



Fluid evolution of the Paleoproterozoic Hujiayu copper deposit in the Zhongtiaoshan region: Evidence from fluid inclusions and carbon–oxygen isotopes

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ABSTRACT

The Zhongtiaoshan region, located in the southern margin of the North China Craton, is the host to a number of metamorphosed sediment-hosted stratiform copper deposits. These deposits are hosted by dolomitic marble and silicic albitite of the mid-Paleoproterozoic Zhongtiao Group and contain economically significant copper and cobalt. The formation of these deposits is considered to be closely associated with the evolution of the Paleoproterozoic “Zhongtiao” rift. The Hujiayu deposit, the second largest Cu deposit of this type, is mainly hosted in silicic albitite and dolomitic marble in the upper part of the Bizigou Formation but locally extends into carbonaceous shales at the bottom of the Yujiashan Formation. Mineralization of the Hujiayu Cu deposit can be divided into an early stage (diagenetic stage) with disseminated to veinlet sulfides and a late stage (metamorphism stage) with coarse-vein sulfides. Mineral assemblages are similar for the two stages, with major minerals as chalcopyrite, pyrite, and pyrrhotite and main gangue minerals as dolomite and quartz. Sulfide veinlets formed in the early stage are thin and discrete, and have irregular boundaries with the host rocks; whereas the ore-bearing veins of the late stage are controlled by fractures.

Five types of fluid inclusions are recognized in the Hujiayu Cu deposit and they are: (1) pure vapor and vapor-rich inclusion (V-type), (2) pure CO₂ inclusion (PC-type), (3) CO₂–H₂O inclusion (C-type), (4) liquid-rich inclusion (L-type), and (5) daughter mineral-bearing inclusion (S-type). Microthermometric analysis shows that the ore-forming fluids of the early mineralization stage are characterized by high salinity (22–40 wt.% NaCl equiv.) and moderate temperature (120–280 °C). The ore-forming fluids of the late mineralization stage are characterized by CO₂ enrichment, high salinity, high temperature and underwent significant unmixing at a temperature interval of 240–480 °C. Compositions of the ore-forming fluids in the early and late stages are interpreted to be mainly basinal brine and metamorphic hydrothermal solution, respectively. Carbon and oxygen isotope compositions suggest possible carbon isotope exchange between the ore-forming fluids and organic-rich carbonaceous shales during the early stage. In the late mineralization stage, both degassing of CO₂ and isotopic exchange with organic carbon may have contributed to the formation of the more negative $\delta^{13}\text{C}_{\text{V-PDB}}$ values of mineralized carbonates.

The early stage mineralization of the Hujiayu Cu deposit may have occurred via interaction of oxidized Cu-bearing brines from the red-bed in the lower segment of the Bizigou Formation with the overlying reductive carbonaceous shales. Late stage mineralization at Hujiayu was mainly triggered by CO₂ escaping from metamorphic hydrothermal solutions.

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1. Introduction

Sediment-hosted stratiform copper deposits are an important type of Cu resource globally, constituting approximately 23% of the world's discovered copper (Singer, 1995; Hitzman et al., 2010). They are formed in evolving basin-scale fluid-flow systems and are comprised of disseminated and veined copper and copper-iron

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sulfide mineralization in dolomitic or silica clastic sedimentary rocks (Brown, 1997; Hitzman et al., 2005). It is widely accepted that the migration of oxidized ore-bearing fluids into a reducing environment leads to the precipitation of ore minerals (Rose, 1976; Brown, 1992; Hitzman et al., 2010). However, details of the ore-forming fluid system are still unclear (Hitzman et al., 2005, 2010), mainly due to the absence of syn-ore gangue minerals that contain fluid inclusions representative of the ore-forming fluids (Hitzman et al., 2010).

The Hujiayu copper deposit is located in the Zhongtiaoshan region on the southern margin of the North China Craton. The Hujiayu copper deposit is geologically similar to the nearby Bizigou, Laobaotan, and Tongmugou deposits (Fig. 1) and is classified as a “Hu-Bi type” copper deposit in literature (CGGCDZM, 1978; Sun and Hu, 1993). The “Hu-Bi type” copper deposits are similar to sediment-hosted Cu deposits in many respects. They are stratiform orebodies composed of disseminated and veined Cu and Cu–Fe sulfides. The orebodies are hosted within dolomitic marble and carbonaceous shales of the mid-Paleoproterozoic Zhongtiao Group (Sun and Hu, 1993). Red beds composed of weakly metamorphosed hematitic siltstone and dolomitic marble underlie the stratiform orebodies (Wei et al., 1984). Many studies have been conducted on the statistical interpretation of microthermometry and H–O–C isotope compositions regarding the ore-forming fluids of the Hu-Bi type deposits (Sun and Ge, 1990; Zhen et al., 1995; Pang, 2010; Huang et al., 2013). In this paper, we focus on the syn-ore quartz and dolomite of the early stage and ore-bearing quartz-dolomite veins of the late stage. Using field and petrographic observations, microthermometric analyses, laser Raman spectroscopy analyses and carbon–oxygen isotopic study, the composition, origin, and evolution of the ore-forming fluids at the Hujiayu copper deposit as well as their implications on ore formation are discussed.

2. Regional geology

The Zhongtiaoshan region is located in the south segment of the Trans-North China Orogen (Zhao et al., 2001; Liu et al., 2012). A Paleoproterozoic “Zhongtiao” rift has been formed in this region (Sun and Hu, 1993; Sun et al., 1995; Zhen, 1997; Fig. 1). More than 30 copper deposits in the Zhongtiaoshan area are believed to have been formed during the evolution of “Zhongtiao” rift. This yields a total metal endowment of approximately 400 Mt of metal Cu (Xu, 2010).

