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Arsenic and Fluorine Contents and Distribution Patterns of Early Paleozoic Stonelike Coal in the Daba Fold Zone and Yangtze Plate, China

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ABSTRACT: Stonelike coal (SLC) is combustible black shale with low caloric value and a high degree of coalification, which is hosted in the early Paleozoic strata. The SLC is widely used for domestic purposes in the Daba fold zone in southern Shaanxi Province, China. Forty three channel samples of stonelike coal (SLC) were collected from the Daba fold zone to determine their elemental content. The results show that the contents of F, As, and Se in the Daba SLC are about 10−50 times more than those in the coals from the Permo-Carboniferous or later stages. The content of As varies from 8 to 277 mg/kg, and its average in the carbonate-hosted SLC of the Cambrian, mainly distributed in the southern Ankang district, is 112 mg/kg, while the average in the igneous-rock-hosted SLC of the Silurian, mainly distributed in the north Ankang district, is 78 mg/kg. The content of Se ranges from 1 to 62 mg/kg, and its average in the carbonate-hosted SLC is 29.21 mg/kg, while the average in the igneous-rock-hosted SLC is 9.91 mg/kg. The content of F ranges from 42 to 4532 mg/kg, with most samples ranging 600−2000 mg/kg. The average content of Hg is 0.66 mg/kg. Most of the SLC is enriched in As, Se, F, and Hg. The contents of F and As in the Daba SLC are about 10−50-times more than those in the coals of Permo-Carboniferous or later stages. As and Se are mainly enriched in the lower Cambrian carbonate-hosted SLC, and F is mainly enriched in the igneous-rock-hosted SLC of Silurian. The contents of As and F are comparatively lower in the carbonate-hosted SLC of the middle and upper Cambrian. The SLC of the middle and upper Cambrian is recommended for indoor use by local residents. It is suggested that local residents do not use the lower Cambrian SLC and igneous-rock-hosted SLC of Silurian for heating and cooking indoors as far as possible.

1. INTRODUCTION

The Daba fold zone of South Qinling Mountains in central China is the main producing area of anthracite rank "stonelike coal" (SLC) (Figure 1) and has over 1000 Mt reserves. The coals usually occur as discontinuous and irregularly lenticular or podiform bodies within the trachytic agglomerate or as sandwiched in fault zones and inserted into the top of fold axes. All are hosted in late Neoproterozoic to lower Paleozoic strata, mainly hosted in Cambrian carbonate and Silurian trachytic agglomerate. Most of the SLCs have no distinct stratigraphic position nor can they be correlated laterally.

The term stonelike coal was sanctioned by the China Natural Science Terms Examination and Approval Committee (CTC) in 1994. SLC was defined as "combustible shale with low heating value and high degree of coalification derived from the remains of thallophyta during the action of paludification and coalification in shallow seas, lagoons, and gulfs in the early Paleozoic".[1]

The Daba fold zone [geotectonic unit] of the South Qinling Mountains consists of a series of deep fault zones that separate it from the Yangtze Plate (Figure 2). It is located in Ziyang, Langao, Hanbing, and Pingli counties of the Ankang district in the southern Shaanxi Province (Daba area), adjacent to Chongqing City and Henan Province in central China (Figure 1).[2−5] The Daba fold zone is the eastern part of the well-known tectonic unit in central China, the Kunlun−Qinling fold zone,[2−5] and is also the (current) geographical boundary between North China and South China.

In the Daba fold zone, only the lower Paleozoic strata are distributed and well developed, lacking the later Paleozoic and late-age strata as well as humic coal. The Daba area is an impoverished area in China. The communication conditions are very poor. Because most places have no highway access, the transport of Permo-Carboniferous and later age coals is very difficult and expensive. So, the Daba SLC is the main source of energy in the Daba area where the local residents (3 Ma populations) have to use it for heating and cooking.

The Daba area, Ankang district, residents have used this SLC as a cooking fuel and as a source of winter heat for thousands of years,[5] causing considerable human health issues. The rate of occurrence of dental fluorosis and skeletal fluorosis is about 60% in the Ankang district in the southern Shaanxi Province. Endemic fluorosis is most serious where the citizens use the SLC for warmth and cooking.[6−10]

Endemic arsenism accompanied by fluorosis, linked to the burning of SLC, is distributed throughout all of the Ankang district and is more serious in the southern Daba area (South Ziyang County and South Langao County in the South Ankang district).[6,7] The prevalence rate of endemic arsenism from SLC burning reached 19.26% in all of the Ankang district in 2004;[6] in a study by Bai et al. in 2004,[6] where 58256 participants were randomly selected, 11219 were found with arsenism, incidences of which increased with age and were higher for males than for females.[6] Most of the patients suffered from mild arsenisms, mainly with skin depigmentation or hyperpigmentation, and the

