

Article

The Occurrence and Chemical Composition of Bismuth-Bearing Minerals in the Niuxingba-Liumukeng Ag-Pb-Zn Deposit, Jiangxi Province, South China

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Abstract: The Niuxingba-Liumukeng deposit, located in the Yinkeng ore field (Jiangxi province, South China), is a typical Ag-Pb-Zn deposit hosted in the Yudu-Ganxian metallogenic belt. Based on the field investigation and mineralogical studies, the mineralization of this deposit can be divided into three stages: quartz-pyrite-arsenopyrite stage (I), quartz-galena-sphalerite-sulfosalt stage (II), and quartz-carbonate stage (III), with stage II being the main Ag mineralization stage. In this contribution, we reported the occurrence of bismuth-bearing minerals in this hydrothermal deposit and its implications for ore formation. Based on the results of electron microprobe analyses, we infer that the dominant occurrence of bismuth at Niuxingba-Liumukeng is primarily marked by solid solutions within the crystal lattice of galena and as visible independent bismuth-bearing minerals. The independent bismuth minerals consist of berryite [Pb₃(Ag,Cu)₅Bi₇S₁₆], emplectite (CuBiS₂), and aikinite (PbCuBiS₃). Most bismuth minerals replace chalcopyrite or fill in the cracks of pyrite and chalcopyrite. Meanwhile, we found a large number of Bi-bearing minerals closely coexisting with Ag-bearing minerals, indicating that bismuth may have played a crucial role in silver deposition from hydrothermal fluids. We considered that the existence of bismuth-rich melts associated with the ore-forming hydrothermal systems could help to promote the enrichment and precipitation of silver to form economic ores.

Keywords: bismuth mineral; silver occurrence; Ag-Pb-Zn mineralization; Niuxingba-Liumukeng deposit; south China



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1. Introduction

Bismuth has been identified as a significant metal in some hydrothermal deposits, however, ore deposits in which bismuth is the primary product are very rare and their main occurrences are associated components of other metal ores [1]. China hosts the largest proven bismuth reserves in the world, which are mainly distributed in the Nanling area including Jiangxi, Hunan, Guangdong, and other provinces [2].

The Niuxingba-Liumukeng Ag-Pb-Zn deposit is located in the Yinkeng ore field of Jiangxi Province in south China [3]. In addition to silver, lead, and zinc, bismuth is also an important accompanying metal in this deposit. Previous studies have conducted in-depth exploration of the Niuxingba-Liumukeng deposit and preliminarily identified the scale and distribution of the mineralized ore bodies [4]. Until now, the Niuxingba-Liumukeng deposit has undergone numerous exploration work, but few studies for ore mineralogy have been conducted. Only several authors attempted to discuss this aspect. For example, Sun [5] studied a series of mineralogical characteristics on chalcopyrite in the deposit, which showed that chalcopyrite is one of the main carrier minerals for Ag-Au and can

serve as a prospecting mineral. Lu et al. [2] suggested that bismuth is one of the important associated elements in the deposit, and bismuth was formed in medium to low temperature and low fluid salinity conditions.

Overall, there is still insufficient research on the occurrence and physicochemical conditions for bismuth in the Niuxingba-Liumukeng deposit, and another issue is that several studies indicate that bismuth and silver could coexist in some ore deposits [6,7]. However, no relevant research has been conducted to reveal how bismuth plays a crucial role in silver transport and deposition in hydrothermal systems. In this paper, we present a comprehensive investigation of bismuth minerals at Niuxingba-Liumukeng. We aim to constrain the occurrence and chemical composition of bismuth and discuss the role of bismuth in silver transport and deposition.

2. Regional Geology

The South China Block (SCB) is famous for its large-scale mineralization and is one of the most important metallogenic provinces in the world. It was composed of the amalgamation of the Cathaysian block from the southeast and the Yangtze block from the northwest along the Qinzhong-Hangzhou tectonic joint belt during the Neoproterozoic [8,9]. The Nanling region lies in the central part of the SCB (Figure 1a,b), and is endowed with a large amount of bismuth resources [2,10].

