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Constraints of C–O–S isotope compositions and the origin of the Ünlüpınar volcanic-hosted epithermal Pb–Zn ± Au deposit, Gümüşhane, NE Turkey

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ABSTRACT

The Eastern Pontide Orogenic Belt (EPOB) constitutes one of the best examples of the metallogenic provinces in on the Alpine-Himalayan belt. This study focuses on the genesis of the Ünlüpınar Pb–Zn ± Au deposit in the southern part of the Eastern Pontide Orogenic Belt. The main lithological units in the study area are the Early Carboniferous Kurtoğlu Metamorphic Complex the Late Carboniferous Köse Granitoid and the Early-Middle Jurassic Şenköy Formation. The studied deposit is hosted by the Şenköy Formation, which consists predominantly of basaltic-andesitic rocks and associated pyroclastic rocks that are calc-alkaline in composition. Silicic, sulfidic, argillic, chloritic, hematitic, carbonate and limonite are the most obvious alteration types observed in the deposit site. Ore microscopy studies exhibit that the mineral paragenesis in deposits includes pyrite, chalcopyrite, sphalerite, galena, gold, quartz and calcite. Electron microprobe analyses conducted on sphalerite indicate that the Zn/Cd ratio varies between 84 and 204, and these ratios point at a hydrothermal deposit related to granitic magmas. Fluid inclusion studies in calcite and quartz show that the homogenization temperature of the studied deposit ranges between 90–160 °C and 120–330 °C respectively. The values of sulfur isotope analysis of pyrite, sphalerite and galena minerals vary between 1.6‰ and 5.7‰, and the results of oxygen and carbon isotope analysis range between 8.4‰ and 18‰ and −5‰ and −3.6‰, respectively. The average formation temperature of the ore was calculated as 264 °C with a sulfur isotope geothermometer. All of the data indicate that the Ünlüpınar deposit is an epithermal vein-type mineralization that was formed depending on the granitic magmatism.

1. Introduction

Epithermal deposits were originally defined by Lindgren (1933) as precious or base metal deposits forming at shallow depths and low temperatures. Epithermal systems can be grouped into high and low-sulfidation types based on variations in their hypogene sulfide assemblages (Sillitoe and Hedenquist, 2003). The Eastern Pontide Orogenic Belt, has been the subject of numerous studies due to the economically important deposits as massive sulfide, porphyry, skarn and vein-type (Akaryalı and Tüysüz, 2013; Eyuboglu et al., 2014; Akaryalı, 2015).

The Northern Zone of the EPOB contains generally volcanic-associated massive sulfide (VMS) and vein type deposits as well as skarn and porphyry (e.g. Yalçınalp, 1992; Tüysüz, 2000; Demir et al., 2008; Yaylalı-Abanuz and Tüysüz, 2010; Sipahi, 2011; Sipahi et al., 2014; Eyuboglu et al., 2014; Abdioğlu et al., 2015; Demir et al., 2015). Yalçınalp (1992) asserted in his research in Güzelyayla (Maçka-Trabzon) that the Güzelyayla porphyry Cu–Mo deposit had a mesothermal characteristic and emerged between 280 and 460 °C. Demir et al. (2008) suggested that the formation of the Köstere mine was related to the emplacement of the Late Cretaceous Torul Pluton, which is the youngest unit in the district; additionally, meteoric waters were also effective in ore formation as per the average salinity values of 5.4% that were obtained from fluid inclusion studies. Yaylalı-Abanuz and Tüysüz (2010) suggested that the presence of framboidal and colloidal ore minerals and textures indicated that Akoluk (Ordu) vein-type mineralization occurred at low temperatures in an epithermal system. Eyuboglu et al. (2014) suggested that the geodynamic setting and host rock geochemical characteristics of the eastern Pontides volcanic-hosted massive sulfide deposits are different from those

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of classic Kuroko-type VMS deposits and named them as "Black Sea-type Volcanogenic Massive Sulfide Deposits".