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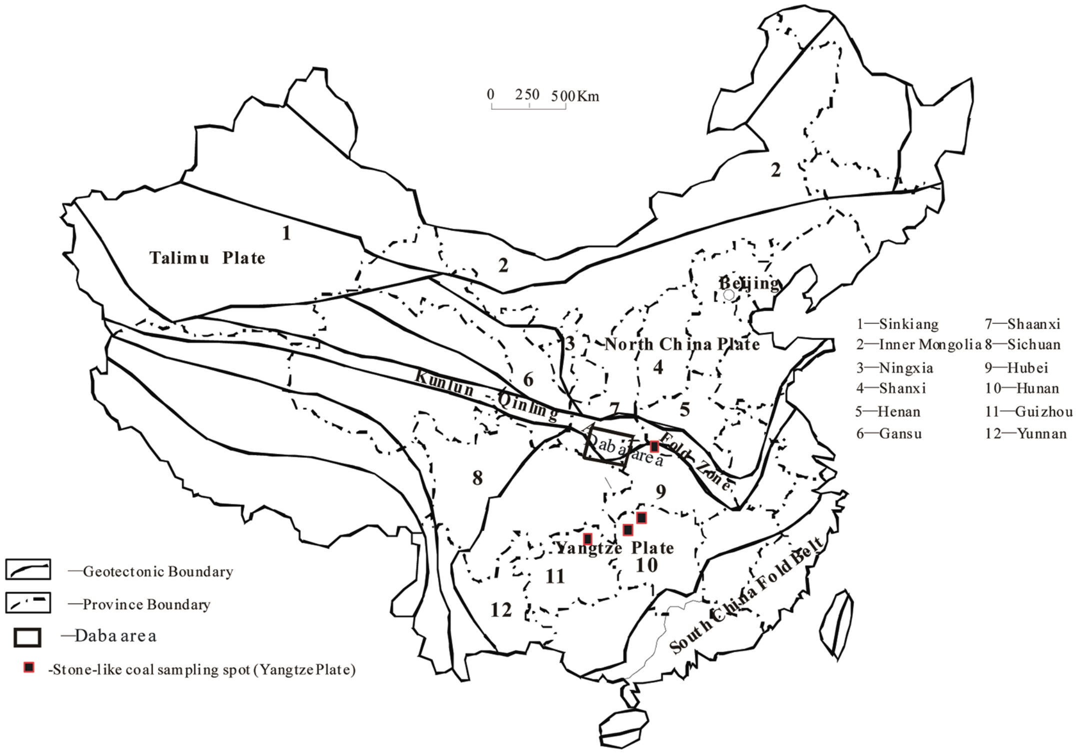

Figure 1. Map showing the study area and the sampling localities for lower Paleozoic SLC in the Daba fold zone (Daba area) in the South Qinling Mountains and the tectonic units of the Yangtze Plate and the North China Plate.

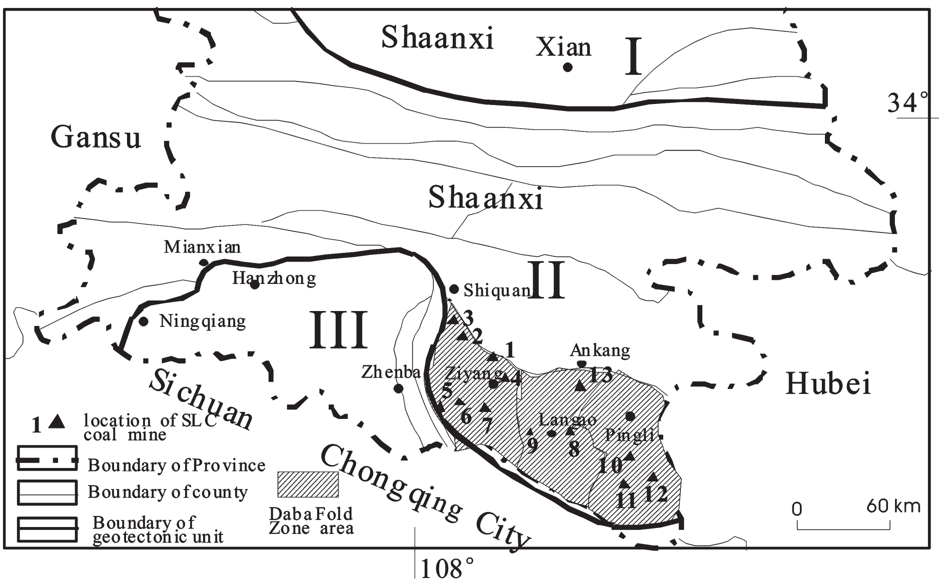

Figure 2. Lower Paleozoic SLC sampling locations in the in Daba fold zone and the geotectonic position of the Daba fold zone. Map key: I, North China plate; II, Kunlun−Qinling fold zone; III, Yangtze Plate; 1, Haoping Coal Mine, Ziyang, Shaanxi; 2, Shuangan Coal Mine, Ziyang, Shaanxi; 3, Hanwang Coal Mine, Ziyang, Shaanxi; 4, Donghe Coal Mine, Ziyang, Shaanxi; 5, Lujiaping Coal Mine, Ziyang, Shaanxi; 6, Jianzhuba Coal Mine, Ziyang, Shaanxi; 7, Lixin Coal Mine, Langao, Shaanxi; 8, Xiaozhen Coal Mine, Langao, Shaanxi; 9, Menshiling Coal Mine, Langao, Shaanxi; 10, Jiutai Coal Mine, Pingli, Shaanxi; 11, Gu-Baxian Coal Mine, Pingli, Shaanxi; 12, LX-Baxian Coal Mine, Pingli, Shaanxi; 13, Bashan Coal Mine, Hanbing of Ankang, Shaanxi.

number of patients with skin depigmentation was larger than that with hyperpigmentation.[6]

The illness rate of arsenic poisoning was 10.7%, which increased with age and was higher for males than for females in Haoping, North Ziyang, and Shimen, North Langao of the Ankang district in 2000.[7] In a study by Shi et al. in 2000,[7] where 439 participants were randomly selected, 47 were found with arsenism. Most of patients suffered from mild arsenism, mainly with skin depigmentation.[7]

A series of epidemiological investigations have confirmed that these health issues result from burning fluorine- and arsenic-rich

SLCs, and they have mentioned that the As and F concentrations of Daba SLC varied greatly in their investigations.[6−11] Chen et al.[10] reported that the average F content of 38 SLC samples collected from resident homes in Ankang was about 809.60 mg/kg, varying from 197.40 to 4688 mg/kg. Bai et al.[6] reported that the F content of Daba SLC from 20 SLC samples collected from resident homes was 3.76−715 mg/kg and that the As content from the 20 SLC samples ranged from 26.12 to 97.36 mg/kg. Luo et al.[12] synoptically summarized the contents and distribution patterns of the trace elements Ag, As, Be, Cd, Cr, Cu, F, Ga, Ge, Mn, Mo, Ni, Pb, Se, Sr, Ti, V, and Zn of lower Paleozoic SLC in South Qinling Mountain region, and they reported the F content of Daba SLC to be 870−1400 mg/kg, the As content to be from 5 to 60 mg/kg, and the Se content to be from 10 to 50 mg/kg. However, only 34 lump samples were collected, and the element (including As, Se, and Hg) contents of most of those SLC samples were measured by a semiquantitative spectrometric method during 1991−1995. Some of those SLC samples were randomly collected from resident homes.[12] So, until today, there has not been a systematic study of the As, F, or other harmful elements distribution patterns of the Daba SLC. The As, F, and Hg contents and distribution patterns of the Daba SLC still remain unclear. Why do the F and As concentrations of the Daba SLC vary so greatly? Where is the high F and As SLC distributed, and what is the distribution of low F and As SLC ? What are the differences in some aspects of SLC, such as the geological age and the geological occurrence?

