



# Article Genesis of Cu-Sn Mineralization in the Shuangjianzishan Super-Large Silver Deposit, Inner Mongolia: Trace Element Constraints from Chalcopyrite and Cassiterite

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Abstract: The Shuangjianzishan silver polymetallic deposit is located in the copper-tin-lead-zincsilver polymetallic metallogenic belt in the Southern Great Xing'an Range, with silver resources of more than 18,000 t, which is the largest silver polymetallic deposit in Asia. Early studies concluded that the Shuangjianzishan deposit is typically an epithermal Ag-Pb-Zn deposit that lacks a hightemperature mineralization stage. In recent years, with the deepening of research, a large amount of Cu-Sn mineralization has been found in the deep part of the Shuangjianzishan deposit, but it is less studied. The laser-ablation inductively coupled mass spectroscopy (LA-ICP-MS) technique is used to investigate the distribution and substitution of trace elements in chalcopyrite and cassiterite. In this paper, the trace element study of chalcopyrite and cassiterite from the Shuangjianzishan deposit reveals that Sn, In, As, Se, Sb, and Tl mainly exist in chalcopyrite in isomorphic form, while Pb, Bi, and Ni mainly exist in chalcopyrite in the form of mineral inclusions. The enrichment of the hightemperature elements Sn and Se in chalcopyrite, and the deficit of the middle- and low-temperature elements Ga, Sb, etc., reflect that the chalcopyrite in the Shuangjianzishan deposit was formed in a middle- and high-temperature environment, and it also indicates that the early ore-forming hydrothermal solution may be rich in Sn. Fe, In, Co, and Ni mainly exist in cassiterite in isomorphic form, and the content of W in cassiterite is high. There are two main forms, one is isomorphic and the other is wolframite inclusion. Cassiterite has Fe-rich and W-U-poor characteristics, indicating that cassiterite from the Shuangjianzishan deposit was formed under relatively oxidized conditions, and the relative enrichment of elements such as Fe, W, Zr, and Hf indicates that the temperature of cassiterite formation was high. The elemental content and inter-ionic coupling relationships suggest that the cassiterite from the Shuangjianzishan deposit may have an elemental replacement mechanism of  $W^{6+} + Fe^{2+} \leftrightarrow 2Sn^{4+}$  or  $Fe^{3+} + OH^- \leftrightarrow Sn^{4+} + O^{2-}$ . The trace elements in cassiterite of the Shuangjianzishan deposit are rich in Fe and Mn and depleted in Nb and Ta, according to the Fe-W diagram, and the tin mineralization of the Shuangjianzishan deposit belongs to cassiteritesulfide-type tin mineralization. Chalcopyrite Co/Ni ratios >1 are consistent with the characteristics of chalcopyrite genesis in hydrothermal deposits.

Keywords: the Shuangjianzishan deposit; tin mineralization; deposit genesis; trace element

# 1. Introduction

The Great Xing'an Range is in a region where two global tectonic mineralization domains, the Paleozoic Paleo-Asian Ocean Tectonic Mineralization Domain and the Mesozoic Paleo-Pacific Ocean Tectonic Mineralization Domain, are strongly superimposed. On the basis of the ancient basement tectonics and the Late Paleozoic orogenic belt, the Mesozoic volcanic–magmatic activities were intense, and the polymetallic metallogenetic belts of Cu-Sn-Mo-Pb-Zn-Ag were formed. As an important Pb-Zn-Ag polymetallic ore-concentrated area in China, the southern section of the Great Xing'an Range has more than 30 Ag-Pb-Zn



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). deposits in the area, with a total Ag resource of more than 57,000 t, making it the largest silver-metallogenic province in China [1]. Important Ag-Pb-Zn hydrothermal deposits include the Shuangjianzishan, Bianjiadanyuan, Weilasituo, and Bairendaba deposits. With the deepening of theoretical research and geological work, a number of tin polymetallic deposits have been discovered in the district, such as the Huanggang, Maodeng, Baiyinnuoer, Baiyinchagan, Weilasituo, and Bianjiadayuan. These hydrothermal tin polymetallic mineralizations are closely related to vein Pb-Zn-Ag polymetallic mineralization, showing good prospects for finding tin polymetallic resources [2]. Overall, the Sn-Cu-Pb-Zn-Ag polymetallic system has a similar vertical zonation, with Sn-Cu(-W) mineralization developed at depth and associated with highly fractionated granite bodies, while Ag-Pb-Zn is close to the shallow surface and fracture-controlled [3]. The intrinsic genesis relationship between medium- and high-temperature tin mineralization and medium- and low-temperature Cu-Pb-Zn-Ag mineralization has long been debated. The debate centers on the spatial distance, and the age difference between the Pb-Zn-Ag mineralization and the rock mass makes it difficult to establish a genesis link between the mineralization and the rock mass [4], restricting the exploration of the mineral sources of Pb-Zn and Cu-Sn mineralization [5]. A previous study held that the Shuangjianzishan deposit is typically an epithermal Ag-Pb-Zn deposit that lacks a high-temperature mineralization stage [6-9]. In recent years, some scholars found abundant Cu-Sn mineralization in the ore and drill holes of the Shuangjianzishan deposit and concluded that the Shuangjianzishan deposit has great potential for Cu-Sn mineralization [10,11]. As the discovery of copper–tin mineralization in the Shuangjianzishan deposit is still recent, less work has been carried out on the metallogenic chronology and mineralogy of chalcopyrite and cassiterite. Chalcopyrite and cassiterite, as important ore minerals in the copper-tin mineralization stage, often contain a variety of trace elements [12,13] and contain rich metallogenic information, which is an important indication of the formation process and genesis type of the deposit [14,15]. At present, there are more studies on pyrite [16], sphalerite, and galena, but the trace element characteristics of chalcopyrite and cassiterite are seldom reported. In this paper, we carry out detailed mineralogical and LA-ICP-MS trace element studies on chalcopyrite and cassiterite from the Shuangjianzishan deposit to reveal the trace element characteristics of chalcopyrite and cassiterite and their relationship with the genesis of the deposit.

