

Mineralogy and Chemistry of Sulfides from the Longqi and Duanqiao Hydrothermal Fields in the Southwest Indian Ridge

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Abstract: Recent investigations found that hydrothermal activity and sulfide mineralization occurs along the Southwest Indian Ridge (SWIR). The Longqi and Duanqiao hydrothermal fields between 49° E and 53° E of the SWIR are two prospective mineralization areas discovered by Chinese scientists. With the aim to determine the mineralogical and chemical characteristics of sulfide minerals, we have conducted detailed studies for samples from the two areas using an optical microscope, X-ray diffractometer, scanning electron microscope, and electron microprobe. The mineralization processes in the Longqi area are divided into three main stages: (1) the low-medium-temperature stage: colloform pyrite (Py I) + marcasite → euhedral pyrite (Py II), (2) the high-temperature stage: isocubanite (±exsolved chalcopyrite) + pyrrhotite → coarse-grained chalcopyrite (Ccp I), and (3) the medium-low-temperature stage: sphalerite + fine-grained chalcopyrite inclusions (Ccp II) → aggregates of anhedral pyrite (Py III) ± marcasite → Fe-oxide (-hydroxide) + amorphous silica. The mineralization processes in the Duanqiao area are divided into two main stages: (1) the medium-high-temperature stage: subhedral and euhedral pyrite (Py I') → coarse-grained chalcopyrite (Ccp I') and (2) the medium-low-temperature stage: sphalerite → fine-grained chalcopyrite (Ccp II') + chalcopyrite inclusions (Ccp II') → silica-cemented pyrite (Py II') + marcasite → Fe-oxide + amorphous silica. We suggest that the fine-grained chalcopyrite inclusions in sphalerite from Longqi and Duanqiao were formed by co-precipitation and replacement mechanisms, respectively. Primary sphalerites from both fields are enriched in Fe (avg. 5.84 wt% for the Longqi field vs. avg. 3.69 wt% for the Duanqiao field), Co (avg. 185.56 ppm for the Longqi field vs. 160.53 ppm for the Duanqiao field), and Cd (avg. 1950 ppm for the Longqi field vs. avg. 525.26 ppm for the Duanqiao field). Cu contents in pyrite from the Duanqiao field (Py I': avg. 849.23 ppm and Py II': avg. 1191.11 ppm) tend to be higher than those from the Longqi field (Py I: avg. 26.67 ppm, Py II: avg. 445 ppm, and Py III: avg. 179.29 ppm). Chalcopyrite from both fields is enriched in Zn (Ccp I: avg. 3226.67 ppm, Ccp II: avg. 9280 ppm, Ccp I': avg. 848 ppm, Ccp II' (inclusions): avg. 1098 ppm, and Ccp II' (fine-grained): avg. 1795 ppm). The varying contents of Zn in the different pyrite and chalcopyrite generations may result from the zone refining process. An integrated study of the mineralogy and mineralogical chemistry suggests that the hydrothermal fluids of the Longqi area are likely conditioned with higher temperatures and relatively lower f_{O_2} and f_{S_2} than those of the Duanqiao area, but in contrast to the former, the latter is much affected by the compositions of the surrounding rocks.

Key words: mineralogy, mineralogical chemistry, Longqi, Duanqiao, Southwest Indian Ridge (SWIR)

1 Introduction

Mid-ocean ridges are important tectonic environments for modern seafloor hydrothermal activities and massive sulfide formation (De Ronde et al., 2003; Hou Zengqian et

al., 2003; Hannington et al., 2005, 2011). Precipitated directly from hydrothermal fluids, sulfide minerals record water-rock interactions and submarine hydrothermal ore-forming system mineralization environments (Hannington et al., 1995; Reed, 2006; Kawasumi et al., 2017).

Previous studies on mineralogy of sulfides from

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seafloor hydrothermal systems have contributed to better understanding of metallization mechanisms at mid-ocean ridge environments (Humphris et al., 1995; Pirajno, 2009). The mineral associations of the sulfide deposit at the mid-ocean ridges are dominantly controlled by basement rock compositions, although fluid chemistry and complexation also affect the mineralogy. The mineralogical features of sulfide deposit vary widely between basaltic, ultramafic, and sedimentary environments at mid-ocean ridges (Zierenberg et al., 1998; Fouquet et al., 2010; Nayak et al., 2014). Several studies have systematically modeled the sulfide and sulfate precipitation sequence from the hydrothermal fluids, whose results generally indicate that precipitation occurs in two groups: 1) an early high-temperature chalcopyrite, pyrrhotite, and anhydrite group followed by 2) a later lower temperature sphalerite and pyrite group (Haymon et al., 1983; Janecky and Seyfried, 1984; Hannington et al., 1995; Wang et al., 2017). Copper-rich or Zn-rich mineralization zonation is common in hydrothermal chimneys and mounds, which are related to the precipitation history and zone refining processes (Haymon et al., 1983; Hannington et al., 1995; Hannington et al., 1998; Petersen et al., 2000; Pirajno, 2009). Additionally, according to experimental simulations, sulfide mineral associations and their chemical compositions are good indicators of fluid physicochemical conditions (e.g., temperature, pH, salinity, and f_{O_2} - f_{S_2}) and hydrothermal system advection

rates (Tivey et al., 1995a, 1995b; Fontboté et al., 2017).

Because the Longqi field is an active vent field and the Duanqiao fields is an inactive field, the two fields have received significant attention and previous study shows that the two areas have the greatest mineralization potential in the SWIR. In this study, we conducted the systematic mineralogical analysis of the samples from the Longqi and Duanqiao hydrothermal areas in the SWIR, and compared typical mineral paragenesis and element accumulation characteristics so as to understand their mineralization conditions and processes. The goal of this study reveals similarities and differences between the active and inactive hydrothermal fields. Considering investigation difficulty and exploration costs associated with mid-ocean ridge environment, this study may provide some implications for determining future research and prospecting targets.

2 Geological Background

The Southwest Indian Ridge (SWIR), which extends from the Bouvet triple junction (BTJ) in the west to the Rodrigues triple junction (RTJ) in the east, is a major plate boundary that separates the African and Antarctic plates (Fig. 1a) (Fisher et al., 1997; Muller et al., 1999; Georgen et al., 2001). Among the global mid-ocean ridge systems, the SWIR is classified as a typical ultraslow-spreading ridge with a full spreading rate of approximately 14–16

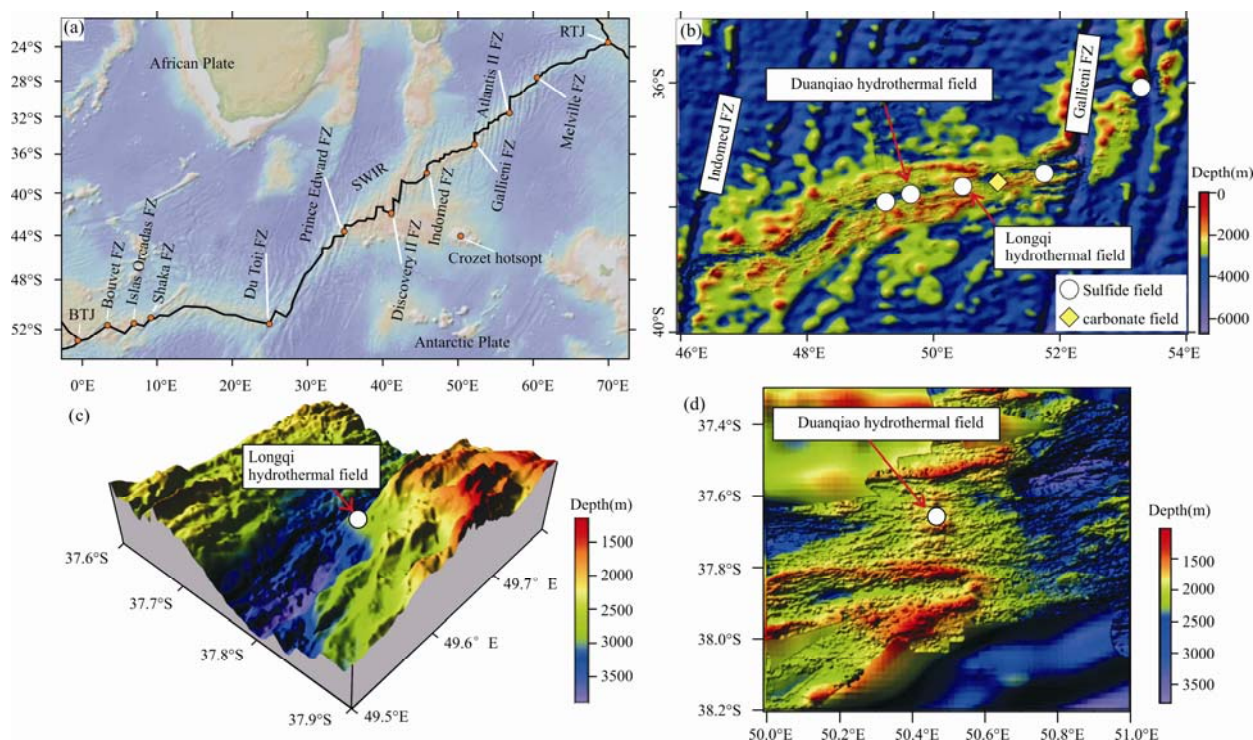


Fig. 1. Generalized geologic map of the studied areas (modified from Tao et al. (2014)).

(a), Tectonic setting of the SWIR; (b), mineralization distribution of the 49°–53°E segment of SWIR; (c), bathymetric map of the Longqi hydrothermal field; (d), bathymetric map of the Duanqiao hydrothermal field.

mm y^{-1} (German et al., 1998; Dick et al., 2003; Hannington et al., 2005). The length of the SWIR is approximately 8000 km, which makes up a significant proportion (approximately 10%) of the total global ridge length (Georgen et al., 2001; Sauter et al., 2010). Both geochemical and geophysical evidences point to the presence of significantly thinner crust at the SWIR compared with that of other fast spreading ridges (approximately 4 vs. 6.3 km) (Reid and Jackson, 1981; White et al., 1992, 2001; Baker et al., 2004). Three types of seafloor geomorphology exist at the SWIR: volcanic seafloor (volcanic cones and flat-topped volcanoes), smooth seafloor, and corrugated seafloor (Cannat et al., 1999, 2006). The SWIR's axial valley is offset by sets of N–S trending transform faults, which are the result of lateral ridge extension throughout its evolution (Royer et al., 1988; Fisher et al., 1997; Georgen et al., 2001). Rocks exposed along the seafloor are mainly basalts, with some gabbros, pyroxenites, and serpentinized peridotites, which locally outcrop adjacent to the fracture zones (Fujimoto et al., 1999; Dick et al., 2000; Tao et al., 2011; Wolfgang et al., 2013). Compilations of the geophysical and geochemical data along the axial valley of the SWIR reveal extensive variations in valley geometry, crustal thickness, topography, mantle composition, and mantle supply (Meyzen et al., 2003; Seyler et al., 2003; Sauter et al., 2004a, 2004b; Font et al., 2007; Tao et al., 2014).

Systematic investigations of hydrothermal activities within the SWIR have not been conducted until recent years. The major hydrothermal fields observed in the SWIR are located in three segments: 10°–16°E, 49°–53°E, and 63°–64°E (Münch et al., 2001; Wolfgang et al., 2013; Tao et al., 2014). Our study areas, the Longqi hydrothermal field (49°39'E, 37°56'S) and the Duanqiao hydrothermal field (50°24'E, 37°39'S), first discovered in 2007 during the Chinese DY115–19 cruise, are situated in the 49°–53°E segment, which is the most extensively surveyed and studied hydrothermal field along the SWIR (Tao et al., 2012).

The 49°–53°E segment lies in the central part of the SWIR between the Indomed and Gallieni transform faults, with water depths varying significantly from 1700 to more than 3000 m (with an average depth of 3180 m; Fig. 1b) (Tal et al., 2011, 2012). Outcropped rocks dredged during the DY115–19 cruise include pillow basalts, some of which may have experienced chloritization or montmorillonitization (Tao et al., 2012; Ye et al., 2012; Qiu Bibo, et al., 2015). Central ridge morphology is marked by numerous flat-topped seamounts, indicating a higher supply of magma (Tao et al., 2014). Geophysical data from this segment suggests that this portion of the SWIR has experienced a dramatic magma supply increase

since 8–10 Ma, characterized by shallower depths and thicker crust than adjacent areas (Georgen et al., 2001; Sauter et al., 2001, 2004a; Tao et al., 2009). The interaction between the ridge and the Crozet hotspot may have induced this enhanced magmatic event and provided a heat source for hydrothermal circulation, although the specific SWIR-Crozet interaction processes are not clearly understood at present (Sauter et al., 2009; Tao et al., 2011, 2014; Zhang Tao et al., 2013).

The Longqi hydrothermal field, located on a high mound at the junction point between a small non-transform offset and ridge valley, is an active field with a water depth of 2775 m (Fig. 1c). The surrounding seafloor is covered by basalts with rough topography (Tao et al., 2012, 2014). Previous studies have detected the presence of massive sulfides and both active and inactive black smoker chimneys (Tao et al., 2012, 2014; Ye et al., 2012). In contrast, the Duanqiao hydrothermal field lies on an axial basaltic topographic high with a shallow water depth of 1739 m (Fig. 1d). The surrounding terrain is relatively flat. There are no temperature or turbidity anomalies in this area, which suggests that it is an inactive field. Residual massive sulfides and chimneys generally contain considerable amounts of Si-bearing minerals (e.g., opal and amorphous silica) (Tao et al., 2012, 2014).

3 Samples and Methods

Eight massive sulfide samples were collected by TV-Grab during the Chinese DY115-19, DY115-20, DY115-21, and DY125-34 cruises successively. Four of the samples are from the Longqi field (49°39'E, 37°56'S), and the other four are from the Duanqiao field (50°24'E, 37°39'S). Hand specimens from the two hydrothermal fields have similar macroscopic features: a black-brown color, an anhedral granular texture, and a massive structure (Fig. 2). Anhedral granular pyrite and sphalerite are visible to the naked eye. Fe-hydroxide and atacamite are visible locally on the surface of the ores (Fig. 2).

We performed a systematic mineralogical study of the eight above-mentioned massive sulfide ores. Mineral associations and structures were primarily analyzed and photographed using a Leica DM4500P polarizing microscope on thin sections. Portions of the samples were crushed and further examined using a PANalytical XPERT-PRO X-ray diffractometer (XRD) at the Center for Testing and Measurement, Second Institute of Oceanography, SOA.

Detailed micro-textural analyses of the minerals were performed using a Nova NanoSEM 450 scanning electron microscope (SEM), equipped with an OXFORD X-Max 50 energy spectrometer, at the Mineral Laboratory of the

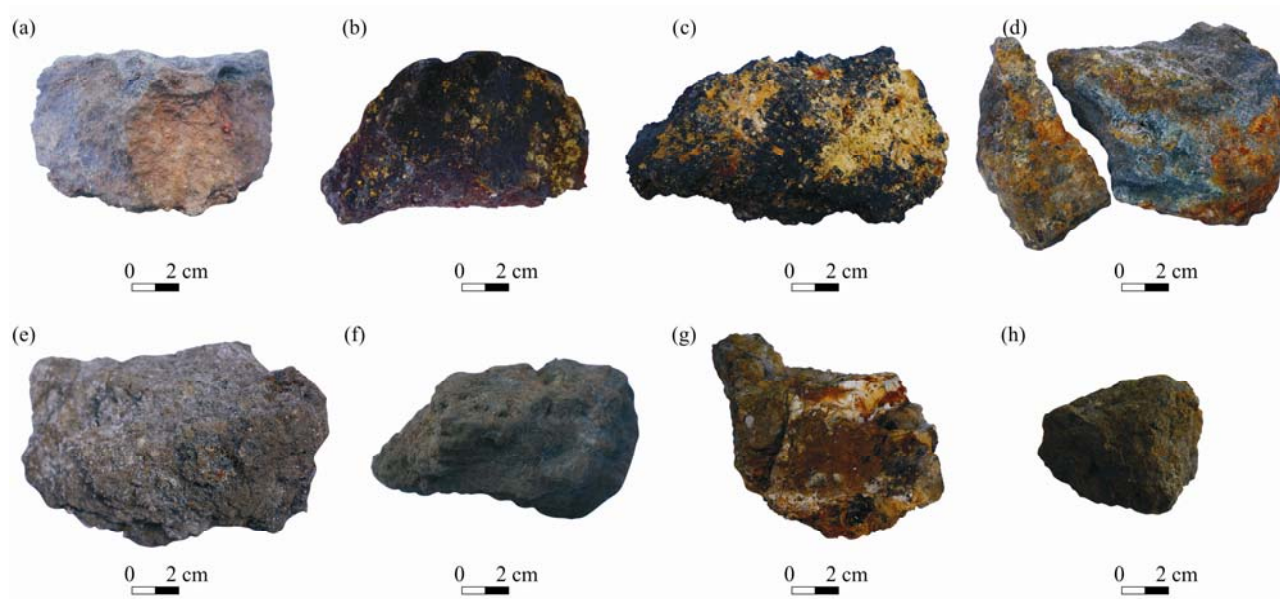


Fig. 2. Hand specimens of massive sulfides from the Longqi field and the Duanqiao field. (a-d), massive sulfides from the Longqi field; (e-h), massive sulfides from the Duanqiao field.

