## Genesis of Strata-bound Sulfide Orebodies in the Tongling Polymetallic Mineralization Cluster, SE China: Evidence from Colloform Pyrite



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Abstract: Colloform pyrite (CPy) is widely distributed in the Tongling mineralization cluster of the Middle-Lower Yangtze River Mineralization Belt (MLYRMB), China. There have many debates as to whether such CPy is associated with Late Mesozoic igneous or Carboniferous sedimentation. CPy from the Xinqiao deposit, a representative of the stratabound sulfide deposits in the MLYRMB, was studied by powder X-ray diffraction (XRD), field-emission scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (TEM). The results show that CPy mainly comprises pyrite, pyrrhotite, quartz, and illite. Pyrite in CPy shows cubic, globule, and xenomorphic morphologies. No octahedral or pyritohedron was observed. Most of the quartz crystals display xenomorphic morphology, where pyrite mold are popular on the surface. Organic matter (OM), which is usually bound to illite, is an important component in CPy. Morphological investigations which exhibit detrital features of quartz and clay minerals indicate that they were derived from continental weathering. Specially, some hexagonal pyrrhotite nanoparticles which show mackinawite morphology are coexisted with OM. The results indicate that the transformation process of sulfides possibly is mackinawite (the precursor) -hexagonal pyrrhotite-pyrite. Thus, compositional and micro-textural characteristics of CPy in Xingiao deposit suggest it to be a sedimentary origin rather than a hydrothermal origin which is associated with Yanshanian magmatism. Moreover, the coexistence of CPy and stratabound sulfide orebodies in the MLYRMB suggests a causal link between the two. It is considered that CPy might have served as a Cu mineralization geochemical barrier for the Cu-bearing ore-forming fluids, which originated from the Mesozoic magma in the MLYRMB.

Key words: nano-mineralogy, colloform pyrite, organic matter, Xinqiao sulfide deposit, Yangtze metallogenic belt, Anhui Province

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## **1** Introduction

The Middle-Lower Yangtze River Mineralization Belt (MLYRMB) is one of the most important regions of mineralization in China. It can be divided into seven main clusters from east to west: Ningzhen, Ningwu, Luzong, Tongling, Anqing-Guichi, Jiurui, and Edong (Pan and Dong, 1999; Deng et al., 2016; Yang and Lee, 2011; Pirajno and Zhou, 2015) (Fig. 1). More than 200 Cu (Au, Pb, Zn, and Mo) polymetallic sulfide deposits have been identified in this belt. The sulfide orebodies in these deposits are classified into three spatially associated types according to their occurrence and mineral associations: (1) porphyry orebodies in Yanshanian granitoid intrusions; (2) skarn orebodies in the contact zones between the Yanshanian intrusions and sedimentary strata; (3)stratabound sulfide orebodies in late Paleozoic-early Mesozoic sedimentary strata (Pan and Dong, 1999; Yang and Lee, 2011). Copper orebodies in the MLYRMB mainly belong to stratabound sulfide deposits, including Wushan, Chengmenshan, Yongping, and Yangjishan Cu (Au) deposits in the Jiurui cluster, and the Tongguanshan, Tianmashan, Xinqiao and Dongguashan deposits in the Tongling cluster (Wang et al., 1994b; Fu et al., 2019), which have been proposed as the like- sedimentary exhalative (SEDEX) deposits in the MLYRMB (Gu and Xu, 1986; Li, 1989; Hou et al. 2011).

In recent decades, stratabound sulfide orebodies have received considerable attention owing to their significant role in understanding the genesis and formation processes of these deposits. Most sulfide orebodies show considerable lateral extension, are strictly stratabound in Upper Carboniferous marine carbonate rocks, and are conformable on the host sedimentary rocks. They also have some sedimentary, e.g., laminar, structures (Gu and Xu, 1986). However, sulfur (S) isotope compositions of the main sulfide minerals, e.g., pyrite and chalcopyrite, show the source of S to be magmatic hydrothermal fluids rather than sedimentary rocks (Xu et al., 2010; Yang and Lee, 2011; Li et al., 2019). Some other geochemical characteristics of these orebodies also provide evidence of hydrothermal origin (Pan and Dong, 1999; Xie et al., 2009; Yang and Lee, 2011; Zhang et al., 2017). In addition, Re-Os dating results show two isochron ages for pyrite in stratabound orebodies:  $319 \pm 13$  Ma and  $143 \pm 16$ 

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Fig. 1. Distribution map of metallogenic districts of the Middle–Lower Yangtze River Metallogenic Belt, SE China (modified after Pan and Dong, 1999 and Yang and Lee 2011).

