

## Research Article

# Compositions of Cu-(Fe)-Sulfides in the 109 Reduced Granite-Related Cu Deposit, Xinjiang, Northwest China: Implications to the Characteristics of Ore-Forming Fluids

Rui Liu <sup>1,2,3</sup>, Genwen Chen <sup>2</sup>, and Jianxing Yang<sup>2</sup>

<sup>1</sup>Guangdong Provincial Key Lab of Geodynamics and Geohazards, School of Earth Sciences and Engineering, Sun Yat-sen University, Guangzhou 510275, China

<sup>2</sup>CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>3</sup>Southern Laboratory of Ocean Science and Engineering (Guangdong Zhuhai), Zhuhai 519000, China

Correspondence should be addressed to Genwen Chen; [chengw@gig.ac.cn](mailto:chengw@gig.ac.cn)

Received 11 September 2019; Revised 20 November 2019; Accepted 25 January 2020; Published 11 February 2020

Academic Editor: Ling-Li Zhou

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In general, porphyry Cu deposit is related to the highly oxidized ore-forming system. However, there are many porphyry Cu deposits that are related to the reduced ore-forming system, and the ore-forming characteristics of reduced porphyry Cu deposit are unclear. Cu-(Fe)-sulfides are the main Cu-hosting minerals in porphyry Cu deposits and are also economically important, and the composition of Cu-(Fe)-sulfides has closely relationship with ore-forming characteristics. In this study, concentration data obtained via laser ablation inductively coupled plasma mass spectrometry are reported for chalcopyrite, bornite, and chalcocite from the 109 porphyry Cu deposit formed in a reduced granite-related mineralization system in western Tianshan, Xinjiang, northwest China. The results show that the chalcopyrite hosts several trace elements including Zn, Ge, Se, In, and Sn; the bornite hosts Mo, Ag, Zn, Se, and Bi; and the chalcocite hosts Mo, Ag, Zn, Sn, Se, and Bi. The smooth time-resolved depths profiles and limited variations of trace element concentrations in these sulfides suggest that their presence is isomorphic. The microstructures of the chalcopyrite and bornite were observed by high-resolution transmission electron microscopy. Their lattices are neatly arranged, also indicating that the trace elements exist mainly as isomorphisms in the chalcopyrite and bornite. Ge, Sn, and In are hosted in the chalcopyrite but absent in bornite and chalcocite, indicating that chalcopyrite has a high potential for hosting these elements. Ge and Sn are preferentially hosted in the chalcopyrite, possibly due to relatively high temperatures and low oxygen fugacity during its formation. Indium is preferentially hosted in the chalcopyrite, possibly due to the In<sup>2+</sup> substitution for Fe<sup>2+</sup> controlled by Goldschmidt's rules, which state that substitution occurs between a substituent and host owing to similarities in their radii and charges. However, the concentration of Ag is low in chalcopyrite but significantly high in bornite and chalcocite, indicating that this element is preferentially hosted in the latter two minerals. The abundance of Ag, a low-temperature element, in Cu-(Fe)-sulfides may largely be dependent on temperature. The Au content is below the minimum level of detection in all sulfides, which is obviously different from the classic porphyry copper deposits. In addition, the concentrations of Zn, Ge, As, Sb, and Te in the chalcopyrite and those of Zn, Se, As, Sb, and Bi in the bornite from the 109 porphyry Cu deposit show obvious differences from those of classic porphyry Cu deposits. Therefore, some elements in Cu-(Fe)-sulfides can be used as indicators of ore-forming oxygen fugacity. Bornite and chalcocite are generally enriched in Ag, indicating that the mining of porphyry Cu deposits may be concerned with the precious metal Ag in bornite and chalcocite. In addition, chalcopyrite may host sufficient Se and Zn, and bornite and chalcocite could host sufficient Se, Zn, and Bi, suggesting that sulfides may be hosts for deleterious elements.

## 1. Introduction

Porphyry Cu deposits, which are currently the world's largest sources of copper, host Cu-(Fe)-sulfides as major Cu carriers. For classic porphyry Cu deposits, which are spatially and genetically related to highly oxidized, magnetite-series I-type granitoids [1–4], sulfur is present mainly as  $S^{6+}$  owing to high oxygen fugacity, and sulfide is formed through the reduction of sulfate. However, for reduced porphyry Cu deposits that are related to reduced granitoids [5–7], sulfur is present mainly as  $S^{2-}$  owing to low oxygen fugacity, and sulfide is formed by  $S^{2-}$  in direct combination with metals such as Cu, Fe, Mo, Pb, and Zn, among others. Therefore, the formation mechanism of sulfide in a reduced porphyry Cu deposit is different from that in a classic porphyry Cu deposit.

In addition, an understanding of sulfide mineral chemistry has both processing and exploration implications for this type of deposit because knowledge of the minor and trace elements carried by host sulfide is essential for evaluating the distribution and partitioning of potential economically valuable components such as Au, Ag, and In between coexisting minerals. In addition, such information can be used to optimize processing and thus to ensure improved recovery of economical by-products such as Ag in sulfides that are commonly extracted during copper smelting and refining [8]. The minor and trace element concentrations in sulfides and their distribution also have potential as vectors to assist in mine-scale exploration. Therefore, understanding how hypogene processes affect Cu-(Fe)-sulfides and influence their surface properties also has implications for mineral processing and environmental geochemistry [9, 10]. Elements such as As, Sb, Hg, Bi, and Se may become enriched in copper concentrates during ore processing; if present at sufficiently high concentrations, this can result in substantial financial penalties and environment risks [11].

