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Anomalous Enrichment of Silver in Organic Matter of the Songxi Shale-hosted Ag-Sb Deposit in Northeastern Guangdong

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Abstract The silver contents of organic matter in the host rocks of the Songxi shale-hosted Ag-Sb deposit of northeastern Guangdong, South China, have been directly determined using the electron microprobe technique. The silver contents in two types of organic matter, marine vitrinite and solid bitumen, vary in the range from 100×10^{-6} to 350×10^{-6}, which are from tens of times to thousands of times higher than those of the host rocks in the ore deposit. The average silver content of the organic matter is also several times higher than the pay grade of silver for commercial mining of the ore deposit. It is quite obvious that the organic matter of the host rocks in the ore district is characterized by an anomalous enrichment of silver. The results of this study indicate that the silver anomalies in the organic matter have been derived from both the host rocks and the silver-bearing fluids of the Songxi black shale ore source. In the course of sedimentation and later hydrothermal reworking, organic matter was able to entrap the element silver from source rocks and silver-bearing fluids through complexation and reduction, so that silver could be further enriched (or precipitated) in the solid bitumen. The quantitative assessment in this study suggests that the distribution of solid bitumens in the ore district may be considered an indication for mineral exploration.

Key words: silver, organic matter, solid bitumen, anomalous enrichment, organic mineralization

1 Introduction

Silver is an element with a low average abundance and very dispersed in the continental crust, and generally occurs in ore deposits as an accompanying element or coexists with other metal elements. There are cases reported both in China and abroad in which silver occurring in organic-rich black shale formations is concentrated to form a deposit (Badham, 1976; Chen and Xie, 1986; Zhang et al., 1995; Yao et al., 1996; Zheng, 1996; Xiao et al., 1997). In some literatures, attention has been focused predominantly on the close genetic relationship between silver mineralization in the black shale formations and organic matter of the host rocks. Studies of some shale-hosted deposits in particular emphasized the importance of organic-metal mineralization as a favourable indication for ore exploration (Parnell, 1988; Zhuang et al., 1997; Xiao et al., 1998; Hu et al., 1999). In further revealing the association of silver mineralization with organic matter, however, a key problem is that we know little about the modes of occurrence and geochemical data of silver within the organic matter.

Recently, we have successfully determined the silver content in organic matter by using the electron microprobe technique, taking the Songxi black shale-hosted Ag-Sb deposit as an example. This technique is particularly advantageous because it can determine granulated organic matter in samples in situ, in a direct and non-destructive way. In this study we have obtained some important geochemical data, and discovered anomalous enrichment of silver in organic matter based on 134 measurements of silver contents of organic matter in the ore district. In combination with organic petrology and the metallogenic characters of the Songxi Ag-Sb deposit, we now present a further discussion on the potential use of bitumen distribution in the ore district and/or silver enrichment within the organic matter for mineral exploration.

2 Samples and Analytical Methods

A total of 20 samples were collected from the host rocks of the Songxi As-Sb deposit (drill holes ZK609 and ZK1011) and from the ore zone V4. The Songxi deposit has been found in northeastern Guangdong Province of South China, and explored recently as an independent large deposit with a silver-antimony association, occurring in a suite of Lower Jurassic black shale formation. The formation mainly consists of black shale, siltstone, argillite, fragmental biogenic limestone, sediment-tuff and basalt, and is the most important ore-bearing bed. The location, regional geological setting and characteristics of the ore deposit are shown in Fig. 1 and described in detail in some papers (Yao et al., 1996; Zheng, 1996; Xiao et al., 1997; Xiao et al., 1998; Hu et al., 1999). In this study each sample was generally separated into two portions. One was polished into a polished section or a thin section for optical microscopic examination of organic matter and determination of silver contents in the organic matter of the rocks. The other was crushed into grains as fine as 100 mesh for analyses of the total organic carbon and whole-rock silver content.