TLF-Tangcheng-Lujiang fault, XGF-Xiangfan-Guangji fault, YCF-Yangxing-Changzhou fault.

Ma, agreeing with those of the host sedimentary strata and Yanshanian magmatic-hydrothermal process, respectively (Guo et al., 2011a; Xie et al., 2009; Li et al., 2017). Thus, the origin and formation mechanism of these stratabound sulfide orebodies remain controversial. Hypotheses include: (1) syn-sedimentary models including terrigenous sedimentation or volcanic-exhalative sedimentation (Gu and Xu, 1986; Li, 1989; Liu and Liu, 1991); (2) magmatic hydrothermal mineralization (Mao et al., 2011; Li et al., 2017; Li et al., 2018); (3) Carboniferous syn-sedimentary origin overprinted by Mesozoic hydrothermal replacement (Zhou et al., 2010; Guo et al., 2011a; Hou et al. 2011; Du et al., 2015; Xie et al., 2020).

A unique feature of these stratabound deposits is the ubiquitous presence of colloform pyrite (CPy) and its close spatial association with early Cretaceous magmaticporphyry–skarn systems. CPy is often characterized by colloform or lamellar structures and is the key to reveal whether there was primary sulfide sedimentation in the Carboniferous. In addition, the close correlations between ore structures and Mesozoic magmatism intensity, Cu mineralization scale, and Fe-sulfide mineral zone (from pyrrhotite and granular pyrite to CPy in stratabound sulfide orebodies) has been widely identified, and is likely associated with the hydrothermal processes induced by Mesozoic magmatism (Wang et al., 1994a; Xiao et al., 2018).

The occurrence of CPy in stratabound sulfide deposits

in the MLYRMB was reported over 30 years ago. However, the micro-texture and mineralogy of CPy remain unrecognized. In addition, the genetic relationship between CPy and stratabound sulfide orebodies, and the metallogenic implications of CPy for Cu polymetallic sulfide deposits are unclear. Hence, in this work, the mineral morphologies, micro-textures, and paragenetic associations of CPy from stratabound sulfide deposits are investigated. Our investigations have revealed similar information about all CPy analysed, indicating that they have similar origins.

Herein, we present the detailed results of the morphology, mineralogy, and associated organic matter (OM) of CPy from the Xinqiao Fe–S deposit, which is representative of the stratabound sulfide deposits in the MLYRMB. With the new dataset, we further discuss the genesis and formation process of CPy, and the function of CPy in the formation of strata-bound sulfide orebodies.

## 2 Geological Settings and Sample Localities

The Xinqiao sulfide deposit is a representative for the strata-bound sulfide deposits in the Tongling mineralization cluster. It is located about 24 km east of Tongling, Anhui Province, China (Xie et al., 2009). The stratabound sulfide orebodies in this deposit are situated in the Middle Carboniferous Huanglong–Chuanshan formations. The underlying and overlying formations of

the orebodies are the Devonian Wutong Formation (Fm.) and Lower Permian Qixia Fm., respectively. The main host rocks are the carbonates of the Huanglong and Chuanshan formations. The sedimentary rocks at Xinqiao were intruded by the Jitou stock at 138.5±1.0 Ma as determined by SIMS zircon U–Pb method (Li et al., 2017), which, in general, is lithologically homogenous diorite and quartz diorite. It shows an approximately elliptical shape and an outcrop area of about 0.5 km<sup>2</sup> (Fig. 2).

