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Abstract: Gold and Bi-bearing parageneses are pivotal to understanding gold concentration and deposition processes. The large-scale Laozuoshan gold deposit is located in the Jiamusi Block, northeastern China, and has experienced complex mineralization processes with abundant gold and Bi-bearing minerals. However, the relationship between Bi-minerals and gold is unclear, preventing our understanding of the gold enrichment and precipitation mechanism in the Laozuoshan gold deposit. Optical microscope and SEM results show three stages of gold mineralization: pyrrhotite (Po-1) + arsenopyrite (Apy-1) + Bi-bearing minerals (Bis-1) + Au-1; arsenopyrite (Apy-2) + chlorite + Bi-bearing minerals (Bis-2) + Au-2; and arsenopyrite (Apy-3) + graphite + Bi-bearing minerals (Bis-3) + Au-3. The abundant amount of gold (Au-1~Au-3) is associated with Bi-bearing minerals (Bis-1~Bis-3), which coexist as inclusions and fill in fractures in these minerals. The mineral assemblages of arsenopyrite, Bi-minerals, and gold exhibit a clear As-Bi-Au mineralogy in the ores, and the ternary diagram of the chemical compositions of the Bi-minerals shows that Bi-minerals all fall in reducing regions, indicating that Bi-minerals are precipitated under reducing conditions. The gold compositions demonstrate a positive correlation ($R^2 = 0.58$) between Au and Bi. Consequently, we propose that the gold experienced the ore-forming fluids concentration and further Bi-melts scavenging for the Laozuoshan gold deposit mineralization. The Bi collector model is essential in interpreting the high-grade gold in the Laozuoshan gold deposit, indicating that the geochemical anomalies observed with bismuth may be a critical potential exploration target for the high-grade gold deposits in the Jiamusi Block.

Keywords: arsenopyrite; gold; Bi-minerals; Laozuoshan; enrichment

1. Introduction

Bismuth is widely found in various sulfide-rich gold deposits [1], including in orogenic deposits [2,3], Cu-Au porphyry-epithermal deposits [4,5], skarn Au deposits [6–10], Iron-Oxide-Copper-Gold (IOCG) deposits [11], Au-rich Volcanogenic Massive Sulfide (VMS) deposits [12], and intrusion-related gold deposits [13–16].

Gold and Bi-bearing parageneses are pivotal to understanding gold deposition and remobilization processes [1]. Bismuth acts as an effective Au scavenger in the liquid phase and dissolves ~20% of Au at 300 °C [17]. This process has been called the Bi collector model, an important mechanism for gold enrichment [10,15,17–19]. Gold scavenging using Bi-melts processes is facilitated at temperatures >271 °C, which tends to contribute to the formation of high-grade ore bodies with complex minerals [17,19]. In this context, elements such as Bi are considered as gold pathfinder elements in mineral exploration [1].

The Laozuoshan gold deposit is a large gold deposit in the north-central part of the Jiamusi Block, NE, China, and has an indicated reserve of 32 t and an average grade of



Citation: Meng, L.; Huang, F.; Gao, W.; Gao, R.; Zhao, F.; Zhou, Y.; Li, Y. Multi-Step Gold Refinement and Collection Using Bi-Minerals in the Laozuoshan Gold Deposit, NE China. *Minerals* 2022, *12*, 1137. https:// doi.org/10.3390/min12091137

Academic Editor: Stefano Salvi

Received: 16 August 2022 Accepted: 5 September 2022 Published: 7 September 2022

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7.38 g/t [20]. Previous reports indicate that the study area experienced regional metamorphism in the early Paleozoic era, skarn mineralization (the early hydrothermal mineralization) in the late Paleozoic era (264.6 \pm 2.6 Ma), and magmatic-hydrothermal superimposition (the late hydrothermal mineralization) in the Mesozoic era (104.6 \pm 1.8 Ma) [21,22], resulting in multiple sulfidation stages as well as the development of complex textures and intricate mineral patterns in the Laozuoshan gold deposit [21–24]. The early hydrothermal mineralization was found to have occurred in the East and Central ore belts of the Laozuoshan gold deposit. In contrast, the late hydrothermal mineralization mainly occurred in the West ore belt, with minor occurrences in the East and Central ore belts [23,25]. C-O-S-Pb isotope data indicate that the ore-forming materials have a magmatic origin [20]. According to mineral paragenesis, there are two metallogenic periods and seven mineralization stages, and arsenopyrite and pyrrhotite are the main gold-bearing minerals [23,25,26]. We found abundant Bi-minerals coexisting with gold in the ores, occurring as inclusions in arsenopyrite or filling in arsenopyrite fissures. However, the relationship between Bi-minerals and gold is unclear, which restricts our understanding of gold enrichment and the precipitation mechanism in the Laozuoshan gold deposit.

In the present study, we focus on describing the arsenopyrite and Bi-minerals found in association with gold in the Laozuoshan gold deposit. We provide detailed information on the mineral paragenesis, chemistry, and textures of the arsenopyrite, Bi-minerals, and gold using ore microscopy, SEM-EDS (scanning electron microscopy with energy dispersive spectrometry), and EPMA (electron probe micro-analysis). These results might reveal the gold enrichment and precipitation mechanism.