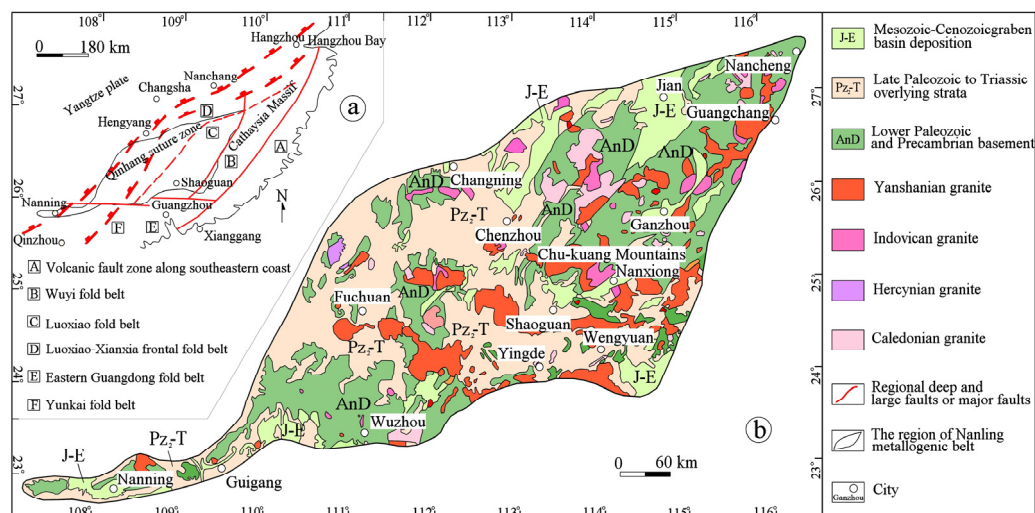


Figure 1. Tectonic location (a) and geological map of the Nanling metallogenic belt (b) (modified from [11]).

The sedimentary strata exposed in the Nanling Range consists of a basement comprising the Neoproterozoic to Ordovician clastic rocks, the Devonian to Triassic marlstone, carbonate, and clastic rocks, and the Jurassic to Cretaceous clastic rocks, red beds, and volcanic rocks [8,12,13]. In addition, this region has experienced multiple tectonic evolution processes, including the Sibao, Xuefeng, Caledonian, and Indosinian events [14]. A significant Au-Ag-Pb-Zn-Cu mineralization has developed in the Yinkeng ore field in the eastern section of the Nanling region. In recent years, scientific deep drilling has been conducted in the Yinkeng ore field, which has received extensive attention [15].

The ore field has an exposed area of 70 km², and the exposed stratigraphy is composed of Neoproterozoic (Qingbaikou, Nanhua, and Sinian systems), Early Paleozoic (Cambrian system), Late Paleozoic (Devonian, Carboniferous, and Permian systems), Mesozoic (Jurassic and Cretaceous systems), and Cenozoic Quaternary. The Qingbaikou-Cambrian system forms a nearly NS-trending folded basement, while the Devonian-Permian system forms a nearly NE-trending folded cover. Inside, the Qingbaikou Kuli Formation is dominated by the Carboniferous fine clastic rock, which is characterized by rich tuffaceous matter. The lithology of the Shangshi and Shabahuang Formation of the Nanhua system is composed

of clastic rocks, slate, and siltstone. The fault structures, including NNE- and NE-trending faults, are developed, belonging to the components of the Dayu-Nancheng and Yingtan-Dingnan tectonic zones through the Yinkeng ore field [3]. Among them, the NNE-trending fault is the largest group of faults in the study area, with obvious mylonitization and schistosization zones. The NE-trending fault was formed during the Indosinian period and was still active during the Yanshanian period, which also developed mylonitization and schistosization zones [3].

The Yinkeng ore field is characterized by the production of W-Sn-Mo deposits related to biotite granite (e.g., the Huameiao tungsten deposit and the Yanqian tungsten deposit; [3]), and Ag-Pb-Zn deposits related to granite (e.g., the Niuxingba-Liumukeng Ag-Pb-Zn deposit and the Laohutou-Qiaozikeng Pb-Zn deposit; [2,5]). Previous research has shown that bismuth could exist in many magmatic-hydrothermal deposits and commonly act as a co-product in the Nanling area [1]. Therefore, the Ag-Pb-Zn deposits in the Yinkeng ore field are representative in the element assemblage of the Nanling area and are an ideal area for studying bismuth mineral assemblages and mineralization (Figure 2a,b).