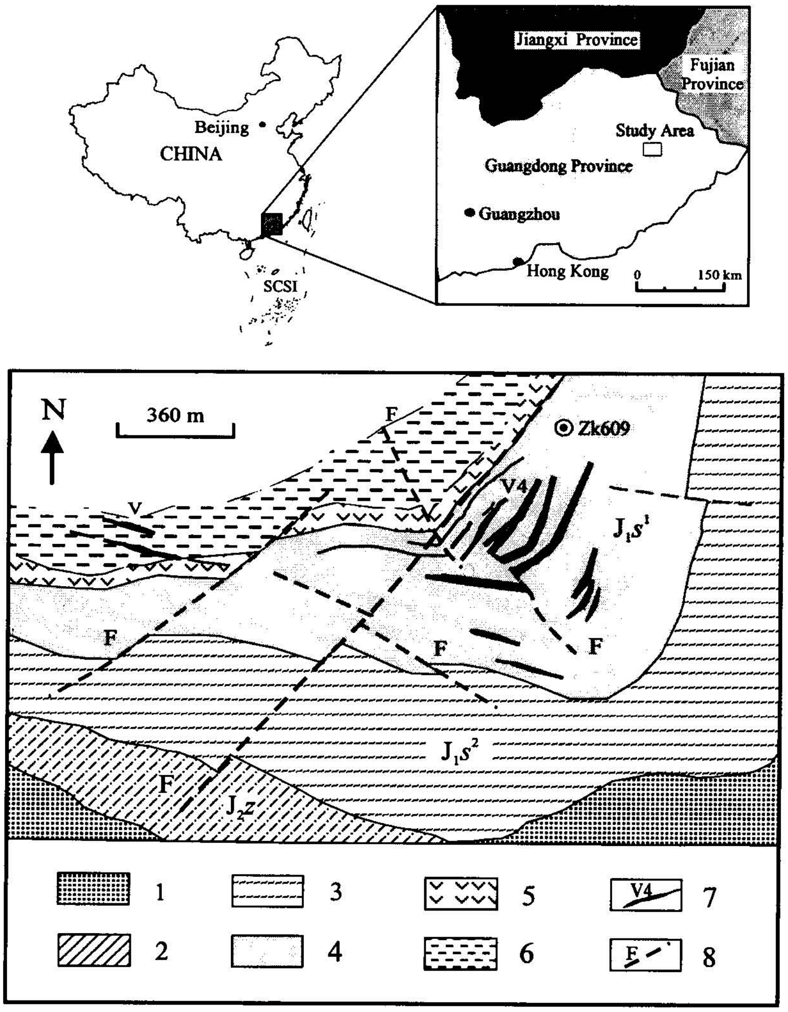

Fig. 1. Location and simplified geological map of the Songxi Ag-Sb deposit (modified from Zheng, 1996).

1. Continental pyroclastic rock; 2. Zhangping Formation, Middle Jurassic (J_2z); 3. middle member of the Songling Formation, Lower Jurassic (J_1s^2); 4. lower member of the Songling Formation, Lower Jurassic (J_1s^1); 5. basalt; 6. clastic rock; 7. Ag-Sb ore vein; 8. fault.

The determination of silver contents in individual organic matter were made in the State Key Laboratory for Mineral Deposit Research, Nanjing University of China, using a JEOL JXA-8800A electron probe micro-analyser. The experiment was operated at 15kV and 2×10^{-8}A, with 500–1000 fold magnification. After a careful optical microscopic examination, areas were selected that did not have any visible mineral agglomerates on the surface. Ag_2S was used as the reference sample. The electron microprobe was estimated to have a detectable limit of approximately 0.01% (SD±5%) under the experimental conditions. A Leco CS 224 carbon-sulphur analyser was used for the whole-rock organic carbon analysis. Before the organic carbon content was determined, the unextracted rocks were treated with hot HCl (6N) to remove the carbonates. The whole-rock silver contents were determined by the atomic absorption spectrophotometry (precision 0.1×10^{-9}) or the X-ray fluorescence spectrometry (precision 0.1×10^{-6}) respectively, depending on the their contents in the samples. Organic matter reflectance measurement was performed on the whole rock polished sections, using an Opton universal reflecting microscope under oil immersion at a 250-fold magnification.