There are two main mineralization types in the Xinqiao deposit, i.e., skarn and stratabound. The skarn orebodies are developed at the contact zone between the Jitou stock and the Middle-Upper Carboniferous limestone and dolomite. The stratabound orebody, which makes up more than 90% of the total ore reserves, contacts concordantly with the host strata and presents laminar, stratiform-like, and lenticular forms. It extends northeastward along strike with a length of 2.56 km and has an average thickness of 21 m. The hanging wall of the stratabound orebody only experienced weak alteration, with the exception of the development of calcite and serpentine along pyrite veins intruding the Qixia Fm. limestone. The footwall of Wutong Fm. sandstone, experienced intensive alteration, represented by the ubiquitous development of silicification and sericitic alteration assemblages. The mineral assemblages in these orebodies are mainly pyrite (with variable textures including colloform and fine- to coarsegrained granular), siderite, chalcopyrite, galena, sphalerite, and magnetite. The gangue minerals include calcite, dolomite, gypsum, quartz, and skarn minerals.

The CPy orebody, which is far from Jitou stock, is located in the southwestern part of the stratabound orebody in the Xinqiao deposit. As it approaches the Jitou intrusion, the CPy gradually evolves into granular pyrite. However, there is no obvious boundary between these two types of pyrite (Fig. 3a). Furthermore, CPy is commonly surrounded by hydrothermal pyrite (Fig. 3b), and CPy in the Xinqiao deposit is characterized by well-developed and commonly colloform texture associated with blocky structures (Fig. 3c, d). CPy samples in the present study were taken from the southwest end of the Xinqiao open-pit stope. They have typical colloform textures (Fig. 3c) and no coarse-grained/hydrothermal pyrite is present, indicating that the original genetic information of the CPy is well preserved.

## **3** Analytical Methods

#### 3.1 Pre-treatment of samples

Large blocks of CPy from the Xinqiao deposit were divided into several sub-samples. The fresh and pollution-free sub-samples were selected and treated with deionized water to dissolve and remove soluble salts (including Fe-sulfate). The post-water treatment samples were rinsed three times for 15 mins in a mixture of dichloromethane and methanol (DCM: MeOH at 9:1 vol:vol) to remove surficial organic contaminants before being air-dried in a vacuum glove box.

## 3.2 Extraction of insoluble HCl-HNO<sub>3</sub> composition

The separation of quartz and clay minerals in the CPy samples was conducted using a mixture of 60% HNO<sub>3</sub> and 35% HCl at a volume ratio of 3:1. Each studied approximately 1 g sample was placed in a 250 ml beaker



Fig. 2. Geological sketch of the Xinqiao deposit in the Tongling mineralization cluster (after Xie et al., 2009).



Fig. 3. Photographs of distribution and microtexture of colloform pyrite (CPy) in the Xinqiao iron sulfide deposit. (a) Field photo showing that no absolute boundary occurs between the coarsely crystalline pyrite ore body and the CPy ore body. Lumpy relicts of the CPy are visible in the coarsely crystalline pyrite section (white unclosed circle on left of white line); coarse-grained pyrite veins occur locally in the region (right of white line). The right man length 176 cm; (b) photograph of a hand sample of CPy: the area circled in white contains relict CPy that is cut by pyrite veins; (c) photograph of a hand sample of CPy, which is gray, colloid-like, with colloform texture and massive structure; (d) photomicrograph of recrystallized CPy textures: gray area is a CPy relict. Pyrite particles are too small to be identified under the optical microscope.

with 50 ml of the acid mixture, and then set in a 30°C water bath for several hours. The residual solids (RS) obtained after acid treatment were washed three times using deionized water, and then dried at 40°C in a drying oven.

## 3.3 XRD analyses

XRD patterns of the raw CPy and RS samples were characterized using a D/MAX2500V diffractometer with Cu–K $\alpha$  radiation at a scanning rate of 2°/min from 3 to 70°. The accelerating voltage was set as 40 kV. The diffraction peaks of different minerals were analysed by JADE 5.0 and Crystallographica Search-Match software.

## **3.4 SEM observations**

SEM analyses were conducted using a SIRION 200 field scanning electron microanalyzer at an accelerating voltage of 0.2–30 kV with a resolution of 1.5 nm. The instrument was equipped with an INCA energy spectrometer system to determine the elemental contents for the areas selected during SEM observations. The

samples were Au-sputtered before observation to improve their conductivity. All SEM investigations were conducted at the Hefei National Laboratory for Physical Sciences, University of Science and Technology of China.

