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Enrichment of arsenic, antimony, mercury, and thallium in a Late Permian anthracite from Xingren, Guizhou, Southwest China

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Abstract

Mineralogy and geochemistry of nine Late Permian coal-seam channel samples (anthracite) from Xingren, Guizhou, Southwest China were examined. Results showed that As, Sb, Hg, and Tl are significantly enriched in a Late Permian anthracite (sample XR-M1) in the study area, and their contents are as high as 2226 μg/g, 3860 μg/g, 12.1 μg/g, and 7.5 μg/g, respectively. However, the contents of the four elements in other coal-seam channel samples from Xingren, even the two channel samples (samples XR-M2 and XR-M3) that are from the same bed as sample XR-M1, are close to the ordinary coal average, indicating that these four elements varied greatly in different coal beds and different locations of the same bed, and such coals highly enriched in these hazardous elements are very local and restricted. The main carrier of As, Sb, Hg, and Tl in sample XR-M1 is an epigenetic getchellite rather than syngenetic pyrite and clay minerals. Getchellite occurs only in the veined kaolinite of hydrothermal origin. The high As, Sb, Hg, and Tl in coal are derived from an arsenic- and antimony-rich hydrothermal fluid.

Keywords: Coal; Arsenic; Antimony; Mercury; Thallium; Getchellite; Guizhou; China

1. Introduction

Anthropogenic sources of As and Hg, including coal-fired power plants, receive much more attention than natural sources (weathering, biologic activities, and volcanic emissions) because they are potentially reducible through technological advances and environmental regulations and restrictions (Hower et al., 2005a, b; Ruppert et al., 2005; Yudovich and Ketris, 2005). Previous studies showed that most of arsenic in coal is associated with pyrite, most commonly as As-rich inclusions in the pyrite lattice (Coleman and Bragg, 1990; Minkin et al., 1984; Ruppert et al., 1992; Huggins and Huffman, 1996; Finkelman, 1994; Hower et al., 1997; Goodarzi, 2002; Eskenazy, 1995; Zhang et al., 2002; Tang and Huang, 2004; Dai et al., 2005b; Yudovich and Ketris, 2005); but sometimes associated with clay minerals (Swaine, 1990; Tang and Huang, 2004; Cui and Chen, 1998), phosphate minerals (Swaine, 1990), and arsenic minerals including orpiment, realgar, and arsenopyrite (Ding et al., 2001). However, occurrences of organically associated arsenic have also been reported in some coals (Kryukova et al., 1985; Goodarzi, 1987; Finkelman et al., 1990; Belkin et al., 1997; Zhao et al., 1998; Zhang et al., 2002). A study

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by Hower et al. (2005a,b) showed that As and Tl in the Pond Creek coal bed, northern Pike and southern Martin counties, Kentucky, occur mainly in Tl–As sulfides. Endemic poisoning caused by domestic arsenic-rich coal combustion is locally very severe in southwestern Guizhou, China. More than 3000 patients in the mountainous region of southwestern Guizhou have been diagnosed with arsenosis (Ding et al., 2001). There are many studies on the high arsenic coals from Guizhou, Southwest China (Dai et al., 2005b; Zheng et al., 1999; Belkin et al., 1998, 1999, 2000; Ding et al., 2001; Finkelman et al., 2002; Zhao et al., 1998). In this paper, on the basis of new data of coal geochemistry and mineralogy, the authors describe the enrichment of arsenic, as well as antimony, mercury, and thallium in a Late Permian coal (anthracite) from Shimenkan, Xingren, Guizhou, Southwest China.

2. Geological setting

Guizhou Province, located in Southwest China (Fig. 1), contains one of the major coal resources of China. Tectonically, western Guizhou Province has a complicated geological setting because of extensive faulting (Zhou et al., 2000). The frequent eruptions of volcanic ashes during the Late Permian age (Chen et al., 2003; Wang, 1996) and epigenetic low-temperature hydrothermal fluids penetrating into coal seams after coal-formation could have led to the geochemical and mineralogical anomalies of coal (Dai et al., 2004,