2. Geological Setting

The Jiamusi Block is situated in the easternmost segment of the Central Asian Orogenic Belt (Figure 1a). The exposed geological units mainly include the Paleozoic Mashan Group, the Majiajie Group, Paleozoic–Mesozoic granitic rocks, and sedimentary rocks (Figure 1b) [27,28]. The Mashan Group is the Precambrian metamorphic basement portion of the Jiamusi Block [29]. The Mashan Group comprises graphite and phosphorus and is rich in aluminum and intercalated with marble, calcium silicate, and quartz schist that has undergone high-amphibolite–granulite facies metamorphism [30]. The Majiajie Group is mainly composed of aluminum-rich and carbon-rich sedimentary clastic rocks that have undergone contact metamorphism [31,32]. The Paleozoic–Mesozoic sedimentary strata are mainly distributed on the southern margin of the Jiamusi Block [27,33]. The early Paleozoic granitic rock is a late Pan-African magma product, as is the Mashan Group, and it constitutes the metamorphic crystalline basement of the Jiamusi Block (Figure 1b). The late Paleozoic magmatic rocks result from the southward subduction of the Paleo-Asian Ocean tectonic domains. In contrast, the Mesozoic magmatic rocks are the result of the superimposition and transformation of the Mongolia-Okhotsk Ocean's and Paleo-Pacific Ocean's tectonic domains [34–36]. The Jiamusi Block has experienced complex tectonicmagmatic activities, forming large- to medium-scale gold deposits such as the Laozuoshan, Tuanjiegou, and Malian deposits (Figure 1b) [23,37].





Figure 1. (a) Sketch tectonic map (modified according to Hao et al. [38]) and (b) simplified geological map of the Jiamusi Block (modified after Wilde et al. [39]). Gold deposit in (b) 1—Lianzhushan gold deposit; 2—Pingdingshan gold deposit; 3—Malian gold deposit; 4—Tuanjiegou gold deposit; 5—Dujiahe gold deposit; 6—Taipinggou gold deposit; 7—Dongfengshan gold deposit; 8—Yangbishan gold deposit; 9—Xinli gold deposit; 10—Jiazhuagou gold deposit; 11—Laozuoshan gold deposit.

3. Deposit Geology

The stratigraphic units of the Laozuoshan gold deposit include the Early Paleozoic Mashan Complex, the Jurassic Chengzihe Formation, and Quaternary unconsolidated sediments (Figure 2a) [27]. The Mashan Complex is exposed in the northeastern part of the mine and is dominated by biotite plagioclase granulite, biotite plagioclase gneiss, marble, and migmatite (Figure 2b). The Jurassic Chengzihe Formation consists of sandstone and carbonaceous shale exposed in the western area of the ore district (Figure 2a). The late Paleozoic gneissic granites ($262 \pm 3.9 \text{ Ma}$) are widespread in the center and western areas of the mine and make minor intrusions into the Mashan Complex and make contact with the marble in those areas to form skarn (Figure 2b) [22,40]. The magmatic activity in the late Mesozoic era resulted in the emplacement of diorite ($103 \pm 1 \text{ Ma}$), felsite ($100.9 \pm 1.6 \text{ Ma}$), granite porphyry ($104.6 \pm 1.8 \text{ Ma}$), plagiogranite, and granodiorite, as well as in widespread diorite porphyry dykes (Figure 2a) [21]. The ore-controlling structures in the ore are mainly NW-NWW- or EW-trending faults or ductile–brittle shear zones (Figure 2a,b), which provide channels for magmatism and hydrothermal fluids.



Figure 2. (a) Geological map of the Laozuoshan gold deposit; (b) and the East ore belt of the Laozuoshan gold deposit (modified after Meng et al. [23]).

The Laozuoshan gold deposit experienced two periods of metallogenesis activity (the early hydrothermal mineralization and the late hydrothermal mineralization), resulting in the formation of three ore belts (East, Central, and West) (Figure 2a). Seven stages of mineralization are recognized based on field and microscopic observations (Figure 3) [23].



Figure 3. Photographs show the textural relationships and paragenesis features of ore samples at the different ore-forming stages in the Laozuoshan gold deposit: (a) Skarn alteration dominated by garnet and diopside (polarized light); (b) Gold-bearing arsenopyrite occurs along contact with pyrrhotite (reflected light); (c) Colloidal pyrite occurs along contact with pyrrhotite and then cut by arsenopyrite (reflected light); (d) Gold is distributed in the fissure of arsenopyrite and pyrrhotite (reflected light); (e) Gold and Bi-minerals occur as inclusion in arsenopyrite (reflected light); (f) Carbonate minerals such as calcite fill chlorite interstitial spaces (cross-polarized light); (g) The alteration of feldspar into sericite in alteration belt (cross-polarized light); (h,i) Bi-minerals and gold occur as the inclusion or fill in the fissure-developed arsenopyrite, and the arsenopyrite fissure is filled with graphite, quartz, and calcite (reflected light); (j) The fined pyrite and marcasite aggregates which containing fine chalcopyrite inclusions are surrounding by arsenopyrite and pyrite (reflected light); (k) Arsenopyrite occurs with pyrite and marcasite (reflected light); (1) Fine-grained euhedral pyrite occur in oriented banded marcasite (reflected light). Abbreviation: Apy—arsenopyrite; Au—gold; Bis—Bi-minerals; Cal-calcite; Chl-chlorite; Ccp-chalcopyrite; Di-diopside; Elt-electrum; Fsp-feldspar; Gn-Galena; Gr-graphite; Grt-garnet; Mrc-marcasite; Po-pyrrhotite; Py-pyrite; Qtz-quartz; Sersericite. The geochronological data come from Wu et al. [40] and Bai et al. [21].

The early hydrothermal mineralization mainly occurred in the East and Central ore belts [27], with a similar occurrence with the wall rock (Figure 2b). The contact zone and the NW-NWW- or EW-trending faults zones controlled the ore bodies (Figure 2b). These ore bodies occur as vein- and lenticular-type bodies and mostly have lengths of 13–330 m, thicknesses of 0.43–9.62 m, and downward plunge depths of 6–400 m and generally dip in the NE direction at an angle of 50° – 80° [27].

