17	7.26	1.75	3.89	No data
SiO$_2$	27.2	9.52	17.1	19.4	30.7	16.2	15.7	14.2	5.36	10.4	19.3	12.5	16.4	16.5	8.47
Al$_2$O$_3$	2.56	7.23	1.58	1.20	1.15	1.57	1.03	5.15	0.46	0.72	6.75	1.52	0.42	2.41	5.98
Fe$_2$O$_3$	5.32	0.84	2.30	1.67	6.11	3.00	0.54	1.67	2.14	1.58	2.43	19.1	1.37	3.70	4.85
CaO	0.31	0.25	0.32	0.37	0.22	0.36	0.29	0.19	0.32	0.25	0.24	0.26	0.37	0.29	1.23
MgO	0.68	0.68	0.77	0.67	0.58	0.56	0.32	0.71	0.51	0.56	0.53	0.25	0.59	0.57	0.22
K$_2$O	1.83	1.29	1.50	1.33	1.07	0.83	1.54	3.62	2.00	2.72	3.66	0.80	1.26	1.80	0.19
Na$_2$O	2.27	0.90	1.42	1.30	1.09	1.30	0.93	1.16	1.10	1.14	2.20	0.57	1.12	1.27	0.16
MnO	0.015	0.014	0.016	0.016	0.015	0.012	0.004	0.003	0.014	0.004	0.010	0.018	0.007	0.011	0.015
TiO$_2$	0.120	0.170	0.100	0.052	0.045	0.100	0.045	0.120	0.030	0.037	0.150	0.100	0.032	0.085	0.330
P$_2$O$_5$	0.037	0.038	0.042	0.045	0.039	0.042	0.032	0.026	0.022	0.029	0.032	0.035	0.026	0.034	0.092

world are 163, 65, 3.6, 12, 4.2, 11, and 4.2, respectively. Various research has discussed the processes accounting for the enrichment of TEs in coal within the study area. The formation of coal in the study area is thought to have been deposited after the end of Emeishan basalt extrusion, and the enrichment of TEs in coal may be related to the extrusion of Emeishan basalt [4]. Moreover, epigenetic low-temperature hydrothermal fluids accompanying the formation of gold and antimony deposits can penetrate into coal seams after coal-formation. This process could have led to the geochemical and mineralogical anomalies of coal [4,5,28,29]. The frequent eruptions of volcanic ash during the Late Permian age may also be the origin of TEs for coal [30,31].

Table 4 shows the Pearson correlation matrix for TEs and some major elements of HZ coal. Among the highly enriched TEs mentioned above, Sb, Pb, Zn, W, Mo, and Cr show a highly positive correlation with each other, whereas As only shows a weak correlation with other elements. The relationship between As and other elements is complex, possibly because As in HZ coal has a diversity of origins and modes of occurrence. Previous research suggests that As in coal from southwest Guizhou may be associated with pyrite, arsenopyrite, arsenic-bearing sulfide, scorodite, and arsenic-bearing clays [4,5,8,32].

Antimony, Pb, Zn, W, Mo, and Cr show a strong correlation with SiO$_2$ but a weak correlation with CaO + MgO, which suggests that these TEs may have originated from deep hydrothermal fluid rich in siliceous components. Among these elements, a much stronger correlation can be found between some element pairs, such as Sb–Pb, Zn–W, and Mo–Cr, which implies that these element pairs may exhibit similar behaviors during the formation of coal [33,34].

Barium and Rb exhibit a high correlation with K$_2$O + Na$_2$O, suggesting that they may have a strong relationship with both clay mineral and feldspar. Iron and Mn exhibit a relatively high correlation with the total sulfur, indicating that Fe and Mn may have a close relationship with the sulfide mineral. In previous studies,

a high level of Mn in pyrite (18–332 $\mu g\,g^{-1}$) has been reported in coal from southwest Guizhou [35,36].