Institute of Mineral Resources, CAGS. The analyses were conducted at a voltage of 15 kV and an electrical current of 11 nA.

Selected thin polished sample sections were analyzed for their chemical compositions using a Jeol JXA-8230 electron probe microanalyzer (EPMA) at the Institute of Mineral Resources, CAGS. The following elements were analyzed: S, Fe, Cu, Zn, Co, Ni, As, Se, Cd, Sb, Pb, Ag, and Au. The operating conditions were as follows: an accelerating voltage of 15 kV, 20 nA of beam current, and a beam size of 5 μm . Natural minerals and synthetic materials were used as standards, and all of the standards were tested for homogeneity before quantitative analysis. Matrix corrections were carried out using the ZAF correction program supplied by the manufacturer.

Individual sphalerite crystals containing small chalcopyrite inclusions were selected for bulk chemical

analysis via inductively coupled plasma mass spectrometry (ICP-MS) at the National Research Center for Geoanalysis, Beijing.

4 Results

4.1 Mineralogical study

4.1.1 The Longqi field

Mineral associations. The main sulfide minerals at the Longqi field identified by XRD and SEM were pyrite, marcasite, sphalerite, chalcopyrite, isocubanite, and pyrrhotite (Figs. 3 and 4). Other minerals include silica and Fe-oxides or Fe-hydroxides (e.g., goethite).

Pyrite is the dominant sulfide mineral and occurs in three forms: (1) colloform pyrite (Py I), which is trapped in sphalerite, generally associated with coexisting marcasite (Fig. 4a), (2) euhedral pyrite (Py II), contained

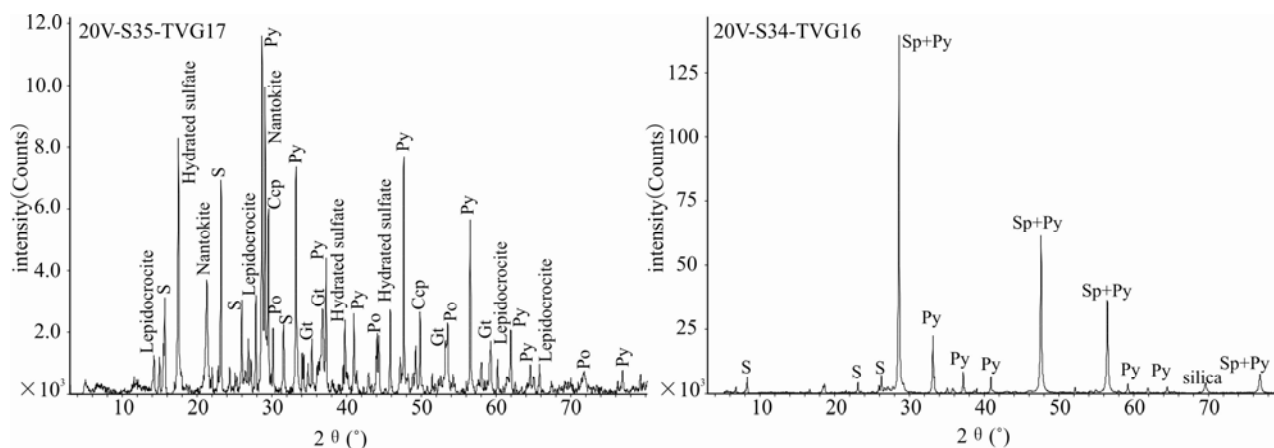


Fig. 3. Typical X-ray diffraction patterns of selected samples from the Longqi field. Py-pyrite, Sp-sphalerite, Ccp-chalcopyrite, Gt-goethite, Po-pyrrhotite.

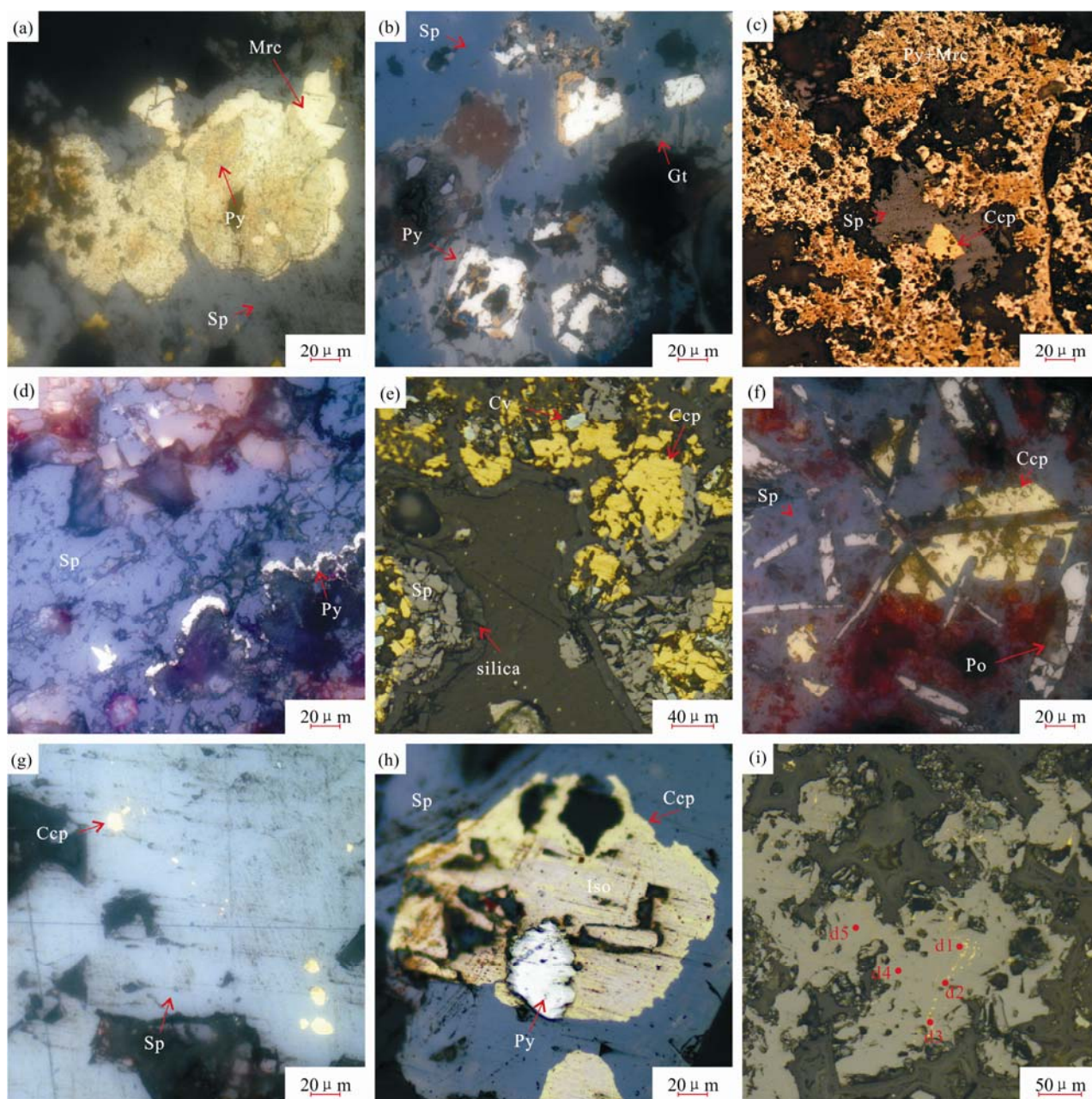


Fig. 4. Photomicrographs of the sulfides from the Longqi field.

(a), colloform pyrite (Py I) and marcasite replaced by sphalerite. (b), euhedral pyrite (Py II) in sphalerite. (c), late stage pyrite (and marcasite, Py III) replacing chalcopyrite and sphalerite. (d), pyrite (Py III) replacing sphalerite along dissolved holes. (e), sphalerite replacing the coarse-grained chalcopyrite. (f), pyrrhotite locally contained in chalcopyrite. (g), bleb-like chalcopyrite inclusions randomly distributed in the cores of the host sphalerite without cleavage or cracks. (h), isocubanite with exsolved chalcopyrite. The chalcopyrite present as lamellas and rings. (i), an example showing the testing locations in the sphalerite containing chalcopyrite inclusions. The red solid circles are targets for EPMA numbered from d1 to d5. Py-pyrite, Mrc-marcasite, Sp-sphalerite, Ccp-chalcopyrite, Po-pyrrhotite, Iso-isocubanite, Cv-covellite, Gt-goethite.

within sphalerite and isocubanite (Fig. 4b and h), and (3) aggregates of anhedral pyrite (Py III), which surround sphalerite and chalcopyrite (Fig. 4c) or adhere to dissolution holes in sphalerite (Fig. 4d). Sphalerite occurs in irregular sheeted or colloform patterns, with a minor axis length of 40–60 μm and along axis length of over 200 μm (Fig. 4c, e, and i). The surface of the sphalerite has numerous pits and commonly shows dissolution-replacement textures (Fig. 4d). Locally, a small quantity of

elongated subhedral pyrrhotite exists, surrounded by sphalerite or partly contained in chalcopyrite (Fig. 4f), and some pyrrhotite is replaced by Fe-hydroxides, leaving a skeleton crystal (Fig. 4f). Chalcopyrite is not as abundant as pyrite or sphalerite and can be classified into two groups: the subhedral coarse-grained chalcopyrite (Ccp I; Fig. 4e) and fine-grained chalcopyrite inclusions (Ccp II; Fig. 4g). The maximum coarse-grained chalcopyrite grain size is approximately 60–80 μm (Fig. 4e), and

chalcopyrite inclusion sizes are no more than 10 μm (Fig. 4g). The pinkish-brown isocubanite, a polymorph of orthorhombic cubanite, is generally surrounded by sphalerite and has typical exsolution textures (Fig. 4h), where the chalcopyrite lamellas and tiny edges are exsolution products. Fibrous Fe-oxide (-hydroxide) and amorphous silica fill in interstitial spaces among the sulfide minerals.

Mineral paragenetic sequences. Previous studies have demonstrated that pyrite can occur at different stages throughout the chimney growth history (Hannington et al., 1995; Maslennikov et al., 2009; Keith et al., 2016). In this study, colloform pyrite (Py I) and euhedral pyrite (Py II) are well preserved in sphalerite and isocubanite (Fig. 4a–b, and h), which indicates that these pyrite phases occur relatively early. Colloform pyrite and marcasite are typical low-temperature non-equilibrium products, which generally occur during initial stages of hydrothermal processes (Wang Yejian et al., 2011; Berkenbosch et al., 2012; Wohlgemuth-Ueberwasser et al., 2015; Ketith et al., 2016). Euhedral pyrite, however, formed during relatively mature chimney stages at higher temperature conditions. Therefore, both the colloform pyrite (Py I) and marcasite should have precipitated earlier than the euhedral pyrite (Py II) in the Longqi field. Isocubanite, coarse-grained chalcopyrite (Ccp I), and pyrrhotite have similar precipitation temperatures (Haymon and Kastner, 1981; Koski et al., 1984, 1994; Caye et al., 1988; Hannington et al., 1988, 1995; Paradis et al., 1988; Large et al., 1989; Mozgova et al., 1996) and are generally formed at the mature stages of the chimney growth. In this study, we observed that isolated crystals of pyrrhotite are locally surrounded by chalcopyrite (Fig. 4f), which implies that pyrrhotite formed earlier than the coarse-grained chalcopyrite (Ccp I). Sheeted sphalerite surrounded or replaced the other sulfides, mentioned above, which precipitated later (Fig. 4a–b, f, and h). As mentioned

above, sphalerite commonly contains fine-grained chalcopyrite inclusions (Ccp II; Fig. 4g). Here, we infer that they formed at approximately the same time. Possible formation mechanisms are discussed later. Aggregates of anhedral pyrite (Py III) and marcasite (Fig. 4c–d) replace sphalerite, which indicates that Py III and marcasite are the last sulfide phases to crystallize during hydrothermal processes.

Consequently, the hydrothermal mineral formation in the Longqi field is divided into three main stages: (1) a low–medium-temperature stage: colloform pyrite (Py I) + marcasite $\rightarrow$ euhedral pyrite (Py II), (2) a high-temperature stage: isocubanite ($\pm$ exsolved chalcopyrite) + pyrrhotite $\rightarrow$ coarse-grained chalcopyrite (Ccp I), and (3) a medium–low-temperature stage: sphalerite + fine-grained chalcopyrite inclusions (Ccp II) $\rightarrow$ aggregates of anhedral pyrite (Py III) $\pm$ marcasite $\rightarrow$ Fe-oxide (-hydroxide) + amorphous silica.

4.1.2 The Duanqiao field

Mineral associations. Pyrite and sphalerite are the dominant sulfide minerals, with a small amount of chalcopyrite and trace amounts of galena (Figs. 5 and 6). Silica and Fe-oxide are present as gangue minerals.

We identified two types of pyrite: sub- or euhedral pyrite (Py I'; Fig. 6a and b) and silica-cemented anhedral aggregates (Py II'; Fig. 6c and h). The euhedral pyrite has a triangular or square shape, mostly surrounded by chalcopyrite or sphalerite, with a grain size of approximately 20–30 μm (Figs. 6a–b). The anhedral pyrite commonly coexists with marcasite, eroding sphalerite along their contacts (Fig. 6h). Locally, these silica-cemented pyrite and marcasite grains are directionally arranged, which may be related to mini fluid channels (Fig. 6c). Sheeted sphalerite is common, which has numerous corrosion pits on the surface (Fig. 6d–e). On the basis of the grain size, three types of chalcopyrite were

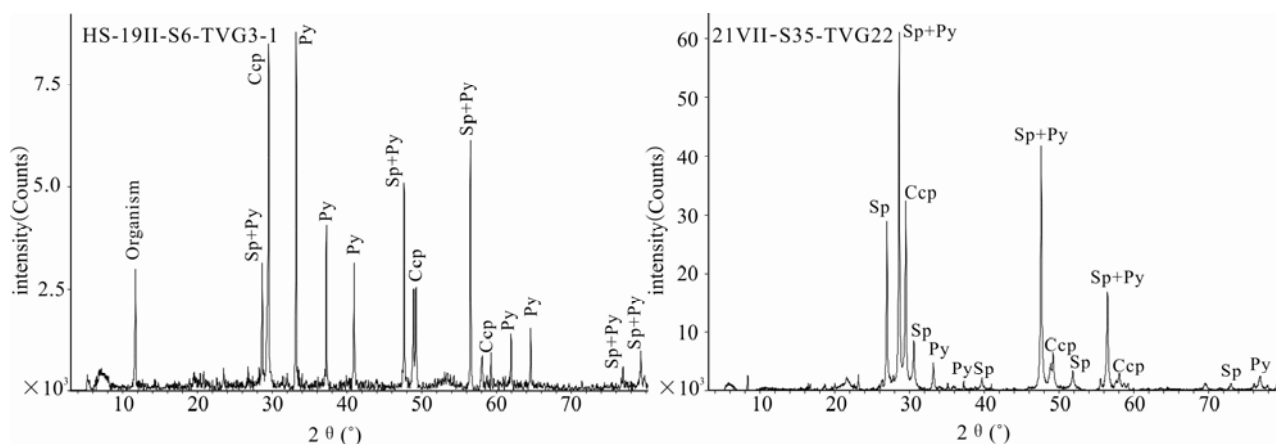


Fig. 5. Typical X-ray diffraction patterns of selected samples from the Duanqiao field. Py-pyrite, Sp-sphalerite, Ccp-chalcopyrite.