## **3.5 TEM investigations**

Powder samples were placed in 10 ml of pure ethanol and dispersed ultrasonically for 20 mins. TEM imaging and energy dispersive spectrometer (EDS)-based elemental mapping were performed on a JEM 2100F TEM equipped with a spherical aberration-corrector and Gatan image filtering.

## 4 Results

## 4.1 XRD and chemical treatment

As shown in Fig. 4a, only the reflections of pyrite can be observed in the raw CPy. After treatment with HCl– HNO<sub>3</sub> (Fig. 4b), the reflections of quartz are present in the RS patterns whereas no peaks of pyrite were detected, indicating the complete decomposition of the pyrite.



Fig. 4. X-ray diffraction patterns of CPy from the Xinqiao deposit. (a) Raw CPy; (b) post-treatment of CPy using HCl–HNO<sub>3</sub>.

Qz-quartz; Py-pyrite.

Based on the calculation of the difference in weight between pre- and post-acid treatment of CPy samples, the amount of quartz in each sample is approximately 3%. Therefore, the CPy samples used in this work mainly comprise pyrite and a small amount of quartz.

## 4.2 SEM

The micro-textures and morphologies of pyrite in CPy are illustrated in Fig. 5. As shown in Fig. 5a, pyrite has various morphologies, including cubic, spherical, and ellipsoidal, in which the euhedral cubic particles are dominant. The particle size of the pyrite varies from nano scale to sub-micron. In addition, many subhedral and xenomorphic grains of pyrite with particle sizes smaller than that of the cubic particles were observed. The EDS measurements (Fig. 5a) show that the Fe:S ratio is approximately 1:2.01, indicating а pyrite-like composition. The quartz is randomly distributed in CPv in the shape of single, very round, granular crystals (Fig. 5b). The pyrite has no recrystallization near the boundary of the quartz and pyrite. Moreover, two types of mineral



#### Fig. 5. SEM images of raw sample and remnants after HCl-HNO<sub>3</sub> treatment of CPy.

(a) SEM image showing CPy consisting mainly of cubic euhedral-subhedral pyrite measuring several nanometers to half a micrometer in size. EDS pattern of samples shows the main elements are Fe and S with a Fe/S ratio of  $\sim$ 2.01 (lower left corner), which reflects the stoichiometry of pyrite; (b) quartz is randomly distributed in CPy in the shape of a single well-rounded granule. The pyrite has no recrystallization near the boundary of quartz and pyrite; (c) SEM image of mold structure consisting of quartz within the remnants after HCl–HNO<sub>3</sub> treatment, which shows the association of syn-sedimentary quartz and pyrite. The cross-sectional morphology (arrow) is similar to that of the pyrite in (a). The EDS pattern of the sample is shown in the lower right corner. (d) SEM image of the surface of clastic quartz coated by clay particles and containing voids resulting from the dissolution of pyrite. The inserted EDS spectrum (lower right corner) shows quartz element composition (Si and O), and the squares are the area selected for EDS analysis.

aggregates are found in the RS. The aggregate in Fig. 5c is composed of particles with irregular morphology. EDS analysis (Fig. 5c) indicates that these particles are quartz. Small holes with sizes similar to pyrite are present in the assemblage, indicating an impression of pyrite into the quartz assemblage. The other assemblage (Fig. 5d) comprises mainly lamellar and xenomorphic clay minerals.

## 4.3 TEM

The TEM images of the raw CPy and RS samples (Fig. 6) show that pyrite comprises submicron-sized euhedral crystals (100–400 nm) and nanosized aggregates where individual particles of pyrite are difficult to identify. Some sheet-like Fe-sulfide particles of 10–100 nm are surrounded by thin films (Fig. 7a). They could be pyrrhotite because the EDS analysis yields an Fe:S ratio of 1:1.03 (FeS<sub>1.03</sub>) (Taylor, 1970) and a high-resolution TEM image (Fig. 7b) exhibits lattice fringes of (007)(d  $\approx$  4.96 Å) and (206) (d  $\approx$  2.65 Å) of hexagonal pyrrhotite. EDS measurements indicate that the thin films are OM because

they contain abundant C and only small amounts of Fe and S. Therefore, it can be concluded that the Fe-sulfide encapsulated by the organic film is pyrrhotite rather than mackinawite (FeS, precursor mineral of pyrite formation), troilite, or pyrite.

