Geologic, Fluid Inclusion and Stable Isotope Constraints on Mechanisms of Ore Deposition at the Datuanshan Copper Deposit, Middle–Lower Yangtze Valley, Eastern China

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Abstract: The Datuanshan deposit is one of the largest and most representative stratabound copper deposits in the Tongling area, the largest ore district in the Middle–Lower Yangtze River metallogenic belt. The location of the orebodies is controlled by the interlayer-sliping faults between the Triassic and Permian strata, and all the orebodies are distributed in stratiform shape around the Mesozoic quartz monzodiorite dikes. Based on field evidence and petrographic observations, four mineralization stages in the Datuanshan deposit have been identified: the skarn, early quartz–sulfide, late quartz–sulfide and carbonate stages. Chalcopyrite is the main copper mineral and mainly formed at the late quartz–sulfide stage. Fluid inclusions at different stages were studied for petrography, microthermometry, laser Raman spectrometry and stable isotopes. Four types of fluid inclusions, including three-phase fluid inclusions (type 1), liquid-rich fluid inclusions (type 2), vapour–rich fluid inclusions (type 3) and pure vapour fluid inclusions (type 4), were observed. The minerals from the skarn, early and late quartz–sulfide stages contain all fluid inclusion types, but only type 2 fluid inclusions were observed at the carbonate stage. Petrographic observations suggest that most of the inclusions studied in this paper are likely primary. The coexistence of different types of fluid inclusions with contrasting homogenization characteristics (to the liquid and vapour phase, respectively) and similar homogenization temperatures (the modes are 440–480°C, 380–400°C and 280–320°C for the skarn, early and late quartz–sulfide stages, respectively) in the first three stages, strongly suggests that three episodes of fluid boiling occurred during these stages, which is supported by the hydrogen isotope data. Laser Raman spectra identified CH₄ at the skarn and early quartz–sulfide stages. Combined with other geological features, the early ore-forming fluids were inferred to be under a relatively reduced environment. The CO₂ component has been identified at the late quartz–sulfide and carbonate stages, indicating that the late ore-forming fluids were under a relatively oxidized environment, probably as a result of inflow of and mixing with meteoric water. In addition, microthermometric results of fluid inclusions and H–O isotope data indicate that the ore forming fluids were dominated by magmatic water in the early stages (skarn and early quartz–sulfide stages) and mixed with meteoric water in the late stages (late quartz–sulfide and carbonate stages). The evidence listed above suggests that the chalcopyrite deposition in the Datuanshan deposit probably resulted from the combination of multi-episode fluid boiling and mixing of magmatic and meteoric water.

Key words: Stratabound skarn deposit, fluid inclusions, stable isotopes, Datuanshan deposit, Middle–Lower Yangtze Valley

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1 Introduction

The Lower Middle–Yangtze River metallogenic belt (MLYRB), which extends from Wuhan (Hubei Province) in the west to Zhenjiang (Jiangsu Province) in the east, contains more than 200 polymetallic (Cu–Fe–Au, Mo, Zn, Pb, and Ag) deposits (Fig. 1; Chang et al., 1991; Pan and Dong, 1999; Mao et al., 2006, 2011), making it one of the most important metallogenic belts in China. The stratabound deposits are the most abundant and economically important ore type in the MLYRB (Chang et al., 1991; Zhai et al., 1992; Tang et al., 1998). The orebodies of the stratabound deposits in the MLYRB are commonly spatially and temporally associated with skarns. Both skarns and orebodies in these deposits are commonly distributed around Mesozoic intermediate–acidic intrusions, and occur as tabular or semi-tabular bodies along interlayer–slipping faults in upper Devonian to Lower Triassic strata (Mao et al., 2006). However, despite their having been mined since ancient times and being well described in the literature (Chang et al., 1991; Tang et al., 1998; Yang et al., 2004; Mao et al., 2006, 2011; Deng et al., 2011; Guo et al., 2011; Yang et al., 2011; Cao et al., 2012; Li et al., 2013; Xu et al., 2014), there is still considerable uncertainty about key issues related to the genesis of these deposits, such as the source and evolution of ore-forming fluids, and the mechanism(s) of ore deposition. A variety of ore fluids have been invoked, with emphasis on primary magmatic fluids, but also including meteoric waters, basinal brines (formation waters), and their mixtures (Xu et al., 2005; Lai and Chi, 2007; Lai et al., 2007; Zhou et al., 2007; Gu et al., 2011; Cao et al., 2012; Liu et al., 2014a). With regard to the meteoric fluids, the timing of their circulation and interaction with magmatic fluids may be relatively early or occur only in the waning stages of the hydrothermal systems (Xu and Lin, 2000; Li et al., 2006; Gu et al., 2011). Various mechanisms have been proposed for evolution of ore-forming fluids and ore deposition, including wall-rock alteration, boiling, and fluid mixing (Xu and Lin, 2000; Xiao et al., 2002; Zhou et al., 2002, 2007; Lai et al., 2007; Cao et al., 2012). Among these, mixing between magmatic and meteoric waters is thought to be the most effective cause of ore deposition (Xu and Lin, 2000; Lai and Chi, 2007; Lai et al., 2007). However, some recent studies show that although fluid mixing occurred in many large-scale stratabound deposits in the MLYRB, fluid boiling may have also played a significant role in ore deposition (Xu et al., 2005; Cao et al., 2012, 2015; Liu et al., 2014b).

Fig. 1. A simplified geologic map of the Middle–Lower Yangtze river belt, East China. The inset is a simplified tectonic map of China (modified from Mao et al., 2011).