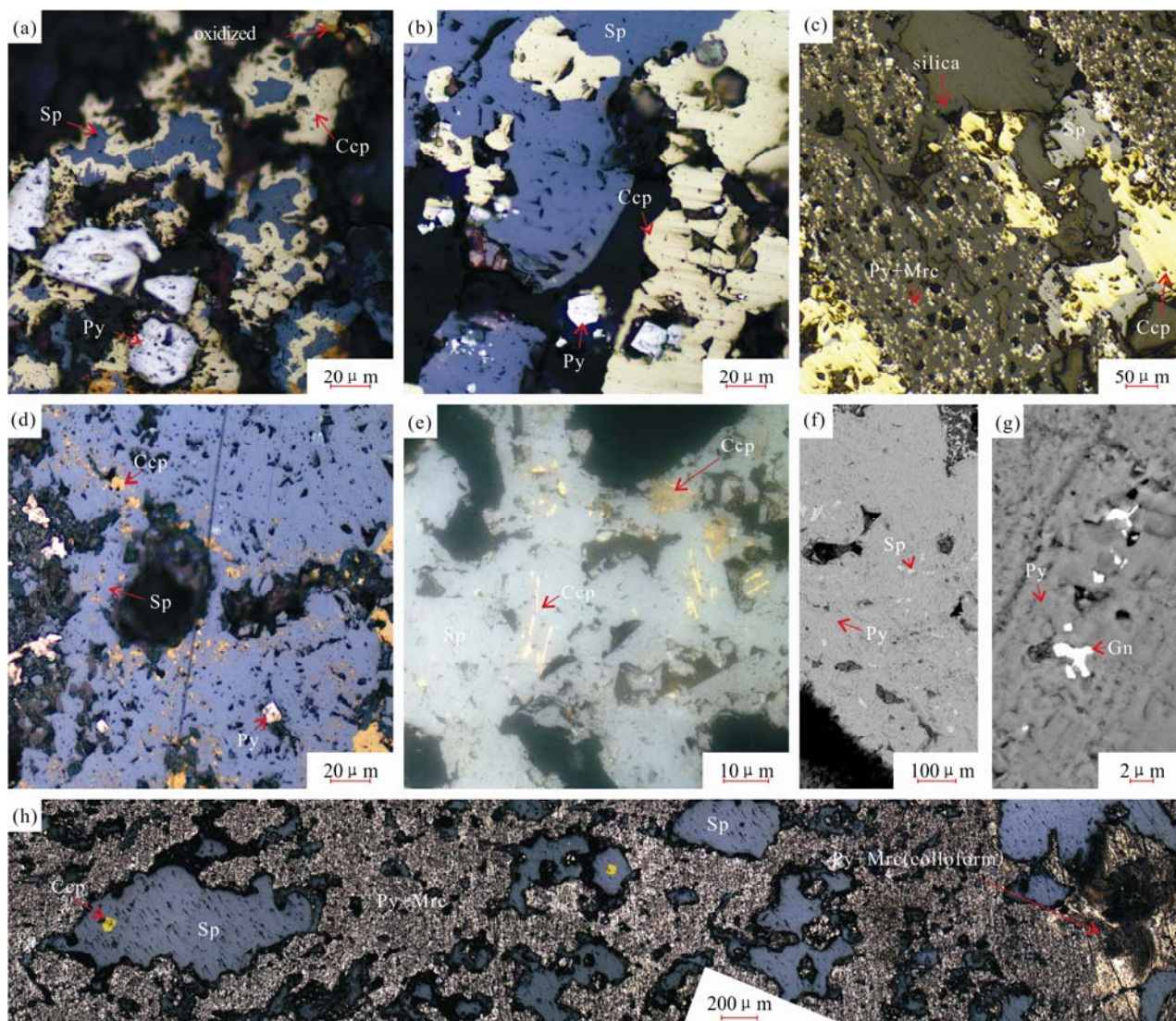


Fig. 6. Photomicrographs of the sulfide from the Duanqiao field (pictures (f-g) are photographed by SEM; the others are photographed by optical microscope).

(a), Enhedral pyrite (Py I') and sphalerite replaced by fine-grained chalcopyrite (Ccp II'). (b), enhedral pyrite (Py I') trapped by sphalerite and coarse-grained chalcopyrite (Ccp I'). (c), oriented pyrite and marcasite indicating the relic of fluid channels. (d), chalcopyrite inclusions distributed along the dissolved pores or edges of the host sphalerite. (e), lamella-like chalcopyrite inclusions arranged in parallel approximately in the sphalerite. (f), sphalerite particles in pyrite. (g), galena particles in pyrite. (h), a spliced picture showing the contact relationship between the pyrite (Py II'), sphalerite and chalcopyrite (Ccp I'). Py-pyrite, Mrc-marcasite, Sp-sphalerite, Ccp-chalcopyrite, Gn- galena.

identified: (1) coarse-grained chalcopyrite (Ccp I'; Fig. 6b–c, and h), commonly surrounded by sheeted sphalerite, (2) chalcopyrite inclusions in the sphalerite (Fig. 6d–e), and (3) fine-grained chalcopyrite or veinlet-like chalcopyrite that occurs along sphalerite edges or fissures (Fig. 6a). The grain size of the coarse-grained chalcopyrite can be more than 50 μm, and the size of the chalcopyrite inclusions or the fine-grained chalcopyrite is less than 10 μm. Moreover, chalcopyrite inclusions occur as “dusts” or chains around dissolution holes or cracks in the sphalerite (Fig. 6d) or as lamellas that are arranged in parallel (Fig. 6e). Traces of microscopic galena and sphalerite particles are distinguishable inside the pyrite, as revealed when using the SEM (Figs. 6f–g). Fe-oxide and silica occur as

interstitial material among the sulfides (Fig. 6).

Mineral paragenetic sequences. Similar to the Longqi field, the subhedral and euhedral pyrite (Py I') formed at relatively high temperatures and precipitated first since they are surrounded by both sphalerite and chalcopyrite (Fig. 6a–b). As described earlier, three types of chalcopyrite occur in the Duanqiao field. The coarse-grained chalcopyrite (Ccp I'; Fig. 6b–c, and h) is generally surrounded by sheeted sphalerite. In Figure 6h, we observe a clear contact relationship between Ccp I', sphalerite, and anhedral pyrite aggregates (Py II'): the coarse-grained chalcopyrite (Ccp I') is surrounded by sphalerite, and sphalerite is surrounded and replaced by pyrite aggregates (Py II'). Locally, Py II' exhibits colloform morphological

features (Fig. 6h), suggesting that they formed at low temperatures (Berkenbosch et al., 2012; Wohlgemuth-Ueberwasser et al., 2015; Gao et al., 2016; Ketith et al., 2016). This means that coarse-grained chalcopyrite (Ccp I') formed earlier than sphalerite, and sphalerite formed earlier than Py II'. On the basis of the observation that fine-grained and veinlet-like chalcopyrite replaces sphalerite as well as no evidence of other new high-temperature hydrothermal processes, we preliminarily infer that fine-grained chalcopyrite formed between the precipitation of sphalerite and Py II'. Moreover, we suggest that chalcopyrite inclusions in the sphalerite probably formed concurrently with the fine-grained chalcopyrite.

In summary, the hydrothermal minerals in the Duanqiao field formed in two main stages: (1) a medium-high-temperature stage: sub- and euhedral pyrite (Py I') → coarse-grained chalcopyrite (Ccp I') and (2) a medium-low-temperature stage: sphalerite → fine-grained chalcopyrite (Ccp II') + chalcopyrite inclusions (Ccp II') → silica-cemented pyrite (Py II') + marcasite → Fe-oxide + amorphous silica.

4.2 Sulfide chemistry

EPMA analyses were performed for pyrite, sphalerite, and chalcopyrite (and isocubanite) from the Longqi and Duanqiao fields. A total of 160 individual mineral chemical composition results are shown in Tables 1–4.

4.2.1 Sphalerite

Major constituent elements. The sulfur concentrations in sphalerite from the Longqi and Duanqiao fields are 32.52–33.99 wt% and 33.11–34.68 wt%, respectively. The zinc concentrations in sphalerite are 50.09–65.69 wt% in the Longqi field and 54.76–64.98 wt% in the Duanqiao field (Table 1).

Minor and trace elements. Sphalerite from both fields is enriched in Fe. In the Longqi field, sphalerite without dissolution pores or fissures (i.e., undamaged) has Fe contents of 1.11–11.19 wt% (avg. 5.84 wt%), and sphalerite micro-zones adjacent to the dissolution pores or fissures has higher Fe contents of 8.78–15.59 wt% (avg. 12.58 wt%). As for the Duanqiao field, the Fe contents of undamaged sphalerite are 1.16–9.36 wt% (avg. 3.69 wt%), and corroded micro-zones have higher Fe contents from 7.87 to 9.67 wt% (avg. 8.91 wt%).

Copper, cobalt, and cadmium have relative enrichment compared with other trace elements in sphalerite from both of the study fields. The Cu contents of the sphalerite show no obvious association with dissolution textures and are generally lower than 1 wt% (avg. 0.385 wt% for the Longqi field and 0.223 wt% for the Duanqiao field), with only a few specific samples reaching approximately 2 wt%

(Table 1).

On the whole, cobalt tends to have concentrations in sphalerite from the Longqi field (up to 1690 ppm), although the Co content of the sphalerite from the Duanqiao field is considerable as well (up to 440 ppm). As for the Longqi field, cobalt also tends to be more enriched in micro-zones adjacent to sphalerite dissolution areas. The average Co contents of undamaged and corroded sphalerite are 185 and 734 ppm, respectively. However, Co contents are relatively stable in the Duanqiao field (avg. 165.53 ppm for the undamaged sphalerite and avg. 150 ppm for the corroded zones; Table 1).

Sphalerites from both of the study fields have very high contents of Cd. Similar to Fe and Co, the highest Cd content occurs in sphalerite micro-zones adjacent to the dissolution areas. In the Longqi field, the Cd contents of undamaged and corroded sphalerites range from 40 to 5340 ppm (avg. 1950 ppm) and from 0 to 7190 ppm (avg. 1781.11 ppm), respectively. With respect to the Duanqiao field, the corresponding contents are 110–3200 ppm (avg. 525.66 ppm) and 2590–5870 ppm (avg. 3617.5 ppm), respectively.

The contents of Ni, As, Se, and Sb are not abundant in sphalerite from the two fields, with general concentrations lower than a few hundred ppm. Lead, Ag, and Au are poorly preserved in sphalerite (most below the detection limits), although a few analytical spots show abnormally high contents (Table 1).

Furthermore, sphalerites that contain fine inclusions of chalcopyrite were analyzed separately, especially for Fe content (Table 2). For the Longqi field, the sphalerite Fe contents in small areas adjacent to or free of chalcopyrite inclusions are relatively constant within the samples (e.g., sample dy1306-3: 7.45–8.33 wt% Cu; Table 2). With respect to the Duanqiao field, the sphalerite Fe contents in small areas adjacent to the chalcopyrite inclusions are 2.05–3.03 wt%, and the corresponding contents in areas without inclusions are 4.97–5.06 wt% (sample dy1306-2).

4.2.2 Pyrite

Major constituent elements. The major element contents in pyrite are relatively constant in both of the studied fields (Table 3). In the Longqi field, the S contents in the three generations of pyrite range from 52.65 to 53.58 wt%, and the Fe contents are in the range from 44.51 to 46.99 wt%. As for the Duanqiao field, the S contents in the two generations of pyrite are 52.87–53.40 wt. %, and the Fe contents in pyrite are 39.84–45.91 wt% (Table 3).

Minor and trace elements.

Copper tends to be more concentrated in pyrite from the Duanqiao field than the Longqi field as a whole. In the