3.3. Modes of occurrence of elements in HZ coals

Trace elements exist in coal through different modes of occurrence, which result from both the coal-forming environments and the subsequent geologic activity. Methods of sequential extraction can provide quantitative information about the speciation of TEs in coal. Two HZ coals with significantly different ash content were chosen for sequential extraction. HZ$_1$ exhibits a high ash content of 40.1%, whereas HZ$_2$ exhibits a low ash content of 13.8%. The occurrence modes of TEs in these coals are shown in Fig. 2.

The residue form of the eleven TEs in HZ$_1$ is higher than in HZ$_2$, whereas the organic form of the TEs in HZ$_1$ is lower than in HZ$_2$. This corresponds to the higher ash content of HZ$_1$ than HZ$_2$. High ash content results in a high fraction of silicate minerals and a low fraction of organic carbon. The eleven TEs in HZ coal exist predominantly as three occurrence modes: the sulfide form, organic form and residue form. Among these TEs, the proportion of the sulfide form varies widely, and As, Pb, and Mo exhibit the highest proportion of the sulfide form. The residue form is the most important occurrence mode for most TEs, except for As and Mo.

The proportion of As in the sulfide, organic and residue forms are 33.1%, 22.6%, and 42.4% in HZ$_1$, and 50.6%, 29.3%, and 18.2% in HZ$_2$, respectively. In contrast, As associated with the water-soluble plus ion exchangeable form and carbonate form accounts for less than 2%. The existence of As in these three main forms has also been reported in previous studies. Arsenic is a typical chalcophile element, and in some types of coal, it is primarily associated with pyrite [37]. In addition to its sulfide form, organic As is also important in coal. Zhao et al. [38] have reported that the occurrence of organically associated As in Guizhou coal has been proved by X-ray absorption fine structure (XAFS); however, the detailed structure of

Table 3
Trace element composition in HZ coals ($\mu g\,g^{-1}$).

|	HZ$_1$	HZ$_2$	HZ$_3$	HZ$_4$	HZ$_5$	HZ$_6$	HZ$_7$	HZ$_8$	HZ$_9$	HZ$_{10}$	HZ$_{11}$	HZ$_{12}$	HZ$_{13}$	HZ average	China average [41]	World average [32,41]
As	386	228	288	253	676	494	2979	237	1617	432	1922	955	120	814	3.8	5.0
Sb	111	51.1	75.0	523	309	455	165	47.2	81.8	44.7	140	49.8	477	195	2.3	3.0
Pb	79.4	44.3	68.7	277	97.8	139	27.0	67.4	51.6	57.1	34.4	40.3	181	89.6	15	25
Zn	587	550	536	689	704	616	501	583	545	518	580	567	571	580	42	50
Cd	0.53	0.47	0.45	0.65	0.73	0.67	0.27	0.27	0.30	0.28	0.39	0.41	0.36	0.44	0.3	0.3
W	21.2	8.6	6.2	25.8	20.6	13.1	5.5	10.9	3.4	4.9	11.2	2.5	1.5	10.4	2.0	2.5
Mo	162	55.7	106	51.6	83.2	61.5	13.6	45.5	28.7	10.2	20.6	32.8	15.8	52.9	3.1	5.0
Rb	31.8	20.9	30.4	19.9	24.1	16.2	21.5	21.4	20.4	23.4	45.8	21.9	19.1	24.4	8.0	26.0
Sr	118	112	181	304	166	259	104	40.0	78.5	570	48.3	65.2	129	167	136	100
Ba	93.7	44.8	72.2	87.7	71.9	55.2	67.7	92.3	80.6	162	160	71.4	104	89.6	82	70
Cr	165	58.6	156	59.7	204	63.2	34.5	103	38.5	41.9	63.5	52.6	46.4	83.7	15.3	20
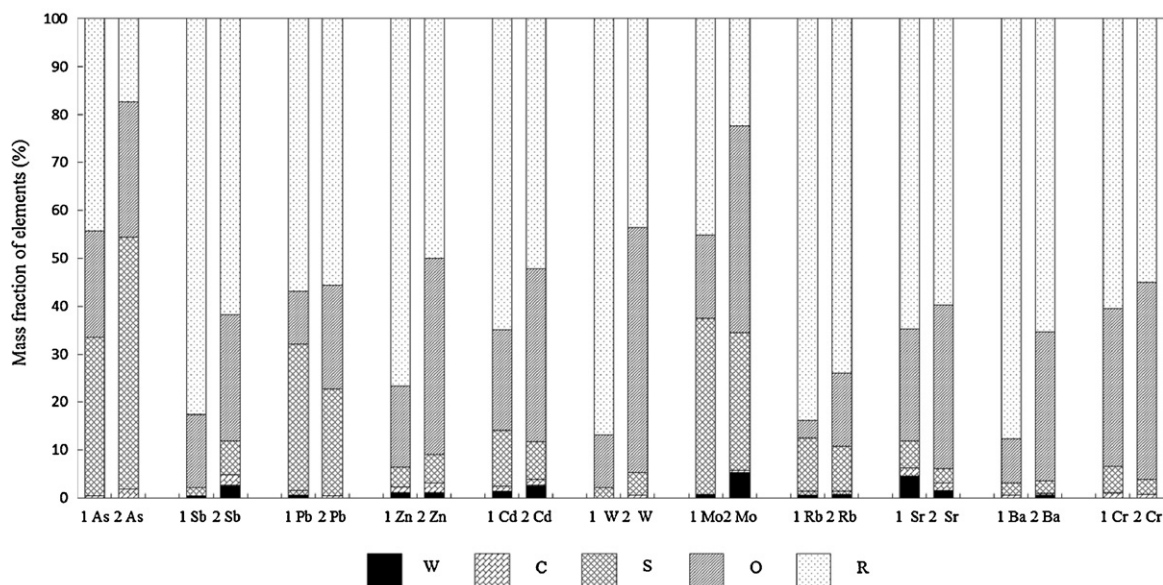
Fig. 2. Mode of occurrence of TEs in HZ coals (1. HZ_1 coal; 2. HZ_2 coal; W: water soluble plus ion exchangeable form; C: carbonate form; S: sulfide form; O: organic form; R: residue form).