3 Results and Discussion

3.1 Composition and distribution of organic matter in the host rocks

The Songxi Lower Jurassic black rock series formation, which is located in the Songxi Ag-Sb deposit, consists of black carbonaceous shale, siltstone, grey mudstone and argillaceous limestone. The black carbonaceous shale is a widespread component in the Songxi Formation, comprising up to 60% of the formation in thickness. Table 1 lists the depth, lithology, whole-rock total organic carbon (TOC) and organic composition of the 20 samples collected from the drill-holes ZK609 and ZK1011 and the ore zone V4. It can be seen from the table that the 16 carbonaceous shale samples in the ore district generally have high whole-rock TOC contents, varying between 0.16 and 5.60 wt%, averaging 1.76 wt%. The whole-rock TOC contents of the 5 carbonaceous shale samples analyzed are over 2.0 wt%, while the other non-shale samples have very low organic carbon contents. Microscopic petrographic observations of the polished sections of the host rocks under the reflected light indicate that the host rocks are distributed with fine and dispersed organic matter, which is closely syngenetic with clay minerals. As shown by the morphologic features of the organic matter in the host rocks, the depositional environment and organic geochemical data (Hu et al., 1999), the fine and dispersed organic matter is generally derived from aquatic plants such as marine algae.

According to the classification of organic petrology (Zhong and Qin, 1995), the organic matter can be clearly divided into two basic types: marine vitrinite and solid bitumen. The geneses of the two are quite different. The former is a type of primary organic matter generally derived from humification of aquatic plants at an early stage of diagenesis, while the latter is a type of secondary (or epigenetic) organic matter that remains in the residues left during petroleum generation and migration processes (Liu et al., 1990; Zhong and Qin, 1995). In the ore district, the marine vitrinite is a widespread micro-organic component of various host rocks, and is generally oriented parallelly to primary sedimentary beddings of the rocks, mostly present in the granular shape and associated with sedimentary pyrite and framboidal pyrite in source rocks (Fig. 2-1a and 1b). The solid bitumen can be identified as structureless organic matter infiltrating along rock cracks or filling into the intergranular space of minerals (Fig. 2-2a and 2b). Data of organic matter reflectance measurements of the host rocks are also presented in