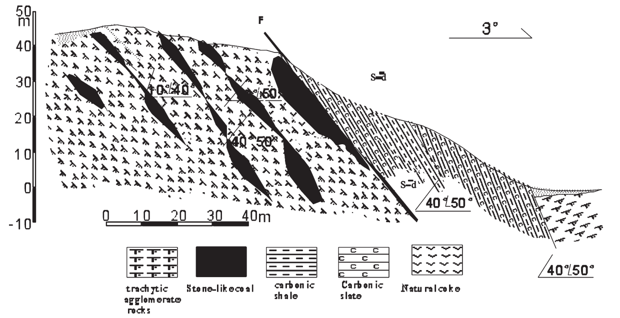

Figure 3. Lenticular SLC bodies enveloped in Silurian trachytic agglomerate rocks in the Haoping Coal Mine of Ziyang County, Shaanxi Province.

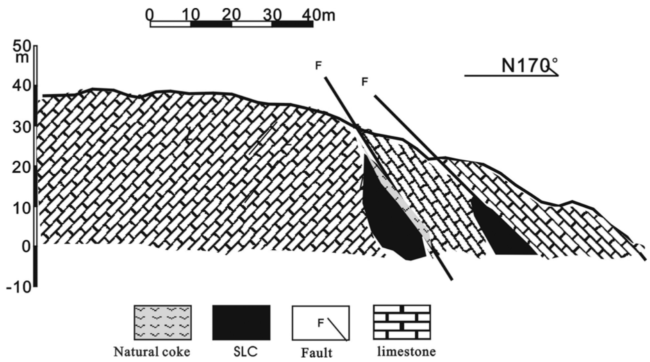

Figure 4. Measured section showing SLC sandwiched in the top of the thrust fold axes associated with thrust faulting in upper the Cambrian limestone at the Tiefu Coal Mine of Ziyang County, Shaanxi Province.

Further study on the composition, especially of As and F contents, of the Daba SLC in the South Qinling Mountains is needed. In this study, about 40 SLC channel samples were collected from 12 SLC mines from the Daba fold zone (Figure 2) and six SLC samples from the lower Cambrian from four sites in the Yangtze Platform were sampled (channel samples) (Figure 1) by our research group, mainly after 2000. The As, Se, and F contents and distribution patterns of the SLC of the early Paleozoic in the Daba fold zone of the South Qinling Mountains are studied.

2. SAMPLING AND ANALYTICAL METHODS

2.1. Samples. The SLC samples used for this paper are channel samples collected according to GB 482-1995(GB 482, 1995)[14] from 12 large SLC mines (43 channel samples) in the Daba area (Figure 2) and four large SLC mines (six channel

Table 1. Content of Major Elements of Igneous-Rock-Hosted SLC of Silurian and Their Typical Surrounding Rocks in Daba Fold Zone, Southern Shaanxi (%)

	age[a]	ash	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
HP-1#′ contact rock[b]	S[c]	59.58	3.69	25.29	6.48	0.38	1.37	0.38	0.73	0.34	18.12	0.11
HP-1#′ contact rock	S	86.01	3.46	16.92	2.23	1.09	0.35	0.37	1.41	1.25	60.81	0.2
HP-1# SLC	S	45.41	5.12	3.96	0.95	2.1	1.62	0	0.88	0.12	29.17	0.37
HP-1# SLC	S	46.09	3.99	2.77	1.47	1.67	1.86	0	0.65	0.25	32.62	0.34
HP-1# trachytic agglomerate	S	86.89	14.45	1.33	1.74	4.02	1.29	0.06	5.39	0.2	55.34	1.63
HP-3# SLC	S	44.25	4.04	1.24	1.18	1.63	1.63	0.11	0.58	0.18	31.13	0.3
HP-4# SLC	S	44.31	3.92	1.22	2.03	1.67	1.9	0.01	0.58	0.24	30.66	0.33
HP-1# natural coke	S	10.48	0.82	2.93	0.01	0.41	0.56	0.01	0.12	0.11	4.54	0.2
DH-1# natural coke[d]	S	17.69	0.53	1.21	0.96	0.17	0.23	0.13	0.03	0.20	13.61	0.02
DH 1#SLC- 2*	S	51.26	4.42	4.35	5.41	1.24	3.55	0.10	0.10	0.28	30.35	0.40
DH 3−1 trachytic agglomerate	S	91.62	12.40	5.12	5.33	3.10	2.78	0.10	1.88	0.65	59.39	0.30
DH 3−2 trachytic agglomerate	S	91.62	15.91	0.93	3.39	3.87	0.72	0.22	6.31	0.21	65.22	1.33
AB- SLC[e]	S	57.43	5.65	3.57	2.82	1.81	1.30	0.12	0.43	0.46	40.94	0.33
HP- SLC	S	40.25	3.48	2.69	2.01	2.02	1.95	0.02	0.12	0.46	27.21	0.30
HP- SLC	S	40.22	3.56	2.84	1.88	2.00	1.80	0.02	0.10	0.45	27.29	0.28
HP-SLC-A17	S	48.42	2.86	2.58	3.49	1.45	1.71	0.04	0.13	0.56	33.13	0.13
HW-SLC-20[f]	S	71.45	2.57	1.78	2.83	2.44	1.09	0.09	0.31	0.27	49.74	0.28

[a] Age, show the age of strata that the SLC hosted in. [b] HP, Haoping Coal Mine, Ziyang. [c] S, Silurian Period. [d] DH, Donghe Coal Mine, Ziyang. [e] AB, Bashan Coal Mine, Hanbing. [f] HW, Hanwang Coal Mine, Ziyang.

