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Ore geology and fluid inclusions of the Hucunnan deposit, Tongling, Eastern China: Implications for the separation of copper and molybdenum in skarn deposits

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ABSTRACT

The Hucunnan ore deposit is a representative skarn Cu–Mo deposit in the Tongling district, an important ore district of the renowned Middle–Lower Yangtze River metallogenic belt of China. The deposit shows distinct zonation of metals, with Cu mineralization distributed mainly in the exoskarn zone at shallow depths, and Mo mineralization occurring chiefly in the endoskarn zone located at deeper depths. Field evidence and petrographic observations indicate that the ore-forming processes can be divided into the skarn, quartz–molybdenite, quartz–chalcopyrite, and carbonate stages. Five types of fluid inclusions (FIs) are present in the deposit: solid-bearing (type 1), liquid-rich (type 2), vapor-rich (type 3), pure vapor (type 4), and CO_2-bearing (type 5). The skarn stage contains mainly type 1 and 2, but also minor type 3 and 4 FIs; the FIs display homogenization temperatures of 434–570 °C and salinities of 2.07–66.0 wt.% NaCl equiv. The existence of hematite daughter minerals in the type 1 inclusions, together with the presence of magnetite in skarn, implies that the skarn-stage fluid was oxidizing. The skarnization of the granodiorite porphyry is commonly accompanied by potassic alteration, suggesting that the fluids were rich in alkali. Similar to the skarn stage, the quartz–molybdenite stage contains type 1 and 2, and minor type 3 and 4 FIs, which yield homogenization temperatures of 280–458 °C and salinities of 1.40–54.2 wt.% NaCl equiv. The presence of sulfide instead of hematite daughter minerals in the type 1 inclusions in quartz–molybdenite veins associated with sericitization indicates that the fluids of the quartz–molybdenite stage were more reducing and more acidic than the fluids in the skarn stage. The decrease in oxygen fugacity and increase in acidity could have resulted from magnetite crystallization and the consumption of alkali cations and OH^-, respectively, during the skarn stage. The quartz–chalcopyrite stage contains all types of FIs, which show homogenization temperatures of 203–392 °C and salinities of 1.22–46.6 wt.% NaCl equiv. Observations of hematite-bearing type 1 FIs in quartz–chalcopyrite veins containing anhydrite associated with biotitization suggest that the fluids of the quartz–chalcopyrite stage were oxidizing and alkali-rich, probably on account of the inflow of meteoric water and boiling in an open system. In the carbonate stage, only type 2 FIs are present; these FIs yield the lowest homogenization temperatures of 156–276 °C and the lowest salinities of 1.05–12.3 wt.% NaCl equiv. Microthermometry and H–O isotope data indicate that the ore-forming fluids were dominated by magmatic water in the early stages (skarn and quartz–molybdenite stages), and that the magmatic water gradually mixed with circulating meteoric water during the late stages (quartz–chalcopyrite and carbonate stages). The coexistence of saline and vapor-rich FIs as internal trails or clusters within individual crystals, with similar homogenization temperatures but contrasting salinities and homogenization modes (to the liquid and vapor, respectively), in the first three stages strongly suggests that three episodes of fluid boiling occurred in these stages, as further supported by the hydrogen isotopic compositions of the fluids, which are lower than those of magmatic water. Based on the above data, we conclude that temporal changes in redox conditions, acidity, and temperature in the mineralizing fluids resulted in the temporal separation of Cu and Mo by selective sulfide precipitation in the Hucunnan skarn deposit. The competition among metals (e.g., Mo and Cu) for sulfur in magmatic fluids, along with vapor–brine immiscibility (fluid boiling), are major factors that contributed to the spatial separation of Cu and Mo in the deposit.

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1. Introduction

The Mo–Cu ± Au association is common in magmatic hydrothermal deposits, as for example in polymetallic porphyry–skarn deposits/orefields (Meinert et al., 2005; Sillitoe, 2010; Seo et al., 2012). However, many such deposits/orefields show a clear separation of Mo versus Cu ± Au mineralization, in both space and time (e.g., Meinert et al., 2005; Simon et al., 2006; Xu et al., 2011; Seo et al., 2012; Cao et al., 2015). For example, the metal grades in some porphyry–skarn deposits show a rough correlation with formation depth; i.e., deep deposits tend to be enriched in Mo but are Cu and Au poor, as in Butte, Montana, and Bingham Canyon, Utah, USA (Singer et al., 2005; Rusk et al., 2008; Murakami et al., 2010; Seo et al., 2012). In some deposits, molybdenite precipitation postdates the precipitation of Cu sulfides ± Au, as for example in the Bingham Canyon deposit (Seo et al., 2012), but the opposite is observed in other deposits, such as in the Datuanshan and Fenghuangshan deposits in East China (Lai and Chi, 2007; Li et al., 2014; Cao et al., 2015) and the Bangpu deposit in Tibet (Wang et al., 2015a). Although the separation of Mo and Cu (Au) at deposit/orefield scales is known and is of economic importance, the geological causes for the partitioning and precipitation of the minerals remain poorly known.

The Tongling region in the renowned Middle–Lower Yangtze River metallogenic belt (MLYRB) of eastern China is an important district of Cu–Au–Fe–Mo mineralization (Fig. 1A) containing numerous skarn deposits (Tang et al., 1998; Pan and Dong, 1999; Mao et al., 2006, 2011). The polymetallic district (approximately 40 km long in an E–W direction and 20 km wide, with a total area of ~800 km^2; Fig. 1B) contains >50 known mineralized skarn occurrences that are closely associated with Early Cretaceous intermediate–acid intrusions (Wu et al., 2014). Some of these mineralized skarns show porphyry-style alteration (Mao et al., 2011; Yang et al., 2011; Wang et al., 2015b).