The Gümüşhane region, which is one of the important metallogenic provinces in the Southern Zone of EPOB, hosts various economic mineralizations such as vein-type Pb–Zn and specially epithermal gold–silver (e.g., Tüysüz et al., 1994; Çubukçu, 1998; Lermi, 2003; Aslan, 2011; Akaryalı and Tüysüz, 2013; Akaryalı, 2015). Tüysüz et al. (1994) and Çubukçu (1998) presented the mineral paragenesis of the gold mineralization in Kaletaş (Gümüşhane) and suggested that the mineralization formed as a sedimentary-type (Carlin-type) epithermal gold deposit. Lermi (2003) focused on the Pb–Zn deposit within Liassic Şenköy Formation in the Midi (Gümüşhane) and indicated that the deposit settled along the faults in the form of discontinuous lenses. Aslan (2011) discovered, as a result of their isotope and fluid inclusion studies in the Mastra Au mine of Gümüşhane that mineralization was magmatic-derived and the mineralization appeared within the wide temperature range of 113–390 °C. Akaryalı (2015) emphasized that Altınpınar Pb–Zn deposit is an epithermal vein-type deposit and is related to non-adakitic granitic magmas produced in the Southern Zone of the EPOB in Lutetian.

Although the general geological characteristics of the region, where the Ünlüpınar deposit is located, were determined (Güner and Yazıcı, 2011), no detailed studies have been conducted on the chemical properties of the ore minerals, formation temperature and the genesis of the hydrothermal fluids that form the deposit. Therefore, this study, which was conducted in the Ünlüpınar deposit site, focused on determining the chemical properties of the ore minerals, the formation temperature of the deposit with the fluid inclusion measurements, the origin of the hydrothermal fluids, based on the deposit with $\delta^{18}O$ and $\delta^{14}C$ isotope analyses, and the heat source for the ore based on $\delta^{34}S$ data and formation temperature.

2. Geological background

The Eastern Pontides Orogenic Belt represents one of the most important metallogenic provinces in the Alpine-Himalayan belt and consists of a mountain chain extending parallel to the southeastern coast of the Black Sea (Fig. 1). This belt can be divided into three subzones as Northern Zone, Southern Zone and Axial Zone depending on the tectonic, stratigraphical and sedimentological characteristics.

The Northern Zone, which hosts the massive sulfide mineralizations in the region, is dominated by late Cretaceous and Cenozoic volcanic–pyroclastic rocks, granitic intrusions and gabbroic intrusions (e.g., Kaygusuz and Aydınçakır, 2011; Kaygusuz et al., 2014; Eyuboglu et al., 2015a). The Hercynian basement, which is represented by Pre-Mesozoic metamorphic massifs such as Pulur, Ağvanis and Tokat, as well as non-metamorphic granitic intrusions such as Gümüşhane and Köse plutons, is widely exposed in the Southern Zone of the Pontides (Topuz et al., 2007, 2010; Dokuz, 2011; Dokuz et al., 2013, 2015). Mesozoic time is commonly represented by Jurassic and Cretaceous sedimentary rocks (Tokel, 1972; Pelin, 1977; Eyuboglu et al., 2006; Dokuz and Tanyolu, 2006; Kandemir and Yılmaz, 2009; Eyuboglu, 2015). However, Triassic Alaskan-type mafic–ultramafic intrusions and also calc-alkaline lamprophyres (Eyuboglu et al., 2010; Karslı et al., 2014), late Cretaceous shoshonitic and ultrapotassic volcanic rocks (Eyuboglu, 2010; Eyuboglu et al., 2011a), and late Paleocene-early Eocene adakitic rocks (Topuz et al., 2005; Karslı et al., 2010, 2011; Eyuboglu et al., 2011a,b,c, 2013a), are widespread in the Southern Zone of the Eastern Pontides. The Axial Zone includes the ultramafic–mafic bodies and olistostromal ophiolitic mélanges (Eyuboglu et al., 2007, 2013b; Topuz et al., 2013), which separate the Eastern Pontides from the Anatolide-Tauride block to the further south. Miocene sedimentary rocks are the dominant cover units exposed in the Axial Zone.