Ore minerals comprise arsenopyrite, pyrrhotite, and chalcopyrite, with minor pyrite, Bi-minerals, electrum, and native gold accounting for 5%–15% of the ores (Figure 3b–e). Gangue minerals include garnet, diopside, chlorite, epidote, quartz, and calcite (Figure 3a,f). Wall rock alteration is characterized by skarnization and chloritization containing amounts of garnet, diopside, epidote, and chlorite (Figure 3a,f). Three stages (Stage I to Stage III) have been identified based on the paragenetic assemblages of minerals (Figures 3a–f and 4). Stage I (the pyrrhotite–arsenopyrite–calcite stage) is represented by massive aggregates of garnets, diopsides, and pyrrhotite, with minor amounts of arsenopyrite (Apy-1) (Figure 3a,b). Stage II (the colloidal pyrite–quartz stage) is characterized by fine- to coarse-grained aggregates of the colloidal pyrites (Figure 3c). Stage III (the coarse-grained arsenopyrite–calcite stage) is marked by abundant coarse-grained arsenopyrite (Apy-2) with anhedral to subhedral radial chlorites (Figure 3d–f).

The late hydrothermal mineralization mainly occurred in the West ore belt, with minor occurrences observed in the East and Central ore belts. The fault structure controlled the ore bodies and converged in the NE direction, spreading in the SW direction in the West ore belt. These vein-type ore bodies have lengths of 25–482 m, thicknesses of 0.19–4.96 m, and downward plunge depths of 7–390 m and generally dip in the NW direction at an angle of $45^{\circ}-55^{\circ}$ [27].

The ore minerals consist of arsenopyrite, pyrite, chalcopyrite, and marcasite with minor amounts of pyrrhotite, galena, sphalerite, Bi-minerals, electrum, and native gold within gangue minerals such as quartz, feldspar, sericite, calcite, and graphite (Figure 3g–l). Kfeldspar alteration is characterized by quartz, K-feldspar, sericite, and carbonate. According to the mineral paragenetic assemblages, four stages (Stage IV to Stage VII) have been identified (Figures 3g–l and 4). Stage IV (the massive quartz stage) is characterized by a large amount of coarse-grained quartz that is largely precipitated without sulfide (Figure 3g). Stage V (the coarse-grained arsenopyrite–quartz stage) is represented by coarse-grained gold-bearing arsenopyrites (Apy-3) that are associated with graphite, quartz, and calcite (Figure 3h,i). Stage VI (the polymetallic sulfide–arsenopyrite quartz stage) is marked by polymetallic sulfide assemblages consisting of chalcopyrite, pyrite, marcasite, arsenopyrite (Apy-4), sphalerite, and galena (Figure 3j–l). Apy-4 can be euhedral to subhedral in shape, can be medium- to fine-grained, and coexists with pyrite and galena (Figure 3k). The final stage (Stage VII: the quartz–calcite stage) comprises calcite and quartz veins ranging from millimeters to centimeters in length (Figure 3l).

Period/		The early hydrothermal mineralization			The late hydrothermal mineralization			
Alteration/ Mineral Stages Phases/Distributions		Stage-I	Stage-II	Stage-III	Stage-IV	Stage-V	Stage-VI	Stage-VII
Alteration	Skarn alteration							
	Sericite alteration							
	Choritizate alteration							
	Carbonate alteration	—						
	Silicium alteration			-				
	Sulfide alteration							
Mineral Phases	Garnet							
	Diopside							
	Tremolite							
	Epidote							
	Chlorite							
	Sericite						•••••	
	Calcite		•••••				•••••	
	Quartz	•••••	• • • • • • • • • • • • • • •	••				•••••
	Pyrrhotite							
	Arsenopyrite							
	Chalcopyrite							
	Pyrite							
	Marcasite						-	
	Gold							
	Bi-minerals						-	
	Sphalerite							
	Galena							
ions	East Ore Belt	***	*	*		*	*	**
tribut	Middle Ore Belt	***	*	**	*	*	*	* *
Dist	West Ore Belt				***	**	***	*

Notes: * Weak ** General *** Intense

Figure 4. The paragenetic sequence of minerals in the Laozuoshan gold deposit. The shadow bar represents the gold precipitation stages (modified after He [25] and Meng et al. [23]).

4. Samples and Analytical Methods

The No. 401 ore body (which has an average grade of 13.07 g/t) and the No. 2 ore body are the main ore bodies in the East and Central ore bodies, respectively. Both of them developed skarn mineralization. In total, 41 disseminated samples were collected from the No. 401 ore body adit located in the East ore belt (Figure 2b), and 15 samples were collected from the No. 2 ore body adit in the Central ore belt. The No. 304 ore body (which has an average grade of 7.64 g/t) in the West ore belt represents the late hydrothermal mineralization. In total, 14 massive structural samples were collected from No. 304 ore body adit in the West ore belt (Figure 2a). After detailed macroscopic observations of the ore samples, the mineralogy of these samples was analyzed using transmitted and reflected light microscopy to identify silicate and ore mineral assemblages, especially those of arsenopyrite, Bi-minerals, electrum, and native gold.

Further, the microscopic textural and elemental qualitative analyses of the sulfides, Bi-minerals, electrum, and native gold were performed using an Ultra Plus field emission scanning electron microscope (FESEM) (Carl Zeiss, Berlin, Germany) at the Analytical and Testing Center of Northeastern University, China. The device has a back-scattering electron (BSE) detector and an energy-dispersive X-ray spectrometer (EDS). The resolution was 0.8 nm, the magnification ranged from 12 to 1,000,000, and the acceleration voltage ranged from 20 V to 30 kV.

The composition data of arsenopyrite, Bi-minerals, and gold were determined using a JOEL JXA-8350F field emission electron probe microanalyzer (EPMA) (JEOL, Ltd., Tokyo, Japan) in the same laboratory. The microprobe was operated with a beam energy of 20 kV and a beam current of 20 nA with a 1 μ m diameter. The counting time was 40 s for the peak and 20 s for the background of each element. The standards were pyrite–FeS₂ (Fe, S), arsenopyrite–FeAsS (As), Au metal (Au), Ag₂S (Ag), Bi metal (Bi), chalcopyrite–CuFeS₂ (Cu), Co metal (Co), Ni metal (Ni), Sb₂S₃ (Sb), ZnSe (Se), TeCdHg (Te), and ZnS (Zn). Analytical results were processed using the ZAF correction routines.