organic arsenic is still unknown. The third important form of As is a residue form, in which As is primarily associated with clay minerals: illite, montmorillonite, and kaolinite. In a previous study, it was proved that AsO_4^{3-} can replace SiO_4^{4-} in the structure of kaolinite [39].

Antimony can occur in minerals associated with pyrite and clays [40,41]. Finkelman [42] suggests the existence of organic and inorganic antimony in coal, and a previous study suggests that Sb can exchange with organic ions in coal [37]. In HZ coal, Sb occurs primarily as a residue form that accounts for up to 80.3% in HZ_1. The second important form of Sb in HZ coal is the organic form, which constitutes 14.9% in HZ_1 and 26.9% in HZ_2. Moreover, a small fraction (7.3%) of the sulfide form of Sb occurs in HZ_2.

In the two HZ coals, Pb is characterized to exhibit primary modes of occurrence as the residue form (56.4–57%), sulfide form (22.6–30.5%) and organic form (11–21.9%) (Fig. 2). This indicates that Pb is primarily associated with silicate minerals, while sulfide minerals are also an important host to Pb. Previous studies also reported the occurrence of Pb in coal associated with
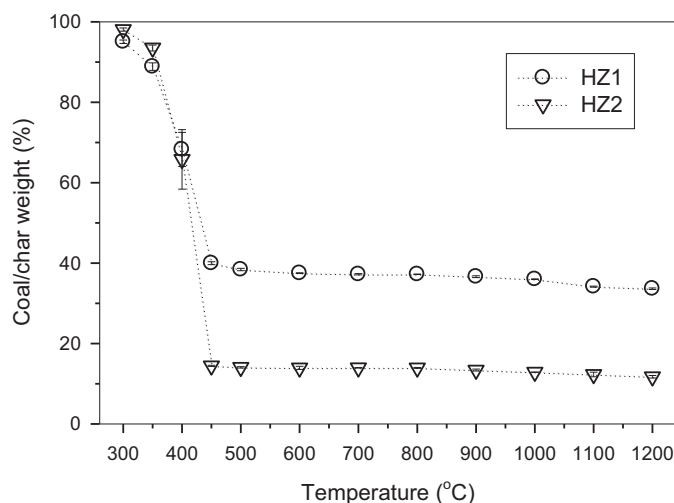
alumino-silicate (residue form) [43,44]. In addition to this, a significant fraction of Pb has been reported associated with sulfides such as pyrite [40,41]. The association of Pb with sulfide minerals conforms to the existence of galena, clausthalite and other sulfide minerals in coal in southwest Guizhou [45].