The element mapping shows that the OM also coexists with quartz and illite in the RS (Fig. 8). Quartz occurs as xenomorphic crystals, and the particle sizes are mainly in the nanometer scale. However, the particle sizes of illite are larger than those of quartz particles. The presence of xenomorphic grains indicates illite to be of detrital terrigenous origin.

## **5** Discussion

## 5.1 Genesis of CPy

The term 'colloform' was first used to describe the rounded and spherical forms that were thought to form from colloidal and metacolloidal substances (Rogers, 1917). Colloform minerals may also be euhedral crystals that are alteration products of original amorphous



Fig. 6. TEM images of raw CPy ores.

(a) TEM image of euhedral cubic pyrite measuring 500 nm to less 1 µm in size; (b) TEM image of sheet and xenomorphic iron sulfide particles.



Fig. 7. TEM analysis of complex particle microtextures of raw CPy ores.

(a) TEM image of complex particles. EDS spectrum of sheet nanocrystals of iron sulfide and films of OM present in the sample (lower right and upper right, respectively); (b) high-resolution TEM image shows 4.96 Å (007) and 2.65 Å (206) lattice fringes and an angle of 62.5° between the two faces of hexagonal pyrrhotite. SAED pattern is shown in the lower right corner.

materials. Roedder (1968) suggested that colloform texture is the direct result of crystallization from a solution. However, most colloform minerals, if not all, occur as lamellar or banded structures that might have under far-from-equilibrium conditions formed of crystallization with diffusion-limited growth and the characteristics of self-organization (Pfaff et al., 2011 and references therein). In addition, colloform textures might be linked to biologically mediated precipitation (Moreau et al., 2004). For now, as the genesis remains debatable, the term 'colloform' used herein refers mainly to shape or morphology and is not used as a genetic term (Pfaff et al., 2011). CPy is found in a variety of environmental settings, including within sedimentary rocks, sulfide deposits (e.g., MVT, SEDEX, and VMS), and at methane-hydrate seep sites in the modern ocean (Conliffe et al., 2013; Zhang et al., 2014; Keith et al., 2016; Wei et al., 2016). The microtexture and morphology of CPy can be used to trace mineralization conditions (Large et al., 2014; Zhang et al., 2014; Wei et al., 2016; Mukherjee and Large, 2016).

Our mineralogical studies (Figs. 4, 6, and 8) indicate that the CPy in the Xingiao deposit is composed mainly of pyrite, less quartz, and a trace of clay minerals (e.g., illite). SEM and TEM analyses show that the nanosized pyrite crystals have cubic and spherical shapes (Figs. 5-7), similar to the CPy described by Rogers (1917). Quartz particles are randomly distributed in CPv in the shape of single granular well-rounded crystals with inset pyrite on their surface, showing that they are detrital grains (Vos et al., 2014). In addition, TEM observation found the hexagonal pyrrhotite nanocrystals are surrounded by OM in the CPy and display mackinawite-like sheet morphology (cf. Wolthers et al., 2003), but do not have mackinawite-like texture and chemical formula (FeS $_{0.92}$ -FeS $_{0.96}$ ). The morphology of pyrrhotite in this study is also different from hydrothermal pyrrhotite (Guo et al., 2011b) and so, given this morphology, the pyrrhotite could be an intermediary phase during the transformation mackinawite (the precursor) to pyrite. This of transformation and then on to pyrite could be a pathway of pyrite formation in diagenesis and metamorphism (Larrasoana et al., 2007; Roberts, 2015), rather than a pathway in the hydrothermal process. Therefore, pyrrhotite with organic films could be an early diagenesis product of CPy (Wilkin and Barnes, 1997; Benning et al., 2000; Larrasoana et al., 2007). As to the transformation mechanism, both irreversible solid-state diffusion and topological phase transition can lead to the transformation of mackinawite to pyrrhotite (Taylor, et al., 1979; Lennie et al., 1995).

