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Occurrence modes of silver in the Ni-Mo-PGE polymetallic layer of the Lower Cambrian black shales in Zunyi, Guizhou Province, South China

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Abstract The Ni-Mo-PGE polymetallic mineralization of the Lower Cambrian black shales locate in Zunyi, South China and contain abundant noble metals such as Ag, Au and PGE, and especially Ag with average concentration of 64×10^{-6}. The occurrence modes of Ag have been investigated using methods of selective chemical dissolution and transmission electron microscopy. The results demonstrate that the occurrence modes of Ag are complex and diversiform. It might be associated with clay minerals, organic matter, sulfides and also occurred as native silver and sulfides with nanometer in size. Combined with results of previous studies, we suggest that the sulfides, clay minerals and organic matter which hosted in the Ni-Mo-PGE polymetallic ores of black shales can play the roles of important reduction and adsorption geochemical barriers for the enrichment and distribution of silver. This study further implies that the selective chemical dissolution and transmission electron microscopy may pave the way to study the occurrence modes of other noble metals in black shales.

Key words silver; Lower Cambrain; black shale; transmission electron microscopy; selective chemical dissolution

1 Introduction

Researches on noble metals in the black shales have been conducted considerably since 1980s, especially after the activity of International Geological Correlation Programmes (IGCP) Project 254 "Metalliferous Black Shales" (Pašava, 1991). Black shales can form in a great variety of environments from suboxic through anoxic to euxinic and provide a new source for the noble metals. In South China, the Ni-Mo-PGE polymetallic mineralization of Guizhou and Hunan provinces hosted in the Lower Cambrian black shales belongs to this type. Previous studies on noble metals mainly focused on geochemical characteristics, metal source and Re-Os geochronology (Jiang et al., 2007; Pašava et al., 2008; Xu et al., 2013). However, the occurrence modes of the noble metals are still problematic because of their lower concentration compared with other major and trace elements.

Previous works have suggested that noble metals in the Ni-Mo-PGE polymetallic layer might be hosted as independent minerals and organometallic compounds in micro to nano scale (Wang and Sun, 2007; Bao, 1997; Liang and Zhu, 1995; Li et al., 1999, Zhang et al., 2005). However, no evidence for the occurrence modes of noble metals has been indicated. In addition, studies on the occurrence modes of noble metals in this region mostly focused on PGE and Au, but rarely involved in Ag which has a relative higher concentration than those of PGE and Au. In this contribution, the occurrence modes of Ag in the Ni-Mo-PGE polymetallic layer of the black shales in Zhongnan village, Zunyi area, Guizhou Province were examined on the basis of the combination of selective chemical dissolution and transmission electron microscope (TEM). Importantly, TEM that equipped with energy dispersive spectroscopy (EDS) for chemical analysis can identify the minerals, especially when we identity a new mineral within micron to nanometer, TEM is the most excellent method (Chen et al., 2003).

2 Geologic backgrounds

The metalliferous Lower Cambrian black shales are mainly distributed along the southern margin of the Yangtze Craton and extend over 1600 km trending northeast along Yunnan, Guizhou, Hunan, Jiangxi to Zhejiang provinces (Mao et al., 2002). The Lower Cambrian black shales at Zunyi, Guizhou Province are exposed at the northwest of the Songlin dome in the Loushan fold belt in Upper Yangtze Paraplatform. The exposed strata are mainly Cambrian, followed by Sinian, Ordovician and Quaternary system and there is not obvious magmatic activity in this region (Fig. 1) (Zeng, 1998). The Lower Cambrian strata is consisting of Niutitang, Mingxinsi, Jindingshan and Qingxudong formations in ascending order, and the Ni-Mo-PGE polymetallic layer is hosted exclusively in the Niutitang Formation which is underlain by the dolomite of the Sinian Dengying Formation uncomfortably (Fig. 1) (Zeng, 1998, Chen, 2006). A comprehensive Niutitang Formation is usually divided into eight units from the bottom to the top as follows, weathered bed, barite bed, phosphatic rock bed, siliceous rock bed, Ni-Mo-PGE polymetallic layer, schistosity black shale, phosphorite nodule and black shale (Fig. 2) (Wang and Sun, 2007). The mineral assemblages of the Ni-Mo-PGE polymetallic layer are mainly clay minerals, organic matter and the sulfides. Detailed descriptions of the mineralogy have been given by Fan et al. (1973), Kao et al. (2001), Chang (2007), Orberger et al. (2007), and Belkin and Luo (2008).