Table 1 Chemical compositions of sphalerite by EPMA analysis

Sample	Dot	Field	Mineral	S (wt%)	Fe (wt%)	Cu (wt%)	Zn (wt%)	Co (ppm)	Ni (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Sb (ppm)	Pb (ppm)	Ag (ppm)	Au (ppm)	Total	Sp precipitation temp.(°C)
dy1306-3	S3-1			33.47	4.80	0.027	60.96	b.d.l.	100.00	300.00	b.d.l.	5340.00	50.00	b.d.l.	b.d.l.	b.d.l.	99.83	287.66
dy1306-3	S3-2			32.87	2.48	0.645	63.98	100.00	210.00	b.d.l.	b.d.l.	320.00	b.d.l.	100.00	620.00	b.d.l.	100.10	256.94
dy1306-3	S3-3			33.52	2.52	0.375	63.34	80.00	b.d.l.	b.d.l.	b.d.l.	490.00	80.00	1020.00	40.00	90.00	99.93	257.74
dy1306-3	S3-4			32.52	1.21	0.432	65.69	b.d.l.	b.d.l.	b.d.l.	b.d.l.	310.00	b.d.l.	480.00	260.00	920.00	100.05	241.29
dy1306-4	S4-1			33.48	7.93	0.076	57.04	50.00	b.d.l.	b.d.l.	b.d.l.	5220.00	450.00	b.d.l.	b.d.l.	110.00	99.11	334.16
dy1306-4	S4-3			33.75	6.05	0.158	58.88	110.00	20.00	210.00	b.d.l.	4220.00	20.00	b.d.l.	b.d.l.	550.00	99.36	306.23
dy1306-4	S4-4			33.83	9.01	0.355	55.82	270.00	20.00	170.00	b.d.l.	5330.00	150.00	b.d.l.	b.d.l.	210.00	99.63	351.33
dy1306-4	S4-5			32.57	1.11	0.444	65.04	b.d.l.	130.00	310.00	b.d.l.	240.00	150.00	1300.00	1190.00	b.d.l.	99.50	240.33
dy1306-4	S4-6			32.55	3.41	1.831	62.77	30.00	b.d.l.	170.00	b.d.l.	40.00	b.d.l.	b.d.l.	250.00	520.00	100.66	268.93
dy1306-9	S9-1		Sp without dissolved pores or fissures	33.24	7.40	0.062	59.34	490.00	160.00	330.00	b.d.l.	2800.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.42	323.09
dy1306-9	S9-5			33.19	11.19	0.162	54.92	480.00	b.d.l.	b.d.l.	b.d.l.	760.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.59	383.88
dy1306-4b	S4b-1			33.02	5.31	0.022	61.33	b.d.l.	10.00	300.00	b.d.l.	2340.00	60.00	b.d.l.	b.d.l.	b.d.l.	99.94	293.71
dy1306-4b	S4b-2			32.87	7.46	0.345	59.25	200.00	b.d.l.	b.d.l.	b.d.l.	230.00	b.d.l.	b.d.l.	20.00	b.d.l.	99.97	323.96
dy1306-4b	S4b-3			33.02	8.64	0.128	58.10	470.00	120.00	90.00	b.d.l.	350.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.99	341.51
dy1306-4b	S4b-4			32.91	7.01	0.265	59.42	370.00	30.00	170.00	b.d.l.	3430.00	100.00	b.d.l.	b.d.l.	b.d.l.	100.01	317.91
dy1306-4b	S4b-5			32.88	6.53	0.404	60.04	b.d.l.	b.d.l.	310.00	b.d.l.	240.00	250.00	300.00	b.d.l.	b.d.l.	99.96	310.82
dy1306-4b	S4b-6			33.20	6.88	0.102	59.34	690.00	180.00	330.00	b.d.l.	2080.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.85	316.34
dy1306-4b	S4b-7			33.02	6.25	0.033	60.54	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1360.00	30.00	b.d.l.	b.d.l.	b.d.l.	99.98	306.57
	average			33.11	5.84	0.326	60.32	185.56	54.44	149.44	b.d.l.	1950.00	74.44	177.78	132.22	133.33		303.47
	mid-value			33.02	6.39	0.214	59.73	90.00	15.00	170.00	b.d.l.	1060.00	25.00	b.d.l.	b.d.l.	b.d.l.		
	min			32.52	1.11	0.022	54.92	b.d.l.	b.d.l.	b.d.l.	b.d.l.	40.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.		
	max			33.83	11.19	1.831	65.69	690.00	210.00	330.00	b.d.l.	5340.00	450.00	1300.00	1190.00	920.00		
dy1306-3	S3-5			33.44	8.78	0.000	56.46	10.00	b.d.l.	b.d.l.	b.d.l.	7190.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.40	
dy1306-4	S4-2			33.99	11.91	0.147	53.21	270.00	110.00	90.00	b.d.l.	60.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.31	
dy1306-9	S9-2			33.22	10.03	0.042	56.47	410.00	b.d.l.	b.d.l.	b.d.l.	260.00	60.00	b.d.l.	b.d.l.	b.d.l.	99.83	
dy1306-9	S9-3			33.27	12.50	0.894	52.28	610.00	b.d.l.	20.00	b.d.l.	3820.00	b.d.l.	b.d.l.	b.d.l.	20.00	99.39	
dy1306-9	S9-4			33.09	12.96	0.131	53.54	500.00	b.d.l.	590.00	b.d.l.	610.00	260.00	b.d.l.	b.d.l.	250.00	99.94	
dy1306-11	S11-1			33.60	12.59	2.243	51.18	580.00	120.00	b.d.l.	140.00	3130.00	b.d.l.	b.d.l.	b.d.l.	230.00	100.03	
dy1306-11	S11-2			33.24	14.38	0.958	50.90	1240.00	b.d.l.	b.d.l.	b.d.l.	460.00	20.00	b.d.l.	b.d.l.	490.00	99.69	
dy1306-11	S11-3			33.67	15.59	0.110	50.09	1300.00	b.d.l.	b.d.l.	40.00	500.00	b.d.l.	170.00	b.d.l.	b.d.l.	99.65	
dy1306-11	S11-4			33.39	14.48	0.005	51.58	1690.00	b.d.l.	b.d.l.	80.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	400.00	99.66	
	average			33.43	12.58	0.503	52.86	734.44	25.56	77.78	28.89	1781.11	37.78	18.89	b.d.l.	154.44		
	mid-value			33.39	12.59	0.131	52.28	580.00	b.d.l.	b.d.l.	b.d.l.	500.00	b.d.l.	b.d.l.	b.d.l.	20.00		
	min			33.09	8.78	0.000	50.09	10.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		
	max			33.99	15.59	2.243	56.47	1690.00	120.00	590.00	140.00	7190.00	260.00	170.00	b.d.l.	490.00		
dy1306-2	S2-1			33.63	9.36	0.057	56.07	370.00	120.00	b.d.l.	30.00	3200.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.48	355.54
dy1306-2	S2-4			33.52	7.78	0.039	58.68	170.00	b.d.l.	b.d.l.	b.d.l.	820.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.11	329.12
dy1306-1	S1-1			33.23	1.16	0.005	64.98	140.00	b.d.l.	20.00	50.00	200.00	390.00	b.d.l.	b.d.l.	b.d.l.	99.46	240.89
dy1306-1	S1-2			34.00	7.11	0.420	57.64	250.00	90.00	b.d.l.	b.d.l.	1040.00	b.d.l.	b.d.l.	b.d.l.	60.00	99.31	322.10
dy1306-1	S1-4			33.11	1.57	0.278	63.82	10.00	b.d.l.	b.d.l.	b.d.l.	610.00	100.00	4110.00	650.00	330.00	99.37	246.11
dy1306-1	S1-5			34.68	1.97	0.012	62.84	90.00	40.00	b.d.l.	b.d.l.	200.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.54	251.26
dy1306-1	S1-6			33.53	2.19	0.036	63.36	b.d.l.	b.d.l.	b.d.l.	b.d.l.	490.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.16	253.69
dy1306-8	S8-1			33.31	2.06	0.185	64.28	150.00	b.d.l.	b.d.l.	b.d.l.	150.00	b.d.l.	170.00	6670.00	40.00	100.56	251.80
dy1306-8	S8-2			33.19	4.38	0.105	61.85	310.00	b.d.l.	b.d.l.	b.d.l.	700.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.64	281.67
dy1306-8	S8-4			33.50	5.41	0.000	60.26	b.d.l.	b.d.l.	b.d.l.	b.d.l.	410.00	330.00	b.d.l.	b.d.l.	110.00	99.26	296.24
dy1306-8	S8-5			33.61	1.78	0.324	63.29	310.00	10.00	580.00	40.00	160.00	90.00	b.d.l.	b.d.l.	b.d.l.	99.12	248.81
dy1306-8	S8-6			33.60	2.00	0.050	63.68	b.d.l.	10.00	b.d.l.	b.d.l.	280.00	b.d.l.	b.d.l.	b.d.l.	60.00	99.36	251.34
dy1306-8	S8-7			33.27	3.31	0.000	62.71	b.d.l.	60.00	160.00	b.d.l.	660.00	20.00	b.d.l.	b.d.l.	60.00	99.39	267.80
dy1510-61	S61-1			33.23	2.05	0.155	64.26	180.00	b.d.l.	10.00	20.00	120.00	140.00	b.d.l.	b.d.l.	b.d.l.	99.74	289.56
dy1510-61	S61-2			33.44	3.13	0.076	63.42	110.00	b.d.l.	b.d.l.	b.d.l.	110.00	100.00	b.d.l.	b.d.l.	b.d.l.	100.10	305.00
dy1510-61	S61-3			33.28	3.61	0.035	62.84	140.00	20.00	b.d.l.	b.d.l.	220.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.81	312.17
dy1510-61	S61-4			33.19	4.39	0.103	62.22	260.00	b.d.l.	b.d.l.	b.d.l.	170.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.95	323.76
dy1510-61	S61-5			33.61	3.84	0.024	62.31	330.00	10.00	380.00	10.00	160.00	40.00	b.d.l.	b.d.l.	b.d.l.	99.88	315.86
dy1510-61	S61-6			33.20	3.03	0.023	63.68	230.00	10.00	b.d.l.	b.d.l.	280.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.98	303.44
	average			33.48	3.69	0.101	62.22	160.53	19.47	60.53	7.89	525.26	63.68	225.26	385.26	34.74	99.64	286.64
	mid-value			33.44	3.13	0.050	62.84	150.00	b.d.l.	b.d.l.	b.d.l.	280.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.54	
	min			33.11	1.16	0.000	56.07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	110.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.		
	max			34.68	9.36	0.420	64.98	370.00	120.00	580.00	50.00	3200.00	390.00	4110.00	6670.00	330.00		
dy1306-2	S2-2			33.31	9.67	0.230	55.28	b.d.l.	170.00	b.d.l.	b.d.l.	5870.00	280.00	b.d.l.	b.d.l.	b.d.l.	99.12	
dy1306-2	S2-3			33.83	8.67	0.335	56.57	90.00	40.00	b.d.l.	b.d.l.	2590.00	140.00	b.d.l.	b.d.l.	b.d.l.	99.69	
dy1306-1	S1-3			33.40	9.44	1.952	54.76	440.00	b.d.l.	b.d.l.	b.d.l.	3250.00	270.00	b.d.l.	b.d.l.	b.d.l.	99.95	
dy1306-8	S8-3			33.92	7.87	0.691	56.36	70.00	b.d.l.	b.d.l.	b.d.l.	2760.00	160.00	b.d.l.	b.d.l.	130.00	99.14	
	average			33.61	8.91	0.802	55.74	150.00	52.50	b.d.l.	b.d.l.	3617.50	212.50	b.d.l.	b.d.l.	32.50		
	mid-value			33.61	8.91	0.691	55.74	90.00	40.00	b.d.l.	b.d.l.	3250.00	212.50	b.d.l.	b.d.l.	b.d.l.		
	min			33.31	7.87	0.230	54.76	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2590.00	140.00	b.d.l.	b.d.l.	b.d.l.		
	max			33.92	9.67	1.952	56.57	440.00	170.00	b.d.l.	b.d.l.	5870.00	280.00	b.d.l.	b.d.l.	130.00		

Note: "b. d. l."=below detection limit.

Table 2 Chemistry of sphalerite containing chalcopyrite inclusions

Sample	Dot	Field	Area	EPMA results					Average bulk compositions of Ccp-diseased sphalerite		
				S (wt%)	Fe (wt%)	Cu (wt%)	Zn (wt%)	Total	CuS (mol.%)	FeS (mol.%)	ZnS (mol.%)
dy1306-3	d1	Longqi	Adjacent to Ccp inclusions	32.78	7.35	0.020	59.51	99.66	4.22	6.98	88.67
dy1306-3	d2			32.85	8.03	0.440	58.47	99.79			
dy1306-3	d3			33.52	8.33	0.390	57.66	99.90			
dy1306-3	d4		Free of Ccp inclusion	32.53	7.49	0.400	59.30	99.72			
dy1306-3	d5			33.45	7.63	0.360	58.44	99.88			
dy1306-4	q1		Adjacent to Ccp inclusions	33.46	7.45	0.020	59.00	99.93			
dy1306-4	q2			32.85	7.63	0.440	58.97	99.89			
dy1306-4	q3		Free of Ccp inclusion	33.52	8.33	0.390	57.76	100.00			
dy1306-4	q4			32.53	7.89	0.400	59.12	99.94			
dy1306-4	q5			32.45	6.83	0.360	60.28	99.92			
dy1306-2	n1	Duanqiao	Adjacent to Ccp inclusions	32.91	3.03	0.080	64.01	100.03	3.18	4.33	92.04
dy1306-2	n2			33.31	2.98	0.187	63.19	99.66			
dy1306-2	n3			33.04	2.05	0.079	64.66	99.83			
dy1306-2	n4		Free of Ccp inclusion	33.50	2.79	0.050	63.08	99.42			
dy1306-2	n5			32.61	4.97	0.001	62.38	99.96			
dy1306-2	n6		Adjacent to Ccp inclusions	33.15	5.06	0.020	61.38	99.61			
dy1306-8	t1			32.99	3.03	0.080	63.51	99.61			
dy1306-8	t2			33.31	1.98	0.187	64.29	99.76			
dy1306-8	t3		Free of Ccp inclusion	33.04	2.05	0.079	64.66	99.83			
dy1306-8	t4			33.22	6.74	0.000	60.12	100.08			
dy1306-8	t5			33.01	6.90	0.010	60.06	99.98			
dy1306-8	t6			33.15	5.06	0.020	61.78	100.01			

Note: an example of the test locations is shown in Fig. 4i. The average bulk compositions of Ccp-diseased sphalerite are calculated based on the chemical analysis by the ICP-MS.

Longqi field, euhedral pyrite tends to have higher Cu contents than colloform or anhedral pyrite (Py I: avg. 26.67 ppm, Py II: avg. 445 ppm, and Py III: avg. 179.29 ppm). With respect to the Duanqiao field, the average Cu contents in sub- or euhedral pyrite (Py I': avg. 849.23 ppm) are slightly lower than those of anhedral pyrite (Py II': avg. 1191 ppm; Table 3).

The zinc contents in pyrite vary significantly (from below the detection limit to over 7 wt%; Table 3), but ultrahigh Zn contents generally occur in Py II' from the Duanqiao field (0–7.25 wt%, avg. 2.17 wt%) when compared with the other samples (Py I: avg. 1495 ppm, Py II: avg. 2008.5 ppm, Py III: avg. 1849.29 ppm, and Py I': avg. 1964.62 ppm).

Cobalt is enriched in pyrite from both fields (Table 3). In the Longqi field, the average Co contents in Py I, Py II, and Py III are 876.67, 4726.67, and 2060 ppm, respectively. As for the Duanqiao field, the average Co contents in Py I' and Py II' are 953.38 and 872.22, ppm respectively.

The Cd contents of most pyrite from the two fields are in the range of tens to hundreds of ppm, but several abnormally high Cd contents occur in Py I from the Longqi field. The As contents of the pyrite from both fields are several hundreds to approximately 2000 ppm. Nickel, Se, and Sb are poor in pyrite from the two fields. Pyrite from the Longqi field shows no enrichment in lead, but pyrite from the Duanqiao field has abnormally high contents of Pb locally, especially for Py II' (up to 5320 ppm). The silver and gold contents of several samples

from the two fields can reach several hundreds of ppm (Table 3).

4.2.3 Chalcopyrite and isocubanite

Chalcopyrite from both of the two fields has similar S, Fe, and Cu contents (Table 4). Zinc is the dominant minor element in chalcopyrite compared with other minor and trace elements (Table 4), and the Zn concentrations of the chalcopyrite from the Longqi field are higher than that from the Duanqiao field (Ccp I: avg. 3226.67 ppm, Ccp II: avg. 9280 ppm, Ccp I': avg. 848 ppm, Ccp II' (inclusions): avg. 1098 ppm, and Ccp II' (fine-grained chalcopyrite): avg. 1795 ppm; Table 4). The Co contents of chalcopyrite from the two study areas are several hundreds to about 1000 ppm. Arsenic and cadmium chalcopyrite contents are no more than a few hundred ppm, but no regular variations exist between the two areas. Nickel, Se, Sb, and Pb are not abundant in chalcopyrite in this study. Silver concentrations are generally several hundreds of ppm. The gold contents of several particular chalcopyrite crystals from the two fields are tens to hundreds of ppm. The detected element content difference between the coarse-grained chalcopyrite and the fine-grained chalcopyrite is not very prominent, except for zinc. The fine-grained chalcopyrite (including the Ccp inclusions) from both areas shows relatively higher concentrations of Zn than that of the coarse-grained chalcopyrite (Table 4).