Crystal morphology is a reflection of the law of atomic arrangement within pyrite. It changes along with the evolution of the growth environment (Huang et al., 2017). Both temperature and supersaturation can influence the crystal morphology and the grain size of pyrite (Rickard, 2012, 2019). In general, multiple textural forms of pyrite, including framboids, microcrystalline clusters, and layers of fine crystals, are typical of syngenetic and diagenetic origins. By contrast, medium-sized and large euhedral crystals (>1 mm) are indications of metamorphic and/or hydrothermal growth (Rickard, 2012; Large et al., 2014; Gao et al., 2016). High supersaturation is beneficial to pyrite nucleation, whereas low supersaturation is beneficial to pyrite growth (Huang et al., 2017 and references therein). Thus, the formation of nano-sized pyrite requires high supersaturation. In the hydrothermal process, supersaturation is usually low and this state can last for a long time, which in turn will leads to growth rather than nucleation of pyrite. The growth kinetics determines hydrothermal pyrite to be larger than syngenetic and diagenetic pyrite.

The CPy in this study mainly comprises submicronsized microcrystalline pyrite, and lacks medium-sized and large euhedral crystals (>1 mm), indicating a sedimentary origin. In addition, CPy contains many nano-sized spherical, rounded, and xenomorphic pyrite aggregates. The recrystallized pyrites with xenomorphic and cubic shape suggest that the CPy has undergone a weak diagenesis and/or later hydrothermal overprinting (Xie et al., 2014). CPy also contains some detrital minerals (e.g., quartz and illite) in addition to OM (Figs. 5 and 8). The mineralogy and micro-textures further indicate that the CPy is a sedimentary production that occurred under stable anaerobic sedimentary conditions rather than in relation to Yanshanian magmatism-related hydrothermal activity (Xu et al., 2019). These results are consistent with the formation of pyrite in a stable and semi-enclosed marine basin where the incursions of terrigenous materials are lacking, similar to the modern Black Sea (Lyons and Severmann, 2006). The mineralogical characteristics of the CPv may furthermore support the hypothesis of the formation of a SEDEX-type-like pyrite deposit before Cu mineralization in the Tongling region and MLYRMB.

## **5.2 Formation processes of CPy**

Pyrite is a common Fe sulfide mineral in natural environments. It holds most of the Fe in  $H_2S$ -rich lakes, sea basins, marine sediments, and pore-fluids. Sedimentary pyrite generally forms under euxinic conditions where dissolved sulfates, and consequently sulfides, and active Fe are available (Berner, 1970, 1984).

Systematic field investigations have shown that the Upper Devonian in the MLYRMB comprises Fe-bearing strata (sometimes Fe oxide nodules) with variable thicknesses (Fig. 9). Under anaerobic conditions, reactive Fe can be released from Devonian sandstones or from contemporaneous sediments. Thus, Fe is not the limiting factor for pyrite formation. In addition, evaporitic gypsum is an important constituent of Carboniferous carbonate strata, indicating that the excessively dissolved sulfate in marine water is a significant sulfate source for the growth of sulfate-reducing bacteria (SRB). Dissolved S produced by SRB then reacted with dissolved Fe<sup>2+</sup> to form sedimentary CPy (Picard, et al., 2018). The organic carbon (OC) (0.2%) varying in the different lithological units is found in the carbonaceous limestones of the lower Oixia Fm. and the dolomites of the Huanglong Fm. (Du et al., 2015). The maximum content of OC in CPy is 0.27%, which is comparable with the total amount of OC in the host sediments. Therefore, dissolved sulfate and sedimenthosted active Fe could have attributed to the formation of sedimentary pyrite in the Tongling cluster.



Fig. 8. TEM analysis of remnants after HCl–HNO<sub>3</sub> treatment of CPy ores. (a) TEM image of remnants after HCl–HNO<sub>3</sub> treatment; (b–f) TEM elements mapping: carbon (C), silicon (Si), oxygen (O), aluminum (Al), potassium (K); (c–d) demonstrates quartz particles (lower right corner of a); b, c, e, and f suggest the association of organic materials with clay (ellipse grain in center of a and quartz in upper right corner of a).



Fig. 9. Field photograph of the top bed of the Devonian Wutong Formation from the Yeshan region, Tongling (human for scale measures 170 cm).