TLF, Tancheng–Luijiang fault; XGF, Xiangfan–Guangji fault; YCF, Yangxinge–Changzhou fault.
The Datuanshan deposit is one of the largest and most representative stratabound copper deposits in the Tongling area, the largest ore district in the MLYRB (Mao et al., 2006). Therefore, this deposit is an ideal natural laboratory for investigating the various genetic issues of the stratabound deposits in the MLYRB, as raised above. Measured and indicated resources of the Datuanshan deposit are about 26.3 Mt of ore grading 1.02% Cu and 0.05% Mo, with potential for economic concentrations of Au, Ag and S. In the Datuanshan deposit, all the orebodies are distributed in stratiform shape in strata around Mesozoic quartz monzodiorite dikes. The mineralization is especially well developed at the boundary between the Triassic and Permain strata (Mao et al., 2006). Several previous investigations have been carried out on the Datuanshan deposit, mainly focused on the general geology (Ling et al., 1998; Chen et al., 2007), related magmatic rocks (Wang et al., 2007), chemical composition of the fluids (Du et al., 2000), and geochronology (Mei et al., 2005; Mao et al., 2006), but little is known about the source and evolution of ore-forming fluids and the mechanisms of ore deposition. As is well known, studies on fluid inclusions can offer direct information about the ore-introducing fluids, and can provide constraints on mineralization processes. In particular, hydrogen and oxygen isotopes of fluids are important monitors for the sources and evolution of ore-forming fluids. Thus, in this paper, we present new field and petrographic observations, H-O isotopes, fluid inclusion microthermometry and laser Raman spectrometry data, and use them to discuss the sources and evolution of ore-forming fluids, and the mechanisms of ore deposition at the Datuanshan stratabound copper deposit. We believe this work will improve our understanding of the formation of the stratabound deposits in the MLYRB.

2 Regional Geology

The Middle–Lower Yangtze River metallogenic belt is located on the northern margin of the Yangtze Craton of Eastern China, to the south of the southeastern margin of the North China Craton and Qingling–Darbeshan orogenic belt (Fig. 1). It is bounded by the NW-trending Xiangfan–Guangji fault (XGF) and the NE-trending Tancheng–Luijiang regional strike-slip fault (TLF) in the north, and the Yangxings–Changzhou fault (YCF) in the south (Fig. 1). Basement rocks of the MLYRB consist of trondhjemite–tonalite–granodiorite gneisses and supracrustal rocks (felsic gneiss and muscovite quartz schist with intercalated amphibolites) that range in age from 2900 to 990 Ma (Chang et al., 1991; Zhai et al., 1992). The metamorphosed basement is unconformably overlain by a thick cover sequence consisting of Neoproterozoic clastic rocks, carbonate and chert, Cambrian chert nodules, mudstone and argillaceous limestone, Ordovician limestone and dolomitic limestone, Silurian clastic rocks, Devonian sandstone, Carboniferous siltstone and limestone, Permian shale, siliciclastic rocks and limestone, and Triassic limestone and argillaceous clastic rocks (Chang et al., 1991; Zhai et al., 1992). In the MLYRB, late Mesozoic magmatism is represented mainly by Late Jurassic to Cretaceous high-K calc-alkaline, shoshonite, and sub-alkaline to alkaline intrusives rocks and their corresponding eruptive rocks (Chen et al., 2001; Zhang et al., 2003; Cao et al., 2009; Yang et al., 2011; Xie et al., 2012; Yang et al., 2014). In addition, small amounts of Cretaceous quartz syenite, syenite, quartz monzonite, and alkaline granite are exposed, which have been classified as A–type granitoids (Cao et al., 2008; Fan et al., 2008; Yan et al., 2012).

The Tongling area, situated in the middle segment of the MLYRB (Fig.1), is the largest copper–iron–gold ore district in the MLYRB (Mao et al., 2006). Cambrian to middle Triassic sedimentary rocks were developed on a stable Precambrian basement, forming a thick sedimentary sequence that became country rocks for later Cu, Au, and Fe deposits (Chang et al., 1991) (Fig. 2a). Marine deposits in the Tongling area, which include clastic sedimentary rocks, carbonates, and evaporates, were formed from the Silurian through to the Middle Triassic, except in the Lower–Middle Devonian. The strata that are closely related to the metal deposits are Carboniferous carbonate, Permian limestone, black shale, and Triassic carbonate and argillaceous rocks (Chang et al., 1991; Pan and Dong, 1999).

Mesozoic magmatic rocks are abundant in the region, forming more than 70 intrusions in the east–west-trending Tongling–Daijiahu magmatic belt occupying approximately 10% of the area (Fig. 2a). The main lithologies of the intrusions are pyroxene monzodiorite, diorite, quartz monzodiorite, granodiorite, and granite porphyry. High–precision zircon U–Pb (SHRIMP and LA–ICP–MS) results for intrusive rocks in the Tongling region have shown that all of them were formed in the Early Cretaceous (mainly 145–137 Ma; Xu et al., 2004; Wu et al., 2008a; Xie et al., 2008, 2009; Cao et al., 2009; Yang et al., 2011; Yang et al., 2014; Wang et al., 2015).

More than 180 ore deposits and occurrences have been discovered in the Tongling district and they are mainly clustered in several orefields, including the Tongguanshan, Shizishan, Xinqiao, Fenghuangshan and Shatanjiao orefields (Fig. 2a). Most of these deposits occur as skarn deposits in the contact zones of magmatic intrusions and stratabound deposits in the country rocks. Porphyry–type
mineralization is generally minor and occurs in the deeper parts of a few deposits (Pan and Dong, 1999). The skarn and porphyry deposits are related to the Yanshanian intermediate–acid intrusions of 145 to 137 Ma (Ling et al., 2009; Xie et al., 2009; Deng et al., 2011). However, the metallogenic mechanisms of the stratabound deposits, e.g., Xinqiao, Dongguashan, Datuanshan, Shimenkou, Laoyaling, and Huangshilao, within the sedimentary rocks has remained controversial (Li et al., 2013).

The Datuanshan copper deposit is located in the Shizishan orefield. The Shizishan orefield is located about 7 km east of Tongling city, in the central part of the Tongling district (Chang et al., 1991; Zhai et al., 1992). The orefield is located on the southeastern limb of the NE–trending Qingshan anticline formed during the Indosinian orogenic event (ca. 230 to 220 Ma; Gu et al., 2007). There are several sets of Late Jurassic to Early Cretaceous faults trending near N–S, E–W, NE and NW (Yang et al., 2011) in this orefield (Fig. 2b). Outcropping strata consist mainly of Triassic thinly-layered limestone, which overlies Permian and Carboniferous limestone and Upper Devonian and Silurian sandstone. The plutons in the Shizishan orefield mainly consist of pyroxene monzodiorite, quartz monzodiorite and granodiorite, and are typically emplaced into Silurian to Triassic sedimentary strata. The stratiform orebodies are widespread throughout this orefield and are hosted by the Devonian to Triassic strata at depths from around −875 m to −90 m (Yang et al., 2011), with individual orebodies and skarns being conformable with the hosting sediments. These orebodies belong to different deposits, including the Dongguashan, Huashupu, Laoyaling, Datuanshan and Hucun deposits. The total reserves of the orefield is more than 1.5 Mt Cu, with the largest single deposit (Dongguashan) containing about 0.94 Mt Cu metal and 22 t Au (Zaw et al., 2007).