Isocubanite is only observed in the Longqi field (Table 4). The S concentrations of the isocubanite range from 34.97 to 35.91 wt%. The Fe concentrations are 35.24–

Table 3 Chemical composition of pyrite by EPMA analysis

Sample	Dot	Field	Mineral	S (wt.%)	Fe (wt.%)	Cu (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Sb (ppm)	Pb (ppm)	Ag (ppm)	Au (ppm)	Total
dy1306-3b	P3b-1			53.20	45.74	30.00	500.00	780.00	14.56	650.00	0.00	330.00	0.00	50.00	30.00	0.00	99.18
dy1306-3b	P3b-2			53.57	45.20	10.00	2690.00	880.00	21.20	330.00	0.00	3250.00	100.00	40.00	170.00	40.00	99.52
dy1306-4b	P4b-1			53.14	44.62	100.00	150.00	680.00	0.00	420.00	220.00	110.00	0.00	20.00	20.00	0.00	97.94
dy1306-11	P11-4			52.83	46.80	20.00	640.00	350.00	0.00	160.00	0.00	50.00	50.00	10.00	0.00	0.00	99.76
dy1306-11b	P11b-1			52.96	45.99	0.00	810.00	470.00	15.64	210.00	10.00	660.00	0.00	100.00	40.00	20.00	99.18
dy1306-11b	P11b-2			52.65	46.07	0.00	4180.00	2100.00	0.00	340.00	0.00	5320.00	0.00	370.00	20.00	0.00	99.96
average				53.06	45.74	26.67	1495.00	876.67	8.57	351.67	38.33	1620.00	25.00	98.33	46.67	10.00	
mid-value				53.05	45.87	15.00	725.00	730.00	7.28	335.00	0.00	495.00	0.00	45.00	25.00	0.00	
min				52.65	44.62	0.00	150.00	350.00	0.00	160.00	0.00	50.00	0.00	10.00	0.00	0.00	
max				53.57	46.80	100.00	4180.00	2100.00	21.20	650.00	220.00	5320.00	100.00	370.00	170.00	40.00	
dy1306-4b	P4b-3			53.32	45.75	470.00	2180.00	5790.00	0.00	770.00	20.00	350.00	0.00	0.00	70.00	650.00	100.10
dy1306-5b	P4b-2			53.67	45.38	870.00	890.00	6800.00	0.00	430.00	0.00	20.00	80.00	20.00	330.00	0.00	100.00
dy1306-9	P9-4			53.34	44.79	1200.00	2001.00	4800.00	30.04	250.00	10.00	0.00	0.00	100.00	30.00	0.00	98.97
dy1306-9	P9-5			52.39	46.83	20.00	3350.00	5620.00	24.56	160.00	0.00	100.00	60.00	40.00	170.00	0.00	100.18
dy1306-9b	P9b-1			52.86	45.84	60.00	2230.00	2140.00	0.00	260.00	0.00	0.00	0.00	60.00	220.00	0.00	99.19
dy1306-11	P11-3			52.87	46.02	50.00	1400.00	3210.00	0.00	330.00	0.00	0.00	0.00	90.00	140.00	50.00	99.42
average				53.08	45.77	445.00	2008.50	4726.67	9.10	366.67	5.00	78.33	23.33	51.67	160.00	116.67	
mid-value				53.10	45.80	265.00	2090.50	5210.00	0.00	295.00	0.00	10.00	0.00	50.00	155.00	0.00	
min				52.39	44.79	20.00	890.00	2140.00	0.00	160.00	0.00	0.00	0.00	0.00	30.00	0.00	
max				53.67	46.83	1200.00	3350.00	6800.00	30.04	770.00	20.00	350.00	80.00	100.00	330.00	650.00	
dy1306-3	P3-1			53.19	45.72	210.00	1250.00	1100.00	0.00	820.00	50.00	150.00	0.00	0.00	0.00	750.00	99.35
dy1306-3	P3-2			53.58	45.00	310.00	3810.00	1020.00	0.00	130.00	0.00	160.00	0.00	0.00	190.00	0.00	99.14
dy1306-3	P3-3			53.00	44.51	620.00	19080.00	540.00	0.00	120.00	0.00	100.00	220.00	0.00	40.00	90.00	99.59
dy1306-3	P3-4			52.97	46.70	330.00	860.00	650.00	0.00	60.00	120.00	0.00	0.00	90.00	100.00	0.00	99.90
dy1306-4	P4-1			52.93	45.98	210.00	890.00	6020.00	0.00	210.00	0.00	100.00	0.00	0.00	350.00	300.00	99.71
dy1306-4	P4-2			52.82	46.06	0.00	0.00	1070.00	0.00	300.00	10.00	0.00	0.00	0.00	0.00	0.00	99.02
dy1306-4	P4-3			52.97	46.11	310.00	0.00	830.00	0.00	0.00	0.00	300.00	90.00	0.00	0.00	370.00	99.27
dy1306-4	P4-4			53.28	45.92	110.00	0.00	1620.00	0.00	0.00	260.00	0.00	0.00	0.00	0.00	0.00	99.39
dy1306-4	P4-5			53.25	45.29	0.00	0.00	5360.00	30.00	180.00	0.00	90.00	0.00	0.00	0.00	160.00	99.12
dy1306-9	P9-1			52.81	46.34	0.00	0.00	1050.00	30.00	180.00	0.00	120.00	0.00	30.00	0.00	0.00	99.29
dy1306-9	P9-2			53.19	46.28	210.00	0.00	2450.00	60.00	180.00	180.00	360.00	330.00	0.00	0.00	0.00	99.85
dy1306-9	P9-3			52.95	46.36	160.00	0.00	4490.00	0.00	570.00	250.00	100.00	0.00	0.00	0.00	20.00	99.87
dy1306-11	P11-1			53.16	46.21	40.00	0.00	1250.00	0.00	220.00	0.00	280.00	380.00	690.00	0.00	0.00	99.65
dy1306-11	P11-2			53.19	46.99	0.00	0.00	1390.00	10.00	70.00	0.00	200.00	200.00	0.00	0.00	70.00	100.37
average				53.09	45.96	179.29	1849.29	2060.00	9.29	217.14	62.14	140.00	87.14	57.86	48.57	125.71	
mid-value				53.08	46.09	185.00	0.00	1175.00	0.00	180.00	0.00	110.00	0.00	0.00	0.00	10.00	
min				52.81	44.51	0.00	0.00	540.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
max				53.58	46.99	620.00	19080.00	6020.00	60.00	820.00	260.00	360.00	380.00	690.00	350.00	750.00	
dy1306-2	P2-1			52.88	46.28	0.00	0.00	890.00	0.00	190.00	70.00	0.00	0.00	0.00	100.00	0.00	99.29
dy1306-2	P2-2			52.99	45.94	30.00	0.00	950.00	110.00	0.00	0.00	60.00	0.00	0.00	0.00	0.00	99.04
dy1306-8	P8-1			53.14	46.06	0.00	0.00	1000.00	0.00	520.00	0.00	10.00	0.00	0.00	0.00	0.00	99.35
dy1306-8	P8-2			53.11	46.46	0.00	0.00	1100.00	0.00	0.00	40.00	150.00	170.00	0.00	0.00	150.00	99.73
dy1510-61	P61-1			53.23	46.32	1520.00	0.00	700.00	120.00	660.00	0.00	70.00	0.00	80.00	170.00	910.00	99.97
dy1510-61	P61-2			52.92	46.68	1960.00	110.00	930.00	0.00	130.00	0.00	10.00	0.00	0.00	50.00	510.00	99.97
dy1510-61	P1-1			52.97	44.69	1400.00	19110.00	1360.00	0.00	200.00	0.00	280.00	90.00	1520.00	50.00	110.00	100.08
dy1306-8	P8-3			53.19	46.29	40.00	380.00	1090.00	50.00	780.00	0.00	0.00	0.00	0.00	0.00	230.00	99.73
dy1306-8	P8-4			52.98	46.41	0.00	380.00	840.00	0.00	360.00	0.00	230.00	0.00	1870.00	220.00	180.00	99.80
dy1306-2	P2-3			53.25	46.33	170.00	640.00	740.00	0.00	2110.00	0.00	490.00	0.00	760.00	0.00	0.00	100.07
dy1510-61	P61-3			52.96	46.26	1140.00	800.00	980.00	0.00	1300.00	10.00	100.00	0.00	1240.00	0.00	30.00	99.78
dy1510-61	P61-4			53.01	45.68	1390.00	1410.00	960.00	110.00	110.00	0.00	0.00	230.00	0.00	0.00	0.00	99.12
dy1510-61	P61-5			53.36	44.99	3390.00	2710.00	1010.00	0.00	470.00	0.00	330.00	0.00	0.00	0.00	240.00	99.16
average				53.08	46.03	849.23	1964.62	965.38	30.00	525.38	9.23	133.08	37.69	420.77	45.38	181.54	
mid-value				53.01	46.28	170.00	380.00	960.00	0.00	360.00	0.00	70.00	0.00	0.00	0.00	110.00	
min				52.88	44.69	0.00	0.00	700.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
max				53.36	46.68	3390.00	19110.00	1360.00	120.00	2110.00	70.00	490.00	230.00	1870.00	220.00	910.00	
dy1510-61	P61-6			52.90	45.55	2840.00	3060.00	1400.00	0.00	0.00	0.00	360.00	0.00	650.00	90.00	410.00	99.34
dy1510-61	P61-7			52.92	45.70	60.00	9830.00	420.00	0.00	440.00	0.00	0.00	0.00	0.00	0.00	30.00	99.70
dy1510-61	P61-8			53.29	44.42	1710.00	12620.00	1030.00	0.00	750.00	0.00	0.00	0.00	5320.00	270.00	0.00	99.88
dy1306-2	P2-4			52.97	45.91	830.00	14450.00	1030.00	20.00	700.00	0.00	170.00	0.00	2470.00	260.00	490.00	100.93
dy1306-2	P2-5			53.31	44.85	480.00	22030.00	1390.00	0.00	0.00	0.00	80.00	0.00	790.00	190.00	0.00	100.66
dy1306-1	P1-2			52.87	43.52	940.00	25890.00	760.00	0.00	120.00	0.00	110.00	80.00	1970.00	0.00	0.00	99.38
dy1306-1	P1-3			52.97	42.85	1840.00	35280.00	610.00	0.00	70.00	0.00	110.00	0.00	1010.00	100.00	510.00	99.78
dy1306-1	P1-4			53.40	39.84	450.00	72540.00	470.00	0.00	20.00	0.00	390.00	0.00	3040.00	100.00	390.00	100.98
dy1306-1	P1-5			53.26	45.75	1570.00	0.00	740.00	0.00	500.00	0.00	0.00	0.00	810.00	340.00	650.00	99.47
average				53.10	44.27	1191.11	21744.44	872.22	2.22	288.89	0.00	135.56	8.89	1784.44	150.00	275.56	
mid-value				52.97	44.85	940.00	14450.00	760.00	0.00	120.00	0.00	110.00	0.00	1010.00	100.00	390.00	
min				52.87	39.84	60.00	0.00	420.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
max				53.40	45.91	2840.00	72540.00	1400.00	20.00	750.00	0.00	390.00	80.00	5320.00	340.00	650.00	

Tabla 4 Chemical composition of chalcopyrite and isocubanite by EPMA analysis

sample	Dot	Field	Mineral	S (wt.%)	Fe (wt.%)	Cu (wt.%)	Zn (ppm)	Co (ppm)	Ni (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Sb (ppm)	Pb (ppm)	Ag (ppm)	Au (ppm)	Total
dy1306-4	C4-5			34.91	31.86	32.04	1180.00	740.00	210.00	b.d.l.	b.d.l.	40.00	250.00	b.d.l.	170.00	b.d.l.	99.07
dy1306-9	C9-1			34.27	30.70	34.53	3430.00	650.00	b.d.l.	60.00	b.d.l.	40.00	b.d.l.	b.d.l.	220.00	b.d.l.	99.94
dy1306-9	C9-2			34.45	30.85	34.18	370.00	960.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	220.00	60.00	170.00	99.66
dy1306-9	C9-3			34.37	30.44	34.35	3420.00	1030.00	b.d.l.	b.d.l.	100.00	b.d.l.	b.d.l.	320.00	200.00	120.00	99.68
dy1306-9	C9-4			34.49	30.79	34.17	5570.00	790.00	b.d.l.	110.00	b.d.l.	50.00	b.d.l.	b.d.l.	330.00	b.d.l.	100.14
dy1306-9	C9-5			34.51	30.80	34.31	4150.00	900.00	b.d.l.	110.00	b.d.l.	350.00	b.d.l.	160.00	260.00	b.d.l.	100.21
dy1306-11	C11-1			34.19	30.78	34.40	2390.00	670.00	b.d.l.	440.00	b.d.l.	200.00	b.d.l.	b.d.l.	450.00	40.00	99.79
dy1306-11	C11-2			34.48	30.65	34.18	4290.00	1270.00	b.d.l.	b.d.l.	b.d.l.	330.00	b.d.l.	b.d.l.	340.00	200.00	99.95
dy1306-11	C11-3			34.26	30.54	33.59	4240.00	570.00	b.d.l.	920.00	b.d.l.	170.00	110.00	b.d.l.	160.00	b.d.l.	99.01
average				34.44	30.82	33.97	3226.67	842.22	23.33	182.22	11.11	131.11	40.00	77.78	243.33	58.89	
mid-value				34.44	30.79	34.18	3425.00	816.11	b.d.l.	85.00	b.d.l.	90.56	b.d.l.	b.d.l.	231.67	20.00	
min				34.19	30.44	32.04	370.00	570.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	60.00	b.d.l.	
max				34.91	31.86	34.53	5570.00	1270.00	210.00	920.00	100.00	350.00	250.00	320.00	450.00	200.00	
dy1306-11	C11-4			34.16	30.84	33.47	7310.00	740.00	b.d.l.	500.00	b.d.l.	340.00	70.00	b.d.l.	290.00	b.d.l.	99.40
dy1306-11	C11-5			34.67	29.20	32.24	29500.00	1210.00	b.d.l.	b.d.l.	b.d.l.	120.00	b.d.l.	b.d.l.	110.00	480.00	99.25
1310-63-Q4-02				34.84	30.70	34.54	2130.00	700.00	b.d.l.	660.00	b.d.l.	50.00	50.00	b.d.l.	300.00	b.d.l.	100.58
1310-58-Q1-01				33.59	29.97	35.04	2180.00	450.00	b.d.l.	190.00	b.d.l.	110.00	200.00	30.00	730.00	750.00	99.06
1310-58-Q6-01				34.32	30.50	34.61	7540.00	590.00	b.d.l.	60.00	b.d.l.	70.00	b.d.l.	b.d.l.	1380.00	b.d.l.	100.40
1310-63-Q2-02				33.80	30.86	34.35	7190.00	500.00	b.d.l.	b.d.l.	b.d.l.	280.00	b.d.l.	b.d.l.	20.00	150.00	99.82
1310-63-Q1-02				34.77	30.50	33.90	8010.00	390.00	b.d.l.	b.d.l.	b.d.l.	90.00	b.d.l.	b.d.l.	80.00	300.00	100.06
average				34.31	30.37	34.02	9280.00	654.29	b.d.l.	201.43	b.d.l.	151.43	45.71	4.29	415.71	240.00	
mid-value				34.32	30.50	34.35	7310.00	590.00	b.d.l.	60.00	b.d.l.	110.00	b.d.l.	b.d.l.	290.00	150.00	
min				33.59	29.20	32.24	2180.00	390.00	b.d.l.	b.d.l.	b.d.l.	50.00	b.d.l.	b.d.l.	20.00	b.d.l.	
max				34.84	30.86	35.04	29500.00	1210.00	b.d.l.	660.00	b.d.l.	340.00	200.00	30.00	1380.00	750.00	
dy1306-3	C3-1			35.81	40.86	21.85	8060.00	840.00	b.d.l.	100.00	90.00	b.d.l.	b.d.l.	b.d.l.	320.00	b.d.l.	99.46
dy1306-3	C3-2			35.55	35.24	27.66	4570.00	790.00	b.d.l.	310.00	b.d.l.	10.00	100.00	30.00	370.00	150.00	99.09
dy1306-3	C3-3			35.91	42.04	21.40	6310.00	760.00	b.d.l.	410.00	b.d.l.	250.00	b.d.l.	280.00	360.00	b.d.l.	100.19
dy1306-4	C4-1			35.10	38.88	25.15	1870.00	2760.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	290.00	b.d.l.	190.00	150.00	99.66
dy1306-4	C4-2			35.31	37.97	25.38	580.00	1670.00	b.d.l.	10.00	b.d.l.	b.d.l.	400.00	240.00	190.00	98.97	
dy1306-4	C4-3			35.44	37.90	24.65	720.00	1320.00	b.d.l.	560.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	240.00	570.00	98.34
dy1306-4	C4-4			34.97	39.28	24.92	550.00	1590.00	b.d.l.	890.00	b.d.l.	80.00	60.00	160.00	130.00	b.d.l.	99.51
average				35.44	38.88	24.43	3237.14	1390.00	b.d.l.	325.71	12.86	48.57	64.29	124.29	264.29	151.43	
mid-value				35.44	38.88	24.92	1870.00	1320.00	b.d.l.	310.00	b.d.l.	b.d.l.	b.d.l.	30.00	240.00	150.00	
min				34.97	35.24	21.40	550.00	760.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	130.00	b.d.l.	
max				35.91	42.04	27.66	8060.00	2760.00	b.d.l.	890.00	90.00	250.00	290.00	400.00	370.00	570.00	
dy1510-61	C61-1			34.93	30.31	34.38	b.d.l.	550.00	b.d.l.	310.00	80.00	70.00	10.00	b.d.l.	310.00	b.d.l.	99.75
dy1306-2	C2-1			35.58	30.26	33.58	900.00	600.00	40.00	70.00	130.00	210.00	b.d.l.	580.00	490.00	99.72	
dy1306-1	C1-1			35.02	30.59	33.27	990.00	670.00	b.d.l.	490.00	b.d.l.	b.d.l.	b.d.l.	470.00	b.d.l.	b.d.l.	99.13
dy1306-1	C1-2			35.09	30.10	33.80	1030.00	790.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.18
dy1510-61	C61-2			35.10	29.98	34.16	1320.00	460.00	b.d.l.	850.00	b.d.l.	100.00	80.00	b.d.l.	b.d.l.	440.00	99.56
average				35.14	30.25	33.84	848.00	614.00	8.00	338.00	30.00	60.00	60.00	94.00	178.00	186.00	
mid-value				35.09	30.26	33.80	990.00	600.00	b.d.l.	310.00	b.d.l.	70.00	10.00	b.d.l.	b.d.l.	b.d.l.	
min				34.93	29.98	33.27	b.d.l.	460.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
max				35.58	30.59	34.38	1320.00	790.00	40.00	850.00	80.00	130.00	210.00	470.00	580.00	490.00	
dy1306-2	C2-2			34.89	31.08	33.12	1570.00	520.00	60.00	b.d.l.	b.d.l.	360.00	190.00	240.00	560.00	50.00	99.44
dy1510-61	C61-3			35.44	30.41	34.44	1600.00	630.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	110.00	100.52
dy1306-1	C1-3			35.36	30.16	34.28	1750.00	780.00	b.d.l.	b.d.l.	b.d.l.	250.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.08
dy1306-2	C2-3			34.94	29.86	34.45	1880.00	600.00	b.d.l.	b.d.l.	100.00	160.00	b.d.l.	b.d.l.	690.00	130.00	99.61
dy1306-2	C2-4			35.14	30.55	33.54	1950.00	870.00	30.00	b.d.l.	b.d.l.	180.00	100.00	b.d.l.	510.00	360.00	99.63
dy1306-2	C2-5			34.62	30.66	33.84	2020.00	350.00	80.00	460.00	b.d.l.	b.d.l.	190.00	b.d.l.	650.00	b.d.l.	99.50
average				35.06	30.45	33.95	1795.00	625.00	28.33	76.67	16.67	158.33	80.00	40.00	401.67	108.33	
mid-value				35.04	30.48	34.06	1815.00	615.00	15.00	b.d.l.	b.d.l.	170.00	50.00	b.d.l.	535.00	80.00	
min				34.62	29.86	33.12	1570.00	350.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
max				35.44	31.08	34.45	2020.00	870.00	80.00	460.00	100.00	360.00	190.00	240.00	690.00	360.00	
1310-59-Q2-01				34.08	31.13	34.81	360.00	760.00	b.d.l.	b.d.l.	b.d.l.	10.00	180.00	b.d.l.	150.00	260.00	100.19
1310-59-Q3-01				34.22	31.30	35.10	860.00	540.00	b.d.l.	360.00	b.d.l.	b.d.l.	350.00	b.d.l.	b.d.l.	b.d.l.	100.84
1310-59-Q1-01				34.14	31.11	34.71	1180.00	510.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	110.00	b.d.l.	100.00	70.00	100.16
1310-58-Q5-01				34.47	30.80	34.52	1710.00	610.00	b.d.l.	b.d.l.	b.d.l.	60.00	b.d.l.	b.d.l.	400.00	170.00	100.09
1310-58-Q2-01				34.05	31.60	34.26	1380.00	620.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	780.00	60.00	100.20
average				34.19	31.19	34.68	1098.00	608.00	b.d.l.	72.00	b.d.l.	14.00	128.00	b.d.l.	286.00	112.00	
mid-value				34.14	31.13	34.71	1180.00	610.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	110.00	b.d.l.	150.00	70.00	
min				34.05	30.80	34.26	360.00	510.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
max				34.47	31.60	35.10	1710.00	760.00	b.d.l.	360.00	b.d.l.	60.00	350.00	b.d.l.	780.00	260.00	