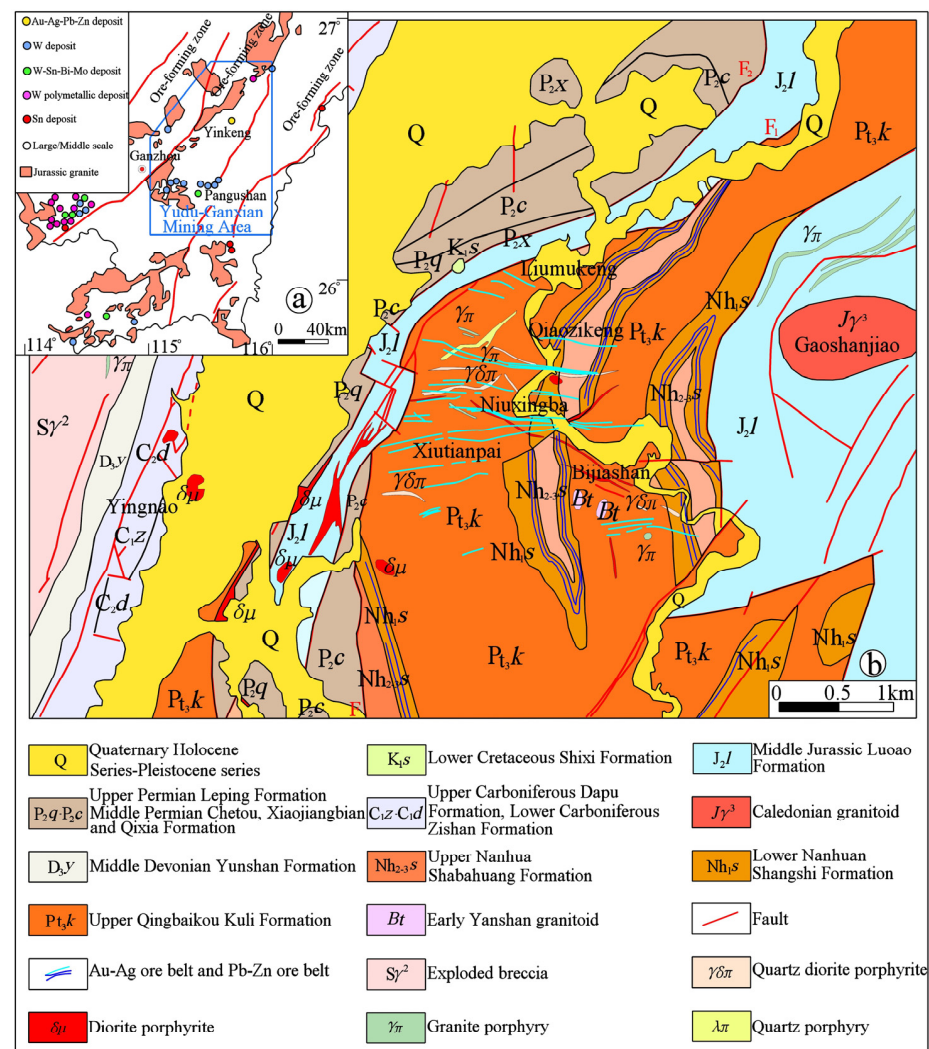


Figure 2. Geological sketch of the Yudu-Ganxian metallogenic belt (a) and geological map (b) of the Yinkeng ore field (modified from [2,16]).

3. Ore Deposit Geology

The Niuxingba-Liumukeng deposit (6.9 Mt @ 187.23 g/t Ag, 1.657% Pb, and 3.956% Zn) is located in the Yinkeng ore field of Jiangxi Province in the Nanling metallogenic belt and has been identified as a medium-sized deposit in terms of silver reserves [3]. The

host rocks of the deposit are mainly granodiorite porphyry, quartz porphyry, and granite porphyry (granodiorite porphyry, 160 ± 1 Ma; quartz porphyry, 153 ± 1 Ma; granite porphyry, 153.6 ± 0.9 Ma; [17]). To date, more than 30 ore bodies have been identified and are controlled by the NE-NNE-trending faults [3], and almost all occurrences of ore bodies are found along the intrusion (approximately 152–160 Ma [3]) and strata boundaries or within the structural fracture zones.

The ore bodies occur mainly in the form of veins followed by net veins. The strike direction of the ore bodies is $80\text{--}120^\circ$, with dip direction towards S or W and dip angles of $75\text{--}88^\circ$ [3]. From south to north, there are No.52 Pb-Zn mineralized zone, No.31-32 Ag-Pb-Zn mineralized zone, No.7 Cu-Ag-Au mineralized zone, No.11 Ag polymetallic mineralized zone, No.42-41 Pb-Zn polymetallic mineralized zone, and No.17 Ag-Pb mineralized zone (Figures 3 and 4; [3]).

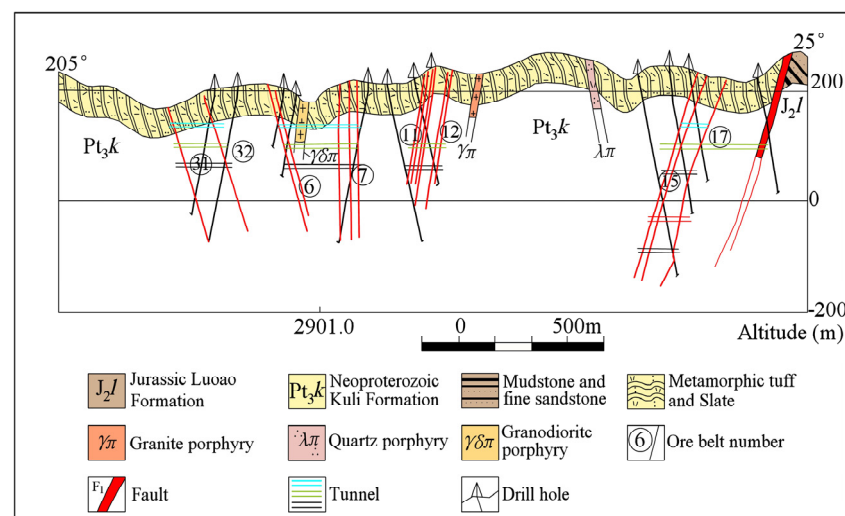


Figure 3. Comprehensive section of silver ore bodies in the Niuxingba-Liumukeng deposit (modified from [3,16]).