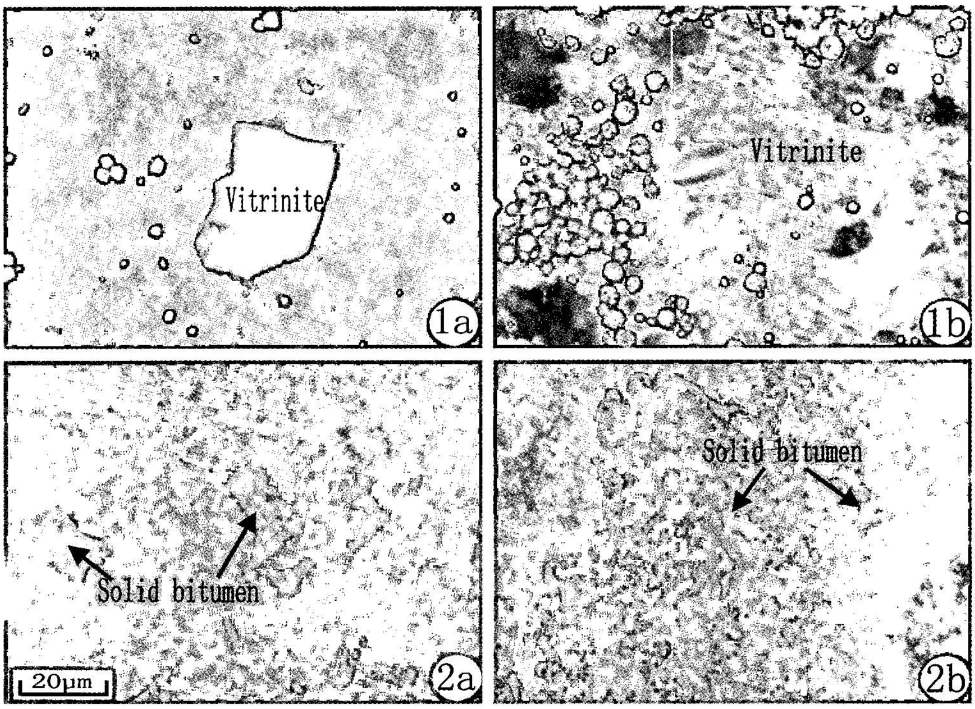

Fig. 2. Distribution of organic matter in the host rocks of the Songxi Ag-Sb deposit.
(1a) Marine vitrinite distributed in a primary sedimentary bedding along the rock stratification, in the diagenetic-supergene enrichment stage, Sample ZK1011-63;
(1b) marine vitrinite associated with framboidal pyrite, in the diagenetic-supergene enrichment stage, Sample ZK1011-72;
(2a) solid bitumen infiltrated along rock cracks, in the hydrothermal-reworking mineralization stage, Sample SXV4-5;
(2b) solid bitumen filling into the intergranular space of minerals, in the hydrothermal-reworking mineralization stage, Sample SXV4-7.

Table 1. The mean reflectance readings of the samples measured range from 2.10% to 4.28%, showing that the organic matter in the ore district has undergone thermal evolution at the stage of over-maturation. Sun and others (1999) analyzed the compositions of organic gases in fluid inclusions of minerals and proved that the light hydrocarbons are mostly composed of saturated alkanes C_1–C_4, while the contents of unsaturated alkenes C_2–C_4 and aromatic hydrocarbons are very low. It can be inferred from the burial depth of the samples measured that the organic matter in the ore district has also experienced an additional thermal alteration after the diagenesis. Obviously, the later epithermal reworking mineralization in the ore district further caused the organic matter to reach the stage of over-maturation.

Two mineralization stages of the Songxi Ag-Sb deposit can be recognized based on detailed observations of the mineral assemblage, rock alteration and features of the mineral deposit: the diagenetic-supergene enrichment stage and the stage of hydrothermal reworking. It is noted through petrographic observations under the microscope that solid bitumens are mainly distributed in the hydrothermal-reworking mineralized rocks. As a matter of fact, it is a common phenomenon in other stratabound metallic deposits that the solid bitumens are distributed within the ore zones (Liu et al., 1990).

3. 2 Silver distribution in organic matter and host rocks of the ore district

The silver contents in both the organic matter and the host rocks of the ore district are presented in Table 2. The silver contents of the 20 samples from the Songxi ore district lie mainly between 0.03×10^{-6} and 16.0×10^{-6}. The average silver content of the 16 black shale samples analyzed is 2.81×10^{-6}, which is obviously higher than that of non-shale rocks. Our results show that the silver contents of the host rocks from the Songxi ore district are generally several times to tens of times higher than those of rocks of the same lithology in the upper continental crust, and the Songxi Lower Jurassic black shale formation itself is a very good source bed for silver.