Note: "b. d. l."=below detection limit.

42.04 wt%. The Cu concentrations are 21.40–27.66 wt%. Zinc and cobalt tend to be enriched in the isocubanite (mean: 3237.14 ppm Zn and 1390 ppm Co). Isocubanite arsenic contents are commonly tens to hundreds of ppm.

However, elements such as Ni, Se, Cd, Sb, and Pb are relatively poor in the isocubanite. Silver concentrations range from 130 to 370 ppm. Several individual isocubanite crystals have Au contents of a few hundreds of ppm

(Table 4).

5 Discussion

5.1 Fine-grained chalcopyrite inclusion formation in sphalerite

The fine-grained chalcopyrite inclusions in sphalerite are found in both of the study areas, which forms the so-called “chalcopyrite disease” texture (Ccp disease; Fig. 4g and Fig. 6d–e). However, genetic interpretations for these chalcopyrite inclusions remain disputed (Bortnikov et al., 1991, 1992; Kojima, 1992). Generally, three possible mechanisms, including exsolution, coprecipitation, and replacement, have been proposed to explain the intimate association between chalcopyrite and sphalerite (Craig, 1973; Barton and Bethke, 1987; Bortnikov et al., 1991; Large, 1992; Halbach et al., 1993; Nagase et al., 1997; Solomon, 2001; Gu Lianxing et al., 2006; Wang et al., 2017). The exsolution mechanism is more suitable for sulfide ores that formed at high temperatures (>350°C), which does not commonly occur in modern seafloor sulfide deposits (Bortnikov et al., 1992; Nagase et al., 1997). In addition, previous experimental results revealed that the Cu solubility limit, in a solid solution determined in the Cu–Fe–Zn–S system, is very limited (<2.4 mol. % Cu at 300°C–500°C) (Kojima and Sugaki, 1987), but the bulk sphalerite Cu contents from both areas are above this limit (4.22 mol. % Cu for the Longqi field and 3.18 mol. % Cu for the Duanqiao field; Table 2). Thus, the chalcopyrite disease texture is attributed to coprecipitation or replacement rather than exsolution in this study.

Previous studies attempted to distinguish the formation mechanisms between coprecipitation and replacement by analyzing the Fe content of the host sphalerite, the distribution or habit of the chalcopyrite, and the anomalous anisotropy of the sphalerite (Barton and Bethke, 1987; Kojima et al., 1990, 1992; Bortnikov et al., 1991, 1992; Nagase et al., 1997). The diagnostic features of these two mechanisms are summarized in Table 5. Although these features are well developed under experimental conditions (Nagase et al., 1997), some of them are equivocal and may not apply to natural

processes.

In the Longqi field, the bleb-like chalcopyrite inclusions are randomly distributed throughout the host sphalerite cores, generally without cleavage or cracks (Fig. 4g and i). The host sphalerite is enriched in Fe, and the Fe contents are relatively constant (6.83–8.33 wt %; Table 2) regardless of the presence of chalcopyrite inclusions (Table 2). No anomalous heterogeneity is found. Although high Fe contents in primary sphalerite favor the replacement mechanism, Bortnikov et al. (1991) suggested that unmodified sphalerite compositions may exclude the replacement hypothesis. Since no obvious structural or chemical evidence for the replacement process, caused by the Cu-bearing fluid, exists, we prefer the coprecipitation mechanism for the formation of the chalcopyrite inclusions.

As for the Duanqiao field, the chain-like chalcopyrite inclusions are generally distributed around the dissolution pores or cracks in sphalerite (Fig. 6d–e). The chalcopyrite lamellas are arranged approximately in parallel, which indicates sphalerite cleavage and crystal planes (Fig. 6e). The sphalerite with chalcopyrite inclusions in the Duanqiao field has a moderate Fe concentration (1.98–6.9 wt %; Table 2). More importantly, the Fe contents of the host sphalerite measurably decrease in areas adjacent to the chalcopyrite inclusions (from over 5 to <2 wt % Fe; Table 2), which agrees with natural chalcopyrite disease texture characteristics reported by Barton and Bethke (1987) and Bortnikov et al. (1991), and the synthesized sample from Nagase et al. (1997). Thus, such features support the replacement mechanism hypothesis: the Cu-bearing fluid replaces the primary sphalerite and consumes the sphalerite’s iron. Chalcopyrite inclusions formed along penetrative areas in the sphalerite (Barton and Bethke, 1987; Kojima et al., 1990, 1992; Bortnikov et al., 1991, 1992; Nagase et al., 1997). The fine-grained chalcopyrite granules or veinlets along the sphalerite edges or fissures (Fig. 6a) also hint at the replacement processes by the Cu-bearing fluid. Thus, we suggest that these fine-grained chalcopyrite granules or veinlets and the diseased chalcopyrite inclusions formed from the same fluid. In conclusion, we prefer the replacement mechanism for

Table 5 Typical mineralogical features of chalcopyrite-sphalerite associations formed by replacement or coprecipitation

Mechanism of formation of chalcopyrite inclusions	Replacement	Coprecipitation
Fe content of the host sphalerite (wt%)	The primary sphalerite is rich in Fe (8 wt% Fe to 14 wt%); The diseased area of the host primary sphalerite shows a decrease in Fe content caused by replacement generally	The primary sphalerite is poor in Fe (0.5 Fe to 2 wt%); The Fe content of the host sphalerite keeps constant relatively
Distribution of chalcopyrite inclusions	Frequently developed along the cleavage, twinning and crack in host sphalerite or late chalcopyrite veinlet	Randomly distributed in the cores of the host sphalerite or along growth zones of the host sphalerite
Chalcopyrite habit	Lamellar, lens-like, ellipsoidal, chain-like	Triangular, dendritic and bleb-like
Anomalous anisotropy (perhaps)	The diseased areas sometimes show anomalous anisotropy under the reflected light	No anisotropy phenomenon
References	Barton and Bethke, 1987; Kojima and Sugaki, 1987; Mariko, 1988; Kojima et al., 1990, 1992; Bortnikov et al., 1991, 1992; Nagase et al., 1997	

chalcopyrite inclusion formation in sphalerite in the Duanqiao field, and the chalcopyrite inclusions precipitate after sphalerite formation.

5.2 Enrichment forms of trace metal elements

Determining the occurrence mode of a particular trace element in minerals is of great importance in genetic mineral deposit studies, exploration, and metallurgy (Huston et al., 1995; Fan Xianke et al., 2016; Xing Bo et al., 2016; Zhang et al., 2017). Previous studies have documented that trace elements within sulfide minerals may occur as (1) lattice substitution (i.e., in solid solution) and (2) micro- to nanoscale inclusions (Winderbaum et al., 2012; Franchini et al., 2015; Genna et al., 2015; Wohlgemuth-Ueberwasser et al., 2015; Cook et al., 2016; Gadd et al., 2016; Nie et al., 2017). In this study, only samples free of mineral inclusions were selected for EPMA analysis. To understand the possible effects of unobserved inclusions (sub-micron to nanoscale) very close to the local sample surface, we follow the analytical method proposed in Huston et al. (1995), taking into consideration factors such as crystal chemistry, element solubility, the presence or absence of important inclusions, and elemental concentration variations among samples. Additionally, some mid-ocean ridge hydrothermal field EPMA data were selected for comparison so as to better understand elemental trends during hydrothermal mineralization (Table 6 and 7). These selected fields are as follows: the TAG field in the Mid-Atlantic Ridge, the Wocan field in the Carlsberg Ridge of the northwest Indian Ocean, the Mt. Jourdanne field in the SWIR, the Karirei field, and the Edmond field in the Central Indian Ridge. Among these fields, only the Karirei field is hosted in an ultramafic environment, and the others are hosted in mafic (basaltic) environments.

5.2.1 Sphalerite

Iron is the dominant minor metal element in sphalerite from both areas (up to 15.9 wt% for the Longqi field and

up to 9.67 wt% for the Duanqiao field; Table 1). It is unavoidable that micro-zones adjacent to the sphalerite dissolution areas may be affected by late overprinting processes or involve some inclusions (e.g., pyrite; Fig. 4b). Nevertheless, undamaged sphalerite still has considerable Fe enrichment (avg. 5.84 wt% for the Longqi field and avg. 3.69 wt% for the Duanqiao field; Table 1). Generally, iron substitutes for Zn and easily incorporates itself into the sphalerite structure via a simple direct substitution of $\text{Fe}^{2+} \leftrightarrow \text{Zn}^{2+}$ (Cook et al., 2009; Lin et al., 2011; Belissont et al., 2014; Keith et al., 2014; Bonnet et al., 2016). The common Fe enrichment in sphalerite in this study supports the above substitution mechanism. Moreover, in this study, there is a good negative correlation between sphalerite Zn and Fe contents from both areas (Fig. 7a). Such phenomenon is also found in other hydrothermal fields at the mid-ocean ridges (Table 6, Fig. 7a). We suggest that the Fe variation in sphalerite is due to the changes in environmental conditions (Scott and Barnes, 1971; Scott, 1983; Keith et al., 2014).

The Cu contents in the sphalerite from the Longqi and Duanqiao fields are generally no more than 1 wt% (avg. 0.45 wt% for the Longqi field and avg. 0.28 wt% for the Duanqiao field; Fig. 7b). This content is within the general range of other hydrothermal systems at mid-ocean ridges (Fig. 7b). Conventionally, Cu^{2+} does not readily incorporate into the sphalerite structure in significant quantities (Craig, 1973). However, recent studies suggest that Cu^+ may be incorporated into sphalerite structure via a coupled substitution (Schorr and Wagner, 2005; Cook et al., 2009; George et al., 2016): $(\text{Cu}^+\text{In}^{3+}) \leftrightarrow (\text{Zn}^{2+}, \text{Fe}^{2+})$. This hypothesis needs further verification since In concentration data in sphalerite from mid-ocean ridge environments are very limited. Moreover, distinct sub-micron Cu-bearing phase inclusions in sphalerite, especially the extensive chalcopyrite disease particles (Cook et al., 2009; George et al., 2016), are important Cu contributors in sphalerite.

Sphalerites from both areas have considerable contents

Table 6 Major element concentrations of sphalerite from different hydrothermal fields of the mid-ocean ridge

Field	S (wt%)	Fe (wt%)	Cu (wt%)	Zn (wt%)	References
TAG	32.02–32.81	0.82–4.72	0.06–1.41	61.88–65.81	Keith et al., 2014
Karirei	31.88–33.36	4.2–12.57	0.12–5.88	46.71–61.37	Keith et al., 2014
Wocan	32.54–34.46	0.13–7.47	0.26–3.52	58.96–66.66	Wang et al., 2017
Mt. Jourdanne	Avg. 32.95	Avg. 9.26	Avg. 1.29	Avg. 52.36	Nayak et al., 2014
Edmond	28.93–42.12	2.06–27.23	0.01–0.53	31.86–66.97	Cao Hong, 2015

Table 7 Major element concentrations of pyrite from different hydrothermal fields of the mid-ocean ridge

Field	S (wt%)	Fe (wt%)	Cu (ppm)	Zn (ppm)	References
TAG	51.29–54.08	44.55–47.43	700–9500	600–13400	Tivey et al., 1995b
Edmond	50.8–53.65	43.15–47.03	200–9000	100–21800	Wang et al., 2012
	48.17–54.27	42.04–49.82	100–6900	100–23800	Cao Hong, 2015
Mt. Jourdanne	Avg. 51.53	Avg. 46.39	Avg. 766.67	Avg. 10600	Nayak et al., 2014
Wocan	49.55–52.55	45.31–47.23	100–1400	100–1400	Wang et al., 2017
Karirei	52.2–54.1	44.4–46.9	100–4000	2.58–1511	Keith et al., 2014

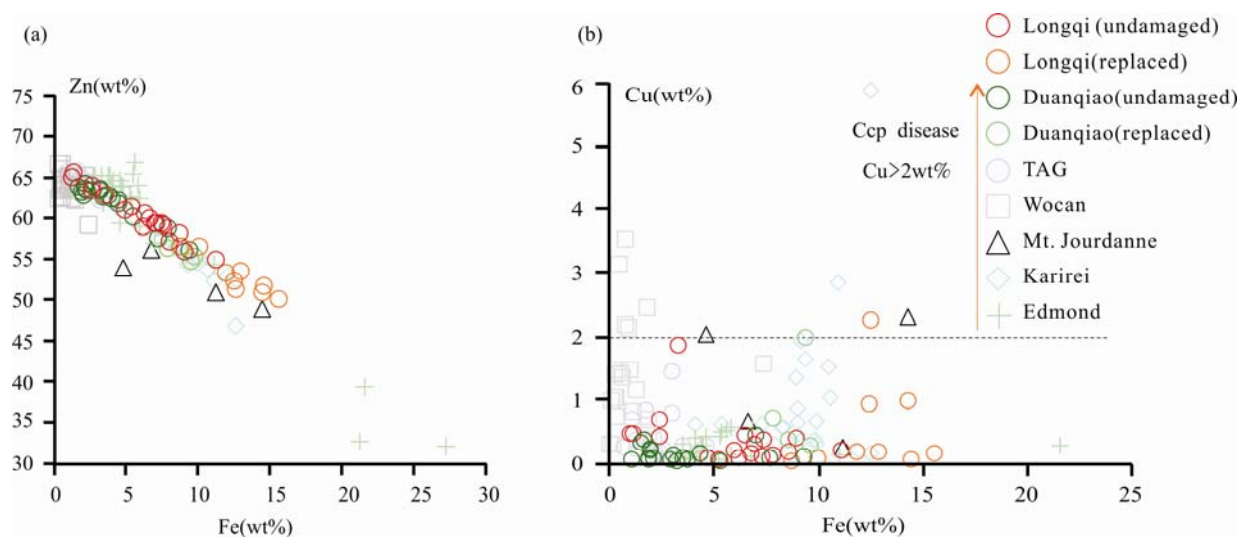


Fig. 7. Distributions of Zn, Fe and Cu in sphalerite from the Longqi field, the Duanqiao field and other mid-ocean hydrothermal fields.