However, despite numerous field studies and experimental works, the processes and mechanisms of pyrite formation in sediments and sedimentary rock are not yet fully understood. The transformation of precursor FeS minerals is considered to be the major process involved in pyrite formation (Schoonen and Barnes, 1991; Rickard, 2012; Peiffer et al., 2015). Amorphous FeS or mackinawite is the precursor species that requires elemental S addition or Fe loss to form pyrite in anoxic sediment; this process can be achieved through the intermediary minerals greigite and/or pyrrhotite (Berner, 1970; Sweeney and Kaplan, 1973; Wilkin and Barnes, 1997). In the Xinqiao deposit, hexagonal pyrrhotite in CPy is surrounded by OM and displays the sheet morphology of mackinawite. These characteristics indicate that CPy from Xinqiao deposit was formed through the pathway of mackinawite–pyrrhotite–pyrite.

As discussed above, during the formation of CPv in the Tongling cluster, sulfate and ferric Fe acted as electron receptors while OM was the electron donor (Berner, 1970; Rickard, 2012). Sulfates in the marine basin were reduced to S<sup>2-</sup> by SRB in the presence of OM. Meanwhile, Fe oxides of the Wutong Fm. were reduced to ferrous.  $S^{2-}$  can react with Fe<sup>2+</sup> to form FeS, including amorphous and ordered mackinawite (Picard, et al., 2018). Due to their low solubility. Fe sulfide minerals can precipitate rapidly from the water column to form hole- and OM-containing aggregates. Subsequently, during sedimentary compaction, iron mono-sulfide minerals continued to react with S<sup>0</sup> (present in the holes) to form hexagonal pyrrhotite, which eventually transformed to pyrite through the addition of  $S^0$ . The processes of transformation from the precursor and intermediary Fe sulfides to pyrite ended during the early stage of diagenesis. The reactions involved are as follows:

$$CH_2COO^- + SO_4^{2-} \rightarrow HCO_3^- + H_2S$$
(1)

$$\begin{array}{l} \text{CH}_2\text{COO}^- + 8\text{Fe}(\text{OH})_3 \text{ (hematite or goethite)} \rightarrow \\ & 8\text{Fe}^{2^+} + 2\text{HCO}_3^- + 5\text{H}_2\text{O} + 15\text{OH}^- \\ \text{H}_2\text{S} + \text{Fe}^{2^+} \rightarrow \text{FeS} \text{ (mackinawite)} + 2\text{H}^+ \end{array} \tag{2}$$

FeS (mackinawite) + 
$$xS^0 \rightarrow$$

$$Fe_{1-x} S$$
 (hexagonal pyrrhotite) (4)

 $Fe_{1-x} S$  (hexagonal pyrrhotite) +  $S^0 \rightarrow FeS_2$  (pyrite) (5)

# 5.3 Implications of CPy for Mesozoic Cu mineralization

In the Tongling mineralization cluster, the large stratabound sulfide orebodies are associated with Carboniferous Huanglong-Chuanshan formations carbonates. These carbonate successions have higher reaction ability and OM than clastic rocks. Interactions between carbonate and intermediate-acidic intrusive rocks might, therefore, have played important roles in the formation of skarn Cu deposits and stratiform-like Cu orebodies (Du et al., 2015). Accordingly, it is proposed that carbonate rock may be the most important factor limiting the formation of stratiform orebodies. However, in the Tongling district, the majority of strata-bound orebodies are closely associated with the Huanglong-Chuanshan formations, which also host sedimentary Cpy orebodies. Thus, it is evident that, in terms of the geological setting, the stratabound orebodies in Tongling and the MLYRMB have genetic relationships with the carbonate rocks of the Huanglong-Chuanshan formations and Hercynian sedimentary Cpy.

Calc-alkaline magmas induce skarn alteration and Cu mineralization in association with related hydrothermal systems and are an important Cu source. Previous researchers have proposed that pyrite might have been a source for Cu mineralization in the Yanshanian (Gu and Xu, 1986). However, according to this work and others on the geochemistry of CPy and coarse-grained pyrite (Chen et al., 2014; Xiao et al., 2016), the CPy could not have acted as an important source of Cu for the large-scale Yanshanian Cu mineralization. Further investigation also indicates that the amount of Cu correlates positively with the intensity of magmatism for each deposit in Tongling (Xu et al., 2011; Fu et al., 2019), while there is a negative correlation between the magmatism intensity and the Cpy content (e.g., Dongguashan and Xinqiao deposits). According to the spatial-temporal distributions of Cu and CPy orebodies, it is considered that CPy controlled Cu mineralization during Mesozoic hydrothermal mineralization through multiple ways, such as providing S and mediating redox conditions.