Research on Cu-(Fe)-sulfides in classic porphyry Cu deposits is focused mainly on chalcopyrite and bornite. Chalcopyrite is generally the main host of many elements owing to its greater abundance in classic porphyry Cu deposits [12], and bornite is generally a poor host for trace elements except Au [12]. Many factors can affect the distribution of trace elements in Cu-(Fe)-sulfides, including physicochemical parameters of the mineralizing fluids, trace element partitioning between coexisting minerals, incorporation in the crystal lattice versus mineral inclusions, and the paragenesis of Cu-(Fe)-sulfides [13–15]. Therefore, comparison of the distribution of trace elements may reveal factors that control the trace element distribution in different Cu-(Fe)-sulfides, particularly for reduced porphyry Cu deposit. Previous studies have indicated that the Cu-(Fe)-sulfides in reduced porphyry Cu deposits, which include chalcopyrite, bornite, and chalcocite, are similar to those in classic porphyry Cu deposits [5, 16–19]. However, owing to the limited number of the reduced porphyry Cu deposits, fewer studies have been conducted on sulfides in this type of deposit.

Considering these factors, we used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to

report the concentration ranges of trace elements typically present at concentrations < 1 wt% in Cu-(Fe)-sulfides from the 109 porphyry Cu deposit. In addition, high-resolution transmission electron microscopy (HRTEM) was used to show the microstructure of chalcopyrite and bornite. The datasets reveal that Cu-(Fe)-sulfides are important trace element carriers in the reduced porphyry Cu deposit and mainly exist in the form of isomorphs. Our data carry implications for both ore genesis and beneficiation of Cu-(Fe)-sulfides in a reduced porphyry Cu deposit.

## 2. Geological Setting and Deposit Background

The Awulale metallogenic belt is a part of western Tianshan, which is situated in the southwestern part of the Central Asian Orogenic Belt (Figure 1(a)). The stratigraphy of the western Awulale metallogenic belt comprises late Carboniferous to Permian sequences and is composed of sedimentary–volcanic rocks including limestone, basalt, andesite, and rhyolite. The eastern part of the Awulale metallogenic belt consists of late Carboniferous sequences that are dominantly composed of volcanic rocks including basalt and rhyolite. Intermediate to felsic intrusions are widely distributed in this belt (Figure 1(b)). The structures are widely developed in this area, including folds, faults, and domes. Numerous Fe-Cu (Au) polymetallic deposits have been recently reported in the Awulale area, which formed an Awulale Fe-Cu metallogenic belt [20]. The western Awulale metallogenic belt is characterized by volcanic–subvolcanic hydrothermal Cu deposits such as Nulasai and Kezikezang and reduced porphyry Cu deposits such as Yinulasai, Qiongbulake, Qunjisayi, Qunji, 109, and Heishantou [18, 19, 21–23].

The 109 porphyry Cu deposit, which has an indicated resource of 0.7–0.8 million tons averaging 0.8% Cu, is located at the middle of the western Awulale metallogenic belt (Figure 1(b)). Three Cu orebodies have currently been found in this deposit (Figure 2), two of which exist as outcrops, and third is underground. These Cu orebodies are plate-like, lenticular, or irregular and vary from 100 to 500 m in length and between 20 and 50 m in thickness. The granitic pluton that hosts this deposit intruded early Permian bimodal volcanic rocks of the Wualng Formation, which is composed of continental intermediate-basic and felsic volcanic rocks. The petrography of the granitic pluton is albite porphyry [18, 19], which contains abundant albite of magmatic origin occurring either as crystals in the groundmass or as erosion products of late-stage minerals or the matrix (Figure 3). The studied deposits contain zones affected mainly potassic alteration with weak phyllic and propylitic zones, sometimes exhibiting brownish-red coloration. The potassic zones comprise the inner and deeper parts of the intrusion. The mineral assemblage is dominated by potassic feldspar and quartz and includes carbonates [19]. Veinlets filled with quartz±alkaline feldspar±sulfides are widespread. Phyllic and propylitic alterations are commonly developed in the outer parts of the intrusion surrounding the mineralized potassic zone and contain chlorite-epidote-carbonate assemblages.

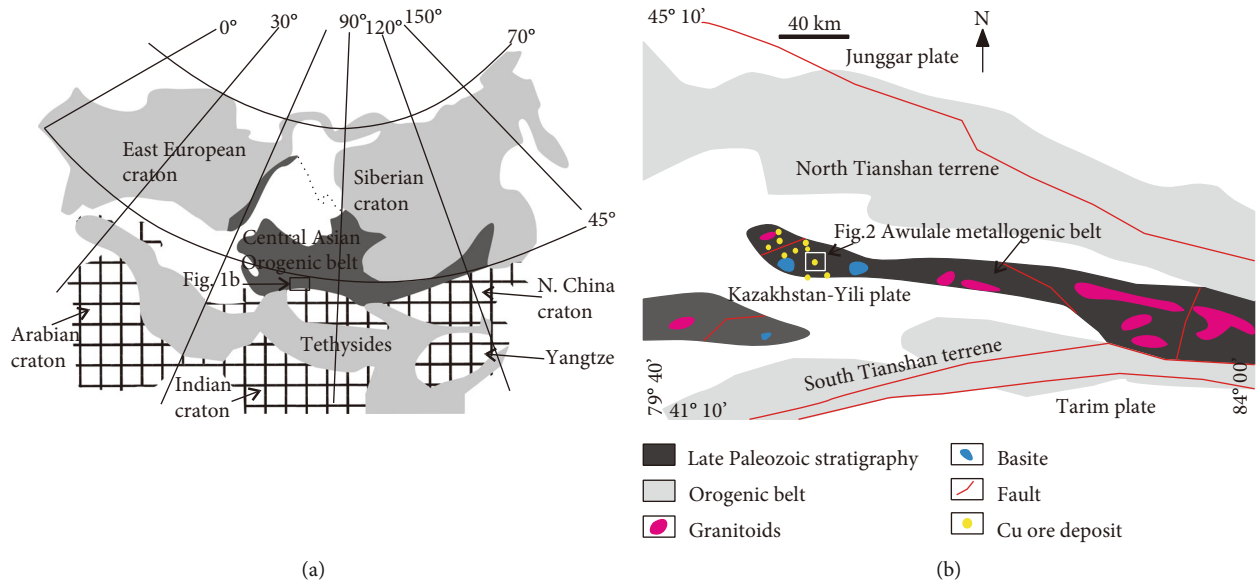


FIGURE 1: (a) Sketch map of the CAOB. (b) Sketch map of western Tianshan (modified from Zhang et al. [24]).