3 Geology of the Datuanshan Copper Deposit

The Datuanshan copper deposit is located in the central part of the Shizishan orefield of the Tongling district (Fig. 2b), at the intersection of the southeast limb of the NE–trending Qingshan anticline and NE trending Baocunghoushan–Shazibao faults and E–W trending Datuanshan–Baoerling faults (Chu, 2003). Orebodies are hosted within the Upper Permian Dalong and Lower Triassic Yinkeg formations (Figs. 3a, b). The Dalong Formation (P2d) is dominated by siliceous shale and chert, and the Lower Triassic Yinkeg Formation (T1y) is composed of muddy limestone and shale.
The Datuanshan quartz monzodiorite, which is closely related to the Datuanshan Cu–Mo mineralization (Chu, 2003; Wang et al., 2007; Wu et al., 2008b), is emplaced into Silurian to Triassic sedimentary strata (Tang et al., 1998), causing strong thermal interaction along the contact zone between the intrusions and country rocks. Quartz monzodiorite is light gray in color, medium- to coarse-grained, and consists of plagioclase (40%–50%), K-feldspar (10%–15%), hornblende (5%–10%), quartz (12%–17%) and biotite (5%–8%), and accessory zircon, titanite, magnetite, and apatite. Plagioclase is subhedral to euhedral, with multiple twins. Alkalifeldspar has Carlsbad twin and poikilitic texture. Hornblende encloses alkali-feldspar, biotite, apatite and metallic minerals, which has been interpreted to indicate magma mixing (Xie et al., 2012). The Datuanshan quartz monzodiorite belong to metaluminous magnetite-series (I-type) granitoids with SiO2 content ranging from 57% to 65% (Wang et al., 2007; Xie et al., 2012). It is classified as high-potassium calcalkaline granitoids for the high alkali content (Wang et al., 2007; Xie et al., 2012). The intrusion shows enrichment of Rb, Ba, Sr, Th and LREE, minor depletion of Nb, Ta and Ti, and slight Eu anomaly with Eu/Eu* values of 0.89 to 0.98 (Wang et al., 2007; Xie et al., 2012). Detailed petrochemistry, a few Sr–Nd–Pb isotope data and experimental simulation of petrogenesis indicate that the Datuanshan quartz monzodiorite was originated from mixing between juvenile mantle and ancient crustal materials (Wang et al., 2007; Yang et al., 2011).

Specifically, the quartz monzodiorite were considered similar to adakite in terms of geochemical composition, even though they formed under intra-continental environment rather than in an island-arc like “normal” adakite (Zhang et al., 2001; Xie et al., 2012). SHRIMP zircon U–Pb ages for the Datuanshan quartz monzodiorite range from 138.7±1.3 to 139.3±1.2 Ma (Wu et al., 2008b; Yang et al., 2011).

In the Datuanshan deposit, all the orebodies are distributed in stratiform shape in the sedimentary rocks around the Datuanshan quartz monzodiorite dikes (Fig. 3). The location of the orebodies is controlled by the interlayer-sliping faults between the Triassic and Permian strata, so that the shape of the orebodies varies with the geometry of the faults. They generally run parallel to the bedding of the host rocks (Figs. 3, 4a–c). There are two types of ores in this deposit: stratiform Cu ores and stratiform Mo ores (Fig. 3). The stratiform copper orebodies are more common and are widely distributed in the Datuanshan deposit. It is spatially and temporally associated with skarn, and is mainly developed at the base of the Lower Triassic Yinkeng calcic skarn intercalated with hornfels (Mao et al., 2006). The skarn is composed predominantly of garnet and pyroxene with lesser actinolite and chlorite. A characteristic feature of this type of alteration is the skarn mineral assemblage commonly occurring as bands intercalated in the host rocks (Figs. 3, 4a–c). Generally, the stratiform Cu orebodies strike N30–35°E and dip 35–50° towards southeast. The major

![Fig. 3. Geological cross-sections of No. 23 (a) and No. 38 (b) exploration lines of the Datuanshan copper deposit (modified from Mao et al., 2006).](image-url)
orebody is about 830 m in length and the thickness ranges from 20.6 to 33.9 m. Ore minerals include chalcopyrite, pyrrhotite, pyrite, sphalerite, and minor galena and molybdenite (Fig. 4c). Gangue minerals include garnet, pyroxene, actinolite, tremolite, chlorite, calcite and quartz (Figs. 4b, c). The stratiform Mo orebodies (also containing Cu) are less important in the Datuanshan deposit. They are stratigraphically below the stratiform Cu orebodies and only exist within the Upper Permian Dalong siliceous shale and chert. The contacts of orebodies and the wall rocks are clear. Orebodies are about 100 to 753 m in length and the thickness ranges from 3.98 to 7.48 m (321 Geological Team of Bureau of Geology and Mineral Exploration of Anhui Province, 1990). Ore minerals are dominantly molybdenite, chalcopyrite, and pyrite. Gangue minerals are mainly epidote, chlorite, quartz and calcite.

4 Mineralization and Alteration

Field evidence and petrographic observations indicate four stages of hydrothermal activity during the formation of the Datuanshan stratabound skarn copper deposit. The mineralogy and associated wall-rock alteration of each stage are illustrated in Fig. 5 and summarized briefly below.

Skarn stage: This is the earliest stage of hydrothermal activity, characterized by the formation of anhydrous mineral assemblages comprising garnet and pyroxene (Fig. 4b). Garnet occurs ubiquitously in the skarn zone as fine- to coarse-grained anhedral to euhedral crystals. Most of them are andraditic–grossularitic (Du, 2013) and some are optically and compositionally zoned on the scale of an individual crystal (Fig. 4d). Pyroxenes occur as fine- to medium-grained anhedral to subhedral crystals. They belong compositionally to the hedenbergite–diopside series (321 Geological Team of Bureau of Geology and Mineral Exploration of Anhui Province, 1990). The skarn mineral assemblage commonly occurs as bands intercalated in the host rocks, however, in some locations, veins from the skarn cut the host rocks, indicating that skarnization postdates the host sedimentary formation.