5. Results

5.1. Texture of the Arsenopyrite, Bi-Minerals, and Gold

The Laozuoshan gold deposit has undergone three gold mineralization stages (Au-1, Au-2, and Au-3), which occurred in Stages I and III during the early hydrothermal mineralization and in Stage V during the late hydrothermal mineralization, respectively (Figures 3 and 4). The aurous minerals (Au-1 to Au-3) are closely related to arsenopyrite (Apy-1 to Apy-3) and the Bi-minerals (Bis-1 to Bis-3) (Figures 5–7).



Figure 5. Reflected light photomicrographs (**a**–**c**), BSE images (**d**–**e**), and element mapping (**g**–**i**) show the textural and chemical features of Apy-1, Au-1, and Bi-minerals (Bis-1) in Stage I. (**a**) Coarse-grained electrum distributed in arsenopyrite margin; (**b**) Pyrrhotite occurs as inclusions in arsenopyrite, while minor electrum and joséite-B fill the fissure of garnet and diopside; (**c**) Bi-minerals and gold occur the fissure between arsenopyrite and pyrrhotite; (**d**) Electrum and Bi-mineral coexisted along the contact with arsenopyrite (Apy-1); (**e**) Native Bi coexisted with the joseite-B as inclusions or in the joseite-B margin, and both of them occurred as inclusion in chalcopyrite; (**f**) Coarse-grained electrum coexisted with joseite-B as the solid solution. Element mappings (**g**–**i**) are the results of (**d**); (**g**) The Bi element mapping of Bi-minerals; (**h**) The Ag element mapping of electrum; (**i**) the Co element mapping of arsenopyrite; Abbreviation: Apy—arsenopyrite; Au—gold; Bi—native Bi; Bis—Bi-minerals; Ccp—chalcopyrite; Di—diopside; Elt—electrum; Grt—garnet; JoB—joséite-B; Po—Pyrrhotite.



Figure 6. Reflected light photomicrographs (**a**–**c**), BSE images (**d**–**e**), and element mapping (**g**–**i**) show the textural and chemical features of Apy-2, Au-2, and Bi-minerals (Bis-2) in Stage III. (**a**) Bi-minerals occur as inclusions in pyrrhotite; (**b**) Gold fills the fissure of arsenopyrite which contains Bi-minerals inclusions; (**c**) Bi-minerals and gold occur as inclusions in arsenopyrite and pyrrhotite, respectively; (**d**) Native gold, native bismuth, and hedleyite coexisted in arsenopyrite; (**f**) Maldonite occurs as inclusions in arsenopyrite or native bismuth, while native gold and electrum occur along the contact with native bismuth; Element mappings (**g**–**i**) are the results of (**d**). (**g**) the Bi element mapping of native bismuth and hedleyite; (**h**) the Ag element mapping of electrum; (**i**) the Co mapping of arsenopyrite; Abbreviation: Apy—arsenopyrite; Au—gold; Bi—native Bi; Bis—Bi-minerals; Ccp—chalcopyrite; Elt—electrum; Mld—maldonite; Po—Pyrrhotite; Py—pyrite.

5.1.1. Stage I (Pyrrhotite–Arsenopyrite–Calcite Stage)

The sulfides are disseminated in garnet and diopside (Figure 3a,b) and are distributed in the skarn ore bodies in the East and Central ore belts. Arsenopyrite (Apy-1) can be medium- to fine-grained (100 to 500 μ m) and is associated with coarse-grained (>500 μ m) pyrrhotite (Po-1), chalcopyrite, and pyrite (Py-1) (Figure 5a–c).

Electrum with minor amounts of native gold usually intergrowths among the Biminerals (Bis-1) (Figure 5). Electrum can be subhedral to anhedral shape, with particle sizes of about 40–120 μ m. It occurs in inclusions in joséite-B, native bismuth, or chalcopyrite (Figure 5b,e) or at the boundary between sulfide (arsenopyrite (Apy-1), pyrrhotite (Po-1), and chalcopyrite (Figure 5c) and related gangue minerals (garnet and diopside, Figure 5b). The surface of the electrum associated with joséite-B is rough and porous (Figure 5f). The Bi-minerals (joséite-B, native bismuth, etc.) can have coarse- to fine-grain (20 to 200 μ m) particles and are distributed at the margins of arsenopyrite (Apy-1) or fill in narrow fractures between pyrrhotite (Po-1) and arsenopyrite (Apy-1) or fissures in garnet and diopside (Figure 5a–d). The joséite-B also occurs as inclusions in arsenopyrite (Apy-1), chalcopyrite, and pyrrhotite (Po-1) (Figure 5e). The EDS results show that Bi, Ag, and Co are evenly distributed in Bi-minerals (Bis-1), electrum (Au-1), and arsenopyrite (Apy-1), respectively (Figure 5g–i).





Figure 7. Reflected light photomicrographs (**a**–**c**), BSE images (**d**–**f**), and element mapping (**g**–**j**) show the textural and chemical features of Apy-3, Au-3, and Bi-minerals (Bis-3) in Stage V. (**a**) Bi-minerals and gold occur as inclusions in arsenopyrite, which surrounding by chalcopyrite, pyrite, and marcasite; (**b**,**c**) Graphite occurs in the fissure of arsenopyrite, which containing gold and Bi-minerals; (**d**) Native gold coexisted with Bi-minerals, which occurs as inclusion in arsenopyrite, while minor electrum occurs along the contact with arsenopyrite; (**e**) Electrum coexisted with maldonite and Bi-minerals such as joséite-A in arsenopyrite, while minor electrum filled the fissure of arsenopyrite. Element mappings (**h**–**j**) are the results of (**g**). (**h**) the Au element mapping of electrum; (**i**) the Ag element mapping of electrum; (**j**) the Co element of arsenopyrite; Abbreviation: Apy—arsenopyrite; Au—gold; Bis—Bi-minerals; Ccp—chalcopyrite; Elt—electrum; Gr—graphite; JoA—joseite-A; Mrc—marcasite; Po—Pyrrhotite; Py—pyrite.