Table 2. Contents of Major Elements in SLC of the Cambrian and the Ordovician in Daba Fold Zone, Southern Shaanxi (%)

	age[a]	ash	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
BX-SLC-LM1[b]	Є$_3$-O$_1$	41.14	4.74	3.4	2.35	1.96	2.3	0.03	0.39	0.47	25.08	0.42
GU-SLC-LM[c]	Є$_3$-O$_1$	40.88	5.1	2.17	2.38	1.68	1.55	0.06	0.22	0.28	27.17	0.28
XZ-SLC-DD[d]	Є$_3$[e]	48.05	5.75	3.12	2.45	1.44	2	0.1	0.35	0.38	32.12	0.35
XZ-SLC-HG	Є$_3$	49.2	7.01	1.54	3.41	1.68	3.71	0.02	0.07	0.64	30.52	0.6
JT-SLC-JG2-1[f]	Є$_3$	29.24	2.73	1.67	1.58	1.4	0.88	0.02	0.11	0.4	20.2	0.26
JT-SLC-IG2	Є$_3$	29.94	0.48	0.32	0.24	0.18	0.21	0	0.03	0.06	28.37	0.04
TF-SLC-A10	Є$_2$[g]	17.73	0.05	5.26	0.1	0.35	3.82	0.01	0.01	2.13	5.9	0.01
TF-SLC-A8[h]	Є$_2$	44.93	1.74	3.85	0.63	0.84	2.68	0.02	0.44	0.21	29.29	0.12
JT-SLC-JGd	Є$_1$[i]	23.92	1.85	5.46	1.32	0.96	1.46	0.02	0.16	0.31	12.26	0.14
XZ-SLC-XH	Є$_1$	28.05	3.38	2.04	2.08	1.84	1.06	0.01	0.08	0.62	16.42	0.51
JT-SLC-63	Є$_1$	50.29	4.41	5.44	2.84	1.67	2.89	0.03	0.94	2.4	30.57	0.41
LX-SLC-56[j]	Є$_1$	41.47	3.82	1.65	2.14	1.47	1.38	0.02	0.52	0.43	28.33	0.36
LX-SLC-57	Є$_1$	41.48	4.37	2.03	2.03	1.42	1.43	0.02	0.05	0.29	28.19	0.35
LX-SLC-58	Є$_1$	42.91	4.68	2.74	2.88	1.51	1.63	0.03	0.05	0.56	30.7	0.36
LU -SLC-32[k]	Є$_1$	59.74	5.05	7. 48	2.03	1.15	3.12	0.21	0.02	3.99	34.11	0.63
TF-natural coke	Є$_3$	11.80	0	0.01	0	0	0	0	0	0	11.56	0.
					Carbonaceous Shale SLC in Daba Fold Zone							
LU-SLC-B39	Є$_1$	80.68	5.35	0.07	5.80	2.06	0.57	0.09	0.21	0.03	62.72	0.61
LU-SLC-B33	Є$_1$	82.06	5.11	0.06	6.43	1.34	0.30	0.04	0.66	0.18	66.69	0.86
LU -SLC-MD1	Є$_1$	83.74	8.97	0.66	4.41	3.81	1.12	0.03	0.11	0.11	62.92	0.51
LU -SLC-MD2	Є$_1$	84.42	11.24	0.34	5.88	3.81	1.49	0.02	0.09	0.09	59.92	0.61
					Carbonaceous Shale SLC in Yangtze Plate							
XC, Henan-Rx2[l]	Є$_1$	74.20	8.31	3.16	3.03	1.42	1.32	0.06	1.12	0.11	54.31	0.18
XC, Henan-Rx3	Є$_1$	72.10	6.33	2.89	4.21	2.13	1.76	0.05	1.23	0.33	49.11	0.79
GZ, Hunan-01-1[m]	Є$_1$	85.24	9.91	1.89	6.56	3.15	0.76	0.06	2.81	0.61	57.48	0.64
GZ, Hunan-01-3	Є$_1$	84.05	8.05	1.59	7.11	2.71	1.05	0.06	2.74	0.13	58.10	0.71
ZJJ, Hunan-16[n]	Є$_1$	81.25	8.82	2.73	10.01	2.63	2.53	0.06	0.50	0.12	52.73	0.50
ZY, HG-2[o]	Є$_1$	83.65	2.76	0.71	5.95	1.17	0.50	0.08	0.23	0.22	72.20	0.75

[a] Age, shows the age of strata in which the SLC is hosted. [b] BX, Baxian Coal Mine, Pingli. [c] GU, Gu-Baxian Coal Mine, Pingli. [d] XZ, Xiaozhen Coal Mine, Langao. [e] Є$_3$, late Cambrian Period. [f] JT, Jiutai Coal Mine, Pingli. [g] Є$_2$, middle Cambrian Period. [h] TF, Tiefu Coal Mine, Ziyang. [i] Є$_1$, early Cambrian Period. [j] LX, Lixin Coal Mine, Langao. [k] LU, Lujiaping Coal Mine, Ziyang. [l] XC, Xichuan, Henan Province. [m] GZ, Guzhang, Hunan Province. [n] ZJJ, Zhangjiajie, Hunan Province. [o] ZY, Zunyi, Guizhou Province.

samples) in the Yangtze Platform (Figure 1) by our research group since 1997.

2.2. Methods. Samples were crushed and ground to less than 200-mesh for geochemical analysis.

Proximate analyses and the ultimate analyses of the samples were performed at the Geological Testing Center of the Coal Academy of the Academy of Sciences and the Coal Testing Center of the Shaanxi Quality Testing Center, the laboratory of the Chenghe Coal Mine bureaus. The reporting limit and relative error is 10^{-3} and 10% for proximate and ultimate analyses, respectively.