Early quartz–sulfide stage: This stage is responsible for the formation of the pyrrhotite-rich orebody, and is marked by the replacement of garnet and pyroxene by retrograde skarn minerals and associated ore minerals (Fig. 6a). Retrograde skarn minerals including actinolite–
tremolite, epidote, chlorite and quartz, typically overprint primary, anhydrous skarn minerals (Fig. 6a). Ore minerals include pyrrhotite, pyrite, and minor chalcopyrite and molybdenite (Figs. 6a–c). Pyrrhotite is the most abundant sulfide in this stage, and occurs mainly as fine- to medium-grained subhedral-anhedral crystals (Figs. 6b, c). Pyrites exist as euhedral–subhedral crystals, and are sometimes surround by pyrrhotite and chalcopyrite (Fig. 6c). Most chalcopyrite occurs as anhedral crystals. Pyrrhotite, pyrite and chalcopyrite fill in the fractures and open spaces of skarn minerals, and the skarn are cut by sulfides-bearing quartz veins (Fig. 6d), indicating that the sulfide minerals formed after primary skarn minerals.

Late quartz–sulfide stage: This is the main copper mineralization stage that formed large amounts of chalcopyrite, sphalerite, galena and pyrrhotite. Chalcopyrite is intergrown with sphalerite, pyrrhotite, quartz, and other minerals (Fig. 6e), and occupies the same veinlets as quartz (Fig. 6f), or exists as chalcopyrite disease in sphalerite. The gangue minerals are mainly quartz, chlorite and calcite. Quartz is mostly granular, and intergrown with chalcopyrite and sphalerite in disseminated ores and veins (Fig. 6g). In some locations, pyrrhotite and pyrite-bearing quartz veins are cut by chalcopyrite and sphalerite-bearing quartz veins (Fig. 6f), and early quartz–sulfide stage pyrrhotite is replaced and crosscut by late quartz–sulfide stage chalcopyrite and sphalerite (Fig. 6h).

Carbonate stage: This is the last stage of hydrothermal activity, characterized by calcite veins filling fissures that crosscut earlier mineral assemblages (Fig. 6i), which indicates that the ore-forming fluid activities were waning. Locally, the veins crosscut the orebody, producing dense stockworks of carbonate.

5 Samples and Analytical Techniques

5.1 Fluid inclusion petrography and microthermometry

The samples in this study were mainly collected from the Datanshan stratiform skarn copper ores. For fluid inclusion measurement, we selected garnet, quartz and calcite from different paragenetic stages and prepared 200 μm-thick doubly polished sections following the procedure of Shepherd et al. (1985). A detailed petrographic study of fluid inclusions was conducted on more than 30 doubly polished sections. From these, 10 sections were chosen for microthermometric analysis. The microthermometric study was carried out at the Laboratory for fluid inclusion, China University of Geosciences, Beijing, China, using a LINKAM THMGS–600 heating and freezing stage with a temperature range of –180 to +600°C. The precision of temperature measurements is about ±0.1°C on cooling runs and ±2°C on heating runs. Salinities of the fluids were calculated from the ice melting temperature for two–phase inclusions.
5.2 Laser Raman spectroscopic analysis

Laser Raman spectroscopic analysis of fluid inclusions was carried out using a LABHR–VIS LabRAM HR800 Raman micro-spectrometer at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, Beijing, China. An argon ion laser with wavelength of 532 nm and a source power of 5 mW×100% was used, and the analyses were conducted at 25°C. The acquisition time is 30s. The spectra were collected between 100 and 4200 cm⁻¹ for the analysis of H₂S, CO₂, N₂, and CH₄, as well as other species in the vapour phase.

5.3 Stable isotope analysis

Mineral separation for oxygen and hydrogen isotope analysis was carried out at the Langfang Geochemical Laboratory in Hebei Province, China. The purity of the garnet and quartz grains was better than 99%.

Oxygen isotope analyses of garnet and quartz were performed at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, China, by a technique modified after that of Clayton and Mayeda (1963). Oxygen was liberated for isotopic analysis using BrF₅, and the resultant oxygen reacted with graphite rods to produce carbon dioxide, the isotopic composition of which was determined using a Finnigan MAT–253 mass spectrometer.

Hydrogen isotope analyses of fluid inclusions were carried out on splits of the samples analyzed for oxygen isotopes, using the following procedure. Aliquots were
enclosed in a stainless tube, dried for about 4 h at 105°C under vacuum conditions to eliminate adsorbed air moisture, and then heated to approximately 1400°C, in an induction oven for 45 min or until the sample stopped giving off gas. Non-condensable gases, CO₂, and any SO₂ were separated cryogenically. The resultant H₂O was reduced to H₂ by hot chromium at 800 °C. This hydrogen was analyzed with a Finnigan MAT-253 mass spectrometer at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, China. The isotope data are presented in the standard δ notation relative to SMOW (Standard Mean Ocean Water) for oxygen and hydrogen. The analytical precisions were better than ±0.2‰ (2σ) for δ¹⁸O and ±1‰ (2σ) for δD. Analytical precision was based on replicate analyses of GBW–04409 quartz (δ¹⁸OSMOW=11.11±0.06‰) and Peking University Standard Water (δD_SMOW=−64.8‰).

6 Results

6.1 Fluid inclusion petrography

To investigate all stages of ore deposition, we focused on the fluid inclusions hosted in garnet and pyroxene of the skarn stage, in quartz of the early and late quartz–sulfide stages, and calcite of the carbonate stage. Based on their compositions and physical properties at room temperature, the inclusions encountered in this study can be classified into four types (Fig. 7): type 1 are three-phase inclusions containing a vapor bubble, an aqueous liquid, and a cubic halite crystal (occasionally opaque ore minerals); type 2 are liquid–rich inclusions with a liquid volume of >60%; type 3 are vapor-rich inclusions with a vapor volume of >60%; and type 4 are pure vapor fluid inclusions.

