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Origin of the Muguayuan veinlet-disseminated tungsten deposit, South China: Constraints from in-situ trace element analyses of scheelite

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ABSTRACT

The Late Triassic Muguayuan W deposit is located in the middle of the Jiangnan Orogen, South China. This deposit is characterized by veinlet-disseminated W mineralization that developed in the Sanxianba granitic porphyry stock. The ore minerals are mainly scheelite with minor molybdenite and wolframite. Scheelite mineralization was closely related to greisenization and phyllic alteration, and took place in two stages. Stage I involved scheelite ± wolframite ± molybdenite + quartz veinlet and disseminated mineralization, whereas Stage II resulted in scheelite + quartz + sericite veinlet mineralization. Sulfide and quartz + calcite ± pyrite veinlets formed during the post-ore stage. Scheelites from the two mineralization stages have different textures and compositions. Cathodoluminescence (CL) images of Stage I scheelites reveal two generations of growth (I-a and I-b). Stage I-a scheelite is dark under CL with oscillatory zoning, and has light rare earth element (LREE)-enriched chondrite-normalized patterns, negative Eu anomalies, and high total REE contents. Stage I-b scheelite forms rim overgrowths on Stage I-a scheelite, is bright under CL, and shows positive Eu anomalies and relatively low REE contents. Although Stage II scheelites are nearly uniform under CL, they can be subdivided into two generations according to their REE systematics. Stage II-a scheelite yields middle REE (MREE)-enriched chondrite-normalized patterns, with negative Eu anomalies, whereas Stage II-b scheelite has MREE-depleted patterns with positive Eu anomalies. Minor amounts of apatite formed in both stages of mineralization. Stage I apatite contains 1370–1930 ppm Mn and 97.7–127 ppm Sr, whereas Stage II apatite has lower Mn (111–158 ppm) and higher Sr (2170–4690 ppm) concentrations. The distinct trace elements compositions of the scheelite and apatite from the two stages identify two ore-forming fluids that had different origins and compositions. The ore-forming fluids in Stage I-a were relatively reduced magma-derived fluids with high Mo, Mn, Nb, and Ta, and low Sr. Fluid modeling shows that the initial fluids of Stage I-a were LREE-enriched with negative Eu anomalies, similar to the Sanxianba granitic porphyry. Precipitation of early apatite and scheelite, as well as plagioclase decomposition, altered the fluid composition and led to relative depletions in REE, Nb, and Ta, and increases of Eu and Sr in the Stage I-b fluids. Cooling of these fluids and the addition of recycled meteoric water led the fluids to become relatively oxidized and Sr-rich; Stage II scheelite precipitated from these fluids. Precipitation of Stage II-a scheelite resulted in the Stage II-b fluids becoming progressively MREE-depleted. Extensive alteration, especially greisenization and phyllic alteration, led to plagioclase decomposition, which provided the Ca necessary for scheelite mineralization. This process was important in generating the W mineralization in the Muguayuan deposit, and perhaps for other granite-hosted, veinlet-disseminated scheelite deposits in the Jiangnan Orogen.

1. Introduction

Scheelite deposits occur mainly as skarn and veinlet-disseminated types. Scheelite skarns are hosted in carbonate-rich rocks at or near the contacts with granitic intrusions, and the Ca-rich wall rocks are thought to be essential for scheelite precipitation (Gaspar and Inverno, 2000; Mao and Li, 1996; Werner et al., 2014; Wu et al., 2014). Veinlet-disseminated scheelite deposits occur mainly in granitic rocks and have previously been considered to be sub-economic (Seedorff et al., 2005; Sinclair et al., 2011). However, in the past decade, some large veinlet-disseminated scheelite deposits have been discovered in the Jiangnan Orogen, South China (e.g., Dahutang, Yangchuling, and Dongyuan; Fu et al., 2011; Huang and Jiang, 2014; Mao et al., 2013, 2017; Xiang et al., 2013), revealing this to be one of the most important W

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mineralization types in the world. For example, the Dahutang deposit has total W (WO_3) resources of > 2 Mt (Mao et al., 2013). These W ore deposit discoveries have led to new research into this type of scheelite mineralization. Unlike scheelite skarn mineralization, veinlet-disseminated scheelite mineralization is developed in granite and granite-granodiorite porphyries. This challenges the previous assumption that Ca-rich sedimentary wall rocks are essential for the formation of large scheelite deposits. A number of petrological, geochemical, and geochronological studies have been carried out on these veinlet-disseminated scheelite deposits (Huang and Jiang, 2014; Mao et al., 2013, 2015; Mao et al., 2017; Wang et al., 2017). However, the origin and evolution of ore-forming fluids in these mineralizing systems remain unclear due to a lack of detailed investigations.