Fluorine content was determined by the combustion−hydrolysis/fluoride-ion selective electrode method (GB/T4633-1997).[15] The sample was combusted in a tubular electric furnace at 1100 °C, and meanwhile, the condensate was introduced into a 0.2 M sodium hydroxide solution; then, 5 ml of total ionic strength adjusting buffer (TISAB) was added to the tested solutions before the content was determined by a fluoride electrode and a calomel reference electrode (Shanghai Precision and Scientific Instrument Co. Ltd., China). The TISAB was prepared as follows: 145 g of sodium chloride and 7.35 g of sodium citrate were dissolved in 143 mL of acetic acid, and then, the pH of the solution was adjusted to 5.0−5.5 using a 40% sodium hydroxide solution (GB/T4633-1997).[15]

Arsenic and Selenium were measured by hydride generation/atomic fluorescence spectrometry method: samples were digested with a mixture of nitric acid and perchloric acid using electric hot plate (GB/T 15555.3-1995; GB/T 17134-1997; NY/T 1104-2006; GB/T 16415-2008)[16−19] and then measured by an AFS-820 dual-channel atomic fluorescence spectrophotometer (Titan Instruments Company, Beijing, China).

The mercury content in these samples was determined by AFS-820 double channel atomic fluorescence spectrometry with a hollow cathode lamp of mercury and high purity argon gas (NY/T 1121.10-2006).[20] The conditions of the AFS-820 double channel atomic fluorescence spectrometry were as follows: the electrical current was 80 mA, the negative high pressure was 300 V, and the air flow was about 400 mL/min. The analysis process was as follows: weigh a sample of 0.2000−0.2500 g; put it into a test tube with a cover; add aqua regia (1 mL high concentration HNO_3/3 mL concentrated HCl); put on the test tube cover and mix the solution; then, place the test tube uncovered in boiling water for 2 h, shaking every 30 min; add 1 or 2 drops of 5% potassium dichromate solution ($K_2Cr_2O_7$), and dilute it to

Table 3. Contents of Trace Elements in the Igneous-Rock-Hosted SLC of Silurian and Their Surrounding Rocks in Daba Fold Zone, Southern Shaanxi (mg/kg)

	age	As	Ba	Co	Cr	Cu	F	Hg	Ni	Se	Sr	V	Zn
HP-1#SLC	S	32.1	2946	8.3	59.9	98.13	1762.3	0.6	126.8	5.1	487.7	700.9	500.7
HP-1#SLC	S	113.6	2575	nd	nd	1.15	1786.7	0.6	nd	4.6	581.9	nd	580.0
HP-3#SLC	S	60.1	2937	nd	nd	61.50	2055.2	0.6	nd	6.8	192.2	nd	553.6
HP-4#SLC	S	214.4	2445	nd	nd	5.40	2232.4	0.6	nd	8.5	225.5	nd	1013.0
HP-SLC	S	80.1	2641	11.8	nd	173.90	1167.9	0.2	nd	17.9	693.9	nd	738.8
HP-SLC	S	122.5	649	nd	nd	2.84	1869.9	1.0	nd	8.96	141.4	nd	851.5
DH1 natural coke	S	8.4	156	1.2	58.6	49.40	42.9	1.9	19.9	1.1	210.5	104.4	15.1
DH1 SLC-2	S	18.3	3012	20.8	187.2	70.25	4532.8	0.8	185.0	8.3	298.9	1332.0	1858.0
HP-SLC-A17	S	122.5	2305	22.8	81.9	166.00	875.0	0.6	97.1	19.6	77.4	648.2	611.9
HW-SLC-20	S	10.4	1862	13.8	47.2	60.60	1591.3	0.4	31.1	4.6	180.6	510.9	214.6
HP- SLC	S	83.7	3292	7.2	151.8	183.60	1526.4	0.2	453.9	18.2	340.2	1947.0	791.8
AB- SLC	S	68.7	2046	13.0	198.0	175.80	834.1	0.3	480.9	15.5	1235.0	2115.0	772.5
avg	12[a]	77.9	2238	12.1	120.8	87.38	1689.8	0.7	211.3	9.9	388.8	1109.6	708.5
						Surrounding Rocks							
HP-contact rock	S	131.7	11462.0	nd	nd	8.5	1186.3	0.2	nd	6.3	1925.0	nd	201.0
HP-1 contact rock	S	8.4	573.7	nd	nd	85.8	259.9	0.2	nd	2.3	3630.0	nd	26.2
HP-1# TA[b]	S	32.5	1311.0	nd	nd	65.3	1263.2	0.2	nd	5.3	267.4	nd	187.3
DH 3-1 TA	S	1.69	3586.00	10.80	51.24	60.13	1108.59	0.23	2.78	11.88	389.90	63.20	103.10
DH 3-2 TA	S	0.23	941.50	23.89	51.70	24.78	1627.41	0.10	30.22	3.74	115.90	40.00	137.50
avg	5[c]	34.89	3574.84	17.35	51.47	48.91	1089.10	0.18	16.50	5.91	1265.64	51.60	131.01

[a] 12 = the number of samples on which the average is based. [b] TA, trachytic agglomerate. [c] 5 = the number of samples on which the average is based.

25 mL with double distilled water. The mercury content was determined in the 5% HCl with potassium borohydride (KBH_4) as the reducing agent, at the same time the blank and the standard substances were also determined (NY/T 1121.10-2006).[20]

For quality control in chemical analysis, the standard reference materials (GBW07406 (soil, China) and GBW11122 (coal, China), Chinese Standard Sample Study Center, Chinese Academy of Measurement Sciences) were randomly analyzed with each batch of rock and SLC samples. In all our As, Se, Hg, and F analyses, the detection limit and relative error were 10^{-9} and less than 10%, respectively.