Fluid inclusions in garnet and pyroxene of the skarn stage comprise mainly three types: type 1, 2 and 3. Rare type 4 inclusions were also found in skarn minerals. These

Fig. 7. Photomicrographs of representative primary fluid inclusion assemblages from the Datushan copper deposit. (a), A three-phase inclusion coexists with a vapour-rich inclusion in garnet (Gr) of the skarn stage; (b), A liquid-rich inclusion coexists with a vapour-rich inclusion in garnet of the skarn stage; (c), Three-phase inclusion coexists with liquid-rich and vapour-rich fluid inclusions in pyroxene (Px) of the skarn stage; (d), Fluid inclusions in quartz (Q) of the early quartz-sulfide stage occur in clusters; (e), Three-phase inclusions coexist with liquid-rich and vapour-rich fluid inclusions in quartz of the early quartz-sulfide stage; (f–h), Three-phase inclusions coexist with liquid-rich and vapour-rich fluid inclusions in quartz of the late quartz-sulfide stage; (i), Two-phase, liquid-rich inclusion in calcite (Cc) of the carbonate stage. L=liquid; V=vapour; S=solid.
fluid inclusions are commonly isolated, 5 to 20 μm in diameter, and round or irregular in shape (Figs. 7a–c). All the inclusions studied in the skarn stage are considered as primary inclusions and were likely entrapped contemporaneously.

Fluid inclusions are abundant in quartz from early and late quartz–sulfide stages, and are of type 1, 2 and 3, and rarely type 4. The proportion of the type 3 and 4 fluid inclusions in the total inclusion population is highest in the quartz from late quartz–sulfide stage compared with other stages. These fluid inclusions are clustered and locally isolated, less than 20 μm in diameter, and round or irregular in shape (Figs. 7d–h). They are also interpreted as primary inclusions. The coexisting fluid inclusions within the same cluster in the same stage minerals display variations in their properties, reflecting either modification after entrapment (e.g., necking down) or heterogeneous trapping of boiling or immiscible fluids (Ramboz et al., 1982; Goldstein, 2001; Chi et al., 2006; Chi and Lu, 2008).

In the carbonate stage, only liquid-rich inclusions (type 2) were found. They occur as isolated inclusions in calcite, and show similar vapor percentages (Fig. 7i). These inclusions are likely primary.

6.2 Fluid inclusion microthermometry

The microthermometric data for fluid inclusions in this study are listed in Table 1, and illustrated in Figs. 8 and 9. The results are described for the different stages as follows.

Skarn stage: Type 1 fluid inclusions within garnet and pyroxene generally homogenize by disappearance of the vapour bubble. The total homogenization temperatures are in the range of 368–561°C, and the mode is 440–480°C (Fig. 8a). The halite dissolution temperatures are in the range of 260–440°C, corresponding to salinities of 35–52 wt% NaCl equiv. (the mode is 46–48 wt% NaCl equiv., Fig. 8b). All type 2 fluid inclusions within garnet and pyroxene also homogenize to the liquid state, at temperatures in the range of 325–542°C, with a mode at 440–480°C (Fig. 8a). They have a calculated bulk salinity of 8.1–23.2 wt% NaCl equiv., with a mode at 18–20 wt% NaCl equiv. (Fig. 8b). Type 3 fluid inclusions generally homogenize to the vapour phase. Homogenization temperatures for these inclusions are in the range of 331–580°C, with a mode at 460–480°C (Fig. 8b). Salinities calculated for these inclusions are in the range of 5.4–8.1 wt% NaCl equiv. (Fig. 8b).

Early quartz–sulfide stage: Type 1 fluid inclusions within the quartz in this stage generally homogenize by disappearance of the vapour bubble. Homogenization occurs at temperatures in the range of 286–432°C, with a mode at 380–400°C (Fig. 8c), and the bulk salinities determined from the dissolution temperatures of halite vary in the range of 28–43 wt% NaCl equiv., with a mode at 38–40 wt% NaCl equiv. (Fig. 8d). Most type 2 fluid inclusions homogenize to the liquid state from 301 to 469°C (the mode is 380–400°C), and have a bulk salinity that varies from 8.6 to 21.1 wt% NaCl equiv. (the mode is 12–16 wt% NaCl equiv., Fig. 8d). Type 3 fluid inclusions homogenize into the vapor phase in the 358–440°C range and have bulk salinities of 4.3 to 5.7 wt% NaCl equiv. (Figs. 8c, d).

Late quartz–sulfide stage: The homogenization temperatures of type 1 fluid inclusions within the quartz of this stage range from 221 to 376°C, with a mode at 280–320°C (Fig. 8e). Bubbles disappear after the dissolution of halite during heating. The daughter minerals dissolve between 120 and 330°C, with corresponding salinities ranging from 28 to 41 wt% NaCl equiv. (the mode is 34–36 wt% NaCl equiv., Fig. 8f). Most type 2 fluid inclusions homogenize to the liquid phase from 221 to 377°C, with a mode at 280–300°C (Fig. 8e), and have bulk salinities from 6.1 to 22.5 wt% NaCl equiv., with a mode at 8–

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<th>Table 1 Summary of microthermometric data for primary fluid inclusions from the Datunshan copper deposit</th>
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<td>Fluid inclusion type</td>
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<td>Early quartz-sulfide stage</td>
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<td>(1) Three-phase inclusions</td>
</tr>
<tr>
<td>(2) Liquid-rich inclusions</td>
</tr>
<tr>
<td>(3) Vapour-rich inclusions</td>
</tr>
<tr>
<td>Carbonate stage</td>
</tr>
<tr>
<td>(1) Liquid-rich inclusions</td>
</tr>
</tbody>
</table>

Note: All temperatures in °C. Salinity expressed as wt% NaCl equivalent; N = number of inclusions analysed; Tm ice = temperature of final ice melting; Tm NaCl = halite dissolution temperature; Tm = temperature of homogenization (L = liquid; V = vapour; S = solid).
12wt% NaCl equiv. (Fig. 8f). Only six inclusions are measured for type 3 inclu-
sions because of the poor visibility of the liquid phase. Type 3 fluid inclusions that
were measured homogenize into the vapour phase from 189 to 382°C, and have bulk salinities ranging from 3.0 to
5.7wt% NaCl equiv. (Figs. 8c, f).

Carbonate stage: The calcite in the carbonate stage contains only type 2 fluid inclusions. These fluid
inclusions always homogenized to the liquid phase. A wide range of homogenization temperatures was recorded (112–375°C, with a mode at 200–220°C, Fig. 8g). Salinities calculated for these inclusions are in the range of 1.9–22.4 wt% NaCl equiv., with a mode at 4–8 wt% NaCl equiv. (Fig. 8h).