Zinc, Cd and W have a similar mode of occurrence. Both the residue and organic forms are the dominant mode of occurrence of these elements. Generally, Zn and Cd exhibit similar geochemical behavior, and in most cases, Cd can exist in sphalerite, smithsonite, and wurtzite through isomorphism to replace other irons [45]. A previous study reported a strong correlation between Zn and Cd in coal [34].

The mode of occurrence of Mo in HZ coal is similar to that of As. The majority of Mo is present as the sulfide form, organic form and residue form. In general, Cr is thought to be associated with the organic form [46]. In addition, Cr shows association with clay minerals and feldspars [41]. Zhang et al. [37] reported that Cr primarily occurs in inorganic mineral matter, which is associated with either clay minerals or pyrite. In HZ coal, Cr primarily occurs in both residue and organic forms (Fig. 2).

3.4. Oxidative pyrolysis of HZ coal

3.4.1. Coal weight loss at different temperatures

Fig. 3 shows the variation of coal or char weight during the pyrolysis of HZ_1 and HZ_2 coals. At a temperature of 350 °C, which is called the cracking temperature, HZ_1 and HZ_2 exhibit a low weight loss of 11.1% and 6.5%, respectively. In the temperature range of <350 °C, the formation and volatilization of low molecular weight species (e.g. water, methane, and carbon dioxide) may occur before organic carbon pyrolysis begins [47,48]. In the temperature range of 350–450 °C, a significant loss of coal weight (HZ_1 – 48.9%, HZ_2 – 79.1%) occurs as a result of the pyrolysis and volatilization of a variety of organic carbon species. These results are in accordance with the organic carbon content of the coal, which is 47.9% and 77.2% (Table 1), indicating that the weight loss in this temperature range is primarily caused by the transformation and release of organic carbon. In the temperature range of 450–1200 °C, the coal weight is only slightly reduced because the organic carbon has almost entirely transformed and volatilized at 450 °C. However, minerals begin to melt and, consequently, the TEs in the mineral

Fig. 3. Coal weight loss during pyrolysis (data are the mean value of three experiments, and the bars represent the standard deviation of three measurements).

Table 4
Pearson correlation matrix for TEs in HZ coals ($n = 13$).

	Sb	Pb	Zn	Cd	W	Mo	Rb	Sr	Ba	Cr	Total S	SiO$_2$	Fe$_2$O$_3$	MnO	CaO+MgO	K$_2$O+Na$_2$O
As	−0.210	−0.482	−0.366	−0.379	−0.259	−0.403	0.259	−0.316	0.082	−0.338	−0.095	−0.031	−0.020	−0.235	−0.670	0.121
Sb		0.876	0.638	0.590	0.417	−0.053	−0.337	0.191	−0.132	−0.052	−0.369	−0.375	−0.194	0.089	0.315	−0.335
Pb			0.654	0.533	0.514	0.065	−0.363	0.309	−0.073	−0.016	−0.195	−0.347	−0.187	0.182	0.513	−0.263
Zn				0.835	0.804	0.303	−0.077	0.031	−0.150	0.464	−0.188	−0.062	0.131	0.425	0.280	−0.126
Cd					0.753	0.536	−0.078	0.115	−0.381	0.522	0.038	−0.085	0.148	0.636	0.347	−0.354
W						0.571	0.134		−0.078	0.532	0.035	0.099	−0.098	0.336	0.427	0.149
Mo							0.217	−0.114	−0.320	0.809	0.421	0.038	0.098	0.528	0.418	−0.036
Rb								−0.226	0.569	0.293	0.124	0.468	−0.004	0.080	−0.100	0.655
Sr									0.368	−0.126	−0.039	−0.401	−0.221	−0.176	0.169	−0.090
Ba										−0.171	−0.162	0.078	−0.160	−0.439	−0.124	0.689
Cr											0.080	0.012	0.111	0.358	0.206	−0.006
Total S												0.014	0.640	0.430	−0.237	−0.162
SiO$_2$													−0.154	−0.067	0.257	0.611
Fe$_2$O$_3$														0.510	−0.596	−0.390
MnO															0.119	−0.438
CaO+MgO																0.166