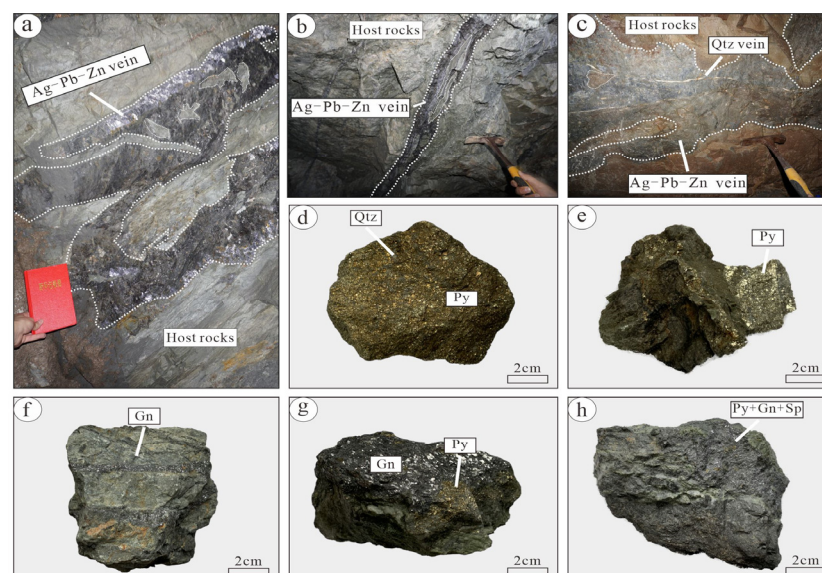


Figure 4. Field and hand-specimen photographs of representative samples. (a,b) Veined galena, sphalerite, and pyrite in contact with host rocks; (c) Clear boundary between the sulfide ore body and host rock; (d,e) Disseminated structure-pyrite; (f) Veinlet structure-galena; (g) Massive structure fine-grained galena and pyrite; (h) Massive sulfide ore comprising sphalerite, galena, and pyrite. Abbreviations: Gn, galena; Py, pyrite; Qtz, quartz; Sp, sphalerite.

Based on the field investigation and mineralogical studies, three stages of the hydrothermal mineralization have been identified, including quartz-pyrite-arsenopyrite stage (I), quartz-galena-sphalerite-sulfosalt stage (II), and quartz-carbonate stage (III). Figure 5 illustrates the paragenetic sequence. The early ore mineral assemblage (Stage I) is dominated by arsenopyrite and pyrite. In this stage, pyrite is euhedral and is associated with quartz; both were replaced by sphalerite, galena, and chalcopyrite. The successive ore assemblage in Stage II are pyrite, galena, sphalerite, pyrrhotite, and sulfosalt minerals. Sulfosalt species include silver-bearing and bismuth-bearing sulfosalt minerals, which commonly coexist with galena, replacing early formed pyrite and arsenopyrite. Stage II is the main bismuth-silver mineralization stage. Stage III is dominated by calcite and quartz, which occur as late veins. The supergene phase is formed by the oxidation of primary sulfides, mainly including hematite and limonite.

Minerals	Mineralization stage			Supergene stage
	Stage I	Stage II	Stage III	
Quartz				
Pyrite				
Arsenopyrite				
Pyrrhotite				
Chalcopyrite				
Sphalerite				
Galena				
Tetrahedrite				
Uytenbogaardtite				
Argentite				
Sericite				
Calcite				
Hematite				
Limonite				
Abundant Common Minor				

Figure 5. Paragenetic sequence of minerals from the Niuxingba-Liumukeng deposit.

4. Sampling and Analytical Methods

A total of 38 ore samples covering all mineralization stages were collected from the underground workings in the mine. They were subsequently observed and identified using an optical microscope and backscattered electron (BSE) imaging, in order to characterize the mineralogy. Major element compositions of minerals were determined with an EPMA-1720 electron probe at the China University of Geosciences, Beijing, with an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam spot of 1 μm (0.01–0.05% detection limit). During the analysis, natural minerals were used as standards including pentlandite (S-Fe), chalcopyrite (Cu), cobaltite (Co-As), sphalerite (Zn), galena (Pb), native silver (Ag), and natural gold (Au).

5. Results

5.1. Bismuth Minerals

The bismuth-bearing minerals present in the studied deposit include aikinite (CuPbBiS_3), berryite [$\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$], and emplectite (CuBiS_2).