It is interesting to us that the determination of silver contents in individual organic matter has been successfully done with the electron probe microanalysis. Except for three samples (ZK1011-72, ZK1011-125 and SXV4-11), the data of silver contents in the organic matter of most samples are higher than the detection limit (90×10^{-6}–110×10^{-6}) of the electron probe microanalysis. This study shows that the data analyzed with the electron probe are authentic. It can be seen from Table 2 that the organic matter generally has a high content of silver, and the data obtained by using the electron probe basically fall in the range from 100×10^{-6} to 350×10^{-6}. The average silver content of the organic matter is several times higher than the pay grade of silver of the Songxi Ag-Sb deposit (50×10^{-6}), and may be considered "mineralized organic matter". The silver content of the organic matter has enormously increased as compared with the source rock, and the silver enrichment coefficients vary from 11 to as high as 2100. To confirm the silver accumulation in the organic matter of the ore district, we simultaneously checked the silver contents in the clay minerals or matrix materials of the samples, but found that very few contained detectable silver. This further proves that silver anomalies occur in the organic matter of the ore district, and that the organic matter has better properties of accumulating silver than clay minerals.

Another interesting phenomenon is that there is a significant difference in silver contents between the marine vitrinite and the solid bitumen. In the same sample, the solid bitumen generally has a higher silver content, which may be higher than that of the marine vitrinite by 10×10^{-6} –20×10^{-6}. It is inferred that the enrichment of silver in the solid bitumen may be partly related to the formation process of the bitumen. The data in Fig. 3 show that the average values of silver content in the solid bitumen and the marine vitrinite from all samples analyzed are 215×10^{-6} and 175×10^{-6}, respectively. At the later hydrothermal-reworking mineralization stage, hydrocarbon-bearing fluids may catch the element silver from the source rock, and/or the silver was initially concentrated within the organic matter through the formation of organic-silver complexes when the silver-bearing and hydrocarbon-bearing fluids met, and then further concentrated in the solid bitumen following petroleum generation, migration and degradation.

Table 1 Organic components of host rocks in the Songxi Ag-Sb deposit

Sample No.	Lithology	Depth (m)	Mineralization stage	Organic matter	C_{org} (%)	Organic matter reflectance R_o (%)			
						Number	$R_{o,\,min}$	$R_{o,\,max}$	$R_{o,\,mean}$
Drill hole ZK609									
ZK609-10	Siltstone	10.2	Diagenetic-supergene enrichment	Vitrinite	0.06	24	2.75	3.88	3.14
ZK609-183	Carbonaceous shale	183.4	Diagenetic-supergene enrichment	Vitrinite, bitumen	0.36				
ZK609-217	Carbonaceous shale	217.6	Diagenetic-supergene enrichment	Vitrinite, bitumen	0.84				
ZK609-246	Carbonaceous shale	246.6	Hydrothermal-reworking	Vitrinite, bitumen	0.82	20	1.40	2.93	2.10
ZK609-277	Carbonaceous shale	277.4	Hydrothermal-reworking	Bitumen	3.04	26	3.30	5.46	4.28
ZK609-301	Carbonaceous shale	301.8	Hydrothermal-reworking	Vitrinite, bitumen	0.85	20	3.04	4.74	3.87
ZK609-336	Shale	336.4	Hydrothermal-reworking	Vitrinite, bitumen	0.55	27	2.07	4.60	3.70
Drill hole ZK1011									
ZK1011-63	Shale	63.4	Diagenetic-supergene enrichment	Vitrinite, bitumen	0.50				
ZK1011-72	Shale	72.5	Diagenetic-supergene enrichment	Vitrinite	0.16				
ZK1011-90	Carbonaceous shale	90.5	Diagenetic-supergene enrichment	Vitrinite, bitumen	2.50	25	2.70	4.39	3.40
ZK1011-101	Carbonaceous shale	101.5	Diagenetic-supergene enrichment	Vitrinite, bitumen	5.60	23	2.50	4.78	3.48
ZK1011-120	Carbonaceous shale	120.4	Hydrothermal-reworking	Vitrinite	0.54	11	0.95	3.12	2.47
ZK1011-125	Carbonaceous shale	125.3	Hydrothermal-reworking	Vitrinite, bitumen	4.20	4	2.81	4.31	3.35
ZK1011-165	Carbonaceous shale	165.9	Hydrothermal-reworking	Vitrinite, bitumen	0.57	25	2.70	4.39	3.40
ZK1011-217	Argillite	217.9	Hydrothermal-reworking	Bitumen	0.09	1	–	–	4.09
ZK1011-236	Muddy limestone	236.5	Hydrothermal-reworking	Vitrinite, bitumen	0.59	31	2.32	3.78	3.02
Ore zone V4									
SXV_4-5	Shale	175.7	Hydrothermal-reworking	Bitumen	0.31	22	1.19	4.42	3.55
SXV_4-6	Carbonaceous shale	175.7	Hydrothermal-reworking	Vitrinite, bitumen	1.61	24	3.30	4.39	3.78
SXV_4-7	Shale	175.7	Hydrothermal-reworking	Bitumen	0.65				
SXV_4-11	Carbonaceous shale	175.7	Hydrothermal-reworking	Vitrinite, bitumen	5.00				