lattice are released [49]. Therefore, this temperature range may be important for the volatilization of TEs bound in minerals.

### 3.4.2. Volatility of hazardous elements during pyrolysis of HZ coals

The release of an element during coal pyrolysis may be controlled by a variety of factors, including its binding form in coal, its interaction with co-existing mineral matter, and the formation of its thermally stable forms at different temperatures [14]. During the initial stage of coal pyrolysis, the structure of organic matter readily decomposes, and the interaction of elements with other elements of mineral matter can occur. This process is summarized by [50]. In the temperature range of 600–850 °C, coal undergoes an intense degradation of its structure, and at a temperature greater than 900 °C, alumino-silicate minerals and sulfides start to decompose. Furthermore, PbCO$_3$ can be completely decomposed into PbO at a temperature greater than 300 °C [14]. In addition, mineral transformation can occur within a wide range of pyrolysis temperatures. At 450 °C, disulfide FeS$_2$ can be transformed into monosulfide FeS, resulting from the decomposition of pyrite [51]. Iron sulfate frequently decomposes at a temperature of <500 °C [52]. Most of the PbS would be transformed into PbO from the pyrolysis of brown coal [14]. Both the decomposition and transformation of organic and mineral matter can release TEs from coal. In addition, the interaction of the elements may form their chlorides or sulfides and then be volatilized [50].

The volatilization of the hazardous elements As, Sb, Pb, Zn, Cd, and Cr in coal during pyrolysis is shown in Fig. 4. A strong contrast of TEs volatility exists between the two coals. The volatility of As in HZ$_2$ below 900 °C is noticeably higher than that in HZ$_1$, with a difference of up to 31.5% at 800 °C. However, the volatility of As in the two coals finally reaches a similar level at a temperature of 1200 °C. Unlike arsenic, Sb, Zn, and Cr exhibit a considerably different volatility between the two coals in the entire temperature range, whereas Pb and Cd generally show a similar volatilization. The difference in the volatility of some TEs between the two coals may be caused by the occurrence mode of TEs in coal.

With regard to the volatility of TEs in coal during pyrolysis, As exhibits the highest volatility of 91.4%, whereas Sb, Pb, Zn, Cd, and Cr exhibit a lower but relatively similar volatility of 48.8–58.9%. This may have resulted from the fact that As is mostly present in both sulfide and organic forms, whereas the other five elements are mostly present in clay minerals (residue form) (Fig. 2). Trace elements bound in both the organic and sulfide forms are considered to vaporize more completely than in the residue form [53]. Alternately, during the coal pyrolysis TEs may transform into element, oxide or chloride prior to volatilization [50]. Arsenic and its compounds of oxide, sulfide, and chloride have a generally lower boiling point than the other five elements (Table 5). As a consequence, As is more likely to volatilize than other TEs during the pyrolysis of coal.

With respect to the influence of the pyrolysis temperature on the volatilization of TEs, the hazardous elements in HZ coal generally present a three-stage volatilization: stage 1 (below 450 °C), stage 2 (450–900 °C), and stage 3 (above 900 °C). The three-stage volatilization of TEs is such a contrast to the coal weight loss, which occurs primarily in stage 1 (below 450 °C).