Berryite [$\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$]: It is grayish white color under the microscope with reflected light. Additionally, it has also been observed to replace pyrite and chalcopyrite.

rite. The main element content includes: $w(\text{Bi}) = 48.43\text{--}49.85\text{ wt\%}$, (mean = 49.07 wt%), $w(\text{Pb}) = 19.91\text{--}20.62\text{ wt\%}$, (mean = 20.23 wt%), $w(\text{S}) = 15.67\text{--}16.45\text{ wt\%}$, (mean = 16.09 wt%), $w(\text{Ag}) = 7.23\text{--}7.74\text{ wt\%}$, (mean = 7.50 wt%), and $w(\text{Cu}) = 6.60\text{--}6.97\text{ wt\%}$ (mean = 6.76 wt%). The calculated formula is $\text{Pb}_3(\text{Ag,Cu})_{5.40}\text{Bi}_{7.21}\text{S}_{15.40}$, which could be simply expressed as $\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$.

Aikinite (PbCuBiS_3): It is characterized by a white reflection color with a light white tinge, forming later than chalcopyrite and pyrite (Figure 6b). Microanalysis indicates mean compositions of 39.99 wt% Bi (35.75–45.47 wt%), 33.47 (28.95–37.33 wt%) Pb, 15.48 (15.27–15.78 wt%) S, and 10.54 (8.74–11.63 wt%) Cu. The calculated formula is $\text{Pb}_{0.97}\text{Cu}_{0.99}\text{Bi}_{1.15}\text{S}_{2.89}$, which can be simply expressed as PbCuBiS_3 .

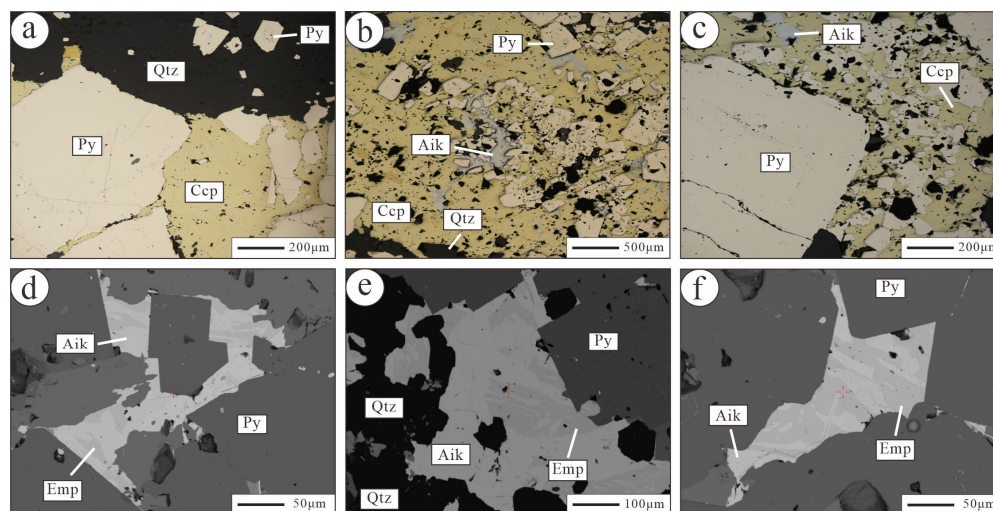


Figure 6. Bismuth minerals and micro-textures for ore minerals in the Niuxingba-Liumukeng deposit. (a) Coexisting pyrite and chalcopyrite (reflected light); (b,c) Coexisting aikinite and chalcopyrite (reflected light); (d–f) Coexisting aikinite and emplectite within pyrite (BSE). Abbreviations: Aik, aikinite; Ccp, chalcopyrite; emp, emplectite; Py, pyrite; Qtz, quartz.

Emplectite (CuBiS_2): The reflection color is light white, showing heteromorphic granular textures. Additionally, it has also been observed to corrode and replace chalcopyrite (Figure 6c). The Bi, Cu, and S contents in this mineral are 61.65–62.36% (mean = 62.04 wt%), 19.45–19.67% (mean = 19.58 wt%), and 17.87–18.04% (mean = 17.94 wt%). The calculated formula is $\text{Cu}_{1.06}\text{Bi}_{1.02}\text{S}_{1.92}$, which can be simply expressed as CuBiS_2 .

5.2. Silver Minerals

Silver mostly occurs as solid solutions within other ore minerals in the studied ore deposit. In addition to the Ag-Bi-S assemblages mentioned above, there are three other silver-bearing independent minerals at Niuxingba-Liumukeng: tetrahedrite $[(\text{Cu,Ag})_{12}(\text{Sb,As})_4\text{S}_{13}]$, argentite (Ag_2S), and uytendogaardite (Ag_3AuS_2).