Table 2 Silver contents of organic matter and host rocks at the Songxi Ag-Sb deposit

Sample No.	Lithology	Mineralization stage	Ag content in rocks ($\times10^{-6}$)	Ag content in organic matter determined with electron probe ($\times10^{-6}$)				Enrichment Coefficient
				OM	Number of tests	Range	Average	
Drill hole ZK609								
ZK609-10	Siltstone	D-S	0.14	Vitrinite	3	110–130	115	821
ZK609-183	Carbonaceous shale	D-S	3.10	Vitrinite	8	150–230	180	58
				Bitumen	4	160–320	250	81
ZK609-217	Carbonaceous shale	D-S	0.65	Vitrinite	6	140–310	226	348
ZK609-246	Carbonaceous shale	H-R	5.57	Vitrinite	1	240	240	43
				Bitumen	5	210–350	310	56
ZK609-277	Carbonaceous shale	H-R	0.65	Vitrinite	8	180–210	190	292
				Bitumen	3	170–240	200	308
ZK609-301	Carbonaceous shale	H-R	0.65	Vitrinite	5	110–250	150	231
				Bitumen	2	130–180	155	238
ZK609-336	Carbonaceous shale	H-R	1.39	Vitrinite	6	90–120	105	76
				Bitumen	4	120–210	150	108
Drill hole ZK1011								
ZK1011-63	Carbonaceous shale	D-S	5.97	Vitrinite	9	110–210	160	27
				Bitumen	5	170–230	200	34
ZK1011-72	Carbonaceous shale	D-S	0.16	Vitrinite	5	nd	nd	
ZK1011-90	Carbonaceous shale	D-S	0.10	Vitrinite	7	140–200	180	1800
ZK1011-101	Carbonaceous Shale	D-S	0.10	Vitrinite	8	100–340	210	2100
ZK1011-120	Carbonaceous shale	D-S	0.21	Vitrinite	6	160–240	190	905
				Bitumen	3	180–230	200	952
ZK1011-125	Carbonaceous shale	D-S	0.03	Vitrinite	5	nd	nd	
ZK1011-165	Carbonaceous shale	H-R	1.49	Vitrinite	4	140–230	210	141
				Bitumen	8	170–340	255	171
ZK1011-217	Argillite	H-R	0.84	Vitrinite	5	120–170	150	179
ZK1011-236	Limestone	H-R	0.84	Vitrinite	1	180	180	214
Ore zone V4								
SXV_4-5	Carbonaceous shale	H-R	0.97	Vitrinite	4	130–160	140	144
				Bitumen	5	170–240	220	227
SXV_4-6	Carbonaceous shale	H-R	4.52	Vitrinite	3	120-180	160	35
				Bitumen	5	180–240	230	51
SXV_4-7	Carbonaceous shale	H-R	16.00	Bitumen	6	130–220	175	11
SXV_4-11	Carbonaceous shale	H-R	3.47	Bitumen	3	nd	nd	

Notes: OM – organic matter; D-S – diagenetic-supergene enrichment; H-R – Hydrothermal-reworking; nd – not determined.