# 2. Regional Geology

The Shuangjianzishan silver-polymetallic deposit in Inner Mongolia is located in the southern section of the Great Xing'an Range's silver-lead-zinc-tin-rare metal metallogenic belt. The geotectonic location belongs to the eastern part of the Xing'an-Mongolia orogenic belt, in the geosynclinal fold system of Middle Inner Mongolia, surrounded by the Siberian Plate and the North China Plate; bounded by the Xilamulun Fault Zone, Erenhot–Hegenshan fault belt, and Nenjiang fault belt; and connected with the North China Craton, Xing'an Block, and Songliao Basin, respectively (Figure 1a). Since the Paleozoic, the study area was successively affected by the subduction collision and splicing system due to the development and demise of the Paleo-Asian Ocean, the continuous subduction of the Mongolia-Okhotsk Plate on the Siberian Plate, and the subduction tectonic system of the Pacific Rim, which realized the obvious transformation from the compressional tectonic system to the extensional tectonic system in the late Mesozoic [17–19]. Under the complex tectonic background, the deep fractures and secondary fracture structures in the region are extremely developed, showing a lattice fracture system based on two northeast-trending deep fractures, namely, the Xar Moron Fault Zone and the Hegenshan-Nenjiang Fault Zone, and the extensive development of NW-, NNE-, and near-EW-trending secondary fractures, which provide transportation channels and metallogenic space. Under such favorable mineralization conditions, there are a series of large-scale and super-large Ag-Pb-Zn polymetallic deposits and Sn polymetallic deposits, such as the Baiyinnuoer large Pb-Zn deposit, Huaaobaote large Ag polymetallic deposit, Bairendaba super-large Ag polymetallic deposit, Haobugao large Pb-Zn polymetallic deposit, Huanggangliang super-large Fe-Sn polymetallic deposit, and Weilasituo Sn polymetallic deposit, owing considerable prospecting potential (Figure 1b). The district is dominated by Late Paleozoic strata and Mesozoic volcanic complex rock mass, except for some small-scale exposures of Early Proterozoic Xilingol metamorphic assemblages in some areas. The area is mainly dominated by emerging Permian strata, the Carboniferous System exposes a set of marine clastic rocks of the Middle Carboniferous Benbatu Formation and the Upper Carboniferous Amushan Formation, and the Permian System from the oldest to the newest exposes the Lower Permian Shoushangou Formation, the Lower Permian Dashizhai Formation, the Middle Permian Zhesi Formation, the Upper Permian Huanggangliang Formation, and the Upper Permian Linxi Formation. Most of the deposits in the southern section of the Great Xing'an Range are hosted in Permian strata [20], and in particular, the volcanic-sedimentary construction of the Dashizhai Formation is an important ore-holding stratum for silver, lead, and zinc polymetallic deposits in the region. The Mesozoic mainly exposed a set of Jurassic–Cretaceous volcaniclastic rock, which are the Xinmin Formation, Manketouebo Formation, Manitou Formation, Baiyingaolao Formation, and Meilertu Formation from bottom to top. There are frequent magmatic activities in the area, and the intrusions of the Hercynian, Indo-Chinese, and Yanshanian period are all developed, which are mainly controlled by the NE-trending fault structure. The Mesozoic magmatic rocks are most widely distributed, and the lithology is mainly granite porphyry, dioritic porphyrite, and quartz syenite, which are closely related to mineralization.



**Figure 1.** (a) Tectonic sketch of NE China (modified after [8]. The red box indicates the approximate scope of (b). (b) Regional geological map of the southern section of Great Xing'an Range (modified after [9]). (c) Geological sketch map of Xinglongshan ore section in the Shuangjianzishan deposit.

# 3. Deposit Geology

The Shuangjianzishan deposit is geographically located in the Fuhe Town, Balin Left Banner, Inner Mongolia. The geographic coordinates of the center of the mine are  $119^{\circ}07'$  E and  $44^{\circ}30'$  N. There are two ore sections in the mine, the eastern Xinglongshan section and the western Shuangjianzishan section, both of which are 4.7 km apart. The mineralization of the Shuangjianzishan section is weaker and the working degree is lower, while the ore body of the Xinglongshan section is larger and the exploration degree is higher. In the mine area, mainly the Lower Permian Dashizhai Formation (P<sub>1</sub>*d*) slate and volcanic-sedimentary rocks, Middle Jurassic Xinmin Formation (J<sub>2</sub>*x*) volcaniclastic and volcaniclastic sedimentary rocks, Upper Jurassic Manketouebo Formation (J<sub>3</sub>*m*) acidic volcanic lava, clastic rocks and volcaniclastic sedimentary rocks, and Quaternary Holocene (Qh) alluvion are exposed (Figure 1c). The ore body is mainly hosted in the stratum of the Dashizhai Formation, and locally extends to the stratum of the Xinmin Formation. Only dioritic porphyrite, granite, granite porphyry, rhyolite porphyry, quartz veins, and other vein rocks are exposed in the area, and the intrusive rocks are mainly granitic rocks, which are not exposed on the surface. Fold tectonics in the mine is relatively simple, the mine is located in the northwest wing of the Linxi-Zhesi anticlinorium, and the Dashizhai Formation strata is generally monoclinic tectonics, NW-trending, with a dip angle of 55°~60°. The fracture structure is very developed in the mining area, controlling the output of the ore body. There are mainly NW-trending, NNE-trending, and near-NS-trending fracture structures, of which the NW-trending ductile shear zone is the most important ore-controlling fracture zone, controlling the output of the NW-trending Ag polymetallic vein group. The ore bodies, in order of mineralization, are the NW-trending Ag polymetallic vein group, the NE-trending ore body, and the near-NS-trending ore body (Figure 2a). The ore bodies are generally lenticular, vein-like, and stratiform-like (Figure 2b). The alteration of the wall rocks near the mine mainly includes silicification, chloritization, pyritization, and carbonatation, followed by sericitization and kaolinization. Among them, silicification and pyritization are closely related to silver, lead, and zinc mineralization. The ore structure is mainly of subhedral-euhedral texture, followed by metasomatic texture, emulsion texture, poikilitic texture, lamellar texture, etc. The ore structures are of brecciated structure, mesh vein structure, banded structure, disseminated structure, dense block structure, and so on. The main metallic minerals are pyrite, galena, sphalerite, chalcopyrite, cassiterite, pyrrhotite, arsenopyrite, canfieldite, kustelite, polybasite, aguilarite, acanthite, stephanite, pyrargyrite, freibergite, native silver, argentite, etc. Gangue minerals include quartz, calcite, chlorite, epidote, and so on.



