Ore Geology Reviews 71 (2015) 263–272

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

Tracing the ore-formation history of the shear-zone-controlled Huogeqi Cu–Pb–Zn deposit in Inner Mongolia, northern China, using H, O, S, and Fe isotopes

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ARTICLE INFO

Article history:
Received 22 December 2014
Received in revised form 27 May 2015
Accepted 7 June 2015
Available online 9 June 2015

Keywords:
H–O–S–Fe isotopes
Huogeqi
Shear zone
Cu–Pb–Zn
Multistage mineralization

ABSTRACT

The original ore-fluid of the Huogeqi Cu–Pb–Zn deposit in Inner Mongolia, northern China, was enriched in heavy oxygen isotopes with $\delta^{18}O$ values ranging from 9.9 to 11.4 per mil, which is characteristic of the metamorphic devolatilization of pelitic rocks. The δD values determined by direct measurement of syn-ore hydrothermal tremolite range from −116 to −82 per mil, lying between the domains of typical metamorphic fluid and meteoric water, which is in equilibrium with organic matter. Oxygen and hydrogen isotope ratios indicate that the ore-fluid was derived from deep-sourced metamorphic fluid and interacted with organic-rich shale during fluid migration, which is consistent with the fluid evolution history revealed by a previous fluid inclusion study. Sulfides in the deposit are characteristically enriched in heavy S isotopes, with an average $\delta^{34}S$ value of 13.4 ± 6.2 per mil (1σ, n = 103). The S-isotope ratios are identical to stratabound sulfides generated through the non-bacterial reduction of Neoproterozoic marine sulfate (with $\delta^{34}S$ values of ~17 per mil). Previous studies on lead isotopes of sulfides revealed that the ore-forming metals (Cu, Pb, and Zn) at the Huogeqi deposit were also remobilized from a stratabound source. This source was syngenetically elevated in its Cu-, Pb-, and Zn-sulfide content as a result of submarine hydrothermal activities forming sulfide-rich layers within a rift tectonic setting. The Fe isotope ratios for sulfides are consistent with those of an intercalated iron-formation within the ore-hosting rocks, suggesting that the Fe in the sulfides was derived from local host rocks during sulfide precipitation and the Fe-rich rocks are favorable lithological units for high-grade mineralization. The heterogeneous sources of ore-fluid, S, ore-forming metals, and Fe are explained by a multistage genetic model, which is supported by the geological characteristic of the deposit. The enriched sulfides were subsequently remobilized and enriched by metamorphic devolatilization during the Permian and Triassic periods. The metamorphic ore-fluid ascended along a shear zone and interacted with organic-rich shale. Sulfides eventually precipitated within the shear zone at a shallower crustal level, especially where the shear zone intersected Fe-rich host rocks. This multistage genetic model has implications for mineral exploration. Greenschist to amphibolite facies terranes containing thick Neoproterozoic rift sequences are ideal regions for potential Cu–Pb–Zn mineralization. In particular, intercalated volcanic rocks within the rift sequences are indicative of high heat-flow and are ideal for the development of submarine hydrothermal systems. The primary structures hosting mineralization and ore shoots in the Huogeqi area are jogs in the shear zones. In addition, Fe-rich lithological units, such as iron-formations, are ideal hosts for high-grade ore.

1. Introduction

The Huogeqi deposit in the Langshan area of western Inner Mongolia has reserves of 0.71 Mt grading 1.35% Cu, 0.97 Mt grading 1.49% Pb, and 0.78 Mt grading 1.46% Zn (Huang et al., 2001), and contains up to 0.1 g/t of Au (Huo, 2011). Although the deposit has been explored and mined since 1958, its genesis has remained unclear. Models include a syngenetic submarine exhalative setting (mainly based on the fact that the Cu–Pb–Zn orebodies are hosted by rift-related sequences and show intimate spatial relations with layered iron-formation). The geochemical characteristics (e.g. S and Pb isotopes) of the deposit are also typical of submarine exhalative systems (Wang and Yang, 1993; Yu et al., 1993; Geng, 1997; Jin et al., 1997; Fei et al., 2004; Peng et al., 2006, 2007; Zhu et al., 2006). Alternatively, an epigenetic model has been proposed on the basis of the observation that Cu–Pb–Zn mineralization is structurally controlled by deformed and faulted host rocks