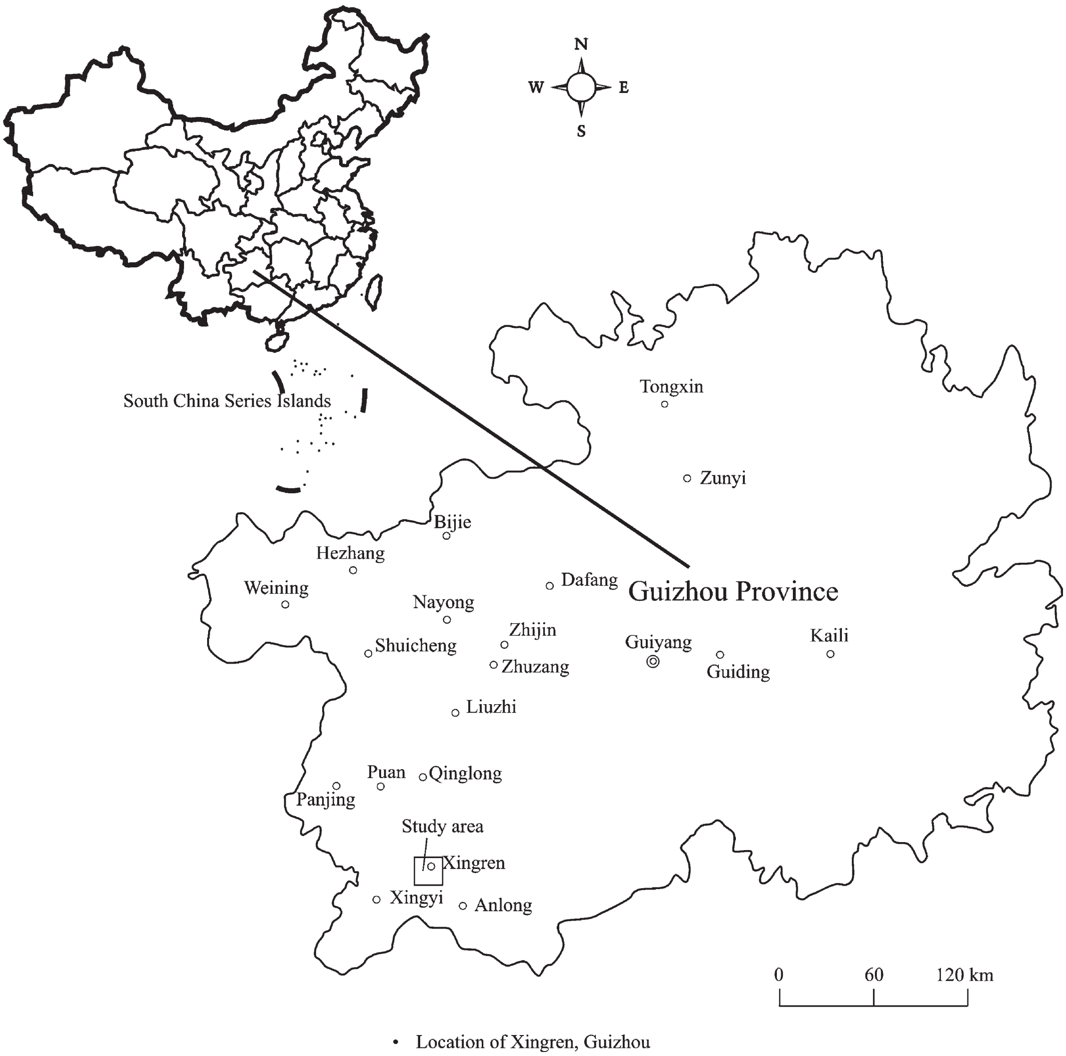

Fig. 1. Location of Xingren, Guizhou, Southwest China.

2005a). Moreover, this area, named the "golden triangle" (He et al., 1993), is enriched with many noble metallic ore deposits, such as gold, antimony, arsenic, mercury, and thallium. The anthracite-rank coals mainly occur in the Late Permian Longtan Formation (P_{2l}), which is made up of an alternating marine facies and terrestrial facies. No igneous rocks are exposed in the immediate vicinity of the study area.

High-arsenic coals are located in Xingren, Xingyi, and Anlong counties of Guizhou (Ding et al., 2001; Ren et al., 1999; Belkin et al., 1999). The area of high-arsenic coal distribution is within the sediment-hosted Au area of Southwest China. Small Au deposits are often found near the high-As coals.

3. Methods of study

Nine coal-seam channel samples from Xingren (including Longchang, Dayakou, Baiwanyao, Xiashan, and Shimenkan Towns; Table 1) of southwestern Guizhou (Fig. 1), were taken from fresh faces in underground mines. Samples XR-M1, XR-M2, and XR-M3 belong to the same bed in different mines of Shimenkan Town, Xingren County. The method of sample collection followed the Chinese Standard for Collecting Channel Samples GB482-1995. The channel sample was cut over an area with 10 cm wide and 10 cm deep, and partings thicker than 3 cm were excluded.

Epoxy-bound pellets were made from the coal samples, crushed and ground to <850 μm and prepared to a final polish with 0.05-μm alumina. Petrologic analysis was performed with oil-immersion, reflected-light optics at a magnification of 500×.

Samples for geochemistry analysis were crushed and ground to less than 200 mesh. X-ray fluorescence spectrometric analysis (XRF) was used to determine the oxides of the major elements, including Si, Al, Ca, K, Na, Fe, Mn, Mg, Ti, and P. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the trace element contents in coal. Mercury was determined by cold-vapor atomic absorption spectrometry (CV-AAS). Selenium and Sb were determined by atomic fluorescence spectrometry (AFS). Fluorine was determined by ion-selective electrode (ISE), and B was determined by inductively coupled-plasma atomic emission spectrometry (ICP-AES).