Arsenic exhibits a typical three-stage volatilization (Fig. 4a). The majority of As is volatilized in stage 3 (HZ$_1$: 62.4%, HZ$_2$: 41.2%); however, a considerably lower proportion of As is volatilized in stage 1 (HZ$_1$: 11.8%, HZ$_2$: 30.6%) and stage 2 (HZ$_1$: 14.5%, HZ$_2$: 22.2%). Arsenic volatilized in stage 1 may correspond to the organic form because organic arsenic frequently vaporizes with coal devolatilization [54]. Arsenic volatilized in stage 3 may correspond to the sulfide form and clay mineral form because sulfide mineral decomposition and alumino-silicate mineral transformation
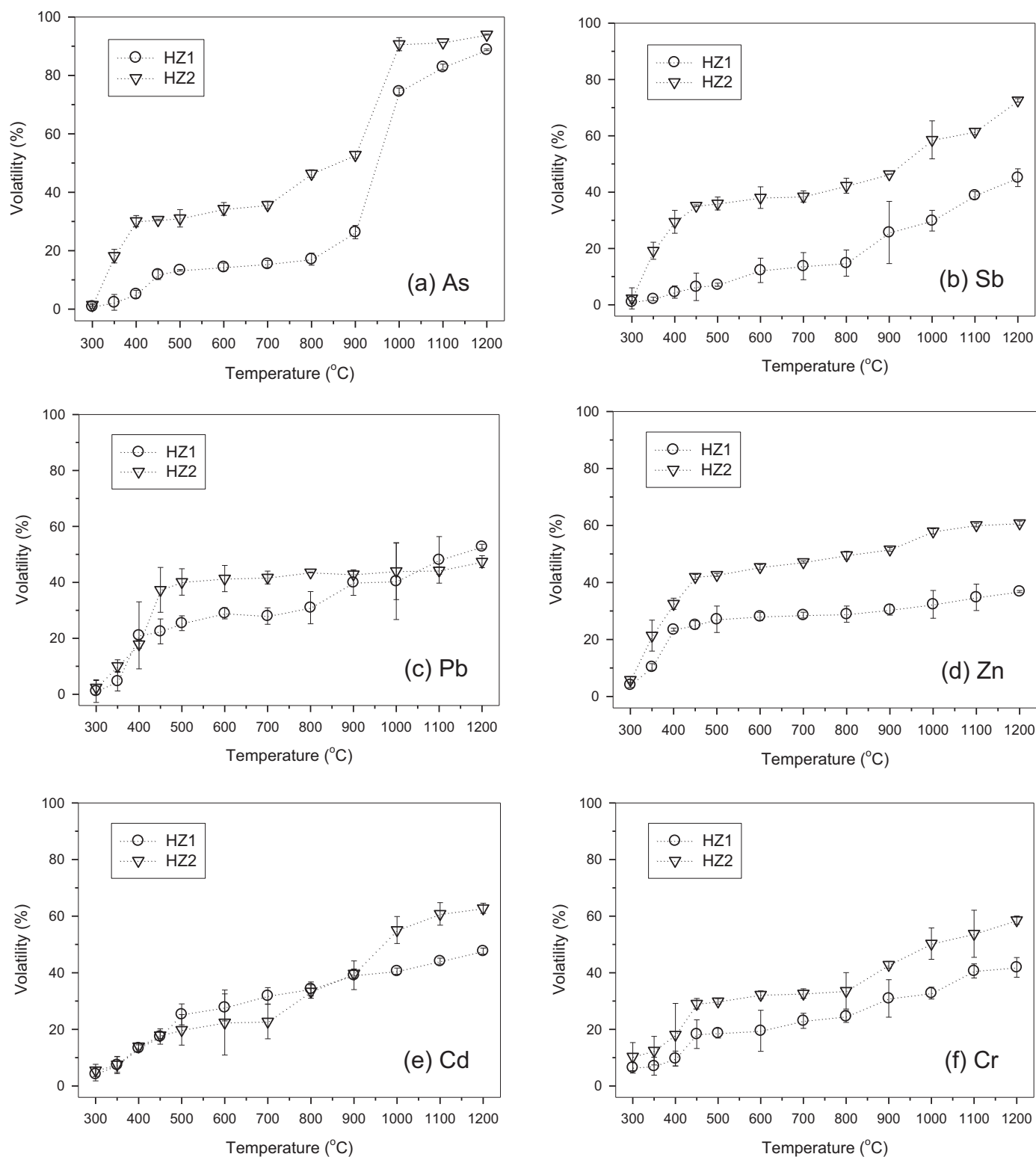
Fig. 4. The volatility of TEs during the pyrolysis of coal (data are the mean value of three experiments, and the bars represent the standard deviation of three measurements).

generally occur above 900 °C. In stage 2, As volatilizes slowly as the temperature increases, possibly because only mineral transformation occurs in this stage. This transformation only results in the release of a small fraction of TEs [55].