The elements Al, Ba, Ca, Cr, Co, Cu, Fe, K, Li, Mg,Mn, Na, Ni, P, Si, Sr, Ti, V, and Zn were measured by inductively coupled plasma−atomic emission spectrometry (ICP-AES), samples were digested with a mixture of nitric acid, hydrofluoric acid, and perchloric acid ($HNO_3-HF-HClO_4$) using electric hot plate, measured by ICP-AES at the laboratory of the Institute of Geographical Sciences and Natural Resources, Chinese Academy of Sciences (Beijing), and Institute of Geology and Geophysics, Chinese Academy of Sciences (Beijing). The following standard reference materials were randomly analyzed with each batch of the samples: GBW07401 (GSS1) and GBW07403 (GSS3) (soil, China), Chinese Standard Sample Study Center, Chinese Academy of Measurement Sciences. The relative error was less than 10%, and the detection limit was 10^{-9}.

3. RESULTS AND DISCUSSION

3.1. Occurrence of Lower Paleozoic SLC in the Daba Fold Zone and Sampling Localities. The quality and occurrence of SLC in the Daba fold zone is different from the traditional sedimentary origin SLC of the Yangtze Plate, South China. In the Daba fold zone, the SLC can occur in any part of the sequence from the late Precambrian, Cambrian, Ordovician, and Silurian, with the largest resource in the Silurian and Cambrian strata. The Daba SLC occurs as lenticular or podiform bodies enveloped in trachytic agglomerate of Silurian (Figure 3) or sandwiched in the fault zones and the top of the thrust fold axes of the carbonate rock of the Cambrian and Ordovician (Figure4). With the exception of the stratigraphical controlled upper Neoproterozoic and lower Cambrian carbonaceous shale SLC (poor quality SLC, not mined and used in Daba area), most occurrences have no distinct stratigraphic position and cannot be correlated laterally. All faults and folds in which SLC bodies are hosted were formed in the orogenesis of the Qingling Mountains in the late Triassic and the superimposed Jurassic folding during the collision of the Yangtze Plate and the North China Plate.[3,4]

The occurrence of SLC in the Daba fold zone is different from the traditional sedimentary origin SLC of the Yangtze Plate, South China. The general sedimentary genesis coal theory can not explain the occurrence of the Daba area SLC.

Most Daba SLC in the Daba fold zone will be more similar to a structural−genetic metamorphic alert coal than the sedimentary−genetic coal. The Daba SLC has been migrated from source rocks during the orogenesis of the Daba Mountain of the Qinling Mountains in the late Triassic collision of the North and South China plates.[3,4] The lower Paleozoic rock lost its volatile material and inorganic minerals as a result of high pressure during the tectonic processes that occurred when the North China Plate collided the Yangtze Plate in the late Triassic and during the process of superposed folding in the Jurassic in the Daba fold zone, or the rock lost its volatile material and minerals as a result of high temperatures during igneous intrusions of the black shale or carbonate rock during the Silurian. It is a pressure and thermally altered coal, different from the sedimentary−genetic SLC of the lower Cambrian in southern China, Yangtze Plate,

Table 4. Content of Trace Elements in the Carbonate-Hosted SLC of Cambrian and Ordovician in Daba Fold Zone, Southern Shaanxi (mg/kg)

	age	As	Ba	Co	Cr	Cu	F	Hg	Ni	Se	Sr	V	Zn
BX-SLC-LM1[a]	Є$_3$-O$_1$	103.2	1187	12.1	353.3	304.7	1408.4	0.6	657.1	39.8	141.2	2823	987
GU-SLC-LM[b]	Є$_3$ - O$_1$	118.4	2993	12.9	155.2	148.7	518.0	0.2	255.7	20.2	272.3	2012	323.1
XZ-SLC-DD[c]	Є$_3$	9.6	3684	10.7	269.4	104.7	529.2	0.3	358.6	4.7	303.9	2048	677.5
JT-SLC-JT2[d]	Є$_3$	16.1	2655	7.6	167.9	123.7	452.9	0.3	332.2	23.9	137.8	1631	890.9
JT-SLC-IG2	Є$_3$	18.7	431.3	12.6	30.97	27.95	248.6	0.3	109	19.3	25.7	410.3	205.2
TF-SLC-10	Є$_2$	92.6	632.8	nd[e]	nd	170	295.4	0.9	nd	7.5	200.5	nd	653.5
TF-SLC-A8	Є$_2$	29.0	457.9	21.9	138.7	249.5	246.8	0.4	147.1	12.3	125.7	1714	1207
XZ-SLC-HG	Є$_1$	72.5	1403	17.5	330	160.2	535.3	1.9	850.8	62.4	58.2	4165	1107
JT-SLC-JGD	Є$_1$	102.3	2362	12.4	369.8	245.9	221.4	0.7	495.6	48.1	183.5	3053	1173
JT-SLC-63	Є$_1$	182.4	1361	19.6	209.9	319.2	683.9	0.7	458.5	32.9	334.3	2.7	1154
LX-SLC-56[f]	Є$_1$	176.9	5632	10.3	268.7	130.2	621.2	0.5	149.8	38.9	190.2	2745	544
LX-SLC-57	Є$_1$	149.1	5215	9.5	237.2	112.7	675.3	0.9	252.5	34.9	196.2	2329	685.4
XZ-SLC-XH	Є$_1$	277.6	4036	18.9	298.5	348	534.5	0.8	931.7	46.3	95.1	3080	1694
LX-SLC-58	Є$_1$	224.7	8220	12.6	266.8	214.9	642.4	1.1	449.5	32.1	225.4	2527	921.3
LU -SLC-A32[g]	Є$_1$	120.4	4179	22.2	49.9	148.7	648.8	0.2	17	28.7	379.8	114	112.4
avg	15[h]	112. 9	2963.3	14.3	224.7	187.2	550.8	0.6	390.3	29.9	191.3	2046.7	822.3
TF-natural coke	Є$_3$	77.8	0	5.3	0	0	6.1	0.3	0	13.1	0	0	0
						Surrounding Rocks							
F6 (limestone)	Є$_3$	0.2	36.0	0.5	6.9	12. 0	88.6	0.0	0.0	0.4	371.8	22.3	12.4
F7 (limestone)	Є$_2$	1.5	302.4	22.7	60.1	28.5	89.6	0.0	82.6	0.0	398.1	128.2	88.0
F8 (limestone)	O	1.3	905.5	10.8	21.9	14.7	347.1	0.0	65.5	0.0	207.0	80.8	49.8
						Lower Cambrian Black Shale (Carbonaceous Shale SLC) in Daba Fold Zone							
B-SLC-B39	Є$_1$	103.1	266.3	7.9	0	30.3	714.7	0.2	10.2	21.2	774.7	544.3	101.4
B-SLC-B33	Є$_1$	151.8	9681	0	84.51	17.2	706.3	0.5	53.3	54.9	77.0	597.5	361.2
LU-SLC-MD1	Є$_1$	68.4	6232.0	19.5	13.78	50.0	740.7	0.4	20.5	22.4	50.5	164.4	372.4
LU-SLC-MD2	Є$_1$	92.9	4950.0	14.3	4.00	106.0	882.6	0.5	5.0	29.27	50.6	280.3	291.3
						Carbonaceous Shale SLC in Yangtze Plate							
XC, Henan-Rx2[i]	Є$_1$	142.4	nd	2.7	20	55	1243.7	0.6	63	41.3	nd	199	275
XC, Henan-Rx3	Є$_1$	231.2	nd	6.3	91	146	1342.0	0.3	140	370.2	nd	587	175
GZ, Hunan-01-1[j]	Є$_1$	119.4	383.4	17.4	84.4	88.5	1835.1	1.0	421.6	36.0	113.7	3637	664
GZ, Hunan-01-16	Є$_1$	223.1	107.1	29.4	113.4	173.8	2104.2	2.1	161.4	56.2	66.5	533	99
ZJJ, Hunan-01-3[k]	Є$_1$	119.2	86.3	23.7	111.7	90.9	1053.0	1.1	382.1	36.5	109.3	3386	821
ZY, HG-2[l]	Є$_1$	273	966	1.2	1413	41.4	639.2	0.1	62.4	45.5	11.1	4247	22.9