A scanning electron microscope equipped with an energy-dispersive X-ray spectrometer was used to study the surface characteristics and determine the distribution of elements in coal using an accelerating voltage of 20 kV and a beam current of 10^{-10} A.

4. Results and discussions

4.1. Proximate analysis and petrography of coals from Xingren, Guizhou

Proximate analysis, rank (vitrinite random reflectance, % R_r), and the petrographic compositions of the channel samples from Xingren are given in Table 1.

Compared with petrographic compositions of the Late Permian coals from western Guizhou as studied by Dai (unpublished data), the coals from Xingren have a higher content of inertinite, although the content of vitrinite is higher than that of inertinite in Xingren coals. The study by Dai (unpublished data) showed that the vitrinite content of the Late Permian coals from western Guizhou varies from 46.4% to 82%, with an average of 68.5%. The vitrinite content of the coal bed from Shimenkan (49.3–53.2%) is lower than that of other coals from Xingren, Guizhou (54.4–69.2%), as listed in Table 1.

Table 1
Proximate analysis and petrographic compositions of coals from Xingren, Guizhou, China (%)

Coal seam	Sample location	Proximate analysis						Petrographic compositions									R_r
		Ash_d	VM_{daf}	$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$	V	I	L	Py	Q	CM	Cal	Getc	T-M	
XR-1	Chengde Mine, Longchang Town	13.03	9.65	2.02	1.43	0.05	0.54	58.6	31.3	0	2.3	5.6	2.2	bdl	0	10.1	2.52
XR-2	Xingchang Mine, Longchang Town	11.43	10.51	1.25	0.70	0.07	0.48	56.8	34.6	0	0.3	5.3	2.4	0.6	0	8.6	2.48
XR-3	Dayakou	27.10	9.22	3.54	2.91	0.04	0.59	54.4	22.7	0	2.2	11.6	7.3	1.8	0	22.9	3.41
XR-4	Baiwanyao	25.20	9.85	4.25	3.46	0.08	0.71	55.6	33.7	0	3.1	4.8	2.5	0.3	0	10.7	3.22
XR-5	Fuxingxiang Mine, Xiashan Town	22.33	10.02	3.05	2.48	0.02	0.55	66.9	8.6	0	3.8	11.3	9.4	bdl	0	24.5	2.73
XR-6	Fuxingxiang Mine, Xiashan Town	13.70	9.95	2.22	1.70	0.04	0.48	69.2	16.0	0	4.1	6.2	4.2	0.3	0	14.8	2.72
XR-M1	Shimenkan	36.44	11.52	5.67	4.95	0.10	0.62	49.3	22.3	0	4.3	14.9	9.2	bdl	bdl	28.4	2.82
XR-M2	Shimenkan	32.82	10.81	6.21	5.52	0.12	0.57	51.4	21.4	0	3.8	13.5	9.6	0.3	0	27.2	2.89
XR-M3	Shimenkan	35.15	11.26	5.84	5.08	0.08	0.68	53.2	21.1	0	4.1	12.9	8.7	bdl	0	25.7	2.85

VM, volatile matter; S_t, total sulfur; S_p, sulfide sulfur; S_s, sulfate sulfur; S_o, organic sulfur; V, vitrinite; I, inertinite; L, liptinite; Py, pyrite, Q, quartz; CM, clay minerals; Cal, calcite; Getc, getchellite; T-M, total minerals; R_r, mean random reflectance of vitrinite; d, on a dry base; daf, on a dry and ash-free base; bdl, below the detection limit.

The ash yield of the coal bed from Shimenkan (XR-M1, XR-M2, and XR-M3) is much higher than that of other coals from the study area. The coal bed from Shimenkan is classified as a high-ash coal on the basis of the Chinese Standard GB 15224.1-2004 (coals with ash yields >29% are considered high-ash coal). Samples including XR-1, XR-2, and XR-6 are low-ash coals (ash yield varying from 10.1% to 16%), while XR-3, XR-4, and XR-5 are medium-ash coals (ash yield 16.01–29.00%).

The content of total sulfur in coals from Shimenkan is high, varying from 4.95% to 5.52%. Other coals (samples XR-1 to XR-6) are also enriched in sulfur, reaching the range of medium- and high-sulfur coals. Sulfur in all coals is dominated by pyrite (Table 1).

XRD data and optical microscope observations showed that mineral matter in the Xingren coal is mainly made up of pyrite, quartz, clay minerals, and a trace amount of calcite.

Quartz in Xingren coals is mainly authigenic, although some of detrital terrigenous origin are found in collodetrinite. The authigenic quartz is distributed in various macerals or occurs as cell-fillings.