Pyrite is a stable mineral phase in a reducing environment. It can act as a catalyzer in the formation of other metal sulfide deposits during late diagenesis, metamorphic remobilization, and hydrothermal processes (Marshall and Gilligan, 1987). Previous studies have revealed that the replacements of pyrite and pyrrhotite by chalcopyrite occur extensively in the stratabound sulfide orebodies in Tongling (Guo et al., 2011b; Hou et al. 2011). Experimental studies have also shown that Cu sulfides can form on the margins of pyrrhotite under medium- to low-temperature conditions (40–200° C) (Pekala et al., 2011). The replacement of pyrite by chalcopyrite has also been discovered experimentally by Zhang and Cai (2016) under medium- to low-temperatures and mildly acidic conditions. It is clear that Fe sulfide minerals including pyrite and pyrrhotite can induce Cu mineralization where Cu-bearing fluids come into contact with Fe-sulfides. CPy has higher reactivity than coarsegrained pyrite due to its lower particle size and higher specific surface area (Xu et al., 2017). Thus, CPy in the Tongling mineralization cluster has better catalytic ability than coarse-grained pyrite to promote Cu mineralization.

Therefore, the reaction of  $Cu^{2+}$ -bearing ore-forming fluids with CPy is an important process in the transformation of Fe-sulfide minerals to Cu-sulfide minerals in Tongling. This reaction can be accelerated by OM in carbonate strata (Greenwood et al., 2013), specifically, in the CPy-involved mineralization process. As a result of these processes, Cpy was replaced by a stratiform Cu-bearing sulfide mineral, and the main transformation reactions are as follows:

$$\begin{array}{l} \operatorname{FeS}_2(\operatorname{pyrite}) \to \operatorname{Fe}_{1-x} S + xS^0 (250-600 \ ^\circ C) & (7) \\ \operatorname{Fe}_{1-x} S (\operatorname{pyrrhotite}) + Cu^{2+} \to \operatorname{CuFeS}_2(\operatorname{chalcopyrite}) \\ & (>150 \ ^\circ C, \operatorname{mainly} 260-340 \ ^\circ C) & (8) \\ \operatorname{FeS}_2(\operatorname{pyrite}) + Cu^{2+} \to \operatorname{CuFeS}_2(\operatorname{chalcopyrite}) \\ & (>150 \ ^\circ C, \operatorname{mainly} 260-340 \ ^\circ C) & (9) \end{array}$$

According to reaction (7), the hydrothermal fluids derived from Yanshanian magmatic activity firstly remobilized CPy to form pyrrhotite via S loss (Bai et al., 2014). Pyrrhotite then reacted with dissolved  $Cu^{2+}$  to form chalcopyrite (reaction 8). In addition, pyrite can be replaced directly by  $Cu^{2+}$  in the ore-forming solutions to generate chalcopyrite (Zhang and Cai, 2016).

In summary, the processes described above explain how stratabound CPy was replaced by Cu-bearing iron sulfide orebodies. Thus, stratabound CPy might have acted as the other important limiting factor on stratabound Cu-bearing Fe sulfide orebodies in the Tongling cluster, and, more generally, in the whole MLYRMB.

#### **6** Conclusions

The systematic field and mineralogical observations demonstrate that nano- to sub-micro scale pyrite is the principal constituent of the CPy in the Xinqiao deposit. Besides, minor amounts of nanoscale hexagonal pyrrhotite, detrital quartz and clay minerals, and OM are present. The hexagonal pyrrhotite displays the sheet morphology of mackinawite and is surrounded by OM. These characteristics indicate that CPy from the Xinqiao deposit was precipitated directly during sedimentation rather than from magmatic hydrothermal fluids. The CPy was formed through the pathway of mackinawitepyrrhotite-pyrite.

The extensive regional distribution of CPy and its microtextures indicate that CPy has served as a reducing agent (or a barrier) for the Cu-bearing ore-forming hydrothermal fluids during the Mesozoic Cu mineralization in the Tongling mineralization cluster and the MLYRMB.

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