6.3 Laser Raman spectroscopy
Laser Raman spectroscopic analysis reveals that the bubbles of type 2 and 3 inclusions in garnet and pyrrhotite-bearing quartz veins contain CH₂ (Figs. 10a–d). Moreover, the bubbles of type 3 inclusions in chalcopyrite-bearing quartz veins contain variable amounts of CH₄, CO₂ and H₂S (Fig. 10e), and the bubbles of type 2 inclusions in quartz–calcite veins contain a minor amount of CO₂ and CH₄ (Fig. 10f).

6.4 Stable isotopes
The oxygen isotopic composition of the host minerals of fluid inclusions and the hydrogen isotopic compositions of fluid inclusions contained in the minerals are listed in Table 2. The calculated δ¹⁸O values of the parent fluids and the measured ΔDSMOW values of inclusion water are plotted in the δ¹⁸O − ΔDSMOW diagram (Fig. 11).

The δ¹⁸O values are in the range of 6.5‰–7.0‰ for garnet of the skarn stage, 11‰–12.4‰ for quartz of the early quartz–sulfide stage, and 11.9‰–14.5‰ for quartz of the late quartz–sulfide stage (Table 2). Using these δ¹⁸O values and the fluid inclusion homogenization temperatures, together with the fractionation equations of Taylor (1976) for garnet and Clayton et al. (1972) for quartz, the δ¹⁸O values of the parent fluids were calculated to be 9.2‰–9.6‰ for the skarn stage, 6.7‰–8.1‰ for the early quartz–sulfide stage, and 5.0‰ to 7.6‰ for the late quartz–sulfide stage (Table 2). These values of δ¹⁸O values are similar to those of magmatic fluids (+5.5‰ to +9.5‰, Ohmoto and Goldhaber, 1997; Ohmoto and Rye, 1979) (Fig. 11).

The ΔDSMOW values of fluid–inclusion water, extracted from quartz of the early and late quartz–sulfide stages, are in the range of −73‰ to −97‰ and −68‰ to −91‰, respectively (Table 2). These values also large overlap with the field of magmatic fluids (Fig. 11).

7 Discussion
7.1 Sources and evolution of ore–forming fluids
The fluid inclusions within skarn-stage garnet are characterized by high homogenization temperatures (the mode of homogenization temperatures is 440–480°C), and high salinities (salinities up to 52 wt% NaCl equiv.), indicating that the fluids are probably of magmatic origin. Hydrogen and oxygen isotopes are important monitors for the sources and evolution of ore–forming fluids. The oxygen isotopic composition of the early fluids, which were in equilibrium with skarn-stage garnet, is very close to magmatic water values (Fig. 11), which further supports the idea that they were magmatic in origin. Different types
of fluid inclusions coexist closely within garnet and pyroxene (as exemplified in Figs. 7a–c); they are commonly isolated and likely primary, and thus are interpreted to have been trapped contemporaneously.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Mineralization stage</th>
<th>$\delta^{18}$O$_{\text{H$_2$O}}$ (‰)</th>
<th>$\delta^{16}$O$_{\text{H$_2$O}}$ (‰)</th>
<th>$\delta^{18}$O$_{\text{fluid}}$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTS001</td>
<td>Garnet</td>
<td>Skarn stage</td>
<td>7.00</td>
<td>9.61</td>
<td>-96.3</td>
</tr>
<tr>
<td>DTS002</td>
<td>Garnet</td>
<td>Skarn stage</td>
<td>6.57</td>
<td>9.18</td>
<td>-97.2</td>
</tr>
<tr>
<td>DTS003</td>
<td>Quartz</td>
<td>Skarn stage</td>
<td>11.5</td>
<td>7.21</td>
<td>-76.0</td>
</tr>
<tr>
<td>DTS004</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>11.0</td>
<td>6.71</td>
<td>-73.0</td>
</tr>
<tr>
<td>DTS010a</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>12.4</td>
<td>8.11</td>
<td>-76.0</td>
</tr>
<tr>
<td>DTS007</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>12.4</td>
<td>8.11</td>
<td>-73.0</td>
</tr>
<tr>
<td>DTS008</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>11.9</td>
<td>5.01</td>
<td>-91.0</td>
</tr>
<tr>
<td>DTS009</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>12.2</td>
<td>5.26</td>
<td>-72.5</td>
</tr>
<tr>
<td>DTS010b</td>
<td>Quartz</td>
<td>Early quartz-sulfide stage</td>
<td>14.5</td>
<td>7.58</td>
<td>-71.7</td>
</tr>
<tr>
<td>DTS011</td>
<td>Quartz</td>
<td>Late quartz-sulfide stage</td>
<td>13.4</td>
<td>6.46</td>
<td>-68.5</td>
</tr>
<tr>
<td>DTS012</td>
<td>Quartz</td>
<td>Late quartz-sulfide stage</td>
<td>12.6</td>
<td>5.75</td>
<td>-71.2</td>
</tr>
</tbody>
</table>

1 Data from Lu (2007); 2 Data from Chu (2003).
These coexisting fluid inclusions homogenize both to vapour and liquid in about same temperature range, indicating boiling in the skarn-stage fluids. Although minor post-trapping modifications may have contributed to the variation of microthermometric data, there is no evidence of intensive deformation that would have significantly breached or stretched the fluid inclusions (Goldstein, 2001).