Clay minerals in Xingren coals are dominated by kaolinite. Two origins of kaolinite in Shimenkan coals can be observed, epigenetic and detrital. Epigenetic kaolinite in Shimenkan coals occurs as fracture-fillings (Figs. 2 and 3), and the detrital materials are distributed along beddings (Figs. 3 and 4). Clay minerals of other Xingren coals are mainly of terrigenous origin.

Pyrite in the coal from Shimenkan occurs as framboidal, isolated euhedral, and nodular forms (Fig. 4), indicating that pyrite in this coal is being of syngenetic or early diagenetic origin (Kostova et al., 1996; Chou, 1997; Dai et al., 2003). However, no fracture- or cleat-filling pyrite was observed in the coal bed of Shimenkan, although fractures are well developed in this coal. Optical microscopy observations showed that pyrite in other coals is mainly of syngenetic or early diagenetic origin, although a trace amount of fracture-fillings occurred in XR-4, XR-5, and XR-6.

Sample XR-3 is enriched in calcite (1.8%), occurring as fracture-fillings in coal. Calcite is low or below the detection limit in other coal samples.

It should be noted that a trace amount of getchellite ($AsSbS_3$) in sample XR-M1 was determined by XRD and under SEM–EDX, but was smaller than the optical detection limit. However, no getchellite was observed in other samples from Xingren, Guizhou, although XR-M1, XR-M2, and XR-M3 were collected from the same coal seam at different mines, and the locations of the three samples distribute within an area less than 2 km^2. The fracture-filling kaolinite in coals from Shimenkan is probably derived from the epigenetic Si- and Al-rich hydrothermal fluid. The idiomorphic morphology of the crystals of kaolinite in fracture-fillings indicates that it

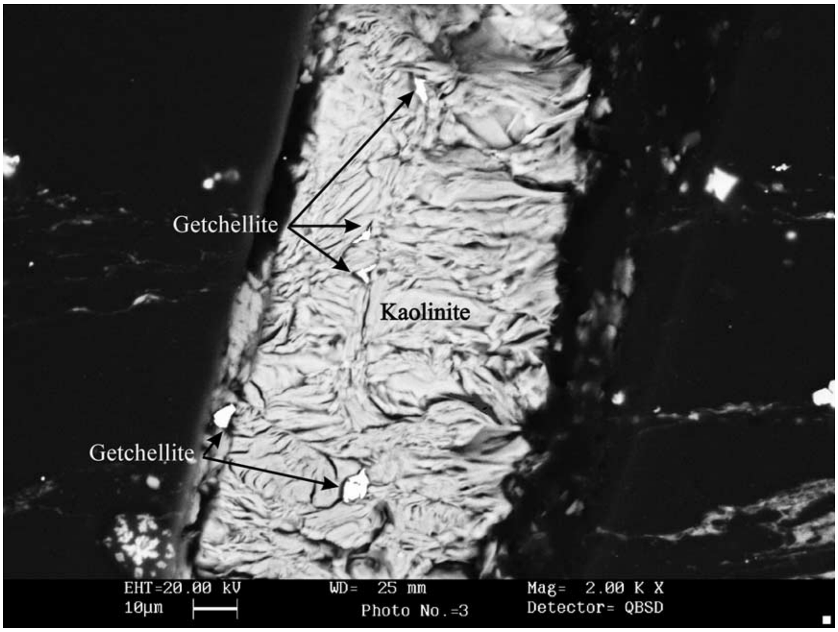

Fig. 2. Fracture-filling kaolinite and getchellite in sample XR-M1 of Shimenkan, Xingren, southwestern Guizhou (back-scattering image).

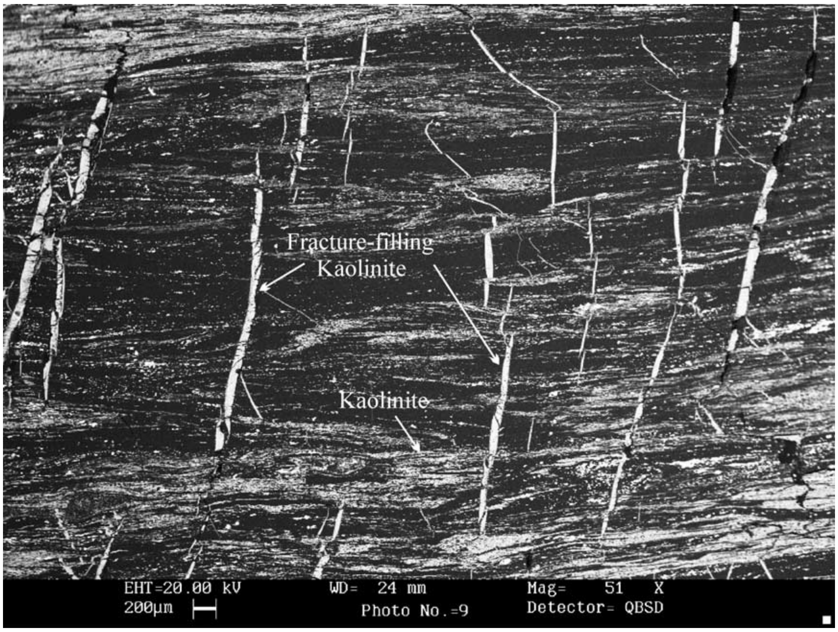

Fig. 3. Fracture-filling epigenetic kaolinite, and syngenetic kaolinite of terrigenous origin distributing along beddings in sample XR-M1 (back-scattering image).