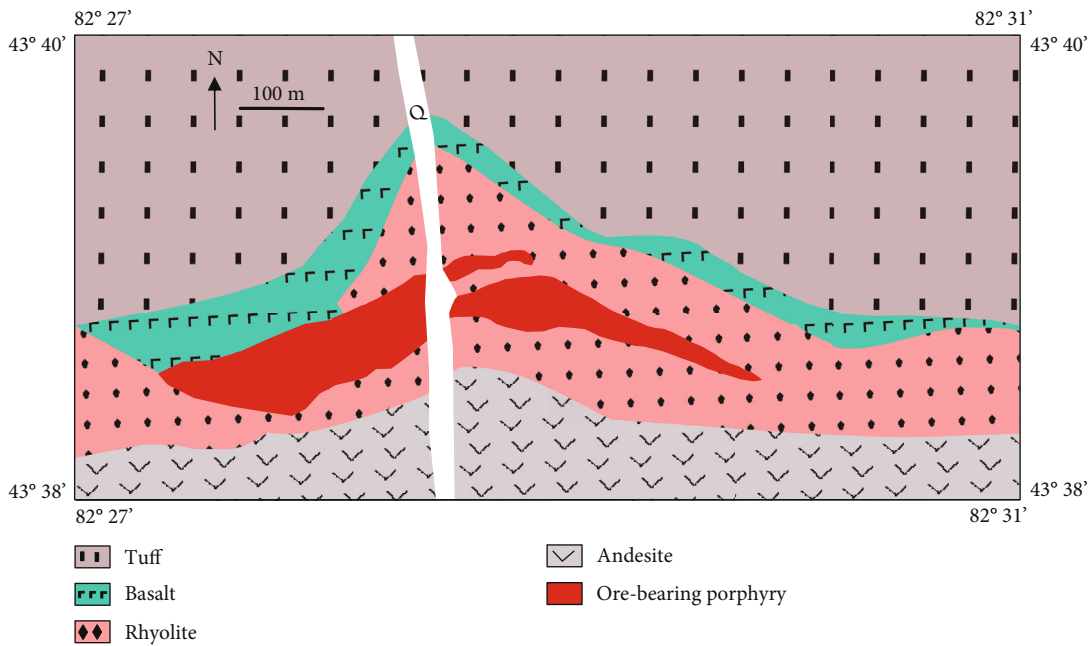


FIGURE 2: Sketch map of the 109 porphyry Cu deposit (modified from Zhao et al. [25]).

### 3. Samples and Analytical Methods

The copper mineralization extends vertically for at least 100 m. The mineralization is broadly coincident with a potassic alteration zone and consists of chalcopyrite-bornite-chalcocite either finely disseminated or forming stockwork veinlets (Figure 4). The source of metals for the 109 porphyry deposits is magmatic, as indicated by the S isotopic signature of the mineralization [19]. The stable O and H isotopic data of this deposit also indicate a predominantly magmatic source for metals and hydrothermal fluids (our unpublished

data). The available fluid inclusion data for this deposit indicate that the temperature of mineralization was 190-300°C [26]. The ore minerals in the 109 porphyry Cu deposit are composed of Cu-(Fe)-sulfides, including chalcopyrite, bornite, and chalcocite (Figure 5). The Cu-(Fe)-sulfides typically show metasomatic and exsolution textures, which indicate the following paragenesis: chalcopyrite → bornite → chalcocite [19].

Crystallographic, trace element, mineral assemblage, and textural observations and measurements have been used to understand the origins of chalcopyrite, bornite, and

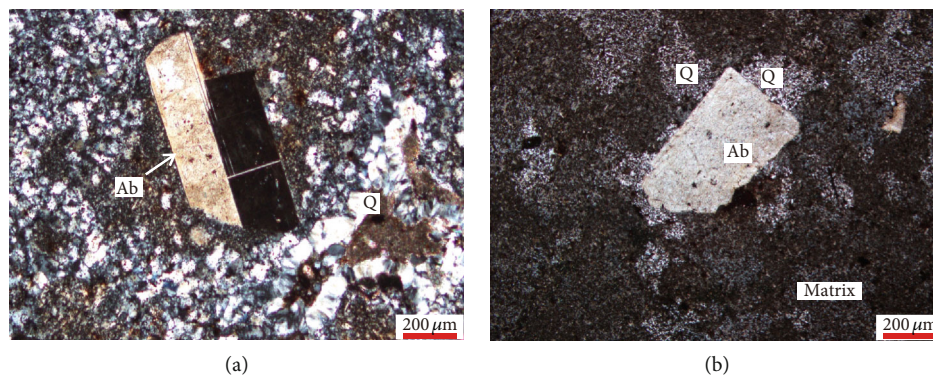


FIGURE 3: Microphotographs of albite porphyry from 109, showing albite occurrences as (a) a crystal in the groundmass and (b) as an erosion product of late-stage minerals or the matrix. Ab: albite; Q: quartz.