The fluid inclusions within quartz from the early quartz–sulfide stage are similar to those within garnet and pyroxene from the skarn stage, containing all fluid inclusion types (type 1–4) identified in this study. As mentioned above, these fluid inclusions are clustered and locally isolated (as exemplified in Figs. 7d, e), and thus are considered as primary inclusions and are interpreted to have been trapped contemporaneously. These fluid inclusions exhibit a very narrow range in homogenization temperature (the mode is 380–400°C) and a wide range in salinity (4.3–43 wt% NaCl equiv., with three modes of 38–40, 12–16 and 4.3–5.7 wt% NaCl equiv.). No quartz showing undulose extinction was found in the early and late quartz–sulfide stages, suggesting the influence of modification after inclusion entrapment on the properties of fluid inclusions is very limited. Therefore, the coexistence of saline and vapour-rich fluid inclusions in areas close to each other within a crystal, and their contrasting homogenization characteristics (to the liquid and vapor phase, respectively) at similar temperatures, suggest that boiling also took place during the early quartz–sulfide stage. The oxygen isotopic composition (6.7‰–8.1‰) of the fluids in equilibrium with quartz from the early quartz–sulfide stage is similar to those of magmatic water. The δD<sub>SMOW</sub> values of water in quartz from the early quartz–sulfide stage vary from −73‰ to −97‰. On the plot of δD<sub>SMOW</sub> versus δ<sup>18</sup>O<sub>water-SMOW</sub> (Fig. 11), two samples (DTS005, DTS006) fall within the magmatic water field, indicating that these fluids are dominantly magmatic water. Two other samples (DTS003, 004) have similar δ<sup>18</sup>O<sub>water-SMOW</sub> values as DTS005 and DTS006, but their δD<sub>SMOW</sub> values are below the magmatic water box, which may have resulted from boiling. Experimental and simulation studies suggest that D preferentially fractionates into the vapour phase relative to H during fluid boiling at temperatures above 250°C (Horita et al., 1993, 1995; Horita and Wesolowski, 1994; Shmuelovich et al., 1999; Driesner and Seward, 2000), and vapour leaving the hydrothermal system may have an isotopic signature similar to seawater, whereas brine residues may become increasingly depleted in D (Shmuelovich et al., 1999).

δ<sup>18</sup>O<sub>water-SMOW</sub> values of the mineralizing fluids for the late quartz–sulfide stage vary from 5.0‰ to 7.6‰. Four of the analyzed samples fall in the range of magmatic water, and three samples have δ<sup>18</sup>O<sub>water-SMOW</sub> values that are slightly lower than those of magmatic water (Fig. 11). δD<sub>SMOW</sub> values of water in quartz from the late the quartz–sulfide stage range from −68‰ to −73‰, which are similar to those of magmatic water, apart from one sample with a δD<sub>SMOW</sub> value of −91‰ (Fig. 11). Four analyses plot within the magmatic water field (Fig. 11), suggesting that the ore-forming fluid of the late quartz–sulfide stage was mainly magmatic water. Two analyses plot within the field between magmatic and meteoric water, but near the magmatic water field, implying that the ore-forming fluids related to these samples were mainly of magmatic origin with minor admixing with meteoric water.

The quartz from the late quartz–sulfide stage also contains all types of fluid inclusions. These fluid inclusions are also clustered and locally isolated (as exemplified in Figs. 7f–h), and thus are considered as primary inclusions and are interpreted to have been trapped contemporaneously. The coexistence of different types of fluid inclusions with similar homogenization temperatures in small areas within a crystal (as exemplified in Figs. 7f, g) strongly suggests that the fluid boiled in the late quartz–sulfide stage. The low δD<sub>SMOW</sub> value of −91‰ of one sample may have also resulted from boiling.

The calcite from the carbonate stage contains only type 2 fluid inclusions. These fluid inclusions have relatively low salinities and low temperatures, indicating late cooling and dilution of ore fluids, probably as a result of incursion of groundwater of meteoric origin, which mixed with
maggmatic fluids.

The concentration effect of losing volatiles during fluid boiling can result in increased salinities (Henley and Mcnabb, 1978; Wilkinson, 2001; Meinert et al., 2003; Liao et al., 2014). However, the microthermometric data show that the salinities of fluid inclusions from the late quartz-sulfide stage are slightly lower than those at the early quartz-sulfide stage (Fig. 9). One possible inference is that another fluid with lower salinity was incorporated into the fluid system. When the microthermometric data for all four paragenetic stages are considered together (Fig. 9), it is evident that the four sets of fluid temperature and salinity recorded for each stage form a linear trend, with salinities and homogenization temperatures decreasing with time. These trends resemble the fluid mixing trend proposed by Kreuzer (2005) and Wagner et al. (2009).

The ore-forming fluids in the skarn stage and the early quartz-sulfide stage are relatively reducing, as reflected by the presence of CH₄ in the fluid inclusions, the lack of iron-oxide daughter minerals (hematite and magnetite) in type 1 fluid inclusions, and the absence of sulfate minerals (barite, anhydrite, and gypsum) in the mineral assemblages. On the contrary, fluids in the late quartz-sulfide stage and carbonate stage are relatively oxidizing, as indicated by the presence of CO₂ rather than CH₄ in type 2 and type 3 inclusions. This change in redox environments from the early to late stages probably resulted from inflow of meteoric water (Chen et al., 2012; Zhang et al., 2012; Liao et al., 2014).

In summary, based on the fluid inclusion and stable isotope data, we suggest that 1) the ore forming fluids were dominated by magmatic water in the early stages (skarn and early quartz-sulfide stages) and it mixed with meteoric water in later stages (late quartz-sulfide and carbonate stages); and 2) at least three episodes of fluid boiling took place during the formation of the Datuanshan copper deposit: the first episode occurred during skarnification, with fluid temperatures of 325–561°C and salinities of 5.4–52wt% NaCl equiv; the second episode occurred during the early quartz-sulfide stage, with fluid temperatures of 286–432°C and salinities of 4.3–43wt% NaCl equiv, and the third episode happened in the late quartz-sulfide stage, with fluid temperatures of 189–382°C and salinities of 3.0–41wt% NaCl equiv. Multi-episode fluid boiling may have resulted from pressure fluctuations or decompression, as suggested for the Dongguashan and Shizishan copper (gold) deposits in the Shizishan orefield by Xu et al. (2005) and Xiao et al. (2002).

7.2 Mineral precipitation mechanisms

In the Datuanshan copper deposit, the main ore-forming elements are copper and molybdenum, which mainly exist as chalcopyrite and molybdenite. The copper precipitation temperature of this deposit mainly ranges from 280 to 400°C, as indicated by fluid inclusion homogenization temperatures (Fig. 8). This temperature range is similar to those reported for other porphyry and skarn copper deposits such as the Sungun, Bingham, El Teniente and Dongguashan deposits (Hezarkhani et al., 1999; Xu et al., 2005; Landwing et al., 2005; Klemm et al., 2007). Experimental studies and chemical modelling have shown that copper is predominantly transported as copper chloride and bisulfide complexes in natural hydrothermal fluids (Barnes, 1979, 1997; Liu et al., 2001; Sherman, 2007; Liu et al., 2008; Mei et al., 2013, 2014; Liao et al., 2014). The precipitation of chalcopyrite can be caused by breakdown of copper chloride and bisulfide complexes during fluid transport, which can be induced by decreases in temperature and ligand ion activity and an increase in pH (Barnes, 1979, 1997; Liu and McPhail, 2005; Seo et al., 2012). These changes in the physico-chemical parameters are produced mainly by fluid-rock interactions, boiling, mixing of the ore fluids with fluids of a markedly different composition, or a combination of some of the above (Wagner et al., 2009; Yoo et al., 2010; Cao et al., 2012, 2015; Li et al., 2013; Huang et al., 2014; Feng et al., 2014). The fluid-rock interaction which accompanied ore deposition at Datuanshan produced a wide envelope of chloritization, but is not considered to have contributed to ore formation because it will lead to an increase in chalcopyrite solubility (Barnes, 1979, 1997; Liu and McPhail, 2005; Simon et al., 2006; Wagner et al., 2009).