Tetrahedrite $[(\text{Cu,Ag})_{12}(\text{Sb,As})_4\text{S}_{13}]$: Tetrahedrite is the main silver-bearing mineral in the Niuxingba-Liumukeng deposit. The reflection color is grayish-white, with particles of approximately 150 µm. Microscopic observations reveal that tetrahedrite is commonly associated with galena, chalcopyrite, and pyrite, and occurs generally as subhedral grains (Figure 7b). The main contents of this mineral are (Cu) = 24.20–25.71 wt% (mean = 25.16 wt%), $w(\text{S}) = 23.29\text{--}24.74\text{ wt\%}$ (mean = 24.14 wt%), $w(\text{Sb}) = 19.77\text{--}27.07\text{ wt\%}$ (mean = 22.42 wt%), $w(\text{Ag}) = 19.33\text{--}19.61\text{ wt\%}$ (mean = 19.46 wt%), $w(\text{As}) = 0.58\text{--}5.53\text{ wt\%}$ (mean = 3.79 wt%), $w(\text{Zn}) = 1.77\text{--}3.66\text{ wt\%}$ (mean = 2.53 wt%), and $w(\text{Fe}) = 0.76\text{--}2.12\text{ wt\%}$ (mean = 1.63 wt%). The calculated formula is $(\text{Cu,Ag,Fe,Zn})_{11.45}(\text{Sb,As})_{4.17}\text{S}_{13.38}$, which can be simply expressed as $(\text{Cu,Ag})_{12}(\text{Sb,As})_4\text{S}_{13}$.

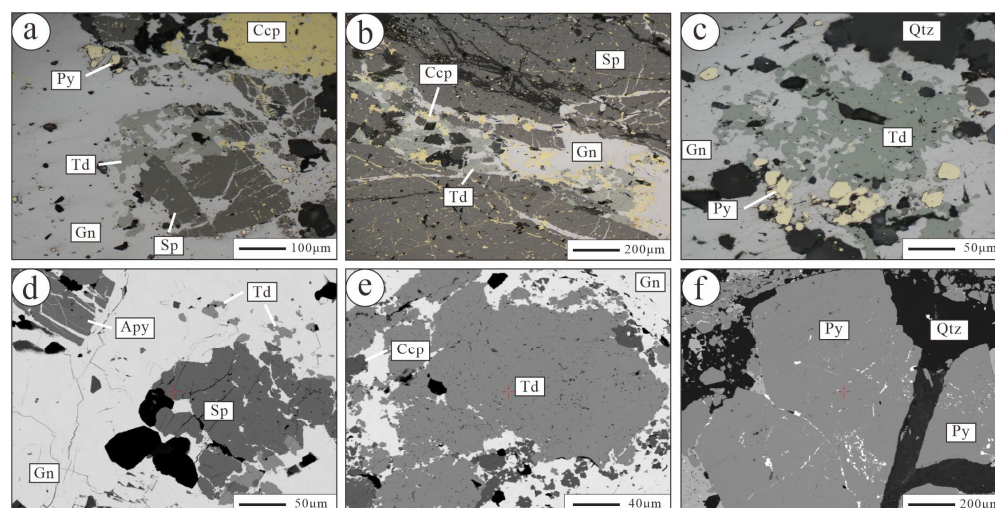


Figure 7. Silver minerals and micro-textures for ore minerals in the Niuxingba-Liumukeng deposit. (a) Sphalerite and chalcopyrite associated with tetrahedrite (reflected light); (b) Coexisting chalcopyrite, sphalerite, and tetrahedrite within galena (reflected light); (c) Early generation galena corroded by tetrahedrite (reflected light); (d) Coexisting sphalerite and tetrahedrite within galena (BSE); (e) Coexisting chalcopyrite and tetrahedrite within galena (BSE); (f) The automorphic pyrite formed in the early stage (BSE). Abbreviations: Apy, arsenopyrite; Ccp, chalcopyrite; Gn, galena; Py, pyrite; Sp, sphalerite; Td, tetrahedrite.

Argentite (Ag_2S): Under the reflecting microscope, the reflection color is grayish-white with a light blue tinge, and the particle size is approximately $85\ \mu\text{m}$. Additionally, argentite is mostly developed in galena and contains Ag and S (73.85 wt% and 13.28 wt%, respectively, Table S1). The calculated formula is $\text{Ag}_{1.87}\text{S}_{1.13}$, which can be simply expressed as Ag_2S .

Uytenbogaardtite (Ag_3AuS_2): The reflection color is light yellow, and the Ag, Au, and S contents in this mineral are 46.80 wt%, 45.81 wt%, and 4.97 wt%. The calculated formula is $\text{Ag}_{3.17}\text{Au}_{1.70}\text{S}_{1.13}$, which can be simply expressed as Ag_3AuS_2 .