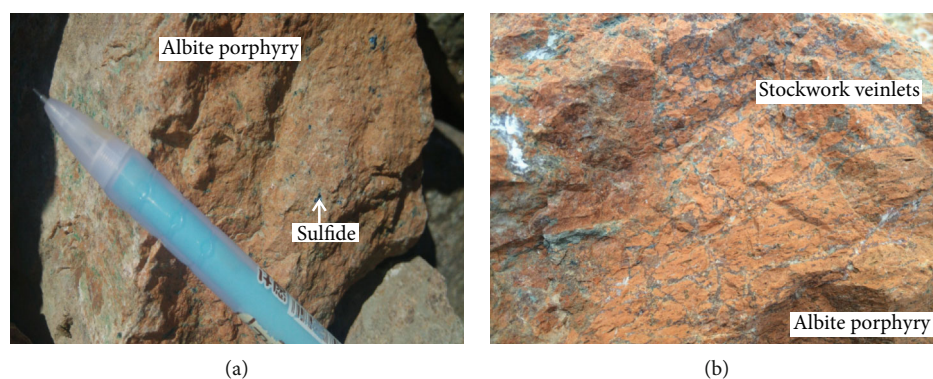


FIGURE 4: Structure of ore in porphyry deposit 109: (a) disseminated ore and (b) stockwork veinlet ore.

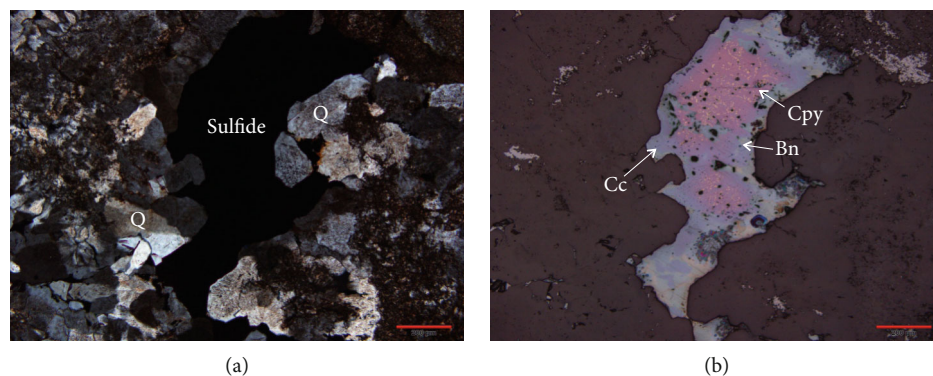


FIGURE 5: Microphotographs of ore minerals including chalcopyrite, bornite, and chalcocite under (a) transmitted light and (b) reflected polarized light. The scale bar is 200  $\mu\text{m}$ . Cpy: chalcopyrite; Bn: bornite; Cc: chalcocite; Q: quartz.

chalcocite [27–30]. As research objects for this study, we selected Cu-(Fe)-sulfides that present metasomatic textures (Figure S1). The concentrations and microstructures of these Cu-(Fe)-sulfides have been analyzed. Five chalcopyrite samples, five bornite samples, and five chalcocite samples were selected for compositional analysis, and two chalcopyrite samples and two bornite samples were selected for crystal structure analysis.

### 3.1. Electron Microprobe Analyzer and Laser Ablation Inductively Coupled Plasma Mass Spectrometry Analysis.

The ore samples were studied under a reflected light microscope, and the paragenesis of the ore minerals was determined on the basis of their textural relationship. Preliminary analysis was conducted using an electron microprobe analyzer (EMPA; JEOL JXA-8230) at the Key Laboratory of Mineralogy and Metallogeny, Chinese Academy of Sciences, to study the major and minor element distribution within the Cu-(Fe)-sulfides, including chalcopyrite, bornite, and chalcocite. Peak calibration on each element was conducted using reference materials. The beam current was 20 nA, the accelerating voltage was 20 kV, and the spot size was 1  $\mu\text{m}$ .

The standards used for measurements included Fe ( $\text{FeS}_2$ ), Cu (Cu), and S ( $\text{FeS}_2$ ). The peak counting times were scaled from 10 s to 60 s and were reduced by half for background counting, depending on the element.

Trace element analysis of the Cu-(Fe)-sulfides was conducted using the LA-ICP-MS, with a 193 nm MicroLas Pro ArF Excimer coupled with an Agilent 4500 quadrupole ICP-MS, at the Nanjing FocuMS Technology Co., Ltd. following the procedure of Gao et al. [31]. The photomicrographs of Cu-(Fe)-sulfides analyzed by LA-ICP-MS are presented in Figure S1. The analytical settings for LA are detailed in Large et al. [32]. LA was performed with a constant 5 Hz pulse rate at 90 mJ laser energy. The ablated material was transported using a constant He flow mixed with Ar in a cyclone coaxial mixer prior to entering the ICP torch and being ionized. The ions were then subjected to sampling, acceleration, and focusing before separation and analysis in the quadrupole mass spectrometer. The data were collected during a 30 ms dwell time per channel to enhance the number of counts for trace elements. Specific areas of the sample plates were ablated with 35–50  $\mu\text{m}$  spot diameters. The total acquisition time was limited to 90 s. To enable quantification of multiphase mineral assemblages, standardization was achieved via external calibration against United States Geological Survey GSE-1G synthetic basaltic glass coupled with ablation yield correction via normalization to 100% total element abundance [33]. To extend the calibration to S, which is not present in GSE-1G, surrogate calibration was applied using S/Fe sensitivity ratios determined by ablation of natural pyrite (NMC-12744). The analytical data were processed using the ICPMSDataCal 7.2 software. Si was used as the internal standard for external standard material. The double internal standard group method using Fe, Cu, and Zn as the blind internal standard elements was used for data processing. By using Si-Fe and Si-Zn or Si-Cu and Si-Zn as the internal standards, the precision of each analysis was better than 15% for most elements ( $>1$  ppm). The mean value and errors for each element in the two standards are listed in Table S1. The average detection limits for the elements analyzed are listed in Table S2.