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http://dx.doi.org/10.1016/j.oregeorev.2015.06.003
0169-1368/

(Niu et al., 1991; Ren et al., 1992; Yang, 1998; Zhang and Wang, 2001, 2002). Others have suggested that the deposit has characteristics of orogenic-type mineralization and have proposed that it was formed by remobilization of submarine exhalative sulfides during Late Paleozoic orogeny (Chen et al., 2004, 2007b, 2009a; Chen, 2006; Pirajno, 2009). Our studies on ore fabrics and fluid inclusions also indicate that the mineralization is shear-zone-controlled and the ore-fluid had a metamorphic origin (Zhong et al., 2012, 2013).

In this study, the enigmatic ore-formation history of the Huogeqi deposit is reconstructed using conventional (H, O, and S) and non-traditional (Fe) stable isotopes to constrain the sources of aqueous fluids, sulfur, and iron in the ore-forming system. Both syngenetic and epigenetic geological processes are modeled in this study for a better understanding of the ore-forming process. A multistage genetic model is proposed on the basis of a synthesis of stable isotope data, geological features and previous geochronological results, lead isotope ratios, and fluid inclusion studies. Finally, the indicators of mineral exploration are discussed on the basis of the multistage genetic model.

2. Geological setting

The Lang Mountains (Langshan) in the northwest corner of the North China Craton (NCC) is dominated by greenschist to amphibolite facies rift sequences assigned to the Langshan Group, which includes metasedimentary schist, shale, quartzite and marble, intercalated with felsic and mafic metavolcanic rocks (Peng et al., 2007; Zhai et al., 2008). These sequences were deposited on Archean high-grade metamorphosed rocks in the NCC during Meso- to Neo-proterozoic rifting events in and around the craton (Lu et al., 2002; Zhai and Santosh, 2013).

The Langshan Group was previously interpreted as Mesoproterozoic rift sequences (Lu et al., 2002); however, recent zircon U–Pb geochronological studies on metasedimentary rocks (<1100 Ma; Gong, 2014) and intercalated volcanic rocks (867–805 Ma; Peng et al., 2010) constrain the depositional age to the Neoproterozoic.

Carboniferous to Triassic (321–228 Ma) intermediate to granitic plutons intrude the Langshan Group (Fig. 1; Pi et al., 2010; Liu, 2012; Wang et al., 2012; Wu et al., 2013). During this period, the northern margin of the NCC was reactivated during tectonic activity along the Paleo-Asian Ocean to the north. This reactivation was marked by widespread magmatism, metamorphism, and deformation. It is still unclear whether the Paleo-Asian Ocean finally closed in the Devonian or in the late Permian–Early Triassic (Sengor and Natal'in, 1996; Chen, 2002; Xiao et al., 2003; Chen et al., 2007a; Chen et al., 2009b; Zhang et al., 2009; Xu et al., 2013). In the former model, the closure of the ocean took place during the Devonian, followed by the formation of a limited intracratonic oceanic basin in a post-collisional setting, which was finally closed under a compressional environment by Early–Middle Triassic times (Chu et al., 2013). The latter model emphasizes that the northern NCC was an Andean-like active continental margin during the Carboniferous–Permian, and the late Permian to Triassic magmatism was related to the final closure of the Paleo-Asian Ocean. Both models include compressional tectonics during the late Permian and Early Triassic following the final closure of either a newly formed oceanic basin or the Paleo-Asian Ocean. This is consistent with the recognized continuous thrust fault activities between 270 and 190 Ma along the northern margin of the craton (Wang et al., 2013).

Northeast-trending thrusts developed throughout the Langshan area, resulting in strong folding and mylonitization of the Langshan Group (Fig. 1). The thrusts dip southeast in the north slope of the Lang Mountains and dip northwest in the south slope, forming back-thrusts associated with a northwest–southeast compressional tectonic setting (Fig. 1). The age of late Permian and Early Triassic thrusting is constrained between 237 ± 3 and 213 ± 2 Ma by $^{39}Ar/^{40}Ar$ dating of muscovite separated from mylonite (Gao, 2010).