[a] BX, Baxian Coal Mine, Pingli. [b] GU, Gu-Baxian Coal Mine, Pingli. [c] XZ, Xiaozhen Coal Mine, Langao. [d] JT, Jiutai Coal Mine, Pingli. [e] nd, no data. [f] LX, Lixin Coal Mine, Langao. [g] LU, Lujiaping Coal Mine, Ziyang. [h] 15 = the number of samples on which the average is based. [i] XC, Xichuan, Hunan Province. [j] GZ, Guzhang, Hunan Province. [k] ZJJ, Zhangjiajie, Hunan Province. [l] ZY, Zunyi, Guizhou Province.

and the South China fold belt and from the humic coal of Permo-Carboniferous system and later ages.

The lenticular or podiform bodies of SLC in the trachytic agglomerate of the Silurian are larger (Figures 3), with lengths of about 420−1350 m (most are about 900 m) and thicknesses of 2−5 m. The lenticular or podiform bodies of SLC in the top of thrust fold axes are mainly hosted in Cambrian and Ordovican limestone strata, and they have general lengths of about 10−150 m, with thicknesses of 1−5 m.[13]

In addition to the carbonaceous shale SLC deposits in the sequence of the late Neoproterozoic through the early Cambrian in the Daba fold zone, most SLC resources can be divided into two types by their geological occurrence: (1) igneous-rock-hosted SLC, mainly hosted in the Silurian trachytic agglomerate, and (2) carbonate-hosted SLC and fault-hosted SLC, mainly hosted in the fault zones and the top of thrust fold axes of the carbonate rock of the Cambrian and Ordovician.

In the Daba area, the Cambrian and Ordovician strata are mainly distributed in the southern Daba area, where there are more carbonate rocks and less volcanic and magma rocks. The Silurian strata are mainly distributed in the northern Daba area, where there are less carbonate rocks and more volcanic and magma rocks.[2−5,13] Corresponding to the strata distribution, the carbonate-hosted SLC is mainly distributed in the southern Daba area (South Ziyang County, South Pingli, and South Langao County in the southern Ankang district). The igneous-rock-hosted SLC of the Silurian is mainly distributed in the northern Daba area (in North Ziyang County, North Pingli, North Langao County, and Hanbing County in northern Ankang district).[5,13]

3.2. Major Element Composition of SLC and Humic Coal. The SLCs of the Daba area have more SiO_2, CaO, and MgO (Tables 1 and 2) than the Carboniferous−Permian coals,[21,22] and they have higher CaO and MgO contents than the gangue associated with the

Carboniferous−Permian coal. The SLC has a higher proportion of SiO_2/Al_2O_3 than does the gangue associated with Carboniferous−Permian coal (Tables 1 and 2); the proportion of SiO_2/Al_2O_3 in the SLC commonly is 4:1 to 8:1, and in the Carboniferous−Permian coal gangue, it is only about 1:1.[21,22] The SLC is harder than the associated gangue because of its higher content of silica.

3.3. Trace Element Composition of SLC. The Daba SLCs are enriched with several of the heavy metals, and their trace element content (Tables 3 and 4) is generally much higher than that of the Permo-Carboniferous and later age coals.[23,24]

The average As contents in the SLC samples are 112 mg/kg in carbonate-hosted SLC and 78 mg/kg in igneous-rock-hosted SLC, ranging 8.39−277 mg/kg, which are much higher than the averages of common Chinese coals[23−28] and those of coals from other countries.[29−37]

Selenium contents ranged from 1.1 to 62.38 mg/kg, and its average contents are 29.21 mg/kg in the carbonate-hosted SLC and 9.91 mg/kg in the igneous-rock-hosted SLC, which are much higher than those of common coals, as reported by Tang and Huang,[23] Ren et al.,[24] He et al.,[25] Dai et al.,[27] Swaine,[29] Chou,[30] and Finkelman.[33] The highest values were found in the carbonate-hosted SLC of the Cambrian strata (Table 4). Comparably lower values were found in the igneous-rock-hosted SLC (Table 3).