3 Materials and methods

Three samples of Ni-Mo-PGE polymetallic layer of the Lower Cambrian black shales are collected from Zhongnan village, Zunyi, Guizhou Province (Figs. 1 and 2). Samples are crushed as fine as 200 meshes and prepared for further determination and observation.

The components of the Ni-Mo-PGE polymetallic ores are mainly clay minerals, sulfides and organic matter. A selective chemical dissolution procedure for variations of Ag concentration in different mineral phases was designed and presented in Table 1 and Fig. 3. Samples for TEM observation were prepared onto copper mesh with organic supporting membrane and carbon coating after dispersed in pure ethyl alcohol by ultrasonic and were measured by a JEM-2000FXⅡ transmission electron microscope (TEM) with an Oxford Link ISIS energy dispersive X-ray spectrometer (EDS). The following conditions were applied in the experiment: accelerating voltage 160 kV and magnification is 20 to 80 K. Both selective chemical dissolution experiment and TEM observations were performed at the State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences (Guiyang) except the determination of Ag concentration which was done by an ICP735 (Varian) at the ALS Chemex (Guangzhou) Co., Ltd; the tolerances for standard and duplicate samples were 3.5% and 5% respectively.

4 Results

4.1 Selective chemical dissolution experiment

The results of the selective chemical dissolution experiment for three samples are listed in Table 2. The concentration of Ag doesn't vary drastically in the different minerals phases. Meanwhile, there was also not showing an obvious enrichment of Ag during the experiment. The whole rock samples of polymetallic ores (Product Ⅰ) contain 62×10^{-6} to 65×10^{-6} Ag (average 64×10^{-6}). The Ag contents of the residue of the Product Ⅰ treated by HF and HCl (Product Ⅱ) range from 58×10^{-6} to 74×10^{-6} Ag (average 64×10^{-6}). Product Ⅲ and Product Ⅳ are the floating section and precipitate of Product Ⅱ separated by $CHBr_3$ (2.89 g/cm^3). The Ag content of Product Ⅲ and Product Ⅳ range from 88×10^{-6} to 101×10^{-6} (average 96×10^{-6}) and 43×10^{-6} to 65×10^{-6} (average 53×10^{-6}), respectively. The Ag concentration of Product Ⅴ ranges from 69×10^{-6} to 94×10^{-6} Ag (average 78×10^{-6}).

Table 1 Experimental procedure of selective chemical dissolution experiment for the Ni-Mo-PGE polymetallic layer in Lower Cambrian black shales, Zunyi, Guizhou, China

Product No.	Experimental procedure
Ⅰ	Whole rock without any treatment
Ⅱ	Residue of the Product Ⅰ dissolved by HF (40%) and HCl (20%), water bath (60℃) for 4 h, repeat once
Ⅲ	Floating section of Product Ⅱ separated by $CHBr_3$ (2.89 g/cm^3)
Ⅳ	Precipitate of Product Ⅱ separated by $CHBr_3$ (2.89 g/cm^3)
Ⅴ	Residue of Product Ⅳ dissolved by HNO_3 (v/v=1:1), room temperature, 10 min

Note: The selective chemical dissolution experimental procedure was designed by reference to Dai et al. (2004), Wang and Sun (2007).