The Huogeqi Cu–Pb–Zn deposit is located at the north side of the Lang Mountains, adjacent to a southeast-dipping thrust fault (Fig. 1). Neoproterozoic amphibolite-facies units assigned to the Langshan Group host the deposit. The group in the area includes quartzite, almandine–biotite schist, andalusite–biotite schist, two-mica schist, and diopside–tremolite marble. The metasedimentary sequences are interlayered with deformed amphibolite units, which are interpreted as metamorphosed basaltic volcanic rocks (Fig. 2; Zhu et al., 2006). Furthermore, an intercalated iron-formation consisting of magnetite, Fe-rich amphibole, and siderite hosts Cu–Pb–Zn orebodies in the area. These Fe-rich host rocks were hydrothermally altered to pyrite and pyrrhotite near mineralized veins.

The Langshan Group is typically mylonitized in the Huogeqi mining area. Orebodies in the area are generally concordant with the mylonitic foliation along jogs in the shear foliation (Fig. 2). The orebodies extend for up to 1500 m along strike, exceed 1200 m down-dip, and are tens of meters thick. They consistently dip at angles of 65°–80° (Fig. 3). Cu–Pb–Zn sulfides are present parallel to shear bands, resulting in the typical banded and laminated mineralization style (Fig. 4A). Disseminated and quartz-vein-type mineralization is also common at Huogeqi. In addition, sulfide-bearing microfractures exhibit characteristics of shear deformation in a brittle–ductile manner and locally crosscut the mylonitic foliation (Zhong et al., 2012).

Ore minerals in the Huogeqi deposit include chalcopyrite, galena, sphalerite, pyrrhotite, and pyrite (Fig. 4B), with minor amounts of arsenopyrite, breithauptine, costibite, gudmundite, and native bismuth. Syn-ore hydrothermal gangue minerals include quartz, tremolite, epidote, chlorite, biotite, muscovite and minor spessartine, which is a typical greenschist-facies assemblage produced in the ore-forming environment. Fluid inclusion microthermometer suggests that the ore-forming temperature was 364° ± 41 °C (1σ, n = 57) and chlorite geothermometer similarly suggests an ore-forming temperature of 362° ± 26 °C (1σ, n = 9; Zhong et al., 2013), which are consistent with greenschist facies temperatures. Peak metamorphic was at almandine-amphibolite facies, as indicated by the presence of minerals such as almandine, plagioclase, pyroxene and biotite, which are locally replaced by sulfides and accompanying shear-zone hosted hydrothermal Cu–Pb–Zn mineralization (Zhong et al., 2014). The mineralization has a metamorphic origin and post-dates the peak metamorphism of the host rocks. The ore-fluid is mesothermal, CH_4-rich, and its low-salinity are characteristic of the equilibrium between deep-sourced metamorphic fluids and organic-rich carbonaceous shale (Zhong et al., 2013).

As a result of the "deep and later" nature of active orogenic belts (Goldfarb et al., 2005), the metamorphic ore-fluid was derived from the devolatilization of an under-thrust rock pile at depth. The fluid subsequently migrated upward and deposited Cu–Pb–Zn sulfides at higher crustal levels during regional uplift and retrograde metamorphism. Consequently, mineralization associated with the metamorphic fluid was during retrograde metamorphism of immediate host rocks.

A $^{39}Ar/^{40}Ar$ geochronological study reveals that ca. 240 Ma Cu–Pb–Zn mineralization took place after amphibolite facies metamorphism during ca. 271 Ma, which is consistent with the post-peak mineralization deduced from petrographic observations by Zhong et al. (in press).

3. Sampling and analytical methods

Syn-ore hydrothermal tremolite was separated from high-grade ore for oxygen and hydrogen isotopic analysis to ascertain the isotopic characteristics of the mineralizing fluid. The tremolite grains form veinlets and are intergrown with sulfides in addition to being surrounded by them (Fig. 4C). This indicates that the tremolite and sulfide are coeval. Furthermore, sulfide inclusions were ubiquitous in the tremolite, verifying the syn-ore nature of the tremolite. Both oxygen and hydrogen isotope ratios were directly determined for the tremolite samples. Sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, galena, and sphalerite