**3.2. High-Resolution Transmission Electron Microscopy Analysis.** Cross-sectional imaging and transmission electron microscopy (TEM) of the chalcopyrite and bornite were prepared on a focused electron ion (FEI)-Helios NanoLab Dual Beam Focused Ion Beam/Scanning Electron Microscope (FIB-SEM). After milling the samples according to the Au ions, the TEM foils, which were attached to Cu grids via Pt welding, were extracted and thinned to 50–70 nm. Images were captured in the immersion mode to obtain the maximum resolution. TEM technology was complementarily used to obtain highly magnified images and the structural/chemical information of both the chalcopyrite and bornite. In situ determination of the morphology and crystal structure was conducted by selecting the area electron diffraction (SAED) of high-resolution images, and the major elemental distribution was qualitatively determined by energy-dispersive spectroscopy (EDS). The selected samples

were observed using an FEI Tecnai G2F20 TEM operated at 200 kV and equipped with an EDS detector with a  $\sim 0.5$ –1 wt% detection limit. All analyses were conducted at Sinoma Test (Guangzhou) Co., Ltd.

## 4. Results

**4.1. Composition of Cu-(Fe)-Sulfides in the 109 Porphyry Cu Deposit.** The average values of the analytical results of EMPA and LA-ICP-MS for the different Cu-(Fe)-sulfides are presented in Table S3. The time-resolved depth profiles are relatively smooth (Figure S2), indicating almost no interference of mineral inclusions.

The chalcopyrite in the 109 porphyry Cu deposit contains S at 31.5–34.7 wt%, Fe at 24.6–28.3 wt%, and Cu at 37.3–43.4 wt%. This chalcopyrite also has trace amounts of Zn, at 1.42–5.79 ppm; Ge, at 0.47–2.05 ppm; Se, at 3.57–15.4 ppm; In, at 3.95–4.47 ppm; and Sn, at 0.58–1.59 ppm. Other trace elements such as Co, Ni, Ga, As, Mo, Ag, Sb, Te, Au, and Bi are present in relatively low concentrations.

The bornite in the 109 porphyry Cu deposit contains S at 25.0–26.8 wt%, Fe at 10.8–11.5 wt%, and Cu at 61.0–63.8 wt%. Zn, Se, Mo, Ag, and Bi show measured values up to 10.8 ppm, 9.69 ppm, 227 ppm, 499 ppm, and 66.2 ppm, respectively. The contents of Co, Ni, Ga, Ge, As, In, Sn, Sb, Te, and Bi are only slightly above the minimum level of detection (MLD).

The chalcocite in the 109 porphyry Cu deposit contains mostly S at 19.9–24.1 wt% and Cu at 69.6–78.3 wt% with minor Fe at 0.03–4.91 wt%. In addition, this chalcocite yielded measured values of up to 12.3 ppm Zn, 13.8 ppm Se, 58.5 ppm Mo, 1133 ppm Ag, and 25.3 ppm Bi. The contents of Co, Ni, Ga, Ge, As, In, Sn, Sb, Te, and Au are slightly above or below the MLD.

**4.2. Microstructures of Chalcopyrite and Bornite in the 109 Porphyry Cu Deposit.** In this study, we used TEM to analyze the microstructural characteristics of the chalcopyrite and bornite to verify whether inclusions are present in the Cu-(Fe)-sulfides. The results show metasomatic texture in both minerals. The chalcopyrite has a high Se content of 15.4 ppm, and the bornite has a high Ag content of 499 ppm. Therefore, these samples are favorable for verifying the forms of Se and Ag occurring in the chalcopyrite and bornite, respectively. The HRTEM and SAED patterns (Figure 6) show that the lattices of chalcopyrite and bornite are regularly arranged, which indicates that no inclusions are present in these Cu-(Fe)-sulfides.

## 5. Discussion

**5.1. The Distribution of Trace Elements in Cu-(Fe)-Sulfides.** The smooth time-resolved depth profiles, the limited variations in the trace element concentrations, and the microstructures all indicate that trace elements may exist mainly in the form of isomorphism in these Cu-(Fe)-sulfides. Chalcopyrite and bornite widely occur in both classical porphyry Cu deposits and reduced Cu deposits [12, 13, 17, 19]; therefore, studies on the distribution of trace elements in these

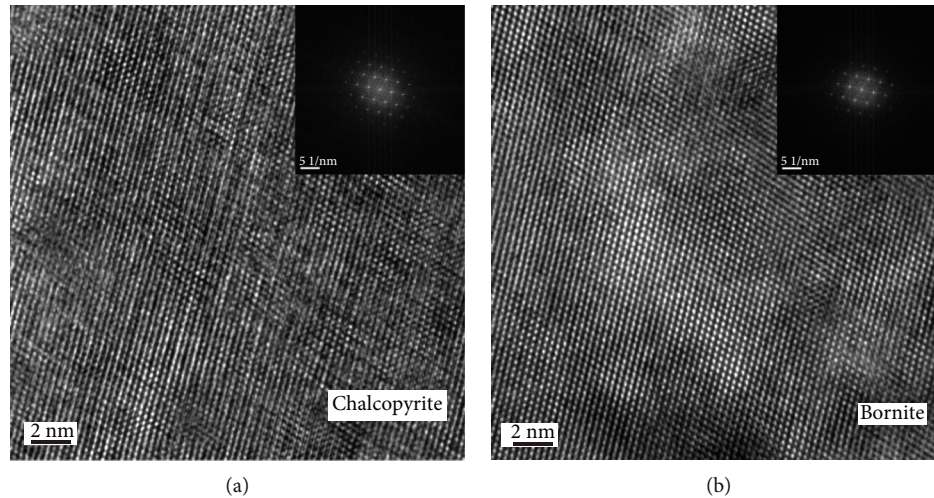


FIGURE 6: Microstructures of (a) chalcopyrite and (b) bornite in the 109 porphyry Cu deposit, showing that the lattices of these Fe-(Cu)-sulfides are regularly arranged. The insets show the corresponding SAED patterns.