6. Discussions

6.1. The Occurrence of Bismuth and Silver

Through the results of electron microprobe analyses, we identify that the dominant occurrence of bismuth-silver at Niuxingba-Liumukeng is primarily marked by solid solutions within the crystal lattice and bismuth minerals, and the later form is the main occurrence of bismuth-silver in the deposit. The contents of bismuth-silver present as a solid solution in sulfides could be Bi of 1.10 wt% in galena and Ag of 0.45 wt% in galena. The main bismuth minerals are emplectite (CuBiS_2), aikinite (PbCuBiS_3), and berryite [$\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$], which occur in the interior, edges, or cracks of sulfide minerals (Figure 6c). Chalcopyrite usually encloses emplectite, which mainly occurs in a micrometer scale at the contact between chalcopyrite and pyrite. The silver minerals are mainly composed of tetrahedrite [$(\text{CuAg})_{12}(\text{SbAs})_4\text{S}_{13}$] and argentite (Ag_2S), and mainly replaced early formed sulfides, e.g., galena and sphalerite (Figure 7a).

The correlation analysis of major elements shows that silver and copper in tetrahedrite yield a negative correlation, which may be due to the varying degrees of isomorphism substitution between silver ions in the hydrothermal solutions and copper ions in the early tetrahedrite, resulting in the formation of early silver minerals (Figure 8a). In addition, silver and bismuth in ores demonstrate a positive correlation, indicating that when the temperature of the hydrothermal system is higher than the melting point of bismuth-silver melts, the Bi melts could strongly absorb and precipitate silver in the ore-forming fluid.

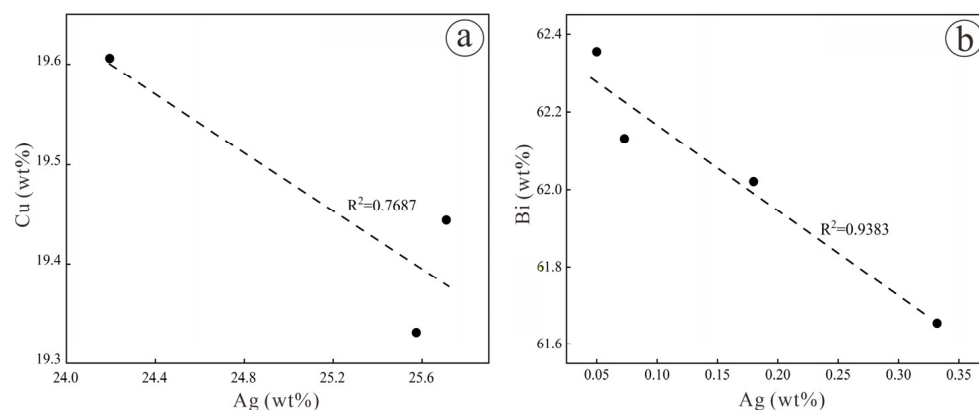


Figure 8. Correlation analysis of major elements in tetrahedrite and emplectite. (a) Correlation of Ag and Cu in tetrahedrite; (b) Correlation of Ag and Bi in emplectite.

6.2. The Possible Source of Bismuth

Numerous studies have shown that bismuth enrichment in hydrothermal Pb-Zn deposits is mainly related to magmatic-hydrothermal fluids, e.g., the Yinshan Pb-Zn deposit in Jiangxi [18], and the Chaijiaying Pb-Zn deposit in Hebei [19]. In addition, due to the similar ion radius of Bi^{3+} (1.16 Å) and Ca^{2+} (1.01 Å), bismuth is more easily enriched in minerals with high Ca contents, favoring a higher abundance of bismuth in acidic magmatic rocks [2,20]. At Niuxingba-Liumukeng, the main ore-forming unit is suggested to be the Mesozoic felsic magmatic rock [3]. Therefore, it is suggested that the granodiorite related to Pb-Zn ore bodies might provide a basis for the source of bismuth in this ore district. Sulfur isotope composition can be used to distinguish different sulfur sources and is widely used to constrain the genesis of mineral deposits [21–23]. The sulfur isotope data (−3.8‰ to −1.4‰) for the Niuxingba-Liumukeng deposit reflect a possible magmatic source for the sulfur contained within metal sulfides [5]. Therefore, bismuth is most likely derived from a magmatic-hydrothermal fluid in the studied deposit.

6.3. Silver Precipitation Mechanism

The epithermal deposit closely related to silver, lead, and zinc mineralization is an important type of deposit [24–30]. In recent years, several studies concluded that bismuth and silver could coexist in many silver deposits, and bismuth may promote the precipitation of silver, providing a new insight into the silver mineralization [2,31–33].