5.1.2. Stage III (Coarse-Grained Arsenopyrite-Calcite Stage)

Au

Sulfides are disseminated in ore and are distributed in the skarn ore bodies in the East and Central ore belts. Arsenopyrite (Apy-2) is the diagnostic mineral of Stage III and is characterized by its coarse grain size (0.2 to 1 mm; Figure 6a–c). Apy-2 fissures are filled in with chlorites and calcites (Figure 3f). Pyrrhotite (Po-1), when replaced by Apy-2, appears to be round (Figure 3d,e). Colloidal pyrite (Py-2) is cut by Apy-2 (Figure 3c) [41].

Native gold and electrum with a minor amount of maldonite coexist with the Biminerals (Bis-2) (Figure 6d–f). Native gold and electrum are subhedral to anhedral shape (30 to 150 μ m, Figure 6d,e). Both of them occur as inclusions in arsenopyrite (Apy-2) or the Bi-minerals (Bis-2) or fill-in arsenopyrite (Apy-2) fractures (Figure 6a–f). Minor amounts of fine electrum (<10 μ m) occur as inclusions in pyrrhotite (Po-1) (Figure 6c). The Bi-minerals (native bismuth, maldonite, and hedleyite) have various particle sizes ranging from 10 to 300 μ m (Figure 6d–f). Hedleyite and native bismuth occur as inclusions in arsenopyrite (Apy-2) and chalcopyrite (Figure 6a–f), with minor native bismuth filling in arsenopyrite (Apy-2) fissures (Figure 6d). EDS element mapping shows that Ag and Bi are uniformly distributed in gold, hedleyite, and native bismuth (Figure 6g,h). There are apparent Co anomalies in Apy-2 (Figure 6i). According to the EPMA data, the Co content is high in Apy-1, while minor contents are present in Apy-2 (Supplementary Materials Table S1). Therefore, the abnormal Co in Apy-2 might indicate that Apy-1 forms Apy-2 through the dissolution–reprecipitation mechanism (Figure 6i) [42].

5.1.3. Stage V (Coarse-Grained Arsenopyrite-Quartz Stage)

Arsenopyrite (Apy-3) is the main sulfide and coexists with graphite (Figure 7a–c). It is mainly distributed in the West ore belts. Coarse-grained arsenopyrite (Apy-3) is about 2 to 3 mm in size and has developed fissures filled in with graphite, quartz, and calcite (Figure 3h,i and Figure 7a–c).

Electrum with minor native gold coexists with Bi-minerals (Bis-3) as inclusions in arsenopyrite (Apy-3) (Figure 7a–f). Additionally, minor native gold particles occur in arsenopyrite fissures and carbonate veins (Figure 7d). Compared to Au-1 and Au-2, the particle sizes of gold (electrum with minor native gold) decrease significantly and range from 5 to 30 μ m (Figure 7a–f). Bi-minerals occur as inclusions in arsenopyrite (Apy-3) or at the edge of Apy-3 (Figure 7a–f). The particle sizes (5–50 μ m) of Bi-minerals also decrease significantly (Figure 7d–f). The Ag in some gold particles (Au-3) shows a trend of enrichment from the center to the edge (Figure 7g–i), something that is further confirmed by EMPA data (Figure 7g and Supplementary Materials Table S2). Meanwhile, there are apparent Co anomalies in arsenopyrite (Apy-3) (Figure 7j).

5.2. Compositions of Arsenopyrite, Gold, and Bi-Mineral Assemblages

5.2.1. Compositions of Arsenopyrite

EPMA data show that the contents of As, S, and Fe in four generations of arsenopyrite vary significantly (Supplementary Materials Table S1 and Figure 8a). The arsenic contents in Apy-1 (average (Ave): 48.41 wt.%; N = 13) and Apy-3 (Ave: 49.65 wt.%, N = 8) are higher than those in Apy-2 (Ave: 46.39 wt.%; N = 7) and Apy-4 (Ave: 46.34 wt.%) (Supplementary Materials Table S1). The sulfur contents in Apy-1 (Ave: 17.90 wt.%; N = 13) and Apy-3 (Ave: 17.98%; N = 8) are lower than those in Apy-2 (Ave: 19.31 wt.%; N = 7) and Apy-4 (Ave: 19.67 wt.%; N = 5) (Supplementary Materials Table S1). The Fe contents in the four generations of arsenopyrite vary significantly, and the mean values are 33.02 wt.% (Apy-1), 35.08 wt.% (Apy-2), 29.08 wt.% (Apy-3), and 34.44 wt.% (Apy-4) (Supplementary Materials Table S1). The Co contents of the arsenopyrites also changed significantly (Supplementary Materials Table S1), e.g., Apy-3 had the highest content (Ave: 4.16 wt.%, N = 8), followed by Apy-1 (Ave:1.69 wt.%, N = 13), Apy-2 (Ave: 0.16 wt.%, N = 7), and Apy-4 (Ave: 0.13 wt.%, N = 5) (Supplementary Materials Table S1). In addition, arsenopyrite with a high arsenic content usually contains elevated Co, even though As is not significantly correlated with Co.