Generally, Sb, Cd, and Cr volatilize evenly as the temperature increases (Fig. 4b, e, and f), with only Sb in HZ_2 showing a

considerable volatilization of 35.2% in stage 1. Trace elements bound in clay minerals (residue form) typically exhibit a slow release when the temperature rises [56]. The steady volatilization of Cd with an increase in temperature is consistent with the results of a previous study. Guo et al. [57] reported an approximately linear volatility of Cd with an increase in the pyrolysis temperature. The

Table 5
Boiling point of TEs and their compounds (°C).

	Element	Oxide	Sulfide	Chloride
As	814	461	707	130
Sb	1750	1570	550	223
Pb	1740	1535	1281	953
Zn	907	1800	1975	732
Cd	765	920	1382	964
Cr	2672	2275	–	950

fraction of Cr associated with the residue form, which is generally considered stable, may be responsible for the steady volatilization of Cr [36,55,58].

Lead and Zn volatilize considerably in stage 1 for the two HZ coals and then volatilize evenly and slowly in stages 2 and 3 (Fig. 4c and d). The considerable volatility of Pb in stage 1 might be caused by the interaction of Pb with other elements and by the decomposition of organic matter. In stages 2 and 3, thermally stable forms of Pb, which particularly occur in HZ_2, may have formed above 450 °C, as the volatility of Pb barely increases in this temperature range. The fraction of Pb associated with clay minerals may be responsible for the formation of the thermally stable form. The high volatility of Zn in stage 1 (25.1% for HZ_1 and 42% for HZ_2) might be caused by the fraction of Zn associated with organic matter. The slight increase

of the volatility of Zn in stages 2 and 3 may show the existence of some inert chemical forms of Zn in the coal.