was precipitated from solutions rather than from fragments of wall rocks outside of the coal. Occurrence of getchellite exclusively in the fracture-filling kaolinite suggests that epigenetic getchellite is carried in from outside of the coal by an Al- and Si-rich fluid.

4.2. Geochemistry of coals from Xingren, Guizhou

4.2.1. Major elements

Concentrations of major and trace elements in coals from Xingren, as compared with the usual range of

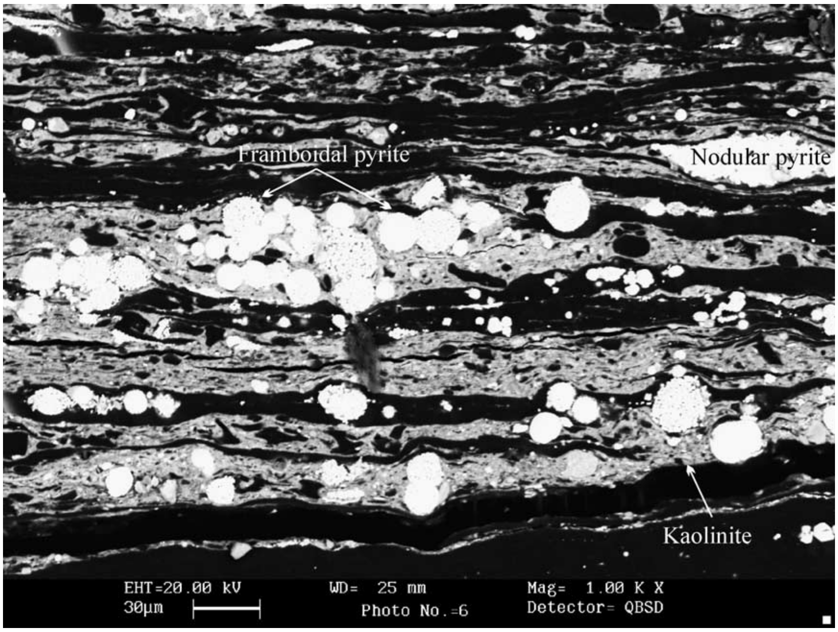

Fig. 4. Framboidal and nodular pyrites and syngenetic kaolinite in sample XR-M1 (back-scattering image).

Table 2
Concentrations of major and trace elements in coals from Xingren, Guizhou, as compared with the ordinary Late Permian coals from western Guizhou Province (in μg/g unless otherwise indicated as wt.%)