Bismuth is one of the low-melting chalcophile elements (LMCE) with characteristics of low melting point and chalcophile behavior, playing a significant role for the effective enrichment and precipitation of gold [34–36]. Previous studies have shown that bismuth could exist stably in the form of Bi melts at temperatures above 271 °C [37]. Because the partition coefficient of gold in Bi melts is significantly higher (~2 orders of magnitude) than that in hydrothermal fluid [34], the occurrence of bismuth melts could efficiently absorb gold from the hydrothermal fluid. When the temperature drops to 241 °C, the Bi-Au melts decomposes, resulting in efficient gold deposition [36]. Therefore, “liquid bismuth collector” [38] is often used as the main mechanism for the enrichment and precipitation of gold in some bismuth-rich magmatic-hydrothermal deposits. Similarly, many studies have also reported that bismuth and silver could coexist in relatively large quantities in some magmatic-hydrothermal deposits [2,31–33]. According to the similar geochemical properties of bismuth-silver [34], the melting point temperature of Bi-Ag melts (262.5 °C) is similar to that of Bi-Au melts (241 °C), which also provides a thermodynamic basis for the co-migration of bismuth and silver [34,35,38]. The Fe/Zn ratio in sphalerite can be used to estimate the formation temperature ($\text{Fe}/\text{Zn}_{\text{sphalerite}} = 0.0013(T) - 0.2953$) [39]. The calculation and analysis show that the Fe/Zn ratios of sphalerite range between 0.013 and 0.090, which indicates the fluid temperatures between 237 and 296 °C (data from [16]). The fluid inclusion data of the quartz-galena-sphalerite-sulfosalt stage demonstrated that the ore-forming

fluids displayed moderate temperature (210–290 °C; [4]). The estimated temperature range for ore formation at Niuxingba-Liumukeng corresponds to the temperature range [4] higher than the melting temperature for Bi-Ag melts (262.5 °C; [36]). Therefore, the Bi melts could exist to absorb much of Ag in the ore fluids and the decomposition of Bi-Ag melts during fluid cooling (the decomposition temperature ~262 °C) could result in the complex Ag and Bi mineral assemblages in the studied ore deposit, e.g., berryite [$\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$] and matildite (AgBiS_2). Furthermore, this intimate Ag-Bi association is supported by the electron probe data of emplectite from Stage II, which reveals a strong positive correlation between bismuth and silver (correlation coefficient = 0.9383) (Figure 8b). In summary, the participation of bismuth melts in silver enrichment is an important mechanism of Ag mineralization in the Niuxingba-Liumukeng deposit, which helps to understand the occurrence and enrichment mechanism of silver in magmatic-hydrothermal deposits.

6.4. Genetic Implications

The phenomenon of coexisting bismuth-silver minerals in the studied deposit suggests a genetic connection, and also provides effective insights for further in-depth research. Many investigations have reported that bismuth-silver could coexist in many ore deposits: (1) the Jiadong gold deposits in eastern China: berryite and aikinite [40]; (2) the Tanshan polymetallic deposit in eastern China: polybasite and pavonite [41]; (3) the Wei-quan silver deposit in eastern Tianshan district: bismuth and matildite [42]; (4) the Hualalin gold deposit in northeastern China: bismuthinite and cupropavonite [43]. Among them, bismuth-bearing minerals are commonly present in hydrothermal deposits [2]. Due to the positive correlation between silver and bismuth, this suggests that if there is a large amount of bismuth minerals in similar ore deposits, it may also indicate the presence of high-grade silver ore. Therefore, Bi could be treated as a pathfinder for ore exploration for some hydrothermal silver deposits. Studying the occurrence and chemical composition of bismuth-bearing minerals is helpful to understand the migration and enrichment mechanisms of silver in ore-forming fluids. This could also contribute to further improving the exploration methods and metallurgical processes and provide a scientific basis for the recovery and utilization of silver.

7. Conclusions

Three stages of hydrothermal mineralization have been identified at Niuxingba-Liumukeng, including the quartz-pyrite-arsenopyrite stage (I), quartz-galena-sphalerite-sulfosalt stage (II), and quartz-carbonate stage (III). The dominant silver and bismuth mineralization occurred mainly in stage II and the identified Bi and Ag minerals include berryite [$\text{Pb}_3(\text{Ag,Cu})_5\text{Bi}_7\text{S}_{16}$], aikinite (PbCuBiS_3), emplectite (CuBiS_2), and tetrahedrite [$(\text{Cu,Ag})_{12}(\text{Sb,As})_4\text{S}_{13}$]. Among them, berryite closely coexists with aikinite and emplectite. The mineralization temperature during the quartz-galena-sphalerite-sulfide stage (II) is estimated between 210 and 290 °C, which is higher than the temperature of bismuth melt formation (271 °C). Therefore, bismuth in the ore-forming hydrothermal fluid mainly exists in the form of melts. We propose that the bismuth melts could efficiently scavenge silver from hydrothermal fluids to form economic Ag ores. The conclusions of this study not only contribute to the understanding of the occurrence and chemical composition of bismuth-bearing minerals in magmatic-hydrothermal deposits, but also have important significance for the comprehensive recovery and utilization of silver.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14010053/s1>, Table S1: Electron microprobe analysis results of ore minerals from the Niuxingba-Liumukeng deposit (wt%).

Author Contributions: Q.Y., writing-original draft; D.Z., writing-original draft; G.Z., investigation; Q.Z., writing-review and editing; J.L., review and editing. All authors have read and agreed to the published version of the manuscript.

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