**Figure 2.** Geological plan of Xinglongshan ore section in the Shuangjianzishan deposit (**a**); typical profile (**b**) (modified after [21]).

## 4. Characteristics of Copper-Tin Mineralization

The newly revealed copper–tin mineralization mainly appears in the Xinglongshan ore section. Wu [10] found a large amount of tin mineralization in the NW-trending ore body and drill core at level 625 of the Xinglongshan ore section. The massive lead–zinc ore at level 625 contains copper (5.67%) and tin (2.35%), and the Cu and Sn grades in the Cu-rich ore in the drilling hole are 12.98% and 4.75%, respectively. There is a lack of Cu-Sn mineralization in the NE-trending ore body. Wu [22] further divided the NW-trending silver polymetallic vein group into silver–copper polymetallic ore bodies developed on the hanging wall of the ductile shear zone and silver–lead–zinc polymetallic ore bodies on the footwall, with the silver–copper polymetallic ore bodies being the main tin-bearing ore

bodies. Tin mineralization is marked by the occurrence of large quantities of canfieldite and cassiterite, accompanied by assemblages of medium- and high-temperature minerals such as chalcopyrite, arsenopyrite, and wolframite. The selenite-rich canfieldite is coeval with sphalerite and galena, and cassiterite is mainly produced in fine grains or fine columns, often parceled by sphalerite, galena, and chalcopyrite (Figure 3d), or may be produced in cassiterite–quartz veins. Ma [11] pointed out that copper mineralization developed sporadically around -300 m and developed on a large scale at a depth of -700 m, and the spatial pattern of change in the vertical direction is as follows: -400 m to the surface is dominated by fine-veined, low-dipping Py-Pb-Zn veins; between -400 and -900 m is characterized by thicker veins, high-dipping, or near-erect Pb-Zn veins; and there are lead-zinc-copper ore bodies below -900 m. From west to east on the plane: At the same elevation, relatively high-temperature Cu-Sn assemblages are more developed in the western part of the mine than in the eastern part of the drill core. Copper ores are produced in massive (Figure 3a), disseminated (Figure 3b), brecciated (Figure 3c), and vein structures. The metallic minerals are mainly chalcopyrite, sphalerite, galena, pyrite, and arsenopyrite. Chalcopyrite in hand specimens is often coeval with quartz, chlorite, and calcite. Microscopic chalcopyrite is often metasomatized for by galena, sphalerite, etc. (Figure 3f), or chalcopyrite is distributed in sphalerite as an emulsion texture (Figure 3e), but it is not the focus of this study.



**Figure 3.** Copper–tin mineralized hand specimen and microscopic characteristics of the Shuangjianzishan silver polymetallic deposit. (a) Massive structure; (b) dense disseminated structure; (c) brecciated structure; (d) chalcopyrite is replaced by sphalerite and cassiterite is parceled by chalcopyrite; (e) chalcopyrite is distributed in sphalerite as emulsion texture; (f) chalcopyrite and arsenopyrite are replaced by galena and sphalerite. Apy—arsenopyrite; Ccp—chalcopyrite; Sp—sphalerite; Gn galena; Cst—cassiterite; Q—quartz.

#### 5. Sampling and Analytical Methods

The chalcopyrite and cassiterite samples used in this study were taken from fresh rock cores and ores in drills ZK0403 and ZK2204 and tunnels. The collected samples were ground into optically thin sections for mineralogical observation, and representative points were selected to carry out electron microprobe analysis (EMPA) and finally LA-ICP-MS in situ trace element analysis.

On the basis of detailed microscopic observation, the major and trace element fractions of cassiterite were determined. The electron microprobe analysis (EMPA) of cassiterite was completed at the Key Laboratory of Mineralization and Resource Evaluation, Institute of Mineral Resources, Chinese Academy of Geological Sciences, and the testing instrument was a JEOL JXA-iHP200F field emission electron microprobe (Figure 4). The accelerating voltage was 15 kV, the beam current was 20 nA, the electron beam spot diameter was 5  $\mu$ m, and the tested elements included F, Si, Mg, Zr, Ca, Fe, Hf, Sn, Sr, and Th, using natural minerals or the national standards of synthetic metal oxides as the standard sets. The data were uniformly corrected by ZAF.



**Figure 4.** Electron probe BES of minerals in the Shuangjianzishan silver polymetallic deposit, Inner Mongolia. (a) Cassiterite is parceled by sphalerite and pyrite; (b) cassiterite is associated with quartz. Cst—cassiterite; Sp—sphalerite; Py—pyrite.

Based on the results of the electron microprobe analysis (EMPA), LA-ICP-MS in situ trace element analysis was carried out on chalcopyrite and cassiterite. A total of 5 samples were collected in this work, including 2 samples of cassiterite with 32 points tested and 13 samples of chalcopyrite with 21 points tested. The specific sampling location and mineral combination characteristics are shown in Table 1. In this paper, we focus on testing early chalcopyrite and cassiterite connected with gangue minerals. As far as possible, samples with clean surfaces and free of fissures and inclusions were selected for testing and analysis. The in situ LA-ICP-MS analysis of chalcopyrite and cassiterite was carried out at the National Research Center for Geoanalysis (CAGS), using a Thermo Element II single-receiver, high-resolution magnetic sector ICP-MS connected to a New Wave UP 213. The denuded material was transported by helium. The operating conditions were a 40  $\mu$ m wide spot beam, 10 Hz frequency, and a laser flow of 10–30 J/cm<sup>2</sup> with an energy of 0.176 mJ. In the analysis process, first, 15 s of background values was collected, followed by 45 s of sample stripping, and finally 15 s of cleaning the system. The specific analysis process and technique refer to [23]. The calibration of trace elements was carried out using MASS1, NIST610, and NIST612 as the joint external standards and KL2G was used as a monitoring standard sample; the analytical precision was  $0.1 \times 10^{-6}$ . GJ-1 and AY-4 were used as standard samples for cassiterite trace element correction. Compared with the electron microprobe analysis, the LA-ICP-MS analysis was characterized by a lower detection limit and higher accuracy.