Element	Xingren, Guizhou									Western Guizhou [a]			
	XR-1	XR-2	XR-3	XR-4	XR-5	XR-6	XR-M1	XR-M2	XR-M3	Sample No.	Min	Max	AM
Al_2O_3 (%)	3.73	3.49	7.39	4.52	6.8	4.18	12.67	15.52	15.21	50	2.44	25.9	4.92
SiO_2 (%)	7.24	5.12	10.59	6.23	10.97	6.19	17.02	18.99	15.69	50	3.03	34.89	9.14
CaO (%)	0.28	1.9	3.21	0.85	0.19	0.5	0.36	0.72	0.62	50	0.05	12.0	1.77
K_2O (%)	0.31	0.33	1.12	0.46	0.32	0.27	0.34	0.32	0.22	50	0.05	1.46	0.25
TiO_2 (%)	0.34	0.14	0.68	0.34	0.59	0.49	0.45	0.36	0.54	50	0.14	0.78	0.36
Fe_2O_3 (%)	1.89	0.83	4.26	3.58	3.52	2.44	4.88	3.54	4.51	50	0.16	6.65	1.88
MgO (%)	0.1	0.09	0.55	0.24	0.24	0.15	0.33	0.34	0.3	50	0.04	1.01	0.21
Na_2O (%)	0.05	0.05	0.09	0.07	0.43	0.19	0.06	0.05	0.06	50	0.05	1.13	0.21
MnO (%)	0.004	0.014	0.093	0.018	0.022	0.015	0.006	0.006	0.007	50	bdl	0.121	0.027
P_2O_5 (%)	0.023	0.166	0.03	0.024	0.072	0.028	0.089	0.102	0.111	50	0.01	0.166	0.036
As	4.0	5.8	10.5	2.3	5.7	2.8	2226	12.6	9.5	39	0.30	10.45	3.9
B	62	48	74	55	68	88	101	68	79	8	42.91	72.66	54.64
Ba	81	73	273	70	109	49	163	192	184	64	10.6	813.2	119.38
Be	0.6	0.5	1.0	0.9	2.1	1.9	2.12	2.1	2.7	62	0.21	12.47	2.19
Bi	0.2	0.2	0.3	0.5	0.3	0.2	0.5	11	0.9	64	0.15	2.05	0.47
Cd	0.1	0.1	0.2	0.2	1.1	0.3	0.3	0.3	0.2	48	0.02	8.19	0.40
Ce	27	33	43	32	70	42	95	60	86	48	10.65	459	59.58
Co	2.4	1.8	6.1	5.4	8.8	4.9	5.6	4.1	2.2	64	0.39	118.6	13.59
Cr	33	13	19	36	64	25	53.3	50	48	57	0.02	139.3	31.91
Cs	0.5	0.4	2.5	2.1	2.3	2.2	3.2	0.9	0.5	48	0.08	3.79	0.84
Cu	58	41	30	36	97	33	122	114	95	64	7.23	369.9	61.12
Dy	2.1	3.6	3.2	3.5	3.8	3.6	5.8	3.4	7.8	48	0.99	12.1	3.36
Er	1.2	2.1	1.7	2.0	2.5	2.2	3.2	1.7	4.4	48	0.52	6.48	1.84
Eu	0.4	0.4	0.9	0.3	0.8	0.6	2.1	1.0	1.3	48	0.24	3.40	0.77
F	52	111	144	89	65	97	85	88	114	50	16.6	500	83.1
Ga	5.7	5.5	11	8.8	16	9.9	11	14	13	64	0.38	99.5	13.05
Gd	2.4	3.5	3.8	3.4	4.3	3.7	8.3	4.3	7.6	48	1.27	20.30	4.66
Hf	1.2	1.3	2.3	1.2	4.9	2.6	5.0	5.1	7.2	39	0.51	55.2	4.25
Hg	0.1	0.11	0.13	0.24	0.22	0.15	12.1	0.19	0.54	33	0.031	0.217	0.09
Ho	0.4	0.7	0.6	0.6	0.8	0.8	1.1	0.7	1.5	48	0.18	2.55	0.67
La	13	17	20	16	37	20	45	29	45	48	5.55	350	32.24
Li	70	58	63	92	111	86	88	82	174	48	0.1	151.6	49.81
Lu	0.2	0.3	0.2	0.3	0.4	0.3	0.4	0.2	0.5	48	0.06	3.00	0.31
Mo	1.0	0.7	16	24	77	44	12	4.8	2.5	48	0.10	76.58	8.24
Nb	7.2	8.5	14	13	34	30	31	28	24	64	2.97	79.9	14.34
Nd	11	14	19	13	26	18	47	24	35	48	1.91	169	23.28
Ni	12	8.1	22	20	44	24	28	13	17	64	4	160	36.74
Pb	9.5	10	9.4	14	10	6.8	12	8.2	10	64	1.26	184.7	14.73
Pr	3.0	3.7	4.9	3.6	7.1	4.8	12	7	10	48	1.24	44	7.87
Rb	7.6	8.2	28	23	9.1	8.0	25	8.1	7.4	39	1.12	78.2	13.03
Sb	0.4	0.3	0.9	8.6	1.0	0.4	3860	0.6	13	44	0.05	6.06	0.97
Sc	3.4	3.3	7.2	4.9	4.1	4.9	15	9.2	8.4	64	1.8	22.74	6.84
Se	0.8	0.9	1.8	1.1	3.8	1.7	1.2	1.1	0.8	48	0.10	6.02	1.65
Sm	2.5	3.2	3.8	3.1	4.8	3.3	9.3	4.6	7.2	48	1.21	27	4.35
Sn	9.6	5.3	9.2	10	7.9	5.9	12	10	11	58	0.05	25.93	5.92
Sr	66	121	231	156	243	100	254	211	304	64	22.12	895.7	134.7
Ta	0.3	0.4	1.1	2.1	3.5	1.0	4.7	3.2	4.1	64	0.06	6.45	0.84
Tb	0.4	0.6	0.6	0.5	0.6	0.6	1.1	0.6	1.3	48	0.18	3.70	0.64
Th	4.4	4.5	5.4	4.7	7.0	4.7	9.2	16	20	48	1.99	47.5	6.52
Tl	0.04	0.02	0.19	0.4	0.51	0.3	7.5	0.7	0.5	48	0.01	0.51	0.11
Tm	0.2	0.3	0.2	0.2	0.4	0.3	0.4	0.2	0.6	48	0.07	1.01	0.26
U	1.4	1.5	14	8.2	77	29	4.5	3.9	5.4	48	0.10	176.2	13.65
V	29	22	94	58	249	116	154	119	126	64	18.01	574.4	123.42