The scatter plot shows that the compositions of Apy-1 and Apy-3 fluctuate greatly (Figure 8a). In contrast, the composition changes observed in Ayp-2 and Apy-4 were relatively stable (Figure 8a). Arsenic was negatively correlated with S ($R^2 = 0.70$) and Fe ($R^2 = 0.43$) in arsenopyrite (Figure 8b,c). There was a strong negative correlation between Fe and Co ($R^2 = 0.88$) in arsenopyrite (Figure 8d), indicating that cobalt may replace Fe during arsenopyrite formation [42].

5.2.2. Compositions of Gold

The EPMA data show that the Au and Ag contents varied greatly from Au-1 to Au-3 (Supplementary Materials Table S2 and Figure 9). The Au content in Au-1 (electrum with minor amounts of native gold) is 68.57%–87.27%, with an average of 83.46 wt.% (N = 14) and a variance of 4.60 (Supplementary Materials Table S2). Au-2 is mainly composed of native gold. The Au content in gold (Au-2) is 89.87–91.42 wt.%, with an average of 90.46 wt.% (N = 5) and a variance of 0.58 (Supplementary Materials Table S2). Au-3 is dominated by electrum and contains minor amounts of native gold. The Au content in Au-3 varies greatly, ranging from 50.23 to 98.43 wt.%, with an average of 62.10 wt.% (N = 10) and variance of 15.38 (Supplementary Materials Table S2).



Figure 8. (a) Ternary plots showing compositions of the Fe, S, and As in different arsenopyrite generations; (**b**–**d**) Binary plots show compositions of selected main elements in different arsenopyrite generations. (**b**) As vs. S; (**c**) As vs. Fe; (**d**) Co vs. Fe. All data based on the results of arsenopyrite analyses by EPMA are given in Supplementary Materials Table S1.



Figure 9. The binary diagrams show the concentration of selected main elements in different gold generations. (a) Au vs. Ag; (b) Au vs. Bi; (c) Au vs. Te. All data based on the results of gold analyses by EPMA are given in Supplementary Materials Table S2.

The above results show that the compositions of Au-1 and Au-2 are relatively homogeneous. In contrast, the compositions of Au-3 vary greatly (Figure 9a). EPMA data reflect that the Au-bearing phases (Au-1 to Au-3) also contain minor amounts of Bi (0.33–0.83 wt.%) and Te (~0.45 wt.%) (Supplementary Materials Table S2). Native gold contains more bismuth (Supplementary Materials Table S2 and Figure 9b). The amounts of Au and Bi in gold (Au-1 to Au-3) are positively correlated (Figure 9b, $R^2 = 0.58$) and are negatively correlated with Te (Figure 9c, $R^2 = 0.50$).

5.2.3. Compositions of Bi-Minerals

The EPMA data show that the Bi-minerals (Bis-1 to Bis-3) that are associated/coexist with gold also demonstrate apparent differences (Supplementary Materials Table S3 and Figure 10). The Bi-minerals (Bis-1) mainly include joséite-B (Bi₄Te₂S: Bi 73.04~75.68 wt.%, Te 20.87~22.10 wt.%, S 2.33~2.76 wt.%), and ingodite (Bi₂TeS: Bi 63.96~69.96 wt.%, Te 21.37~30.33 wt.%, S 4.05~5.29 wt.%), with minor amounts of tsumoite (BiTe), pilsenite (Bi₄Te₃), and native bismuth (Supplementary Materials Table S3). The Bi-minerals (Bis-2) include native Bi with minor amounts of maldonite (Au₂Bi) and hedleyite (Bi₇Te₃) (Supplementary Materials Table S3). The Bi-minerals (Bis-2), native bismuth, and minor amounts of joséite-A (Bi₄Te₂) as well as pilsenite (Bi₄Te₃) and maldonite (Au₂Bi) (Supplementary Materials Table S3). The Bi vs. Te binary diagram of the Bi-minerals shows relatively obvious zoning between the three generations of Bi-minerals in the Laozuoshan gold deposit (Figure 10a). The typical Bi-rich Bi-minerals of joséite-B, native Bi, with minor amounts of ingodite and joseite-A, where Bi/(Te + S) > 1 (Figure 10b), confirm that the ore-forming fluids in reducing conditions [43,44].



Figure 10. (a) The binary diagrams (Bi vs. Te) show the concentration of selected main elements in different Bi-minerals generations; (b) Ternary diagram (Bi + Sb + Pb – Te – S + Te shows compositions of Bi-minerals in the Laozuoshan gold deposit (modified after Cook et al. [45]; Wei et al. [46]). The Bi/Te + S = 1 line is from Ciobanu and Cook [43] and Ciobanu et al. [44], which separates the Bi-minerals formed in reduced fluids from those in oxidized fluids. Noted that the Bi-minerals from reduced fluids usually have Bi/Te + S > 1 and have an assemblage of native gold and pyrrhotite, whereas those from oxidized fluids usually have Bi/Te + S < 1 and have an assemblage of native gold and pyrrhotite. All data based on the results of the Bi-minerals analyses by EPMA are given in Supplementary Materials Table S3.

6. Discussion

6.1. The Physical–Chemical Conditions of the Ore-Forming Fluids Indicated by Minerals Assemblages

Based on the texture and structure of the typical ores and the paragenetic association of the minerals, the Laozuoshan gold deposit can be divided into areas that experienced early hydrothermal mineralization and late hydrothermal mineralization and can be further divided into seven mineralization stages (Figures 3 and 4). Stages I and III are the main gold precipitation stage during the early hydrothermal mineralization. Stage V is the main gold precipitation stage during the late hydrothermal mineralization (Figures 5–7).