Sample No.	Mineral	Sampling Location	Description				
ZK0403-61	Сср	ZK0403 at 171 m depth	Quartz–sphalerite veins with chalcopyrite dotted among them				
ZK2203-19	Сср	ZK2203 at 396 m depth	Vein chalcopyrite ore, gangue minerals are mainly quartz				
ZK2203-20	Сср	ZK2203 at 445 m depth	Vein chalcopyrite ore				
ZK2203-21	Сср	ZK2203 at 498 m depth	Vein-like sphalerite ore with chalcopyrite is sparsely disseminated in it				
ZK2203-23	Сср	ZK2203 at 594 m depth	Chlorite-dense disseminated chalcopyrite ore				
ZK2203-29	Сср	ZK2203 at 993 m depth	Quartz-chalcopyrite-sphalerite veins				
ZK2203-33	Сср	ZK2203 at 1172 m depth	The vented galena ore and chalcopyrite are distributed in disseminated form				
ZK2204-7	Сср	ZK2204 at 280 m depth	Striped galena-sphalerite ore with chalcopyrite dots in it				
ZK2204-9	Сср	ZK2204 at 298 m depth	Chalcopyrite ore with quartz and calcite veins				
ZK2204-10	Ccp	ZK2204 at 308 m depth	Vein sphalerite ore, chalcopyrite sporadic distribution				
ZK2204-12	Ccp	ZK2204 at 389 m depth	Chalcopyrite ore with quartz vein				
ZK2204-14	Сср	ZK2204 at 462 m depth	Quartz vein chalcopyrite ore				
ZK2204-17	Сср	ZK2204 at 625 m depth	Breccia chalcopyrite-sphalerite ore				
ZD5-02	Cst	Level 5 elevation 625 m, vein 75	Dense disseminated chalcopyrite ore with cassiterite				
ZK2204-B3	Cst	ZK2204 at 1386 m depth	Vein sphalerite ore with cassiterite				

**Table 1.** Sampling locations and sample characteristics of chalcopyrite and cassiterite in the Shuangjianzishan deposit.

# 6. Result

#### 6.1. Geochemical Characteristics of Trace Elements in Chalcopyrite

The results of chalcopyrite trace elements (see Table S1, Figure 5) show that chalcopyrite is generally enriched in Ni, Sn, Pb, Se, and Ag; relatively enriched in Cr, Cu, As, Rb, Sr, Cd, and In; contains a small amount of Co, Sb, Ge, Mn, and B; and poor in Cs, Hf, Ta, W, Tl, Ga, Nb, Mo, and Bi elements. The specific characteristics are as follows:

- (1) Rich in Sn, Se, Ni, Pb, and Ag. Sn content ranged from  $20.61 \times 10^{-6}$  to  $14,363.11 \times 10^{-6}$ , average  $2710.5 \times 10^{-6}$ . Se content ranged from  $0 \times 10^{-6}$  to  $4257.89 \times 10^{-6}$ , average  $665.83 \times 10^{-6}$ . Ni content ranged between  $0 \times 10^{-6}$  and  $2776.85 \times 10^{-6}$ , average  $530.23 \times 10^{-6}$ . Pb content ranged between  $3.17 \times 10^{-6}$  and  $3728.26 \times 10^{-6}$ , average  $366.78 \times 10^{-6}$ . Ag content ranged between  $6.15 \times 10^{-6}$  and  $703.47 \times 10^{-6}$ , average  $193.33 \times 10^{-6}$ .
- (2) Less rich in Cr, Cu, As, Rb, Sr, Cd, and In. Cr content ranged between  $0 \times 10^{-6}$  and  $101.01 \times 10^{-6}$ , average  $26.34 \times 10^{-6}$ . Cu content ranged between  $5.52 \times 10^{-6}$  and  $46.61 \times 10^{-6}$ , average  $20.56 \times 10^{-6}$ . As content ranged between  $0 \times 10^{-6}$  and  $59.73 \times 10^{-6}$ , average  $14.53 \times 10^{-6}$ . Rb content ranged between  $0 \times 10^{-6}$  and  $82.66 \times 10^{-6}$ , average  $15.09 \times 10^{-6}$ . Sr content ranged between  $1 \times 10^{-6}$  and  $59.49 \times 10^{-6}$ , average  $20.32 \times 10^{-6}$ . Cd content ranged between  $0 \times 10^{-6}$  and  $394.91 \times 10^{-6}$ , average  $63.24 \times 10^{-6}$ . In content ranged between  $2.39 \times 10^{-6}$  and  $263.41 \times 10^{-6}$ , average  $71.34 \times 10^{-6}$ .
- (3) Contains small amounts of Co, Sb, Ge, Mn, and Ba. Co content ranged between  $0 \times 10^{-6}$  and  $7.66 \times 10^{-6}$ , average  $1.85 \times 10^{-6}$ . Ge content ranged between  $0 \times 10^{-6}$  and  $22.94 \times 10^{-6}$ , average  $4.27 \times 10^{-6}$ . Sb content ranged between  $0.22 \times 10^{-6}$  and  $6.94 \times 10^{-6}$ , average  $1.93 \times 10^{-6}$ . Ge content ranged between  $0 \times 10^{-6}$  and  $22.94 \times 10^{-6}$ , average  $4.27 \times 10^{-6}$ . Ge content ranged between  $0 \times 10^{-6}$  and  $22.94 \times 10^{-6}$ , average  $4.27 \times 10^{-6}$ . Mn content ranged between  $0 \times 10^{-6}$  and  $47.72 \times 10^{-6}$ , average  $9.52 \times 10^{-6}$ . Ba content ranged between  $0.1 \times 10^{-6}$  and  $67.53 \times 10^{-6}$ , average  $10.88 \times 10^{-6}$ .
- (4) Poor in Zn, Cs, Hf, Ta, W, Tl, Ga, Nb, Mo, and Bi. Zn content ranged between  $0 \times 10^{-6}$  and  $3.36 \times 10^{-6}$ , average  $0.6 \times 10^{-6}$ . Cs content ranged between  $0 \times 10^{-6}$  and  $1.02 \times 10^{-6}$ , average  $0.15 \times 10^{-6}$ . Hf content ranged between  $0.08 \times 10^{-6}$  and  $0.63 \times 10^{-6}$ , average  $0.25 \times 10^{-6}$ . Ta content ranged between  $0 \times 10^{-6}$  and  $0.14 \times 10^{-6}$ ,