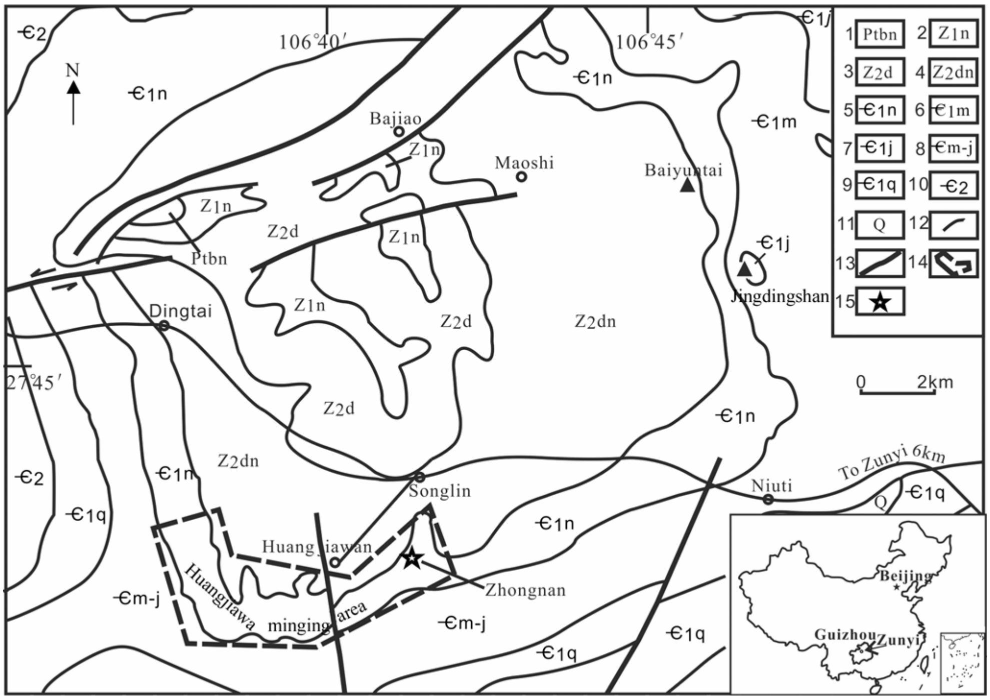

Fig. 1. The regional geological map of Ni-Mo-PGE polymetallic mineralization in Lower Cambrian black shales, Zunyi, Guizhou, China (modified from Zeng, 1998). Note: 1. Lower Proterozoic Banxi Group; 2. Nantuo Formation; 3. Doushantuo Formation; 4. Dengying Formation: dolomite; 5. Niutitang Formation: stone coal and polymetallic carbonaceous pelite; 6. Mingxinsi Formation: carbon-mudstone; 7. Jindingshan Formation: siltstone and mudstone; 8. Mingxinsi Formation and Jindingshan Formation; 9. Qingxudong Formation: dolomite; 10. Middle Cambrian; 11. Quaternary; 12. stratigraphic boundary; 13. fault; 14. Ni-Mo-PGE mining area; 15. sampling site.

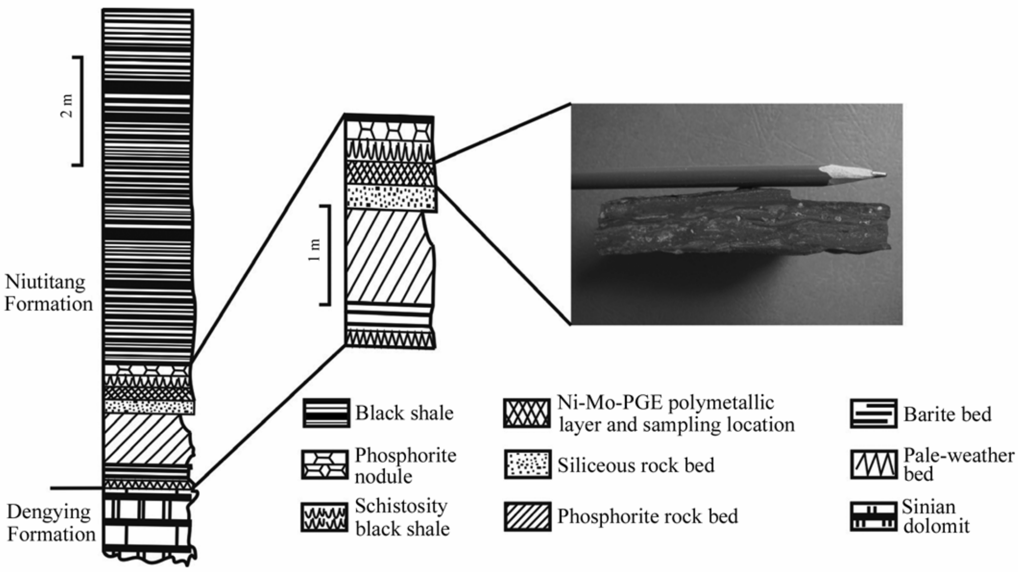

Fig. 2. The profile of Ni-Mo-PGE polymetallic mineralization in Lower Cambrian black shales, Zhongnan village, Zunyi, Guizhou, China (modified from Wang and Sun, 2007).

4.2 TEM observation

The observation were carried out for all products of the selective chemical dissolution experiment and the results show that much more Ag-bearing minerals, such as native silver and Ag-bearing sulfides, were found in the Product Ⅴ. The native silver minerals are in rounded shape and the size ranges from 50 to 500 nm and were melted during the observation by electron beam (Fig. 4a). The Ag-bearing sulfides are in irregular and rounded shape, with the size ranging from 200 to 600 nm (Fig. 4b, c). All of the Ag-bearing sulfides are distinguished from native silver by the melting phenomenon.