The reduced gold skarns are characterized by low garnet/pyroxene ratios and are dominated by hedenbergite and grandite [47]. There is a genetic association with reduced granitoid intrusion during the late Paleozoic era (264.6 ± 2.6 Ma) and a Fe₂O₃/(Fe₂O₃ + FeO) ratio between 0.12 and 0.17 for Laozuoshan granite [21,22,40]. The earliest alteration stage is characterized by potassium hornfels. Following this alteration stage, prograde skarn formation subsequently occurred. This process is characterized by garnet in the grossular– andradite series and pyroxene in the hedenbergite-diopside series in the Laozuoshan gold deposit, similar to the reduced gold skarn deposit [20,40,47,48]. Furthermore, Bi-bearing phases and gold are often developed in later stages and accompanying base metals in reduced gold skarn deposits [47]. Usually, these assemblages postdate previous early sulfidation stages and are dominated by pyrrhotite and arsenopyrite with or without lollingite [47,49]. In the Laozuoshan gold deposits, most of the Au- and Bi-bearing phases are indeed postdated. Both the assemblages marked by coarse-grained pyrrhotite (Po-1) and arsenopyrite (Apy-1) without lollingite are from Stage I and show a distinctive Au-Bi-As \pm Co geochemical association (Figure 5a-f and Supplementary Materials Table S1). Gold was also observed to coexist with the Bi-phases, and both of them occur along the contact with arsenopyrite or pyrrhotite (Figure 5a–f), which are typical mineral assemblages in reduced skarn gold deposits, suggesting their precipitation at reduced conditions (Figure 5) [47].

Arsenopyrite (Apy-1 to Apy-3) is a gold-bearing mineral found in the Laozuoshan gold deposit (Figures 5–7). The As(III) hydroxide complex As(OH)₃ is the most dominant As-bearing species and has a wide range of temperatures ($25 \sim 500 \circ C$) and fluid densities ($0.05 \sim 1.1 \text{ g/cm}^3$) in the natural hydrothermal system, as indicated by experimental studies [50-52]. The decreases in fO_2 induce arsenopyrite crystallization and decrease the H₂S and arsenic concentrations in ore-forming fluid [53,54]. In the Laozuoshan gold deposit, coarse-grained arsenopyrites (Apy-2) are associated with pyrrhotite (Po-1), chlorite, and calcite in Stage III (Figures 3d–f and 6). The chlorite composition belongs to ripidolite, representing reduced conditions that favor arsenopyrite precipitation [23]. In Stage V, the abundance of graphite, quartz, and calcite filling in arsenopyrite (Apy-3) fractures suggests that arsenopyrite was precipitated under the reduced conditions (Figure 3h,i and Figure 7a–f).

After a careful examination of the mineralogy (Figures 5–7), it was possible to recognize that a wide range of disseminated Bi-minerals (Bis-1~Bis-3) coexist with the gold (Au-1~Au-3), something that is not described in Meng et al. [23]. The general forms of Bi-sulfosalts under high fS_2 conditions are associated with pyrite stability. Bismuth–chalcogenides and native bismuth usually form within the fields of pyrrhotite and arsenopyrite under low fS_2 and fO_2 conditions [10,11,55,56]. Accordingly, most of the Bi-bearing phases in the Laozuoshan gold deposit are dominated by joséite-B, ingodite, and native bismuth, with minor amounts of tsumoite, pilsenite, maldonite, hedleyite, and joséite-B and no Bi-sulfosalts (Figures 5–7), which suggest that the Bi-bearing minerals might crystallize under reduced conditions [15]. The ternary diagram depicting the chemical compositions of the Bi-minerals (Bis-1 to Bis-3) shows that the Bi-minerals all occur in the reducing regions, indicating that Bi-minerals are precipitated under reducing conditions (Figure 10b and Supplementary Materials Table S3) [44–46]. Therefore, the mineral assemblages and their chemical compositions indicate that gold mineralization occurs under the reducing conditions in the Laozuoshan gold deposit.

6.2. Gold Scavenging Using Bi-Melts and Refining Processes during the Cooling of the Mineralization System

Previous work shows that gold is commonly transported as thiosulfate and chloride complexes in hydrothermal solutions, depending on their relative fO_2 conditions and temperatures [57]. However, it might migrate by forming [Au, As]²⁻ or [Au(As, S₃)]²⁻ in Asrich reduced hydrothermal fluids [58,59]. In the Laozuoshan gold deposit, Bi-minerals are associated with gold and exist as inclusions or fill in arsenopyrite and pyrrhotite fractures (Figures 5–7), indicating that gold might be transported as a thiohydron complex or as an

As-bearing complex [57–59]. Gold and Bi-minerals occurred as invisible solid inclusions in arsenopyrite and pyrrhotite (Figures 5–7) and were identified using the LA-ICP-MS data of Shi et al. [22], implying that gold and bismuth were available in the fluids that were responsible for forming the earlier sulfide assemblages. The compositions and textures of the Bi-bearing assemblages related to gold where Au and Bi show a positive geochemical correlation ($R^2 \ge 0.5$) have been described in previous studies [1,5,15,60]. The EPMA data for gold (electrum, native gold) show a positive correlation ($R^2 = 0.58$) between Au and Bi (Figure 9b and Supplementary Materials Table S2), suggesting that the Bi collector model might play an important role in gold enrichment in the Laozuoshan gold deposit.

Oxidized Bi³⁺ is the predominant Bi-bearing phase of Bi in hydrothermal fluids [19,55]. If bismuth is present in the Au-bearing solution, with favorable sulfur-oxygen fugacities and temperatures (above 271 °C), Bi-melts form and effectively scavenge Au from the fluids, forming Bi-Au-melts [15,17–19,60]. The ore-forming temperature is identified according to the homogenization temperatures of the quartz and calcite fluid inclusions (366.5~410.3 °C) and of the arsenopyrite (Apy-2) geothermometer (390–420 °C) in the Laozuoshan gold deposit [23,61], all of which are above the melting point of Bi (271 °C) [17], indicating that Bi could exist as melts in the ore-forming fluids in the Laozuoshan gold deposit. Furthermore, the Bi-minerals and gold undergoing typical eutectic crystallization in the Laozuoshan gold deposit (Figures 5d–f and 7d–f) demonstrated similar textures and assemblages to those that have been previously reported in a large number of deposits worldwide [3,7,11,56,60,62]. The Bi-minerals coexist with pyrrhotite and arsenopyrite, and the Bi-bearing phases have Bi/(Te + S) ratios ≥ 1 (Figures 5, 6, 7 and 10b), which suggests that the reduced conditions might facilitate the formation of bismuth immiscible fluids [3,7].