The volatilization of TEs presents a strong contrast to the loss of coal weight during pyrolysis (Fig. 5). In the early stage of pyrolysis (<450 °C), the high loss of coal (60% for HZ_1 and 85.6% for HZ_2) has resulted in average trace element volatility of 16.9% for HZ_1 and 32% for HZ_2, whereas in the late stage of pyrolysis (>450 °C), the minor loss of coal (6.3% for HZ_1 and 2.7% for HZ_2) has resulted in average trace element volatility of 35.2% for HZ_1 and 34% for HZ_2. This result is in agreement with the association of a large proportion of TEs with sulfide and silicate minerals. At high temperatures, TEs can be significantly released because of the transformation and decomposition of these minerals. However, these processes only result in a minor loss of coal weight.
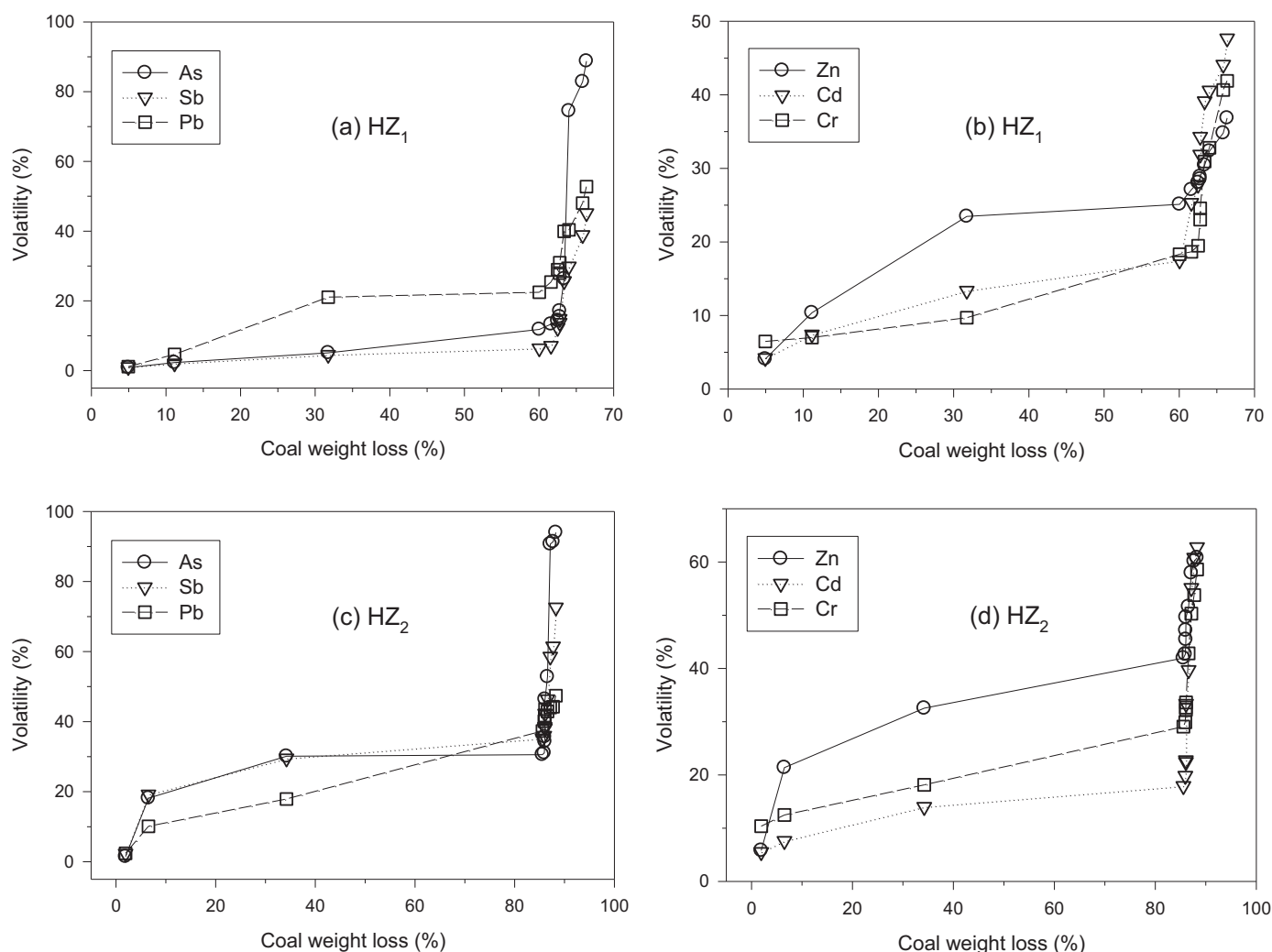
Fig. 5. The volatility of TEs versus coal weight loss during the pyrolysis of coal (based on data from Figs. 3 and 4).

4. Conclusion

In the HZ coal, As, Sb, Pb, Zn, W, Mo, and Cr are highly enriched, and Cd, Sr and Ba are slightly higher than the average values of Chinese coal. Trace elements in the coal are present predominantly as three modes of occurrence: the sulfide form, organic form and residual form.

The trace element volatilization during the pyrolysis of coal is highly affected by the temperature, the mode of occurrence, and the element itself. Generally, TEs show a considerable volatilization below 450 °C, which is thought to correspond to the organic form of TEs. In the temperature range above 450 °C, the volatility of TEs, excluding As, increases slowly with temperature because of their association with silicates. Arsenic exhibits a uniquely high release at 900–1000 °C and, consequently, a higher volatility than Sb, Pb, Zn, Cd, and Cr, which may result from the high proportion of As associated with sulfide.

The volatilization of TEs is not similar to the loss of coal weight during pyrolysis. At high temperatures, a minor loss of coal weight can result in a significant volatility of TEs. This phenomenon is likely caused by the association of a large proportion of TEs with sulfide and silicate minerals.

Acknowledgments

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