average  $0.01 \times 10^{-6}$ . W content ranged between  $0 \times 10^{-6}$  and  $3.21 \times 10^{-6}$ , average  $0.27 \times 10^{-6}$ . Tl content ranged between  $0 \times 10^{-6}$  and  $0.3 \times 10^{-6}$ , average  $0.09 \times 10^{-6}$ . Ga content ranged between  $0 \times 10^{-6}$  and  $4.78 \times 10^{-6}$ , average  $0.85 \times 10^{-6}$ . Nb content ranged between  $0 \times 10^{-6}$  and  $4.2 \times 10^{-6}$ , average  $0.85 \times 10^{-6}$ . Mo content ranged between  $0 \times 10^{-6}$  and  $2.63 \times 10^{-6}$ , average  $0.54 \times 10^{-6}$ . Bi content ranged between  $0 \times 10^{-6}$  and  $2.63 \times 10^{-6}$ , average  $0.74 \times 10^{-6}$ .



I MILCO NI CU ZII GA GE AS KO SI NOMOCU III SII SO CS BA III IA W II FO BI

**Figure 5.** Boxand-whisker plots for different generations of chalcopyrite in situ trace elements from the Shuangjianzishan ore area.

#### 6.2. Geochemical Characteristics of Trace Elements in Cassiterite

Cassiterite is one of the main tin-bearing minerals in the Shuangjianzishan deposit. Containing 78.6% tin, cassiterite is the most common tin mineral and the most important ore mineral of tin. Its chemical component is SnO<sub>2</sub>, which is a rutile tetragonal crystal system oxide mineral. The results of cassiterite trace elements (see Table S2, Figure 6) show that the trace element contents of the two cassiterite samples extracted from the tunnel and the drill, respectively, are similar, generally enriched in Fe, Co, Ni, Cd, In, Sb, and W; relatively enriched in Mn, Zn, and Pb; with a small amount of Cu, Ga, Ge, Sr, Nb, and Ba; and poor in Cr, As, Rb, Mo, Cs, Hf, Ta, Tl, and Bi. Some element contents are even below the detection limit, and the elemental content of tunnel samples is generally higher than that of drill holes. The specific characteristics are as follows:

(1) Rich in Fe, Cd, Ni, In, Co, and W. Fe content ranged between  $1272.46 \times 10^{-6}$  and  $36,766.47 \times 10^{-6}$ , average  $7405.76 \times 10^{-6}$ . Cd content ranged between  $28,522.69 \times 10^{-6}$  and  $31,034.52 \times 10^{-6}$ , average  $29,820.29 \times 10^{-6}$ . Ni content ranged between  $6944.71 \times 10^{-6}$  and  $7731.47 \times 10^{-6}$ , average  $7337.13 \times 10^{-6}$ . In content ranged between  $2475.65 \times 10^{-6}$  and  $2536.9 \times 10^{-6}$ , average  $2651.89 \times 10^{-6}$ . Co content ranged between  $1153.17 \times 10^{-6}$  and  $1274.97 \times 10^{-6}$ , average  $1205.67 \times 10^{-6}$ . W content ranged between  $0 \times 10^{-6}$  and  $9952.13 \times 10^{-6}$ , average  $1193.93 \times 10^{-6}$ .

- (2) Less rich in Mn, Zn, Pb, and Sb. Sb content ranged between  $0 \times 10^{-6}$  and  $802.1 \times 10^{-6}$ , average  $73.89 \times 10^{-6}$ . Mn content ranged between  $0 \times 10^{-6}$  and  $185.46 \times 10^{-6}$ , average  $18.42 \times 10^{-6}$ . Pb content ranged between  $0 \times 10^{-6}$  and  $225.18 \times 10^{-6}$ , average  $9.08 \times 10^{-6}$ . Zn content ranged between  $0 \times 10^{-6}$  and  $117.03 \times 10^{-6}$ , average  $7.43 \times 10^{-6}$ .
- (3) Contains small amounts of Cu, Ga, Ge, Sr, Nb, Ba, and As. Cu content ranged between  $0 \times 10^{-6}$  and  $2.49 \times 10^{-6}$ , average  $0.2 \times 10^{-6}$ . Ga content ranged between  $0 \times 10^{-6}$  and  $36.61 \times 10^{-6}$ , average  $7.08 \times 10^{-6}$ . Ge content ranged between  $0 \times 10^{-6}$  and  $3.59 \times 10^{-6}$ , average  $0.56 \times 10^{-6}$ . Sr content ranged between  $0 \times 10^{-6}$  and  $28.83 \times 10^{-6}$ , average  $2.18 \times 10^{-6}$ . Nb content ranged between  $0 \times 10^{-6}$  and  $5.64 \times 10^{-6}$ , average  $1.02 \times 10^{-6}$ . Ba content ranged between  $0 \times 10^{-6}$  and  $17.25 \times 10^{-6}$ , average  $1.01 \times 10^{-6}$ . As content ranged between  $0 \times 10^{-6}$  and  $51.73 \times 10^{-6}$ , average  $4.46 \times 10^{-6}$ .
- (4) Poor in Cr, Rb, Mo, Cs, Hf, Ta, Tl, and Bi. The contents of Cr, Rb and Cs in all cassiterite samples were lower than the detection limit, and the contents were very low. Mo content ranged between  $0 \times 10^{-6}$  and  $2.89 \times 10^{-6}$ , average  $0.31 \times 10^{-6}$ . Hf content ranged between  $0 \times 10^{-6}$  and  $2.22 \times 10^{-6}$ , average  $0.21 \times 10^{-6}$ . Ta content ranged between  $0 \times 10^{-6}$  and  $0.11 \times 10^{-6}$ , average  $0.02 \times 10^{-6}$ . Tl content ranged between  $0 \times 10^{-6}$  and  $0.06 \times 10^{-6}$ , average  $0.01 \times 10^{-6}$ . Bi content ranged between  $0 \times 10^{-6}$ , average  $0.01 \times 10^{-6}$ .