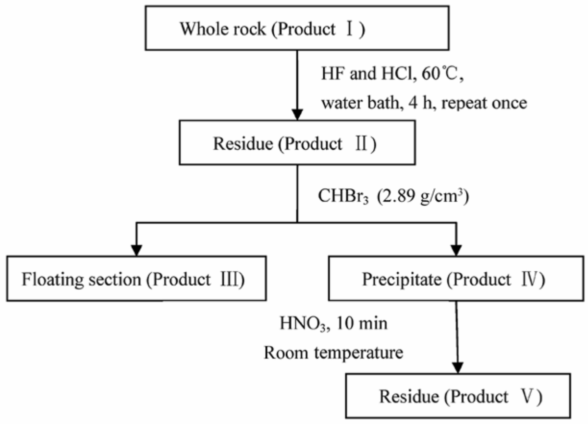

Fig. 3. The experimental flow chart of selective chemical dissolution experimental procedure (designed by reference to Dai et al., 2004, Wang and Sun, 2007).

5 Discussion

Possible occurrence modes of silver were evaluated by the variation of Ag concentration during the selective chemical dissolution experiment (Table 2). Product Ⅰ (average Ag of 64×10^{-6}) was treated by HF and HCl to dissolve the clay minerals and obtain Product Ⅱ (average Ag of 64×10^{-6}). There was no obvious variation for average Ag concentration with the dissolution of clay minerals in this stage, indicating that some silver may be hosted in the clay minerals. Product Ⅲ was mainly composed of the organic matter such as kerogen and its density was relatively low compared with those of $CHBr_3$ (2.89 g/cm^3), the concentration of Ag was 96×10^{-6} average and Ag possibly hosted in the organic matter as organometallic compounds resemble other similar silver deposit (Zhuang et al., 1998; Hu et al., 2002). Product Ⅴ was the residue of Product Ⅳ treated by HNO_3 and has an average concentration of Ag of 78×10^{-6}, higher than Product Ⅳ (53×10^{-6}), indicating a small part of Ag also hosted in sulfides. These results suggest that the occurrence modes of Ag in the Ni-Mo-PGE polymetallic layer of the black shales are not unique, whereas, it can associates with clay minerals, organic matter and sulfides.

Silver is the typical chalcophile element and can usually form sulfide or sulfosalt minerals, native silver and electrum (Liu et al., 1984). As mentioned above, Ag can also associate with clay minerals, organic matter and sulfides except for native silver and sulfide minerals in the Ni-Mo-PGE polymetallic layers. Reason for these results is due to the sedimentary conditions. The Lower Cambrian black shales formed in a sediment-starved, semi-restricted and anoxic basin (Lehmann et al., 2007; Pašava et al., 2008) and the higher amount of organic matter is a notable feature. The presence of abundant organic matter can play an important role for the activation, transportation and enrichment of metals by absorption, complexion and reduction (Tu, 1998). Furthermore, the related simulations experiments show that the presence of abundant clay minerals, sulfide and organic matter also have strong surface effects on adsorption of metals because of large surface area and surface chemical activity (Zhu et al., 2005; Han et al., 2011). Therefore, we concluded that clay minerals, sulfides and organic matter provide favorable geochemical barriers (adsorption and reduction) and constrain the enrichment and distribution of Ag in the Ni-Mo-PGE polymetallic layer of the Lower Cambrian black shales.

6 Conclusions

The occurrence modes of Ag in the lower Cambrian black shales of South China were not composed of a single form but it might be combined with silicate minerals, organic matter and sulfide minerals. In this study, we also indentified native silver and Ag sulfide in size of nanometer. The organic matter, silicate minerals and sulfide minerals might play the roles of geochemical barriers for the enrichment and distribution of Ag.