(a), Zn-Fe correlation of different hydrothermal fields. (b), Plots of Cu vs. Fe (modified after Keith et al. (2014)).

of Co (up to 1690 ppm in the Longqi field and up to 440 ppm in the Duanqiao field). Since Co and Fe have similar ion sizes, sphalerite may also significantly incorporate Co^{2+} into its structure (George et al., 2016), which has been experimentally demonstrated in the CoS–ZnS solid-solution system (Becker and Lutz, 1978). Sphalerite micro-zones adjacent to dissolution areas from the Longqi field have abnormally higher Co and Fe contents (>1000 ppm Co; Table 1 and Fig. 8a), and such characteristics probably indicate the involvement of sub-micron distinct phases (e.g., pyrite). This inference is supported by extensive pyrite particle occurrence along dissolution pores or cracks in the sphalerites (Fig. 4d), where the pyrite

particles are highly enriched in Co (avg. 2060 ppm). For the undamaged sphalerite from the Longqi and Duanqiao fields, we suggest that the general Co contents resulted from lattice substitution (Fig. 8b).

As mentioned above, sphalerites are significantly enriched in Cd (up to 7190 ppm in the Longqi field and up to 5870 ppm in the Duanqiao field). Since Cd^{2+} also has an ionic radius similar to that of Zn^{2+} , significant amounts of Cd can be incorporated into the sphalerite structure via a direct substitution, $\text{Cd}^{2+} \leftrightarrow \text{Zn}^{2+}$ (Cook et al., 2009; Bonnet et al., 2016), especially at high temperatures (Chen et al., 1988; Cook, 2009; Monecke et al., 2016). In this study, sphalerites with the highest Cd contents from both

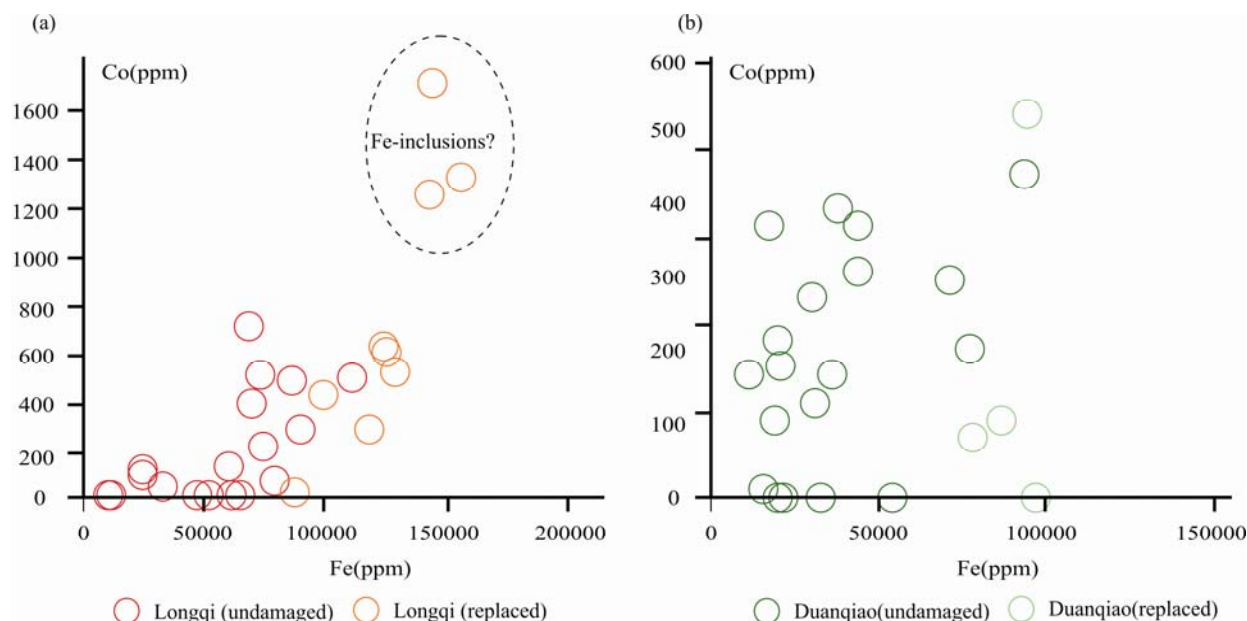


Fig. 8. Correlation of Co and Fe in sphalerite from the Longqi field and the Duanqiao field.

(a), Co-Fe correlation in sphalerite from the Longqi field. (b), Co-Fe correlation in sphalerite from the Duanqiao field.

areas occurred adjacent to the dissolution areas. Such non-constant contents may not be attributed to the involvement of tiny inclusions because no other minerals with such high contents of Cd have been identified. A possible explanation is that late Cd-bearing hydrothermal activities unevenly overprinted early sphalerite along fissures or pores, during which process more Cd was incorporated.

With respect to lead, silver, and gold, since the contents of most samples are close to or below the detection limit, it is difficult to infer their mode of occurrence in sphalerite. However, sub-micron inclusions of unidentified minerals probably cause the locally high contents of Pb, Ag, and Au in several samples.

5.2.2 Pyrite

The Fe and S contents of the pyrite from the two fields are in conformity with that of pyrite from other hydrothermal fields in mid-ocean ridge environments (Table 3 and Table 7). The variations of these concentrations imply variable amounts of trace elements substitution for Fe and S in pyrite (Fouquet et al., 1998; Friedl et al., 1995; Reich et al., 2013).

The Cu contents of pyrite from the two study fields vary significantly between different samples, ranging from below detection limit to approximately 3,000 ppm, and contents are relatively stable within individual samples (Table 3; Fig. 9a). As such, it is not easy to determine the mode of occurrence of Cu in pyrite. Previous studies have reported that the pyrite structure can accommodate Cu (Frenzel and Ottemann, 1967; Einaudi, 1968; Clark, 1970; Radcliffe and McSween, 1970; Pacevski et al., 2008), even reaching levels of several thousand ppm (Reich et al., 2013; Yuan et al., 2018). However, no notable negative correlations are found between Cu and Fe contents to support the $\text{Cu}^{2+} \leftrightarrow \text{Fe}^{2+}$ substitutional mechanism in our results and other mid-ocean hydrothermal fields (Fig. 9a). Most pyrites from the two fields have rough and porous surficial features (Fig. 4a and Fig. 6h), which are favorable for the involvement of (sub-)micron inclusions via sorption processes, especially for fine-grained pyrites with large surface-to-volume ratios that precipitated rapidly at low temperatures (e.g., Py II' in the Duanqiao field) (Scott et al., 2009; Ganna et al., 2015). Thus, we preliminarily infer that sub-micron Cu-sulfide inclusions (e.g., chalcopyrite) may be a possible Cu-carrier in pyrite.

Zinc and cobalt are able to easily enter the pyrite's crystal lattice in significant quantities (Maslennikov et al., 2009; Deditius et al., 2011; Winderbaum et al., 2012; Large et al., 2014; Wang et al., 2017). The negative correlation between Zn and Fe in our study and other mid-ocean fields indicates that iron substitution for zinc is common (e.g., Py II', $R^2=0.92$; Fig. 9b). As for cobalt, the

relatively constant contents within and between samples, in addition to the absence of Co-bearing phases, imply that it is incorporated into the pyrite crystal lattice (Fig. 9c).

The abnormally high contents of Cd in several pyrites (Py I, up to 5320 ppm Cd; Fig. 9d) from the Longqi field may be related to the sub-micron sphalerite inclusions because these particular spots also contain significant Zn contents. With respect to gold, silver, and lead in pyrite, we refer to the results from Reich et al. (2005, 2010, and 2013) and Keith et al. (2016) as follows (Fig. 10). Their results are based on element solubility limit studies and statistical analysis, which show that gold, silver, and lead form triangular wedge-shaped compositional variations with arsenic in a log (Au, Ag, Pb)–log (As) diagram reflecting solid solution or mineral inclusions (Fig. 10). For our samples from both of the study fields, results suggest that most Pb and Ag are in the form of solid solution, only a few are in inclusions (Figs. 10a and b), and Au is mainly present as (sub-)micron- or nano-sized inclusions (Fig. 10c) (Reith et al., 2013).

5.2.3 Chalcopyrite

Chalcopyrite is a relatively poor trace element carrier compared with pyrite and sphalerite (Large et al., 2009; Belousov et al., 2016; George et al., 2016; Keith et al., 2016). Unlike sphalerite, chalcopyrite is not a fully ionic structure, which makes it inefficient at adequately predicting trace element partitioning patterns using Goldschmidt's rules (George et al., 2016, 2017).

In this study, chalcopyrite from both the Longqi and Duanqiao fields is enriched in Zn compared with other trace elements (Ccp I: avg. 3226.67 ppm, Ccp II: avg. 9280 ppm, Ccp I': avg. 848 ppm, Ccp II' (inclusions): avg. 1098 ppm, and Ccp II' (fine-grained chalcopyrite): avg. 1795 ppm; Table 4). Furthermore, chalcopyrite from late stages tends to have higher Zn contents compared with the contents from early stages. Excluding the only excessively high-content sample (Dot C11-5, probably because of Zn-inclusion; Table 4), the general zinc concentrations range from hundreds to several thousands of ppm. Previous experiments in the Cu-Fe-Zn-S system show that certain amounts of Zn may substitute for Fe during specific conditions (Kojima and Sugaki, 1985; Huston et al., 1995). However, for situations with zinc concentrations over 2000 ppm, there are still debates, and controversies still exist over what are the influencing factors: either micro-inclusions or solid solution (Huston et al., 1995; Moggi-Cecchi et al., 2002; Serranti et al., 2002; Shalaby et al., 2004; Helmy et al., 2014; Wang et al., 2015).

With respect to most other trace elements, no obvious trends or patterns were observed between the different generations of chalcopyrite and the two hydrothermal

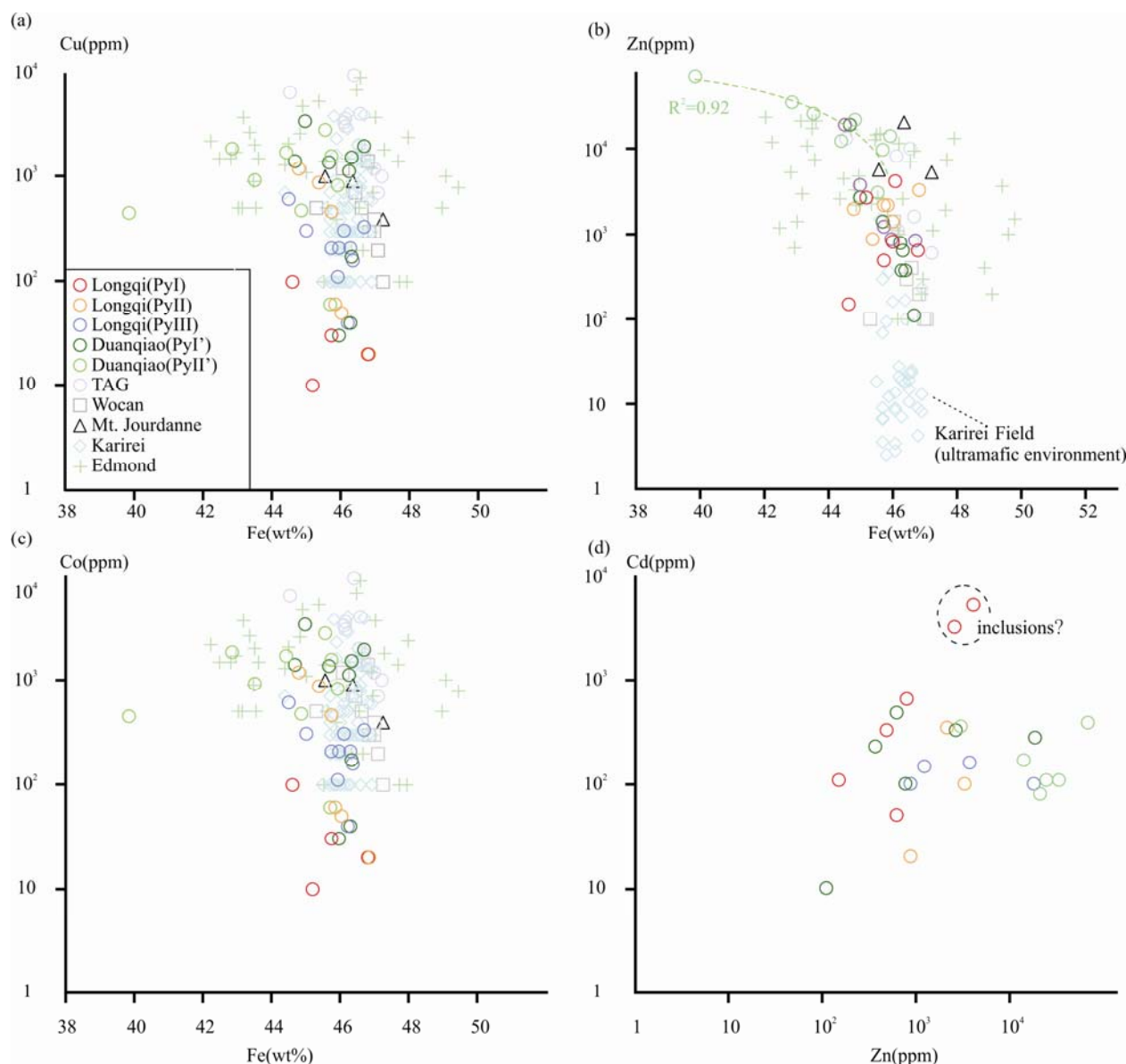


Fig. 9. Elements correlation analysis diagram of pyrite from the studied areas and other mid-ocean hydrothermal fields (The green dashed line in Fig. 9b. is the Zn-Fe correlation trend line of pyrite from the Duanqiao field, $R^2=0.92$).

fields. Owing to the lack of data concerning the trace element occurrence state in chalcopyrite, further investigations are necessary in the future.

5.3 Physicochemical conditions during mineral precipitation

Parameters such as pH, f_{O_2} , f_{S_2} , and temperature have important impacts on hydrothermal mineralization, and detailed studies of the mineral assemblages can reveal the physical and chemical conditions during hydrothermal mineralization (Kingston Tivey, 1995). Hydrothermal solution chemical buffering when mixed with seawater will affect the mineral assemblage equilibrium (Hannington et al., 1995; Fontboté et al., 2017).