**Figure 6.** Box-and-whisker plots for different generations of cassiterite in situ trace elements from the Shuangjianzishan ore area.

#### 6.3. Cassiterite Electron Microprobe Analysis Results

The results of cassiterite electron microprobe analysis (Table 2) show that cassiterite from the Shuangjianzishan deposit is enriched in Si, Fe, Mg, and Ca. The elemental content of Si ranges from 0.57% to 2.69% (average 1.33%), the Fe elemental content from 0.39% to 4.16% (average 1.73%), the Mg elemental content from 0.08% to 0.42% (average 0.18%), and the Ca elemental content ranges from 0.38% to 0.61% (average 0.51%). The contents of F, Zr, Hf, Sr, and Th are very small.

	F	SiO <sub>2</sub>	MgO	ZrO <sub>2</sub>	CaO	FeO	HfO <sub>2</sub>	$SnO_2$	SrO	ThO <sub>2</sub>	Total
ZK2204-17-01	0	1.098	0.227	0.033	0.506	1.564	0	96.252	0	0.038	99.718
ZK2204-17-02	0.131	1.769	0.166	0	0.527	1.706	0	95.086	0	0.022	99.407
ZK2204-17-03	0.058	1.271	0.15	0.056	0.548	2.188	0.15	95.853	0.032	0.019	100.325
ZK2204-17-04	0	1.207	0.152	0	0.384	1.332	0.156	96.38	0.024	0	99.635
ZK2204-17-05	0	2.693	0.42	0	0.498	4.158	0	91.456	0.071	0	99.296
ZK2204-17-06	0	1.844	0.216	0	0.488	3.093	0.388	94.169	0	0	100.198
ZK2204-17-07	0.101	0.993	0.122	0.098	0.407	1.629	0.058	96.288	0	0	99.696
KZ0001-05-01	0	0.571	0.076	0.033	0.535	0.393	0	98.272	0.008	0.008	99.896
KZ0001-05-02	0	0.641	0.115	0.056	0.484	1.111	0	96.667	0.031	0	99.105
KZ0001-05-03	0	1.605	0.162	0.089	0.61	0.99	0	96.381	0.013	0	99.85
KZ0001-05-04	0	0.989	0.157	0.005	0.565	0.904	0.063	97.805	0	0	100.488

**Table 2.** Electron microprobe analysis results of cassiterite in the Shuangjianzishan silver polymetallic deposit.

## 7. Discussion

#### 7.1. Occurrence State of Trace Elements in Chalcopyrite and Its Indicating Significance

Chalcopyrite is the main carrier of Cu in the Shuangjianzishan deposit. Its ideal chemical formula is CuFeS<sub>2</sub>, and the tetragonal variant is the most common in nature. Pauling and Brockway [24] thought that there was a strong covalent bond between Cu and Fe, and the valence states of Cu and Fe fluctuated between monovalent-divalent and divalent-trivalent, respectively. Compared with base metal sulfides such as galena and sphalerite, the situation of trace elements entering the chalcopyrite structure is often more complicated [25], and because of the existence of covalent bonds in chalcopyrite, it means that the GoldSchmidt rule [26] cannot be used to predict the distribution trend of elements just like pure ionic structure minerals, but it still has certain reference significance. The content of trace elements in chalcopyrite is controlled by many factors, such as the chalcopyrite crystal structure, element partition with co-crystallization minerals, and magma/fluid composition [25,27]. The content of Sn is highest in chalcopyrite in this test. Sn, Cu, and Fe have similar ionic radius, so Sn can enter chalcopyrite through isomorphism. Eugster [28] thought that the migration and enrichment of high-concentration Sn were mainly formed under high-temperature and reduction conditions. George et al. [25,27] pointed out that chalcopyrite is not the "first preferred host" of trace elements when there are co-crystallization sulfides such as sphalerite, but it is also beneficial to enrich trace elements in minerals if the ore-forming fluid is rich, so the early hydrothermal solution of the Shuangjianzishan deposit may be rich in Sn, which makes the Sn content in chalcopyrite higher. In the -CPS signal diagram (Figure 7), some In and Sn signals are consistent. The ionic radii of In and Sn are similar, and there is a good positive correlation (Figure 8b). It is speculated that In and Sn enter chalcopyrite in the form of coupling instead of Fe at high temperature [29], forming  $CuInS_2$  and  $Cu_2FeSnS_4$  solid solutions with the same structure as chalcopyrite. Although In and Zn also show a weak positive correlation (Figure 8c), the synchronous change in Zn and In is not observed in the signal diagram, which further proves that there may be a coupling substitution relationship between In and Sn. The positive correlation between Zn and Mn (Figure 8d) shows that Zn mainly exists in chalcopyrite in the form of inclusions. There is a positive correlation between Pb and Bi in chalcopyrite (Figure 8f), but Pb and Bi cannot exist in chalcopyrite in the form of solid solution, but mostly exist in chalcopyrite in the form of inclusions, due to the large difference between the ionic radius of Cu and Fe ions. The content of As is high, which may replace the S element in chalcopyrite. Butler et al. [30] think that As can promote the entry of Au and Ag. There is a weak correlation between As and Sb (Figure 8e), and there may be As-rich inclusions. The content of Se in chalcopyrite is high (the average is 665.83 ppm), and the S element is primarily substituted by other elements through isomorphic replacement, which implies that the formation temperature of chalcopyrite is relatively high [31]. The low content of medium- and low-temperature elements such as Ga and Sb

in chalcopyrite reflects that chalcopyrite was formed in a medium- and high-temperature environment. There is a positive correlation between Sb and Tl (Figure 8a), which indicates that Sb and Tl may enter chalcopyrite through coupling substitution. Chalcopyrite in the Shuangjianzishan deposit has a high content of Ni (with an average of 530.23 ppm), but George et al. [25] think that Ni is not obviously enriched in chalcopyrite, but exists in pyrite, so Ni may mainly exist in chalcopyrite as pyrite or pyrrhotite inclusions, instead of replacing Fe in chalcopyrite by isomorphism.



Figure 7. Typical LA-ICP-MS-time -CPS signal spectrum of chalcopyrite in the Shuangjianzishan deposit.



**Figure 8.** Binary diagrams of trace elements content in chalcopyrite in the Shuangjianzishan deposit. (a) Sb versus Tl; (b) In versus Sn; (c) In versus Zn; (d) Zn versus Mn; (e) As versus Sb; (f) Pb versus Bi.