The Precambrian strata exposed in the Zhongtiaoshan area include, from the oldest to the youngest, the Sushui Complex, Jiangxian Group, Zhongtiao Group, Danshanshi Group, and Xiyanghe Group (Hu and Sun, 1987; Sun and Ge, 1990; Bai, 1997; Fig. 1B). The Sushui Complex, the oldest rock unit identified in the Zhongtiaoshan area, consists mainly of the Neoproterozoic (2.8–2.5 Ga) TTG gneiss (Sun and Hu, 1993; Tian et al., 2006; Zhao et al., 2012a; Liu et al., 2012; Zhu et al., 2013; Wan et al., 2014). Rifting in the Zhongtiaoshan area began at approximately 2.2–2.1 Ga. The North China Craton in this period was in an extensional regime (Zhai et al., 2010; Zhai and Santosh, 2011, 2013), which led to abundant magmatism in the Trans-North China Orogen (Du et al., 2010, 2012). The accumulation of potassic bimodal volcanic rocks and shallow facies clastic sedimentation in this period formed the Jiangxian Group, which hosts Luojiahe Cu deposit (Jiang et al., 2013b). As the rifting entered intermediate stage at 2.1 Ga, the sedimentation was primarily terrigenous clastic, volcanic, and marine carbonate, forming the Zhongtiao Group (Sun and Ge, 1990; Sun and Hu, 1993). The first phase of the “Zhongtiao” movement, occurring at ~1.9 Ga (Sun and Hu, 1993; Zhang, 2012), may have led to the closure of the “Zhongtiao” rift. At ~1.85 Ga, the collision between the Eastern and

Western Blocks formed the Trans-North China Orogen (Liu et al., 2012).

The “Zhongtiao” rift is a triple junction rift system with intense fracturing (Fig. 1). The NE-trending branch near the continent failed during the evolution of the rift. The SE-trending and SW-trending basement fractures controlled the emplacement of the stratiform Cu deposits such as the Tongkuangyu, Luojiahe, and the Hu-Bi type Cu deposits (Sun et al., 1995; Fig. 1).

3. Ore geology

Many sediment-hosted stratiform Cu deposits in the Zhongtiaoshan region are hosted in the Zhongtiao Group. The majority of the deposits occur in silicic albitite and dolomitic marble between the lower parts of the Yujiashan Formation and the top of the Bizigou Formation (CGGCDZM, 1978; Sun et al., 1995; Fig. 2). The Bizigou, Hujiayu, Tongmugou, and Laobaotan Cu deposits, four typical “Hu-Bi type” deposits, are located in an approximately 20 km long belt in the southwest branch of the “Zhongtiao” rift (Fig. 1B). The Bizigou Cu deposit, containing 393, 591 t copper (average Cu grade: 1.492%) and 1, 844 t Co (average Co grade: 0.024%), is the largest “Hu-Bi type” deposit (Huang et al., 2001). The Hujiayu Cu deposit is located 12 km south of Bizigou (Fig. 2), with reserves of approximately 320,000 t Cu (average Cu grade: 1.07%), 1700 t Co (average Co grade: 0.027%), 1.119 t Au (average grade 0.19 g/t Au), and 10 t Ag (average grade 1.25 g/t Ag) (Huang et al., 2001). The Hujiayu mine comprises of 167 orebodies. Number 3 is the largest and is 650 m long and 24 m thick (Sun et al., 1995).

The strata exposed in the Hujiayu mining area include the Yuyuanxia, Bizigou, and Yujiashan Formations (from the oldest to the youngest) (Fig. 2A). The Yuyuanxia Formation is composed predominantly of stromatolite-bearing dolomitic marble. The orebodies are mainly hosted in the Bizigou Formation. The rocks of the Bizigou Formation are generally classified into six types (the deepest to the shallowest): amphibolite, scapolite–biotite schist, red sandstone and dolomitic marble, gray dolomitic marble, silicic albitite, and carbonaceous shales (Fig. 3C). The orebodies are mainly hosted in the silicic albitite and gray dolomitic marble within the upper segment of the Bizigou Formation, but they locally extend into the unraninite and pyrite bearing carbonaceous shales (Figs. 3A and 4A) at the bottom of the Yujiashan Formation. The silicic albitite is spatially associated with dolomitic marble and carbonaceous shales, and is characterized by very fine stratification consisting of albite and quartz. The presence of red beds is ubiquitous in the Zhongtiao Group although its importance is often ignored (Wei et al., 1984; Cen, 1993). The red beds (red dolomitic marble and sandstone) occur discontinuously in the lower segment of the Bizigou Formation with a total thickness of up to one hundred meters (Wei et al., 1984; Fig. 3D). However, the thickness of the individual red beds ranges from 6 to 20 m. The occurrence of red beds is similar to other strata of the Bizigou Formation. Strongly limonitic dolomitic marble can be observed in some parts of the Bizigou Formation.

Fold and fault structures are well-developed in the Hujiayu mine area. The Nanhegou–Xigou congruent inverted syncline is the main structural control of the orebodies (Fig. 2A). Common types of hydrothermal alteration products observed at the Hujiayu Cu deposit include albite, carbonate, biotite, and silica. However, the alteration associated with mineralization can be difficult to identify because post-mineralization regional metamorphism also significantly altered the rocks of Bizigou Formation (CGGCDZM, 1978; Sun and Ge, 1990).

The mineralization observed in the Hujiayu Cu deposit can be divided into early stage (diagenetic stage) and late stage (metamorphic stage):

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