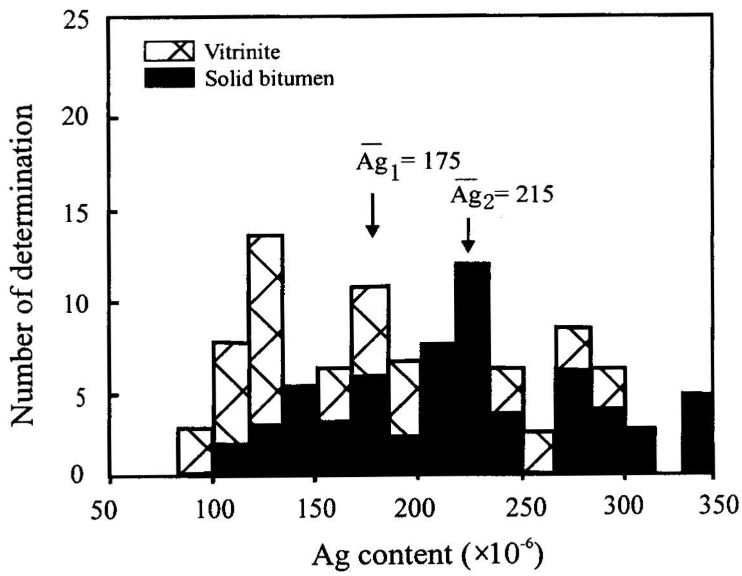

Fig. 3. Histogram of Ag contents in vitrinites and solid bitumens from the Songxi Ag-Sb deposit.

3.3 Occurrence mode of silver in the organic matter and its significance in organic mineralization

Scanning electron micrographs of organic matter show that there is no existence of microscopic inclusions of ore minerals (or silver-bearing minerals) within the organic matter. A qualitative chemical composition X-ray scanning analysis also indicates that the distribution of silver in organic matter is uniform and dispersed from rim to core. It is generally agreed that there are three modes of interaction between the dissolved metals and the organic matter that may result in enrichment of the metals: (1) physical adsorption of metals onto the organic matter, (2) chemisorption of metals into organic matter by forming organometallic complexes, and (3) precipitation of metals reduced by organic matter. The physical adsorption is generally manifested in enrichment of metallic ions onto the surface coat of organic matter, but no evidence has been obtained for this case. As the elements that form organic matter are dominated by C, H, O, N, S and P as well as some halogens (mainly F, Cl, Br and I), their organic groups (such as –OH, –COOH and –SH) have the ability to link with native silver into organic matter, resulting in anomalous enrichment of silver within the organic matter. Therefore, we may conclude that the chemisorption (complexation) and reduction of organic matter are the main ways that cause the anomalous silver enrichment. The fact that silver contents in the solid bitumen are higher than those in the marine vitrinite indicates that a chemical reaction had taken place between the hydrocarbon-bearing fluid and the silver-bearing fluid in the process of petroleum generation and migration.

It is of great significance in finding silver anomalies within the organic matter of the Songxi Ag-Sb deposit. Because bitumen is abundant in the Songxi ore district and the ore zone is often one of bitumen veins, the distribution of bitumen veins in the ore district may be considered a marker for exploration of new orebodies.

4 Conclusion

The electron microprobe technique has been useful in determining the silver content of organic matter and can be used in understanding the rules of metal enrichment in different types of organic matter in the formation of ore deposits in combination with studies of organic petrology and geological characters of ore deposits. In this study we have observed anomalous silver enrichment in the organic matter of the ore district and also found that the silver content of the solid bitumen is generally higher than that of the marine vitrinite. This study also provides geochemical data for further revealing the association of silver mineralization with organic matter and finding the distribution of new orebodies in the ore district. This is of great significance for present-day studies of organic matter and metalliferous mineralization.

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