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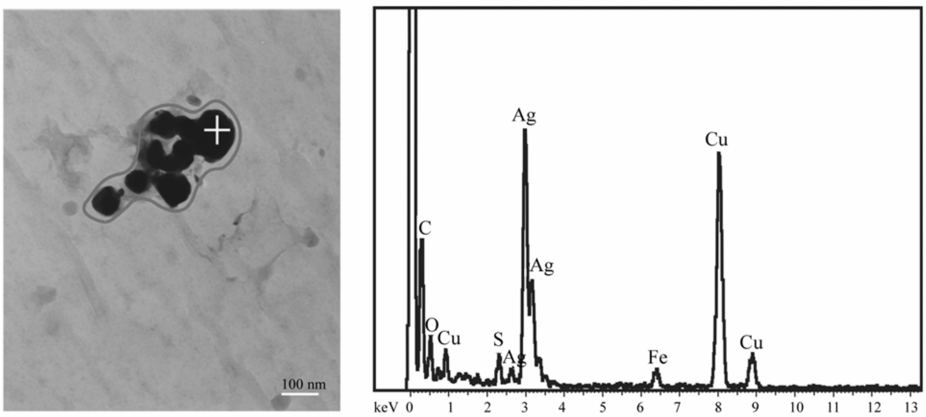
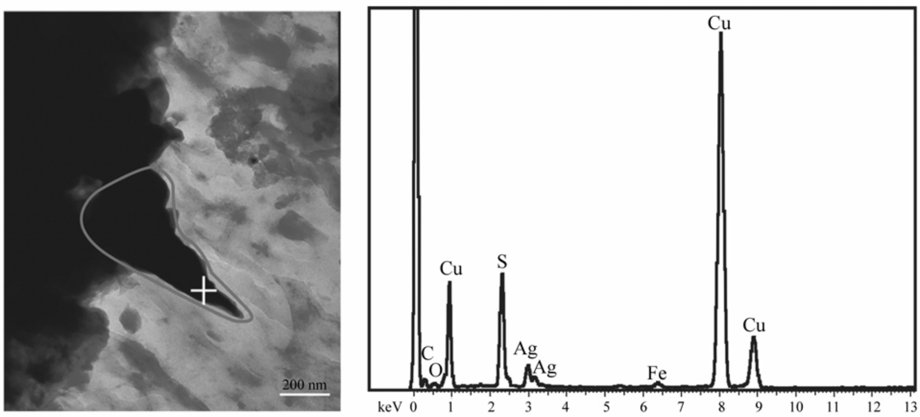
Table 2 The concentrations of Ag in different products during the selective chemical dissolution experiment

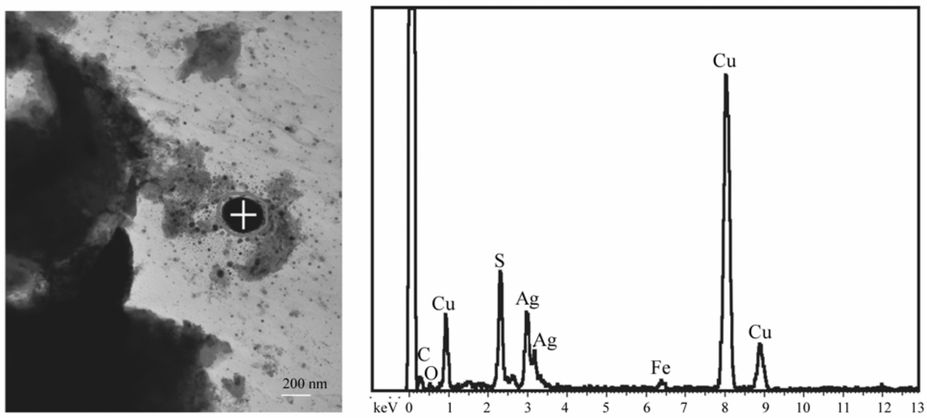
Product No.	Sample No.	Ag ($\times10^{-6}$)	Features of products
Ⅰ	xzh1	62	Silicate minerals, sulfides, organic matter
	xzh2	65	
	xzh3	65	
	Average	64	
Ⅱ	xzh1	59	Sulfide and organic matter
	xzh2	58	
	xzh3	74	
	Average	64	
Ⅲ	xzh1	88	Organic matter such as kerogen
	xzh2	101	
	xzh3	99	
	Average	96	
Ⅳ	xzh1	52	Sulfides
	xzh2	43	
	xzh3	65	
	Average	53	
Ⅴ	xzh1	72	Heavy minerals undissolved by acid solution
	xzh2	69	
	xzh3	94	
	Average	78	



(a) The image and EDS spectrum of native silver



(b) The image and EDS spectrum of Ag-bearing mineral



(c) The image and EDS spectrum of Ag-bearing mineral

Fig. 4. The Ag-bearing minerals in the residue of selective chemical dissolution experiment (Product Ⅴ), "+" is the position for analysis, the Cu characteristic peak was contributed by the sample-carrier Cu grid.

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