Cu-(Fe)-sulfides could reveal the differences in ore-forming materials between classical porphyry and reduced Cu deposits. In addition, primary chalcocite is rare in classical porphyry Cu deposits, but it is an important Cu carrier in the 109 reduced porphyry Cu [19]. Our study also revealed the distribution of trace elements in the chalcocite from the reduced porphyry Cu deposit.

**5.1.1. Chalcopyrite.** Chalcopyrite is generally considered to be a relatively poor host for trace elements compared with other common sulfides such as bornite, chalcocite [12], sphalerite [34], and galena [35]. Indeed, the LA-ICP-MS element maps presented by George et al. [36] demonstrate that chalcopyrite is generally the least preferred host for a range of trace elements when chalcopyrite, sphalerite, and galena cocrystallize. A summary of relevant literature revealed that only Ag, Zn, As, Se, Co, and Pb are usually reported as trace components in solid solutions within chalcopyrite, whereas Mn, In, Tl, Ga, and Hg are seldom referred to, if at all. In addition, empirical concentration data for natural chalcopyrite is scarce compared that for other sulfides, and in cases in which data are reported, the full range of elements is often not checked, or the MLD for many trace elements are too high to identify accurate concentration ranges [28, 37–50]. For the dataset presented in this study, generally lower MLD were analyzed by LA-ICP-MS, thus enabling new evaluation of chalcopyrite in reduced porphyry Cu deposits as a trace element carrier.

The only trace elements commonly present in excess of the MLD in the chalcopyrite from the 109 porphyry Cu deposit are Zn, Ge, Se, In, and Sn. However, despite the low overall concentrations, when chalcopyrite coexists with other sulfides, it is apparent that the chalcopyrite can contain a wide range of trace elements such as Ge, Se, In, and Sn. Significantly, Ge and In are both commonly present at measurable concentrations in chalcopyrite despite rarely being reported in most previous studies. Thus, considering the greater abundance of chalcopyrite relative to other sulfides in many Cu ores, chalcopyrite could be the main sulfide host for many of the aforementioned elements in a given deposit.

**5.1.2. Bornite.** After chalcopyrite, bornite is one of the most commonly occurring Cu-(Fe)-sulfides. Bornite is a major Cu carrier in porphyry Cu deposits such as that in Ertsberg District, Indonesia [51]. Simon et al. [52] and Kesler et al. [53] indicated that high-temperature bornite might at least initially host a significant amount of the total gold budget in some porphyry deposits. Cook et al. [12] studied the minor and trace elements in hypogene bornite from 12 deposits and proposed that bornite could contain significant concentrations of both Ag and Bi. Bornite is a relatively poorer host for Au than other sulfides such as pyrrhotite, pyrite, and chalcopyrite, and most anomalous Au concentrations in bornite can readily be tracked to micron- and submicron-scale inclusions [12]. The Se and Te concentrations in bornite may be as high as several thousand parts per million. In addition, bornite is a poor host for a range of other elements such as Co, Ni, Ga, and Ge, among others.

The bornite in our study is broadly enriched in Mo and Ag, and the Zn, Se, and Bi contents are higher than the MLD. Generally, the concentrations of Ag and Bi show little variation at the sample scale, indicating that bornite may be a major carrier of Ag and Bi. However, Zn, Mo, and Se show significant variation of several to hundreds of orders of magnitude across the sample suite. Zn and Mo have been rarely reported in bornite by Cook et al. [12]; however, that in the 109 porphyry Cu deposit contains up to 19.0 ppm Zn and 227 ppm Mo, indicating that this bornite could be a host of these two elements.

**5.1.3. Chalcocite.** Chalcocite is an economically important copper mineral. Models regarding the genesis of chalcocite vary substantially, with conditions ranging from the highest-temperature hydrothermal systems to ambient temperature weathering solutions; thus, no single model can be used to constrain the formation conditions of this mineral. Published quantitative data of chalcocite are scarce. Thus, the data for Au in chalcocite given by Kesler et al. [53] are significant, with maximum values of 4.24 ppm and 13.0 ppm reported for the chalcocite in the Batu Hijau and Skouries

porphyry deposits, respectively. Support has also been made for lower levels of Ag in the chalcocite of some specific deposits such as Bor in Serbia, for which Jankovic et al. [54] reported up to 123 ppm. Reich et al. [55] reported preliminary data from the Mantos Blancos deposit in northern Chile, which includes Ag maxima of 1057 ppm and 812 ppm in secondary chalcocite. In the same sample suite, the Au concentrations range from lower than the MLD, at 0.07 ppm, up to 6.00 ppm. The Se and Te concentrations are 2.00-96.0 ppm and 0.6-18.0 ppm, respectively. The Bi concentrations are insignificant, generally below the MLD, whereas the As and Sb are in many cases significantly higher, with maxima of 300 ppm and 60 ppm, respectively. In addition, Cook et al. [12] reported that chalcocite can contain Au, Ag, As, and Se and is particularly enriched in Bi. These elements are related to the inherent crystal chemistry differences between hypogene and supergene chalcocite.

The chalcocite from the 109 porphyry Cu deposit evaluated in the present study contains a high concentration of Ag, which indicates that it might be an important host for Ag in reduced porphyry Cu deposits. In addition, Bi and Se were detected in this chalcocite, and Zn, Sn, and Mo, which have not been reported in other deposits, are commonly present at measurable concentrations. However, the Au and As, which are enriched in the chalcocite from other deposits such as the Sveconorwegian Cu-Ag-Au deposit [56], the Baita Bihor Cu-Mo skarn deposit [57, 58], and the Tinnsig Cu-Ag deposit [59], are all lower than the MLD. Thus, chalcocite in the reduced porphyry Cu deposits might be a host for Ag, Bi, Zn, Se, Sn, and Mo.