The total Cu–Au reserves in the Tongling district have been estimated at 5 Mt Cu and 150 t Au (Wu et al., 2010). The Hucunnan deposit, discovered by Team 321 of the Bureau of Geology and Mineral Exploration of Anhui Province, is a representative skarn deposit in the district, and shows mineralization associated with porphyry-style alteration. In the Hucunnan deposits that contain both Cu and Mo, a paragenetic relationship is observed between Cu sulfides and molybdenite, from vein to orebody scales, with molybdenite precipitation predating the precipitation of Cu–Fe sulfides. Drilling has revealed that Cu mineralization in the deposit is developed mainly within exoskarn, whereas the Mo mineralization occurs mainly in endoskarn, and is located deeper than the Cu mineralization.

The Hucunnan deposit is particularly suitable for comparing the mechanisms of copper sulfide and molybdenite precipitation, because the Cu mineralization is temporally and spatially distinct from the Mo mineralization. As is well known, fluid processes are critical for understanding the transport and concentration of metals in hydrothermal systems. Therefore, in this study we examined the interrelationships between Cu and Mo mineralization at field and petrographic scales, combined with data on H–O isotopes, fluid inclusion (FI) microthermometry, and laser Raman spectrometry. The aim is to reveal the sources and evolution of ore-forming fluids and the factors that lead to the separation of molybdenite from copper sulfides in skarn systems.

2. Geologic setting

The Tongling district, located in the central part of the MLYRB (Fig. 1A), is the largest Cu–Au–Fe–Mo ore district in the belt (Tang et al., 1998; Pan and Dong, 1999; Mao et al., 2006; Lai and Chi, 2007). Marine sedimentary rocks in the Tongling district, which include clastic sedimentary rocks, carbonates, and evaporates, were deposited in the Silurian–Middle Triassic, with the exception of the Early–Middle

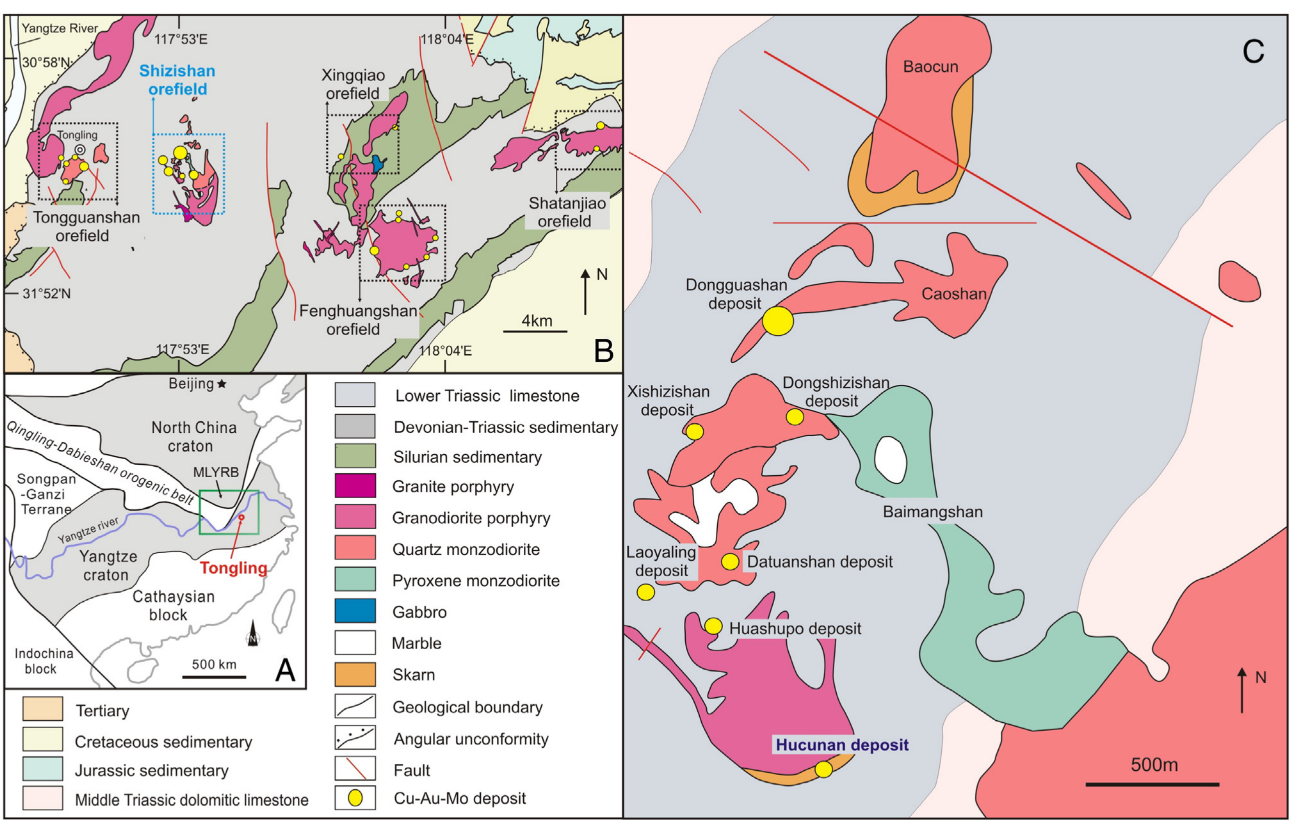

Fig. 1. (A) Simplified structural map showing the locations of the Middle–Lower Yangtze River metallogenic belt (MLYRB) and Tongling district (modified from Metcalfe, 2011; Mao et al., 2011). (B) Geological map of the Tongling district (modified from Chang et al., 1991). (C) Simplified geological map of the Shizishan orefield in the Tongling district (modified from Wang et al., 2015b).