5.3.1 Implications from mineralogy

Pyrite crystals have different textures under different physicochemical conditions in seafloor hydrothermal systems (Maslennikov et al., 2009; Revan et al., 2014; Keith et al., 2016). Colloform, euhedral, and anhedral pyrites are developed in the samples examined in this study. As described earlier, at the initial stage of chimney growth, colloform pyrite (Py I) and marcasite formed during a rapid mixing process between hydrothermal fluids and cold seawater (Hannington et al., 1988, 1995; Berkenbosch et al., 2012; Wohlgemuth-Ueberwasser et al., 2015). With the passage of time, these colloform pyrite and marcasite minerals, together with silica or sulfates (anhydrite), constituted the material for the construction of the initial walls of the chimney, providing good thermal

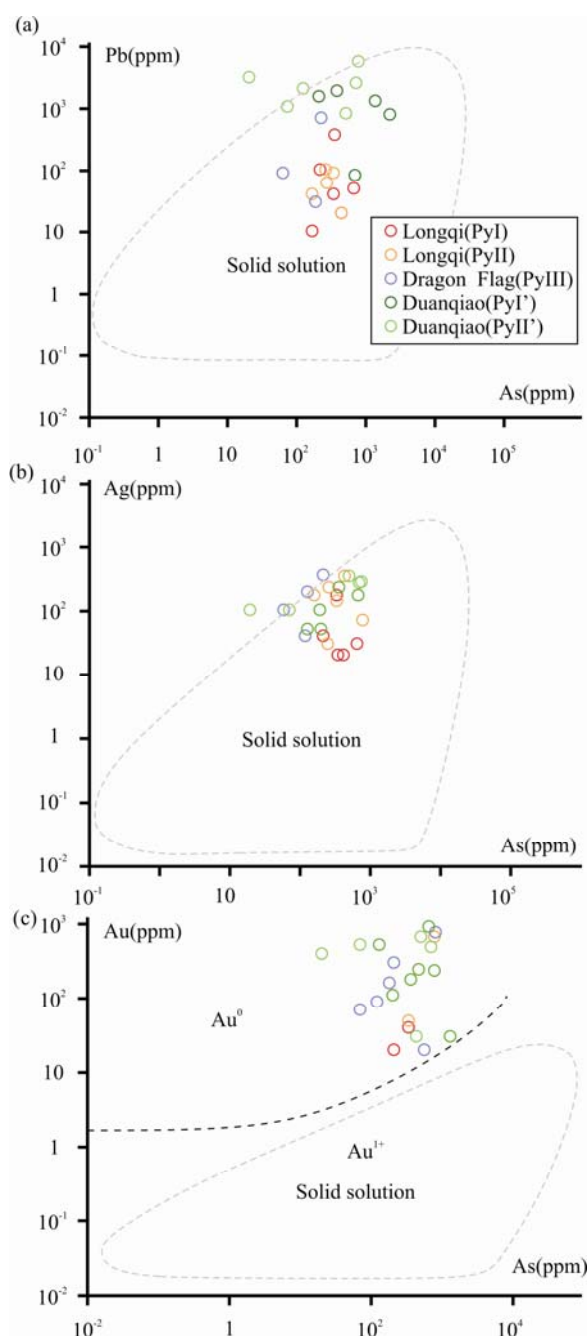


Fig. 10. Concentrations of (a) Pb, (b) Ag and (c) Au vs. As in pyrite from the studied areas and other mid-ocean hydrothermal fields (modified from Keith et al., 2016).

The black dashed curve represents the Au solubility line representing the upper limit of Au solid solution in pyrite (Reich et al., 2005). The gray dashed lines limit the zone of Au, Ag and Pb solid solution (Reich et al., 2005, 2010, 2013).

insulation, which allowed progressively hotter fluids to mix with the seawater. As a consequence, high-temperature minerals (e.g., euhedral Py II) precipitated in a stable environment protected by minerals with good impermeability (Hannington et al., 1995; Wang Yejian et al., 2011; Keith et al., 2016). In this study, we interpreted the absence of anhydrite as retrograde solubility

(Hannington et al., 1995; Petersen et al., 2000). Additionally, during one single hydrothermal stage, the decrease in temperature and the increase in pH are among the most common signs that lead to coarse-grained chalcopyrite precipitation before sphalerite and anhedral pyrite in both of the fields (Hannington et al., 1995; Reed et al., 2006; Pirajno et al., 2009). Therefore, mineral paragenesis in Longqi reveals the entire sulfide-sulfate chimney evolution, from the beginning to its mature stages and finally to its waning stage. Mineral paragenesis in the Duanqiao field, however, only implies chimney evolution from the mature stage to the waning stage.

In addition, different occurrences of mineral assemblages between the two fields imply differences in the hydrothermal conditions. Small amounts of isocubanite and pyrrhotite are only found at the Longqi field (Figs. 4f and h), whereas extensive sphalerite inclusions in pyrite are particular to the Duanqiao field (Fig. 6g). Isocubanite, with typical exsolution textures (Fig. 4h), precipitates at approximately 350°C in seafloor hydrothermal systems (Haymon and Kastner, 1981; Caye et al., 1988; Hannington et al., 1995; Mozgova et al., 1996). Thus, isocubanite occurrences exhibiting exsolution textures at the Longqi field imply that the fluid had a relatively high temperature.

Pyrrhotite is also a characteristic phase in high-temperature chimneys (e.g., black smokers) as it is rarely preserved in low-temperature chimneys (Hannington et al., 1995). According to previous experiments and mineral studies (Vaughan and Craig, 1978; Large et al., 1992; Hannington et al., 1995; Sack et al., 2006), coexisting pyrrhotite and sphalerite likely precipitate from relatively reduced, high-temperature fluids. In this study, pyrrhotite occurrences at the Longqi field and the absence of pyrrhotite at the Duanqiao field indicate that the Longqi field hydrothermal fluids have relatively higher temperatures and lower f_{O_2} and f_{S_2} compared with the Duanqiao field because the latter only has occurrences of pyrite and marcasite as the Fe-S phases (pyrite favors higher f_{S_2} and f_{O_2}) (Hannington et al., 1995).

As described earlier, anhedral pyrite aggregates (Py II') generally contain significant amounts of sphalerite micro-particles (Fig. 6f). Such phenomenon is probably due to a sharp change in the fluid chloride content, which may be due to seawater entrainment during the waning stage. Zinc has a chloride affinity, and a significant decrease in fluid chloride concentrations will induce the rapid oversaturation of zinc, resulting in the formation of abundant micro-sized sphalerite inclusions in pyrite during a short time period (Metz and Trefry, 2000; Pokrovski et al., 2013; Keith et al., 2016).

5.3.2 Implication from sulfide chemistry

We observed negative correlations between Zn and Fe contents in sphalerite at both field sites and other mid-ocean ridge fields (Fig. 7). This trend is related to the substitution of Fe for Zn as discussed earlier (Herzig, 1988; Keith et al., 2014). Previous experimental studies have discussed the hydrothermal fluid conditions based on the FeS compositions within the sphalerite structure (e.g., Scott and Barnes, 1971; Scott, 1983; Sack, 2006; Lepetit et al., 2012; Keith et al., 2014). Proposed relationships between f_{S_2} and temperature derive from the thermodynamic “Gibbs energy” principle (Sack, 2006). Keith et al. (2014) discussed the relationship between f_{S_2} and f_{O_2} in fluids using the equation: $H_2S(aq) + 0.5O_2(g) = H_2O(l) + 0.5S_2(g)$. Their results suggest that the incorporation of Fe into the sphalerite crystal lattice favors higher temperatures and lower f_{O_2} and f_{S_2} . This indicates that sphalerite's FeS content may reflect temperature and f_{S_2} - f_{O_2} , i.e., sphalerite with higher FeS content precipitated from fluids with higher temperature and lower f_{O_2} and f_{S_2} .

In this study, despite a lack of data on fluid chemistry, the abundant Fe-bearing minerals from both sites indicate that iron is a major solution component. In other words, the Fe concentration of the mineralizing fluid is not a key factor that influences the different levels of substitution compared with temperature and f_{S_2} - f_{O_2} . Here, we consider that undamaged sphalerites exclude any effects from late overprinting or replacement processes. The average undamaged sphalerite Fe contents from the Longqi and Duanqiao fields are 5.84 and 3.69 wt%, respectively, which implies that the Fe substitution level for Zn is greater in the Longqi field than in the Duanqiao field. Therefore, we suggest that the sulfides in the Longqi field precipitated from hydrothermal fluids at higher temperatures and lower f_{O_2} and f_{S_2} conditions compared with that of the Duanqiao field during the sphalerite stage. This inference is consistent with implications from mineralogy: the occurrence of coexisting pyrrhotite and sphalerite in the Longqi field, as we just discussed above. Moreover, Keith et al. (2014) have provided an empirical formula to estimate minimum fluid temperatures that induce sphalerite precipitation from hydrothermal fluids: $Fe/Zn_{sphalerite} = 0.0013(T) - 0.2953$. In this study, we excluded sphalerites with micro-zones that have corroded (or cracked) or that are close to late-stage pyrites (e.g., Fig. 4b) to avoid the effects of late-stage hydrothermal processes. The calculated temperatures are 303.5°C for the Longqi field and 286.7°C for the Duanqiao field. The incorporation of Cd into the sphalerite structure also favors higher temperatures (Chen et al., 1988; Cook, 2009; Monecke et al., 2016). The average Cd contents of undamaged sphalerite from the Longqi and Duanqiao

fields are 1950 and 525.66 ppm, respectively (Table 1), supporting the above observation about temperature.

In addition, the cobalt content in pyrite may also reflect fluid conditions. Cobalt is sensitive to temperature, and the substitution of Co for Fe favors higher temperatures (Maslennikov et al., 2009; Deditius et al., 2011; Winderbaum et al., 2012; Wang et al., 2017). The level of substitution is not constant within and between samples. Such variations are probably related to unstable cooling or mixing processes during the waning stage of chimney growth as low-temperature seawater contains only 0.05 ppb Co (Brewer, 1975; Huston et al., 1995). During the low-temperature stage, anhydrite dissolves back to seawater (Hannington et al., 1995; Petersen et al., 2000), locally changing the chimney's permeability, which may perturb the progressive cooling and mixing process. The difference in pyrite Co contents between the two fields implies either that there are differences in fluid temperature or that there are differences in the Co concentration in the initial solutions.

5.4 Implications for important mineralization processes

Zinc in sulfides. In this study, we found that Zn contents correlate to mineral generations. In the Longqi field, the late generation of Ccp II (avg. 9280 ppm Zn) has higher Zn contents than the early Ccp I (avg. 3226.67 ppm Zn). Similarly, in the Duanqiao field, the late Ccp II' (inclusions: avg. 1098 ppm Zn; fine-grained chalcopyrite: avg. 1795 ppm) has a higher Zn content than the early Ccp I' (avg. 848 ppm Zn). For pyrite, zinc also tends to be enriched in later generations (Py II: avg. 2008.5 ppm, Py III: avg. 1849.29 ppm, and Py II': 2.17 wt. %) than the early generations (Py I: avg. 1495 ppm and Py I': 1964.62 ppm). The formation of such Zn enrichment trends in sulfide at late stages is widely documented (e.g., TAG and Okinawa Trough hydrothermal fields), which may be attributed to the zone refining process, where zinc is remobilized and transported to the outer parts of the chimney or deposit (Sangster et al., 1976; Goldfarb et al., 1983; Hannington et al., 1995; Petersen et al., 2000; Keith et al., 2014). The levels of Zn content in pyrite from the study area and other basalt-hosted fields are higher than the Zn levels in pyrite from the Karirei field (ultramafic environment; Fig. 9b). Such differences may be related to the special geologic conditions in the ultramafic environment at the mid-ocean ridges.

Lead and galena in pyrite. We only identified galena micro-particles in pyrites from the Duanqiao field (Fig. 6g). In addition, pyrites tend to have more Pb enrichment at the Duanqiao field (up to 5320 ppm), whereas most Pb contents in pyrites from the Longqi field are near the

detection limit (Table 3). Previous studies have suggested that Pb is mainly derived from the destruction of surrounding rocks (e.g., feldspars) (Hannington et al., 1995, 2005), and the variations in the Pb concentrations in sulfide at the mid-ocean hydrothermal systems may reflect different water-rock interaction processes (Fouquet et al., 2010; Nayak et al., 2014). Recently, Ye Jun (2010) and Yang Weifang (2017) have reported the Pb contents and isotopic data of bulk sulfides from the two fields. The Pb contents of the bulk sulfides from the Longqi field and the Duanqiao field were 52.4–584 ppm (avg. 194.7 ppm) and 263–7500 ppm (avg. 1465.7 ppm), respectively. The sulfide Pb isotopic data consistently indicate that Pb is mainly derived from basalt in both fields (Ye Jun, 2010; Yang Weifang, 2017). Combining these data with our research results, we suggest that the hydrothermal fluids at the Duanqiao field are more likely affected by the surrounding rocks compared with the Longqi field.

6 Conclusions

(1) The hydrothermal processes at the Longqi field are divided into three main stages: (1) the low–medium-temperature stage: colloform pyrite (Py I) + marcasite → euhedral pyrite (Py II), (2) the high-temperature stage: isocubanite (±exsolved chalcopyrite) + pyrrhotite → coarse-grained chalcopyrite (Ccp I), and (3) the medium–low-temperature stage: sphalerite + fine-grained chalcopyrite inclusions (Ccp II') → aggregates of anhedral pyrite (Py III) + marcasite → Fe-oxide (-hydroxide) + amorphous silica. The mineralization processes in the Duanqiao field are divided into two main stages: (1) the medium–high-temperature stage: sub- and euhedral pyrite (Py I') → coarse-grained chalcopyrite (Ccp I') and (2) the medium–low-temperature stage: sphalerite → fine-grained chalcopyrite (Ccp II') + chalcopyrite inclusions (Ccp II') → silica-cemented pyrite (Py II') + marcasite → Fe-oxide + amorphous silica.

(2) Fine-grained chalcopyrite inclusions in sphalerite from the Longqi field may have formed via coprecipitation mechanisms, and the chalcopyrite inclusions in sphalerite from the Duanqiao field were formed by replacement mechanisms.

(3) Primary sphalerites from both field sites are enriched in Fe (avg. 5.84 wt% for the Longqi field and avg. 3.69 wt% for the Duanqiao field), Co (avg. 185.56 and 160.53 ppm), and Cd (avg. 1950 and avg. 525.26 ppm). Copper, lead, silver, and gold may form mineral hosted (micro) inclusions in sphalerite.

(4) Pyrite from the Duanqiao field (Py I': avg. 849.23 ppm and Py II': avg. 1191.11 ppm) tends to have higher Cu contents compared with that of the Longqi field (Py I:

avg. 26.67 ppm, Py II: avg. 445 ppm, and Py III: avg. 179.29 ppm). At both sites, zinc, cobalt, cadmium, lead, and silver may be incorporated into the pyrite structure. Copper and gold may form independent mineral (sub-micron) inclusions hosted in the pyrite.

(5) Chalcopyrite from both sites is enriched in Zn (Ccp I: avg. 3226.67 ppm, Ccp II: avg. 9280 ppm, Ccp I': avg. 848 ppm, Ccp II' (inclusions): avg. 1098 ppm, and Ccp II' (fine-grained): avg. 1795 ppm).

(6) Occurrences of isocubanite and pyrrhotite, together with higher contents of Fe and Cd in the sphalerite structures, imply that sulfides in the Longqi field precipitated from the hydrothermal fluid at higher temperatures and lower f_{O_2} and f_{S_2} conditions compared with that of the Duanqiao field.

(7) The relatively high Zn contents in late-stage pyrites and chalcopyrites may be attributed to the zone refining processes. Sulfides tend to have enrichment in lead from the Duanqiao field, which implies that the hydrothermal fluids at the Duanqiao field are more likely affected by the surrounding rocks than the Longqi field.

Acknowledgements

This research was funded by the Resources Assessment Methods of Polymetallic Sulfides Program (NO. DY125-12-R-02), the Metallogenic Potential and Resources Assessment of the Polymetallic Sulfides in the Atlantic Ridge Program (NO. DY125-11-R-01) and Deep Structure and Mineralization Process of the Lead-Zinc Deposit Systems formed by the Continental Collision in Tibet Plateau (NO. 2016YFC0600306). We thank the reviewers and the editor for their suggestions that helped improve the paper.

Manuscript received Nov. 9, 2017

accepted Mar. 6, 2018

edited by Fei Hongcai

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