#### 7.2. Occurrence State of Trace Elements in Cassiterite and Its Indicating Significance

Cassiterite has strong weathering and erosion resistance and is not easily influenced by hydrothermal alteration in the later period. It often contains siderophile elements such as Ti, V, Cr, Mn, Fe, Co, and Ni; chalcophile elements such as Cu, Pb, and Ag; and some rare elements [32]. The research results in this paper show that cassiterite has relatively high Fe (average 7405.76 ppm) and W (average 1193.93 ppm), and relatively low Sb (average 73.89 ppm) and U (average 1.64 ppm), and W-U has a positive correlation (Figure 9c). Predecessors thought that high temperature was beneficial to the replacement of Sn in cassiterite by Fe [33], and Huang et al. [34] further concluded that the FeO content in cassiterite was positively correlated with the crystallization temperature of cassiterite is basically greater than 1%, and it is considered that the crystallization temperature of cassiterite in the Shuangjianzishan deposit is higher, but Tan et al. [35] think that the universality of this conclusion is still controversial, so this paper only takes it as a secondary reference condition. Generally speaking, the W content in cassiterite is not high, and it is elevated only when it coexists with wolframite or scheelite [36]. In this paper, cassiterite has a higher W content, and there is a certain correlation between Fe and W (Figure 10), which indicates that cassiterite in the Shuangjianzishan deposit may have an element replacement mechanism of  $W^{6+}$  + Fe<sup>2+</sup>  $\leftrightarrow$  2Sn<sup>4+</sup>; it is suggested that the cassiterite formation temperature is higher. At the same time, it also reflects the characteristics that magmatic hydrothermal fluid is rich in W. But at the same time, Wu [37] found wolframite inclusions in cassiterite, and the W content in cassiterite has a large range  $(0 \times 10^{-6} \sim 9952.13 \times 10^{-6})$ , indicating that W may not enter cassiterite mainly in isomorphic form, but in the form of wolframite micro-inclusions. Previous studies have shown that the primary cassiterite rich in W-U(Sb) and poor in Fe was formed under the condition of relative reduction, and  $Sn^{2+}$ can migrate in acidic fluid, while the cassiterite rich in Fe and poor in W-U was formed under the metasomatism of late oxidizing hydrothermal fluid [38]. The cassiterite in the Shuangjianzishan deposit is characterized by being rich in Fe and poor in U and Sb, so it is speculated that it was formed under the condition of relative oxidation. The content of Fe-Ga is high in the relative oxidation environment (Figure 9e).



**Figure 9.** Binary diagrams of trace element content in cassiterite in the Shuangjianzishan deposit. (a) Nb versus Ta; (b) Zr versus Hf; (c) W versus U; (d) Sc versus V; (e) Fe versus Ga; (f) Co versus Ni.

The results of this test show that the content of In in cassiterite is relatively high (with an average of 2651.89 ppm). Pavlova et al. [39] think that the content of In in cassiterite has a certain corresponding relationship with the depth of mineralization, and the content of In in quartz-vein-type tin ore with deep formation is relatively low (<160 ppm), while that in sulfide tin ore with a shallow formation is usually relatively high. At the same time, the hydrothermal fluid is rich in volatiles such as F and Li, which is also beneficial to the enrichment of In and the replacement of Sn in cassiterite. Therefore, the high content of In in cassiterite is not necessarily due to the decrease in temperature and pressure during the formation of cassiterite, but may also be due to the further enrichment of In in cassiterite due to the volatile substances such as F and Li contained in the ore-forming hydrothermal solution [35]. Zhu et al. [40] pointed out that Sn plays an important role in the enrichment process of In. Tin and indium are co-enriched and migrated in ore-forming fluids and separated in the mineralization and precipitation stage. It is especially obvious in skarn deposits and epithermal deposits related to granite (hydrothermal vein type) [41].



Figure 10. W-Fe diagram of cassiterite in the Shuangjianzishan deposit (After [39]).

Nb-Ta and Fe-Mn usually appear in pairs and enter the cassiterite crystal lattice together. Cassiterite often replaces  $Sn^{4+} \leftrightarrow Fe^{2+} + Mn^{2+} + Nb^{5+} + Ta^{5+}$  in pegmatite and high-temperature quartz veins, while  $Fe^{3+} + Nb^{5+} + Ta^{5+} \leftrightarrow Sn^{4+}$  is replaced in middle– low-temperature quartz veins [42]. However, cassiterite in the Shuangjianzishan deposit is rich in Fe and poor in Nb and Ta. It is speculated that Fe may enter the cassiterite lattice through  $Fe^{3+} + OH^- \leftrightarrow Sn^{4+} + O^{2-}$  instead of the above two replacement reactions, which also explains the reason why cassiterite is poor in Nb and Ta. Chen et al. [43] thought that cassiterite of hydrothermal origin was generally poor in Nb and Ta, especially cassiterite in quartz veins, and (Nb, Ta)<sub>2</sub>O<sub>5</sub> was generally less than 1%. Nb<sup>5+</sup> and Ta<sup>5+</sup> have similar ionic charge and ionic radius, and  $ZrO_2$ ,  $HfO_2$ , and  $SnO_2$  have the same structure, so the contents of Nb, Ta, Zr, and Hf and the ratio of Nb/Ta and Zr/Hf have a clear indication for the genesis of cassiterite, and Nb-Ta and Zr-Hf in cassiterite show obvious positive correlation characteristics (Figure 9a,b). The mass fraction of Zr and Hf in cassiterite of high-temperature hydrothermal origin is high. The (Fe + Mn)/(Nb + Ta)indices of cassiterite in the Shuangjianzishan deposit are all less than 2, indicating that it has the characteristics of cassiterite in hydrothermal deposits [44]. The Nb/Ta ratio of cassiterite in the Shuangjianzishan deposit ranges from 9.17 to 201.66, with an average value of 81.51, suggesting that it is related to magmatic hydrothermal solution (Nb/Ta ratio > 1), suggesting that ore-forming materials may mainly come from magma. There is a positive correlation between Sc-V and Co-Ni (Figure 9d,f), indicating the existence of isomorphic substitution reactions between Sc-V, Co-Ni, and Sn.