The As and Se contents of the carbonate-hosted SLC of the Cambrian are generally higher than those in the igneous-rock-hosted SLC of Silurian (Table 3).

The average F content in the SLC samples is 550.82 mg/kg in carbonate-hosted SLC of the Cambrian (Table 4) and 1689.75 mg/kg in igneous-rock-hosted SLC of the Silurian, ranging from 42.91 to 4532 mg/kg, with most of the samples in the 1000−2000 mg/kg range (Table 3). The F content of most Dada SLC samples is much higher than the F contents of the common Chinese coals[23,24,38,39] and worldwide coals.[29−34]

The Hg content of most Dada SLC is about twice as much as that of the Permo-Carboniferous humic coals in the North China Plate.[23,24] The average Hg content of the SLCs from the Daba fold zone is 0.66 mg/kg; moreover, the content of Hg in some fault-hosted SLC reaches 1.446 mg/kg, suggesting that Hg is variable in migratory habits.

The F content of igneous-rock-hosted SLC (Table 3) is higher than that of the carbonate-hosted SLC (Table 4). The Silurian trachytic agglomerate, the surrounding rock of the igneous-rock-hosted SLC, has much higher F content than the carbonate rock surrounding rock the carbonate-hosted SLC (Table 4). The F content of carbonate-hosted SLC is lower than that of the carbonaceous shale SLC of the lower Cambrian in the Daba fold zone and that of the SLC in Yangtze Plate (Table 4).

The contents of Ba, Cu, Zn, Cr, Ni, and Sr in the SLC are about 10 times higher than those in the Permo-Carboniferous humic coals in the North China Plate.[23,24] However, the Co content of the SLC is lower, only 10% of the Co in the Permo-Carboniferous humic coals of the North China Plate.[23,24]

Considerable quantities of highly organic shales, locally used as SLC, occuring in the lower part of the lower Cambrian in the Yangtze Platform and the South China fold belt, have been thoroughly studied.[40−43] However, previous studies excluded the contents and distribution patterns of the toxic elements As, Se, F, and Hg in the lower Cambrian SLC in the Yangtze Platform and the South China fold belt.

Four sites of the SLC of the lower Cambrian in the Yangtze Platform were sampled (channel samples) for this study (Figure 1). Among them, two are from Xichuan, in the east of the Daba fold zone, also in the Yangtze Plate in the western Henan Province. The carbonaceous shale SLC (poor-quality SLC) of the lower Cambrian in the Daba fold zone is in the same level as the lower Cambrian SLC of South China in the trace elements content. This suggests that both were formed under the same paleoenvironmental conditions during the lower Cambrian. However, the SLC of the lower Cambrian and the carbonaceous shale SLC (poor-quality SLC) of the Daba fold zone have somewhat lower F and Se contents (Table 4).

4. CONCLUSION

The As, Se, F, and Hg contents of Daba SLC vary. Most of the SLCs are rich in As, Se, F, and Hg. The contents of F, As, and Se in the Daba SLC are about 10−50 times more than those in common humic coals, and it is a poisonous coal for indoor warmth and cooking.

The F content of igneous-rock-hosted SLC of Silurian is much higher than that of the carbonate-hosted SLC. The As and Se contents of the carbonate-hosted SLC, especially the carbonate-hosted SLC of the lower Cambrian age, are much higher than the those of the igneous-rock-hosted SLC of the Silurian. In the northern Daba area, the main area of igneous-rock-hosted SLC of the Silurian distributed and mined in Daba fold zone, the citizens use a lot of local igneous-rock-hosted SLC of the Silurian for heating and cooking. The endemic arsenism is very serious in the southern Daba area,[6] the main area of the lower Cambrian SLC outcrops and mining in the Ankang district,[13] and is much higher than in the other places in Daba fold zone.[6,7]

Volcanic activity and magma intrusions represent the main natural persistent sources of fluorine.[44,45] The Silurian trachytic agglomerate, the surrounding rock of the igneous-rock-hosted SLC, has a much higher F content than the carbonate rock of the surrounding rock of carbonate-hosted SLC (Table 4). The frequent volcanic activity and magma intrusions of the Silurian might be the main reason for fluorine-rich SLCs in the Daba area. The volcanic activity and magma intrusions of the Silurian brought F to the surrounding rock and inclusions; the origin material of the SLC that wraps the igneous-rock would have adsorbed the F of the magma. So, the igneous-rock-hosted SLC of Silurian has much higher fluorine contents than does the SLCs hosted by other units. The fluorine content of the Cambrian carbonate, especially the middle and late Cambrian, is very low (Table 4), where there are little magma activities; so, the F content is significantly lower in the carbonate-hosted SLC.

In the Daba area, low-fluorine SLCs are mainly distributed in the southern Daba area, where there are more middle and late Cambrian carbonate rocks and less volcanic and magma rocks.

The Daba mountainous area is an impoverished area in China. Lacking humic coal, the local residents have to ignore the higher content of toxic elements such as As, Se, F, and Hg in the SLC and use it for heating and cooking. Future studies may suggest techniques that can reduce the toxic element contents of the SLCs used locally for domestic purposes and encourage local residents not to use the lower Cambrian SLC and igneous-rock-hosted SLC of Silurian as much as possible. The contents of As and F are comparatively lower in the carbonate-hosted SLCs of the middle and upper Cambrian, and these are recommended to local residents for indoor use.

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ABBREVIATIONS

SLC =stonelike coal, burnable black shale.

Daba area =Ziyang County, Langao County, Hanbing County and Pingli County of the Ankang district in the southern Shaanxi Province, in the Daba fold zone of the South Qinling Mountains.

Daba SLC =stonelike coal of the early Paleozoic in the Daba area.

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