The abundant gold and Bi-mineral particles that occur as inclusions in arsenopyrite (Apy-1~Apy-3) and pyrrhotite (Po-1) or that fill in the fractures in these sulfides (Figures 5–7) suggest the existence of Bi melts that scavenged Au, filling in the fractures of earlier sulfides. The major elements (Fe, As, Co) found in arsenopyrite varied, and the positive correlation between Co and Fe in arsenopyrite indicates that Co replaced Fe (Figure 8a,d), which might facilitate the formation of lattice defects in arsenopyrite and the mechanical incorporation of nano-micron gold and Bi-minerals inclusions [22]. Further, element mapping shows abnormal Co in arsenopyrite (Apy-2) (Figure 6i), implying that arsenopyrite (Apy-1) might experience dissolution and reprecipitation and form arsenopyrite (Apy-2) [63]. Therefore, the abundance of native gold and native bismuth particles filling in arsenopyrite (Apy-2) fractures suggests that invisible gold and Bi were remobilized from arsenopyrite during arsenopyrite recrystallization and that part of the Bi-enriched immiscible melts survived and scavenged gold after arsenopyrite crystallization until the waning stages of the hydrothermal system (Figure 6d,g,i) [1]. Similar processes have been proposed by Fougerouse et al. [64] and Morey et al. [65].

In summary, we propose that gold experienced the concentration of ore-bearing fluids and further Bi-melt scavenging during mineralization in the Laozuoshan gold deposit. During the water-rock reaction, the fO_2 of the As-rich gold-bearing fluids decreased under the reducing conditions, which led to the precipitation of base metal sulfides such as pyrrhotite and arsenopyrite [51,52,54]. The Au⁺ and Bi³⁺ thiohydrogen complex in the oreforming fluids desulfurized to form gold and bismuth nanoparticles, which were initially enriched in arsenopyrite or pyrrhotite as visible or invisible inclusions [19,55,64]. Since the melting point of bismuth is lower than the precipitation temperature of pyrrhotite and arsenopyrite [17], bismuth could exist in the ore-forming fluid as immiscible melts to further scavenge Au from the ambient fluids [18,19]. Subsequently, the gold-bearing immiscible bismuth melts precipitated and separated into gold and Bi-minerals as the temperature of the hydrothermal fluids decreased or underwent supersaturation during migration [15], which is confirmed by the gold and Bi-minerals inclusions in arsenopyrite (Apy-1~Apy-3) and pyrrhotite (Po-1) as well as by their presence in the fractures of these sulfides (Figures 5–7). The Bi collector model is essential for interpreting the high-grade gold in the Laozuoshan gold deposit, indicating that the bismuth geochemical anomaly

may be a critical potential exploration target for the high-grade gold deposits in the Jiamusi Block.

7. Conclusions

- 1. The Laozuoshan gold deposit has experienced complex mineralization processes (the early hydrothermal mineralization and the late hydrothermal mineralization), with three gold precipitation processes occurring successively. The abundant gold (Au-1 to Au-3) and Bi-mineral (Bis-1 to Bis-3) particles are associated with pyrrhotite (Po-1) + arsenopyrite (Apy-1), chlorite + arsenopyrite (Apy-2), and graphite + arsenopyrite (Apy-3).
- 2. Bi-minerals (such as joséite-B, ingodite, and native bismuth without Bi-sulfosalts) are associated with gold (electrum, native gold, or minor maldonite) and coexist as inclusions or as fracture fillings in arsenopyrite (Apy-1~Apy-3) and pyrrhotite. The mineral assemblages of arsenopyrite, Bi-minerals, and gold exhibit a clear As-Bi-Au mineralogy in the ores, and the ternary diagram of the chemical compositions of the Bi-minerals shows that the Bi-minerals all fall in reducing regions, indicating that Bi-minerals are precipitated under reducing conditions.
- 3. The gold compositions show a positive correlation ($R^2 = 0.58$) between Au and Bi. The gold experienced the concentration of the ore-forming fluids and further Bimelt scavenging during the mineralization of the Laozuoshan gold deposit. The Bi collector model is essential for interpreting the high-grade gold in the Laozuoshan gold deposit, indicating that the bismuth geochemical anomaly may be a critical potential exploration target for the high-grade gold deposits in the Jiamusi Block.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min12091137/s1, Table S1: Compositions of the different generations of arsenopyrite in Laozuoshan gold deposit; Table S2: Compositions of gold in Laozuoshan gold deposit; Table S3: Compositions of the Bi-minerals and Bi-Au minerals in Laozuoshan gold deposit.

Author Contributions: L.M., F.H. and W.G. devised the project. L.M., F.H., R.G. and W.G. wrote the paper, assisted by Y.Z., and operated the EPMA. F.Z. and Y.L. assisted with data processing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 41272062, the National Natural Science Foundation of China, grant number 41902067, China Postdoctoral Science Foundation, grant number 2021M700713, and Key Laboratory of Mineral Resources Evaluation in Northeast Asia, Ministry of Natural Resources, grant number DBY-KF-18-04.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data used in this study are freely available.

Acknowledgments: The authors would like to thank Yufeng Shao for his help in the fieldwork. We also thank Degao Zhai of China University of Geosciences, Beijing, He Zhang of Nanjing University, and Jin-peng Luan of Northeastern University for their suggestions on paper revision. We appreciate the Editor for editorial help and supportive comments. We thank two anonymous reviewers for their helpful comments and suggestions to improve our paper. Thanks to MDPI for language editing services during the preparation of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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