# 7.3. Genesis of Cu-Sn Mineralization

A cassiterite–chalcopyrite–quartz–arsenopyrite high-temperature mineral assemblage appears in the deep ore of the Shuangjianzishan mining area, which contradicts the previous understanding that the Shuangjianzishan deposit only has a medium–low-temperature mineralization stage [9]. Previous studies have shown that magmatic cassiterite is rich in Nb and Ta, but relatively poor in Fe and Mn, while hydrothermal cassiterite is the opposite [44]. In this study, cassiterite is richer in Fe and Mn, but relatively poor in Nb and Ta, indicating that it was formed in a relatively high-temperature hydrothermal environment, and tin mineralization belongs to the cassiterite–sulfide type. Most tin mineralization in the world is considered related to hydrothermal processes related to highly differentiated and relatively reduced granite bodies [45,46]. Cassiterite related to granite is rich in Nb and Ta, and the

Nb + Ta content is generally higher than 1%, while cassiterite related to sedimentary or metamorphic hydrothermal solution has a low content of high-field elements [44]. The cassiterite in the Shuangjianzishan deposit in this study has a low content of high-fieldstrength elements (Nb is  $1.02 \times 10^{-6}$ , Ta is  $0.02 \times 10^{-6}$ ). It is rich in Fe (7405.76  $\times 10^{-6}$ ) and W (1193.93  $\times$  10<sup>-6</sup>), which is different from typical magmatic hydrothermal deposits and SEDEX/VHMS-type deposits. This shows that the enrichment degree of W, Nb, Ta, Zr, Hf, and other elements in cassiterite is not only related to the source, but also influenced by many factors such as temperature, pH, pressure, and oxygen fugacity, and the source cannot be simply judged by the content of trace elements [32]. Chen [47] thinks that the Co/Ni ratio of chalcopyrite in Cu-Ni sulfide deposits is less than 1, while the Co/Ni ratio of chalcopyrite in porphyry, skarn, and epithermal deposits in hydrothermal deposits is more than 1. Because chalcopyrite contains Ni-rich micro-inclusion minerals in this test, the Ni content is not representative, but according to the data of trace elements of chalcopyrite in the Shuangjianzishan deposit [37], it conforms to the characteristics of chalcopyrite in hydrothermal deposits. The enrichment of high-temperature elements such as Sn, Se, and W in cassiterite and chalcopyrite indicates that the Shuangjianzishan deposit has a hightemperature metallogenic stage of Sn-Cu, which is not a simple medium-low-temperature magmatic hydrothermal deposit.

#### 7.4. Discussion of the Relationship between Tin and Silver Mineralization

Sn is typically a high-temperature element, and a high-temperature environment is more conducive to the migration and enrichment of Sn. A large amount of early tin mineralization was found in the Shuangjianzishan deposit. From the mineralogical characteristics, chalcopyrite and sphalerite grew around the early cassiterite (Figure 4), or early tin-bearing mineral inclusions were found in sphalerite and chalcopyrite. Chalcopyrite and cassiterite coexisted with gangue minerals such as quartz (Figure 3f), and were later metasomatized by galena and sphalerite, indicating that chalcopyrite and cassiterite were formed earlier than sphalerite and galena. From the geochemistry of mineral trace elements, cassiterite is rich in high-temperature elements such as W and In, while the contents of Cu, Pb, Zn, and Ag are all low, indicating that its formation temperature is high, but it is not rich in concentrated low-temperature ore-forming elements. Chalcopyrite is rich in high-temperature elements such as Sn and Se, suggesting that early ore-forming fluids may be rich in Sn, and copper-tin mineralization is closely related. Therefore, according to the observed macroscopic and microscopic characteristics, it is concluded that the metallogenic sequence of the Shuangjianzishan deposit is  $Sn \rightarrow Cu \rightarrow Pb$ -Zn-Ag. Wei [48] speculated that the ore-forming age of cassiterite is about 129 Ma, which is basically consistent with the isochron age of sphalerite of  $133 \pm 4$  Ma [6]. From the perspective of ore-forming age, it is considered that there may be a certain relationship between Cu-Sn mineralization and Pb-Zn-Ag mineralization, but the source of ore-forming materials, evolution of ore-forming fluids, and spatial zonation of high-temperature Sn mineralization and medium-low-temperature Cu-Pb-Zn-Ag mineralization are still unclear. Therefore, it is uncertain whether the tin polymetallic mineralization and silver-lead-zinc mineralization in the Shuangjianzishan deposit are similar to the same metallogenic systems as those in the Weilasituo deposit [49] or the spatial superposition of multi-center mineralization like the Dajing deposit [50,51].

## 8. Conclusions

- 1. Chalcopyrite is rich in medium–high-temperature elements such as Sn, In, and Se, but poor in low-temperature elements such as Ga and Sb, which indicates that chalcopyrite has a high formation temperature, and the early ore-forming fluid is rich in Sn, while Pb, Bi, Ni, and other elements mostly exist in chalcopyrite as inclusions.
- 2. Cassiterite is rich in Fe, W, and In but poor in U and Sb, indicating that cassiterite was formed in a medium–high-temperature oxidation environment, and the early ore-forming fluid was rich in W. Because there are wolframite inclusions in cassiterite, and the W content changes greatly, it is considered that the cassiterite in the

Shuangjianzishan deposit mainly has the element replacement mechanism of  $Fe^{3+} + OH^- \leftrightarrow Sn^{4+} + O^{2-}$ , followed by  $W^{6+} + Fe^{2+} \leftrightarrow 2Sn^{4+}$ .

- 3. Cassiterite is rich in Fe and Mn, but relatively poor in Nb and Ta, indicating that it was formed in a relatively high-temperature hydrothermal environment, and tin mineralization belongs to the cassiterite–sulfide type.
- The metallogenic sequence of the Shuangjianzishan deposit is Sn→Cu→Pb-Zn-Ag, and the copper–tin mineralization is closely related.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app14093822/s1, Table S1: The laser ablation ICP-MS spot analyses of chalcopyrite from the Shuangjianzishan deposit (ppm), Table S2: The laser ablation ICP-MS spot analyses of cassiterite from the Shuangjianzishan deposit (ppm).

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