**5.2. Distribution Feature of Trace Elements in Different Cu-(Fe)-Sulfides.** The S isotopic compositions of the chalcopyrite, bornite, and chalcocite in the 109 porphyry Cu deposit indicate that these Cu-(Fe)-sulfides had the same unique source and trace elements in the ore-forming fluids during their formation [19]. However, the trace element concentrations are different among the Cu-(Fe)-sulfide. The concentrations of Zn and Se in all Cu-(Fe)-sulfides show negligible variation (Figure 7), indicating that neither Zn nor Se is preferentially distributed into chalcopyrite, bornite, or chalcocite. However, other trace elements such as Ge, Mo, Ag, In, Sn, and Bi show significant changes in the Cu-(Fe)-sulfides.

The chalcopyrite contains the highest concentration of Ge, In, and Sn. However, these elements are present at less than 1 ppm in bornite and chalcocite, indicating that Ge, In, and Sn are preferentially distributed into chalcopyrite rather than bornite and chalcocite in the 109 porphyry Cu deposit. Huston et al. [60] inferred that Sn substitutes for Fe in sulfides and noted that the highest Sn concentrations occur in the more reduced and highly metamorphosed deposits. This inference reflects the tendency of Sn to be transported in significant quantities only at reduced high-temperature conditions [61]. According to the homogenization temperature of fluid inclusions in the 109 porphyry Cu deposit, the formation temperature of the chalcopyrite was higher than that of the bornite and chalcocite [26]. In addition, the formation oxygen fugacity of the chalcopyrite was lower than that of the bornite and chalcocite based on the S

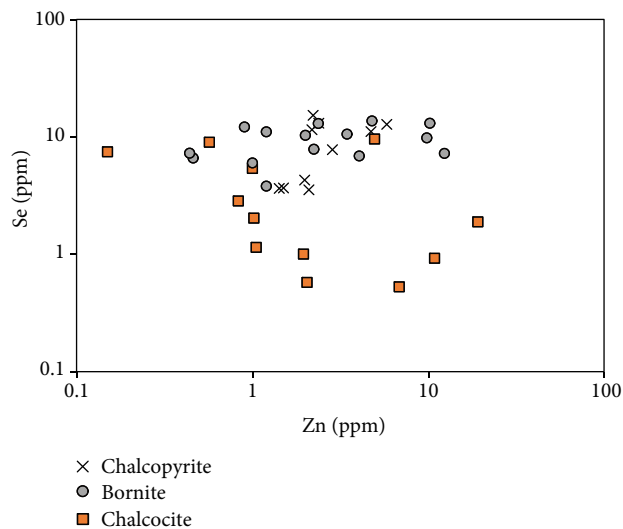


FIGURE 7: Plots showing Zn and Se variation in coexisting Cu-(Fe)-sulfides in the 109 porphyry Cu deposit.

isotopic compositions within these Cu-(Fe)-sulfides [19]. Therefore, our study confirms that Sn is transported in significant quantities at reduced high-temperature conditions. Because the geochemical behavior of Ge is similar to that of Sn [62], the concentration of Ge in chalcopyrite is higher than that in bornite and chalcocite, which also confirms that the quantity of Ge is affected by temperature and oxygen fugacity. Chalcopyrite is isostructural with roquesite ( $\text{CuInS}_2$ ); thus, chalcopyrite can contain significant concentrations of In most likely at the Fe site [63]. However, Fe is also present in bornite, and the concentration of In in this sulfide is low. This finding may indicate that In substitutes for  $\text{Fe}^{2+}$  and not  $\text{Fe}^{3+}$ , which follows Goldschmidt's rules, because the  $\text{In}^{3+}$  has an ionic radius similar to that of  $\text{Fe}^{2+}$ .

Mo and Ag are rare in chalcopyrite but are significantly high in bornite and chalcocite, which indicates that these elements are preferentially distributed into bornite and chalcocite. Mo is soluble under oxygenated conditions in the ore-forming fluid [27]. The trend of the Mo content in Cu-(Fe)-sulfides from the 109 porphyry Cu deposit also provides strong evidence for a relatively high Mo content in oxidized conditions. Ag is a low-temperature element and is preferentially distributed into chalcocite [12], which can explain the trend of the Ag content in the Cu-(Fe)-sulfides examined in the present study.

Overall, the distribution of trace elements is significantly different among Cu-(Fe)-sulfides. The paragenesis of Cu-(Fe)-sulfides is also different based on the texture; therefore, the distribution of trace elements could be controlled mainly by paragenesis. If so, however, chalcopyrite, which is the first Cu-(Fe)-sulfides generated, should contain much higher trace element contents than those in bornite and chalcocite because the Cu-(Fe)-sulfides in this study have same source. In fact, some trace elements, such as Mo and Ag, are higher in the bornite than they are in the chalcopyrite. Therefore, many other factors play contributing roles in the trace element distribution in Cu-(Fe)-sulfides. For example,

Ge, Sn, Mo, and Ag are affected by physical and chemical conditions such as temperature and oxygen fugacity, respectively. The distributed trends for In in Cu-(Fe)-sulfides are controlled by Goldschmidt's rules. In addition, the trace element content of Ag in bornite and chalcocite is also largely dependent on the presence or absence of other sulfides.

*5.3. Implications for Ore Genesis and Scientific Exploitation of Cu-(Fe)-Sulfides.* In porphyry ore deposits, the concentration of trace elements in sulfides is closely related to the concentrations in the ore-forming fluids [64]. Changes in the physicochemical conditions or ore-forming fluid source will result in variation in the trace element signatures of sulfide minerals. Investigation of the trace element signatures of sulfides can thus help to interpret the ore-forming processes. In samples with available trace element data for coexisting chalcopyrite, bornite, and chalcocite, these minerals contain many of the same trace elements such as Zn and Se. In particular, the coexisting bornite and chalcocite contain almost the same trace elements. These findings may indicate that some trace elements in Cu-(Fe)-sulfides can be used to indicate the different source for these minerals.