As discussed above, fluid boiling took place during the skarn stage, the early quartz-sulfides stage and the late quartz-sulfides stage. Fluid boiling may have increased the oxidizing status of the ore fluid, decreased its temperature and significantly increased its pH due to the loss of acidic volatiles (Barnes, 1979; Wagner et al., 2009); the first factor (increased oxidation) is unfavorable, and the latter two factors (decreased T and increased pH) are favorable, for chalcopyrite precipitation. The presence of pyrrhotite and the absence of iron-oxide daughter minerals, CO₂ component and sulfate in the fluid inclusions in the skarn and early quartz-sulfide stages imply that the ore-forming fluids of these two stages were under relatively reduced conditions and sulfur was present in the hydrothermal fluids mainly as reduced sulfur (H₂S). Upon cooling and boiling, H₂S is stabilized in the fluids at high temperatures (above ~400°C) and reduced conditions (Barnes, 1997; Suleimenov and Seward, 1997; Seo et al., 2009). Therefore, the boiling in the skarn stage is unfavorable for ionization of hydrogen sulfide and precipitation of sulfide minerals, but favors precipitations of Ca, Mg and Fe,
which formed skarn minerals such as garnet and pyroxene, and enrichment of copper in the ore-forming fluids. In the early quartz–sulfide stage, the fluid temperatures were still high (mode of fluid inclusion homogenization temperatures at 380–400°C, Fig. 8c) and close to the temperature of H₂S stability (∼400°C, Barnes, 1997; Suleimenov and Seward, 1997; Seo et al., 2009). As a result, the available sulfur ion (e.g., S²⁻ and S₈²⁻) in fluids of the early quartz–sulfide stage is insufficient relative to metals (e.g., Cu and Fe), resulting in precipitation of mainly pyrrhotite and minor chalcopyrite. This process also leads to a further enrichment of copper in the ore-forming fluids. The relatively reduced conditions of the early fluids also imply that the fluids boiling during the skarn and early quartz–sulfide stages occurred mainly under lithostatic pressure, and did not lead to large-scale hydraulic fracturing of wallrocks which would provide conduits for inflow of meteoric water and oxidize the fluid system. In contrast, the CO₂ component identified in inclusions from the late quartz–sulfide stage indicates that the ore-forming fluids in this stage were under relatively oxidized environments, probably as a result of inflow of meteoric water. Interestingly, the fluid inclusion homogenization temperatures in this stage are similar to those corresponding to the conversion from lithostatic to hydrostatic pressure systems (Fournier, 1999). The change in fluid pressure regime in the late quartz–sulfide stage may have resulted in intensive fluid boiling, with volatile substances escaping from the fluid system, causing the pH, Eh, temperature and other properties of the solutions to change significantly (Drummond and Ohmoto, 1985; Hedenquist et al., 1998; Logan, 2000; Meinert et al., 2005). Consequently, chalcopyrite precipitated. A direct link between copper deposition and boiling is supported by the observation that veins exhibiting boiling have the highest copper grades. Thus, multi-episode fluid boiling is probably the most important factor influencing mineralization at Datuanshan.

In many hydrothermal systems, mineralization is generally due to fluid mixing (Audétat et al., 1998; Lu et al., 2003; Zhou et al., 2007; Cao et al., 2012, 2015; Yu et al., 2014). As discussed above, the ore forming fluids were dominated by magmatic water in the early stages (skarn and early quartz–sulfide stages) and mixed with meteoric water in the later stages (late quartz–sulfide and carbonate stages). The overall decrease in fluid salinities with time (Fig. 9) suggests that more and more meteoric water invaded the hydrothermal system from early to late stages, which oxidized the fluid system, increased the overall pH, and decreased temperature and ligand activity (Wagner et al., 2009, Cao et al., 2015). All of these factors may have contributed to chalcopyrite precipitation through destabilization of copper chloride and bisulfide complexes. Therefore, copper deposition in the Datuanshan deposit can be attributed to a combination of multi-episode fluid boiling and mixing of magmatic and meteoric fluids.

8 Conclusions

Field evidence and petrographic observations indicate that the ore-forming processes in the Datuanshan deposit can be divided into four stages, i.e., the skarn, early quartz–sulfide, late quartz–sulfide and carbonate stages, respectively. Chalcopyrite is the main copper mineral, whose precipitation started in the early quartz–sulfide stage, but mainly concentrated in the late quartz–sulfide stage.

Four types of fluid inclusions are identified in the Datuanshan deposit: three-phase inclusions (type 1), liquid-rich inclusions (type 2), vapour-rich inclusions (type 3) and pure vapour fluid inclusions (type 4). The minerals from the skarn, early and late quartz–sulfide stages contain all fluid inclusion types, but only type 2 fluid inclusions were observed in the carbonate stage.

Microthermometric results of fluid inclusions and H–O isotope data indicate that the ore forming fluids were dominated by magmatic water in the early stages (skarn and early quartz–sulfide stages) and mixed with meteoric water in the late stages (late quartz–sulfide and carbonate stages). According to the fluid inclusion assemblages, homogenization temperatures, salinities and stable isotopes, it is inferred that three episodes of fluid boiling occurred during the skarn, early quartz–sulfide and late quartz–sulfide stages, respectively. These fluids boiling are closely associated with chalcopyrite precipitation. First two episodes of fluids boiling led to an enrichment of copper in the ore-forming fluid, and the third episode of fluids boiling resulted in large amounts of chalcopyrite precipitation. In addition, a meteoric fluid mixing process at the late quartz–sulfide and carbonate stages is also suggested, which may have contributed to copper mineralization.

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