The study area is situated in the Southern Zone of EPOB (Fig. 2a). The oldest rock unit exposed in the area is the Kurtoğlu metamorphic complex, which consists mainly of mica schists, gneisses and phyllites, cut by metagranitic dikes (Topuz et al., 2007; Eyuboglu et al., 2013b). According to Topuz et al. (2007), the minimum age for the metamorphic event is the Carboniferous at 320.3 ± 1.7 Ma. Kurtoğlu metamorphic complex is cut by the late Carboniferous Gümüşhane and Köse intrusive complexes, including various rock types such as granite, granodiorite, quartz diorite, rhyolite, and dacite (Topuz et al., 2010; Dokuz, 2011). These basement units, exposed in the study area, are unconformably overlain by the early-middle Jurassic Şenköy Formation (Kandemir, 2004; Kandemir and Yılmaz, 2009), which is characterized by two main phases of the rifting (Eyuboglu et al., 2006). The first phase is represented by basic-intermediate volcanics and coarse clastics deposited in asymmetrical half grabens. These lithologies of Şenköy Formation are overlain by Ammonitico Rosso-type pelagic limestones, showing a short-term thermal subsidence in the region. The second rifting of the Jurassic began with the second sequence of alternating volcanics and epiclastics (Eyuboglu et al., 2006 The early Jurassic rocks are cut by middle Jurassic granitic and quartz dioritic intrusions (Eyuboglu et al., 2015b). The rift-related Şenköy Formation is covered by the late Jurassic-lower Cretaceous carbonates (Berdiga Formation) in the whole Gümüşhane region. The late Cretaceous period is represented by a thick turbiditic sequence with some interlayered felsic tuffs in the Gumushane area (Tokel, 1972's Kermutdere Formation). A recent study (Eyuboglu, 2015) indicated that zircon U-Pb age determinations from the felsic tuffs show that the sequence was deposited on the carbonate platform in Campanian. All exposed rock units are cut by early Eocene adakitic porphyries (Karslı et al., 2010; Eyuboglu et al., 2011a, 2013b) and are uncomformably covered by the middle Eocene Alibaba Formation consisting of basaltic-andesitic volcanic rocks and their pyroclastics. All these lithological units are cut by basaltic dikes of unknown age.

3. Ore deposit geology

The studied Ünlüpınar deposit is hosted by volcanic rocks of the Şenköy Formation (Fig. 2b) is vein-type and characterized by fracture filling of massive sphalerite, galena, pyrite and chalcopyrite. The host rocks are calc-alkaline volcanic rocks, including basalt, andesite, and pyroclastic rock. The andesite in the ore area was strongly altered and deformed. The andesite is dark-gray, with microlitic porphyritic, porphyric (Fig. 3a) and glomeroporphyric texture (Fig. 3b). Wall-rock alteration in the deposit mainly developed along and in the vicinity of mineralized fracture zones. The main alteration types are silicic, sulfidic, carbonate, argillic, chloritic (Fig. 3e and f), hematitic and limonite (Fig. 3d).

The Pekünyayla and Eylenceyayla mineralizations hosted by basaltic-andesitic rocks of Early-Middle Jurassic Şenköy Formation occur within fracture zones that are NE-trending and roughly parallel to each other, indicating the existence of an extensional tectonic regime during their evolution. The sulfide ore-bearing fractures range from 200 to 1000 m in length and from 5 to 15 m in width. Similarly, the distribution of gold-bearing quartz veins in the mineralization field is controlled by NE-trending fractures that vary between 10 and 50 m in length and between 2 and 5 m in width.

The field and also ore petrography studies indicate that there were at least four different stages of ore formation in the Ünlüpınar mineralization. The first stage is represented by chlorite veins. This