Table 2 (*continued*)

Element	Xingren, Guizhou									Western Guizhou [a]			
	XR-1	XR-2	XR-3	XR-4	XR-5	XR-6	XR-M1	XR-M2	XR-M3	Sample No.	Min	Max	AM
W	0.3	0.3	0.6	1.2	1.5	0.7	1.3	1.8	2.2	64	0.11	4.01	0.93
Y	14	23	20	22	25	26	34	20	45	64	6.0	97	24
Yb	1.1	1.8	1.5	1.7	2.4	1.9	3.0	1.6	4.0	48	0.43	17.2	1.98
Zn	26	21	19	62	90	28	87	64	81	64	2.01	561.4	55.1
Zr	74	67	144	222	329	196	322	337	412	64	23.93	1852	223.96

Min, minimum; Max, maximum; AM, arithmetic mean.
[a] From Dai et al. (2005b).

concentrations found for the Late Permian coals from western Guizhou are listed in Table 2.

Concentrations of major elements are in accordance with mineral compositions in coals as described above.

The concentration of SiO_2 is higher than that of Al_2O_3 in all coals, probably due to the occurrence of significant amounts of quartz, in addition to kaolinite. Particularly, SiO_2 and Al_2O_3 in the coal bed from Shimenkan (XR-M1, XR-M2, and XR-M3) are much higher than those of other Xingren coals and the usual range of concentrations found for the Late Permian coals from western Guizhou, as reported by Dai et al. (2005b).

Concentrations of CaO, K_2O, MnO, and MgO in XR-3 are higher than those of the ordinary Late Permian coals from western Guizhou. However, concentrations of these elements in other coals from Xingren are either lower than or close to the usual range of concentrations found for the coals from western Guizhou.

With exceptions of XR-1 and XR-2, Fe_2O_3 in coals from Xingren is higher than the usual concentration range for coals from western Guizhou. The relative high Fe content of these coals from Xingren is attributed to high pyrite in coal.

4.2.2. Trace elements

Four trace elements including As, Hg, Sb, and Tl in sample XR-M1 from Shimenkan, Xingren, particularly received much attention, because they are significantly enriched, as high as 2226 μg/g, 12.1 μg/g, 3860 μg/g, and 7.5 μg/g, respectively (Table 2), compared with their concentrations in ordinary coals from China and USA as estimated by Ren (unpublished data) and Finkelman (1993). Concentrations of As, Hg, Sb, and Tl in ordinary coals of China are 3.75 μg/g (3390 samples), 0.19 μg/g (1401 samples), 0.90 μg/g (506 samples), and 0.47 μg/g (969 samples), respectively (Ren, unpublished data), and they are 24 μg/g, 0.17 μg/g, 1.2 μg/g, and 1.2 μg/g in US coals, respectively (Finkelman, 1993). The remaining trace elements are not enriched in coals from Xingren, Guizhou.

Table 3
Semiquantitative SEM–EDX results for getchellite, syngenetic pyrite, syngenetic kaolinite, fracture-filling kaolinite, and organic matter in XR-M1 (getchellite, syngenetic pyrite, syngenetic kaolinite, fracture-filling kaolinite, and organic matter are based on 12, 18, 9, 15, and 17 test spots, respectively) (in wt.%)

Test aim		Na	Mg	Al	Si	S	K	Ca	Mn	Fe	Ti	Sb	As	Hg	Tl
Getchellite	Min	bdl	bdl	0.02	0.05	35.6	bdl	bdl	bdl	0.01	bdl	28.5	20.6	0.01	bdl
	Max	bdl	bdl	0.14	0.12	42.3	bdl	bdl	bdl	0.08	bdl	33.1	25.3	0.26	0.18
	Mean	bdl	bdl	0.05	0.07	38.7	bdl	bdl	bdl	0.04	bdl	30.7	22.1	0.15	0.08
Pyrite	Min	bdl	bdl	0.08	0.32	46.6	bdl	0.05	bdl	42.1	bdl	bdl	bdl	bdl	bdl
	Max	bdl	bdl	0.21	1.57	55.1	bdl	1.24	bdl	48.5	bdl	bdl	0.02	bdl	bdl
	Mean	bdl	bdl	0.12	1.16	50.2	bdl	0.84	bdl	44.8	bdl	bdl	bdl	bdl	bdl
Syngenetic kaolinite	Min	1.21	0.84	10.5	16.8	bdl	0.17	1.58	bdl	2.12	bdl	bdl	bdl	bdl	bdl
	Max	3.26	1.82	21.6	22.5	0.16	0.33	4.85	bdl	3.56	0.05	bdl	bdl	bdl	bdl
	Mean	2.41	1.22	18.5	20.2	0.08	0.24	3.21	bdl	2.34	0.02	bdl	bdl	bdl	bdl
Fracture-filling kaolinite	Min	0.85	0.35	13.5	15.9	0.02	0.08	0.58	bdl	1.58	bdl	bdl	bdl	bdl	bdl
	Max	2.54	1.79	24.5	24.6	0.15	0.25	3.25	0.07	3.33	bdl	0.05	0.03	bdl	bdl
	Mean	1.87	1.15	20.2	21.5	0.15	0.18	2.54	bdl	2.21	bdl	0.02	bdl	bdl	bdl
Organic matter	Min	bdl	0.19	0.19	0.45	0.32	bdl	0.07	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	Max	0.2	0.38	0.32	1.84	0.89	0.08	1.24	bdl	0.95	0.08	bdl	0.03	bdl	bdl
	Mean	0.04	0.15	0.21	1.15	0.68	0.03	0.6	bdl	0.38	0.02	bdl	bdl	bdl	bdl