In addition, the distributions of some trace elements may be regarded as typomorphic characteristics for Cu-(Fe)-sulfides, such as Zn, Se, In, and Sn in chalcopyrite. Furthermore, the Au content in Cu-(Fe)-sulfides from the 109 porphyry deposit is obviously less than that in classic porphyry deposits. The incorporation of Au into sulfide is in the form of Au<sup>+</sup> [65, 66], which might be less in reduced mineralization systems owing to its low oxygen fugacity. In addition, the concentrations of Zn and Ge in the chalcopyrite and that of Zn in the bornite from the 109 porphyry Cu deposit are significantly higher than those in classic porphyry Cu deposits. However, the concentrations of As, Sb, and Te in the chalcopyrite and Se, As, Sb, and Bi in the bornite from the 109 porphyry Cu deposit are obviously lower than those in classic porphyry Cu deposits such as the Elatsite Els porphyry Cu deposit [12]; the Roşia Poieni, Bucium-Târniţa, Colnic, Rovina, Valea Morii, and Bolcana porphyry Cu deposits [47]; and the Assarel and Bor porphyry Cu deposits [67]. Therefore, these elements might be used as indicators of ore-forming oxygen fugacity.

Cu-(Fe)-sulfides are widespread in both hypogene and supergene Cu deposits worldwide and are considered to be profitable Cu ores because of their high Cu content at 67-80 wt% [68]. The presence of precious metal in Cu-(Fe)-sulfides is a significant concern for many mining operations, which can increase the economic value of the Cu deposit. Silver is one such element and is commonly extracted as an economical by-product during copper smelting and refining [8]. For example, the high-grade, low-tonnage "Manto-type" Cu deposits of northern Chile host 8-25 g of Ag per ton [69], and more than 31.3 tons of Ag have been produced as a by-product of the main Cu-(Fe)-sulfide mineralization in the Mantos Blancos deposit [70]. In porphyry environments, an abundance of bornite is commonly associated with elevated Au and Ag grades [12]. In the present study, the bornite and chalcocite contain relatively high Ag grades. Despite their simple compositions, these Cu-(Fe)-sulfides

are structurally complex and commonly consist of Ag in the form of solid solution [12] or at micro- and nanoscales [55]. In this study, we observed high Ag contents in these Cu-(Fe)-sulfides, and we confirmed that its form in the bornite is isomorphic, which provides an example of Cu-(Fe)-sulfides with high Ag content in reduced porphyry environments. This finding suggests that mining operations of porphyry Cu deposits should be concerned with the precious metal content in bornite and chalcocite.

In addition, Cu-(Fe)-sulfide can also contain many deleterious elements such as Co, Zn, As, Se, Cd, Sb, Hg, Pb, and Bi, which are included in copper concentrates after froth flotation [71]. Such elements reduce the overall grade of the copper concentrate and may require further, often costly, treatment to remove them from the final copper products [67]. Smelters thus impose financial penalties regarding concentrates that contain deleterious elements at greater than tolerated levels. Many mining operations therefore work hard to separate deleterious elements from their final saleable concentrates or to blend ores from different sources. In addition, the concentration of deleterious elements in a concentrate generated from Cu-(Fe)-sulfides is directly related to the concentration of deleterious elements within the Cu-(Fe)-sulfides. Therefore, an understanding of the mineralogical hosts for each element in the primary ore is important for reducing the penalties associated with particular concentrations of deleterious elements in the concentrate. According to the data presented in this study, chalcopyrite, bornite, and chalcocite could host sufficient amounts of Se and Zn to be considered as hosts, which indicates that concentrates produced from the 109 reduced porphyry Cu deposit should be examined to detect deleterious elements contained within them.

## 6. Conclusions

Based on LA-ICP-MS and TEM analysis of Cu-(Fe)-sulfides from the 109 reduced porphyry Cu deposit, western Tianshan, northwest China, the main conclusions are summarized in the following points:

- (1) The chalcopyrite hosts Zn, Ge, Se, In, and Sn; the bornite hosts Mo, Ag, Zn, Se, and Bi; and the chalcocite hosts Mo, Ag, Zn, Sn, Se, and Bi. Compared with those in classic porphyry copper deposits, the Cu-(Fe)-sulfides in reduced porphyry Cu deposits are poor hosts for Au
- (2) Trace elements can exist mainly in isomorphic forms in Cu-(Fe)-sulfides. Other main factors controlling the trace element distribution in Cu-(Fe)-sulfides include physical and chemical conditions, Goldschmidt's rules, and presence or absence of other sulfides
- (3) The bornite and chalcocite are generally hosts of rich Ag. This indicates that the mining of porphyry Cu deposits should also be concerned with the precious metal content. In addition, Cu-(Fe)-sulfides are hosts for many deleterious elements, which should be removed from the copper concentrates



## Data Availability

The (data type) data used to support the findings of this study are included within the supplementary information files.

## Conflicts of Interest

The authors declare no conflict of interest.

## Acknowledgments

This study was financially supported by the Fundamental Research Funds for the Central Universities (Project No. 191GPY75) and the National 305 Project (Project No. 2011BAB06B02-03). The authors are grateful to Dr. Mengxi Wang and Chummier Ma in addition to numerous technical staff members for offering their assistance during this study.

## Supplementary Materials

Figure S1: the photomicrographs of Cu-(Fe)-sulfides analyzed by LA-ICP-MS, indicating that they occurred as metasomatic textures. Figure S2: the smooth time-resolved depth profiles of Cu-(Fe)-sulfides. a: chalcopyrite; b: bornite; c: chalcocite. Table S1: mean value and errors (ppm) for each element of standards. Table S2: average detection limits (ppm). Table S3: EPMA (wt%) and LA-ICP-MS (ppm) results of Cu-(Fe)-sulfides in the 109 porphyry Cu deposit. (*Supplementary Materials*)

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