bdl, below detection limit.

Although XR-M1, XR-M2, and XR-M3 are from the same bed of three different mines in a restricted area, arsenic, Hg, Sb, and Tl are not enriched in XR-M2 and XR-M3, in sharp contrast to that of XR-M1. The content of the four elements varies greatly in the same bed, and this is in accordance with the study by Ding et al. (2001). Thus, the enrichment of As, Hg, Sb, and Tl in coals from Xingren is not ubiquitous, but very local. A study by Dai et al. (2005b) also indicates that high-As coals from Xingren County, southwestern Guizhou, are very restricted, and the high-As coal reservoir of southwestern Guizhou is extraordinary small, although western Guizhou Province is the area of endemic arsenosis related to coal combustion as reported by some authors (Zheng et al., 1999; Belkin et al., 1997; Finkelman et al., 2002).

Previous reports of origins and modes of occurrence of high arsenic in coals from southwestern Guizhou indicate that the high arsenic in coal is mainly attributed to pyrite, arsenopyrite, arsenic-bearing sulfide (realgar?), Fe–As oxide, K–Fe sulfate, scorodite, and arsenic-bearing clays (Belkin et al., 1998; Zheng et al., 1999; Ding et al., 2001; Tang and Huang, 2004; Dai et al., 2005b). Occurrences of organically associated As have also been reported in Guizhou coal (Zhao et al., 1998).

SEM–EDX results show that As, Sb, Hg, and Tl in sample XR-M1 mainly occur in getchellite (Table 3). Arsenic in getchellite varies from 20.6% to 25.3%, with an average of 22.1% (Table 3). The average content of Sb in getchellite is 30.7%, and minor antimony occurs in fracture-filling kaolinite, varying from below detection limit to 0.05%, with an average of 0.02%. Mercury and Tl also mainly distribute in getchellite, with averages of 0.15% and 0.08%, respectively. These four elements are below detection limit in pyrite, syngenetic kaolinite, and organic matter. Thus, the high content of As, Sb, Hg, and Tl is attributed to getchellite in coal.

Tang and Huang (2004) suggested that high-arsenic coals from southwestern Guizhou are predominantly attributed to hydrothermal solutions and generally occur near Carlin type gold deposits. Ding et al. (2001) revealed that the concentrations of As, Sb, Au, and Hg are high in both the high As coals and the Au deposits in southwestern Guizhou, indicating a genetic link. Zhou and Ren (1992) found high As coals in eastern Yunnan, which is adjacent to southwestern Guizhou and also in part of the Au-impregnated area of Southwest China.

To the best of our knowledge, getchellite has not been previously reported in coal (Ward, 2002; Bouška et al., 2000; Tang and Huang, 2004). Getchellite is a typical mineral of low-temperature hydrothermal fluid, and often occurred in As–Au deposits (Wang et al., 1982). In XR-M1 sample of Xingren, Guizhou, getchellite occurs in the epigenetic veined kaolinite probably of hydrothermal origin as described above (Fig. 2). It should be concluded that high As, Sb, Hg, and Tl is derived from low-temperature hydrothermal fluids and probably related to Au mineralization.

5. Conclusions

Arsenic, Hg, Sb, and Tl are significantly enriched in an anthracite (sample XR-M1) from Shimenkan, Xingren of southwestern Guizhou. The content of the four elements is as high as 2226 μg/g, 12.1 μg/g, 3860 μg/g, and 7.5 μg/g, respectively. However, they sharply decrease to normal abundance of elements of the same bed within a restricted area as small as <2 km^2. The predominant carrier of As, Hg, Sb, and Tl is epigenetic getchellite, occurs in vein kaolinite of hydrothermal origin, rather than syngenetic pyrite in coal. Arsenic, Sb, Hg, and Tl in sample XR-M1 are derived from an As- and Sb-rich low-temperature hydrothermal fluids, and are probably related to Au mineralization.

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