In-situ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) trace element analysis of minerals has been widely used to constrain magmatic and hydrothermal processes (Brugger et al., 2000; Ghaderi et al., 1999; Hazarika et al., 2016; Peng et al., 2004; Song et al., 2014; Sun and Chen, 2017; Xiong et al., 2017). Scheelite is a common mineral that forms in various types of hydrothermal deposits, and it can incorporate abundant trace elements, such as rare earth elements (REEs), Sr, Y, Pb, Mn, and Mo, via substitution for Ca^{2+} or W^{6+} in the crystal lattice. These substitutions are controlled mainly by the crystal structure of scheelite and the physicochemical nature of the associated fluids (Brugger et al., 2000, 2008; Ghaderi et al., 1999; Liu et al., 2007; Raimbault et al., 1993; Song et al., 2014; Zhao et al., 2018).

Ghaderi et al. (1999) analyzed the REE compositions of scheelites from orogenic Au deposits and concluded that crystal structure exerts a first-order control on the elemental chemistry of scheelite. Brugger et al. (2000) combined cathodoluminescence (CL) imaging and LA-ICP-MS trace element analyses of scheelite from the Mt. Charlotte and Drysdale Au deposits, Western Australia, and proposed that scheelite chemistry is sensitive to the dynamics of the hydrothermal system. Song et al. (2014) reported that high-Mo scheelite from the skarn-type W-Mo deposits precipitated under oxidizing conditions. Sun and Chen (2017) used scheelite chemistry to show that ore-forming fluids for the giant Dahutang deposit were multistage and derived from multiple sources. Hence, in-situ LA-ICP-MS trace element analyses of scheelite can provide important insights into the origin and evolution of ore-forming fluids in veinlet-disseminated W ore deposits.

The newly discovered Muguayuan W deposit is located in central Hunan Province and is a typical veinlet-disseminated scheelite deposit within the Jiangnan Orogen. In this paper, we describe the geology and ore petrography of the Muguayuan deposit, and present CL imaging and in-situ LA-ICP-MS trace element analyses of scheelite. These observations and data advance our understanding of the evolution of hydrothermal fluids and mineralization processes in this deposit.

2. Geological background

The South China Block (SCB) comprises the Yangtze Block to the northwest and the Cathaysia Block to the southeast (Wang et al., 2007a,b, 2014). At 860–820 Ma, these two blocks collided and amalgamated to form the SCB (Wang et al., 2014; Zhou and Zhu, 1993) along the Jiangnan Orogen (Fig. 1a), which comprises mainly Neoproterozoic lower-greenschist-facies metamorphosed sedimentary rocks along with interbedded mafic-intermediate volcanic and pyroclastic rocks. These rocks have been intruded by undeformed Neoproterozoic granitoids (Wang et al., 2004, 2014; Zhou et al., 2002).

The Central Hunan Metallogenic Province, located in the middle of the Jiangnan Orogen, was intruded by Triassic and subordinate Devonian granitic rocks (Fig. 1b; Chu et al., 2012). There are three types of W mineralization in this province. Sb–Au–W deposits developed in Proterozoic to Paleozoic rocks (Hu et al., 2017), in which scheelite is a minor component. The genetic link between the Sb–Au–W deposits and magmatism is unclear (Ma et al., 2002; Peng et al., 2003). The other two types of W deposits are veinlet-disseminated and skarn types, in which scheelites are the dominant W minerals. These deposits are spatially and genetically related to granitic rocks (Fig. 1b; Xie et al., 2018).

The Muguayuan deposit is a typical veinlet-disseminated W deposit and is located in the northern part of the Central Hunan Metallogenic Province (Fig. 1b). Late Triassic granitoids in this district include the Taojiang granodiorite pluton, the Yanbaqiao granodiorite pluton, and the Sanxianba granitic porphyry stock and dikes (Fig. 1b). The Taojiang pluton, with an exposed area of 239 km^2, is the largest granitic pluton in the district, and was emplaced at ~217 Ma (Wang et al., 2012). The Yanbaqiao pluton has an exposed area of > 70 km^2 and has similar petrological features and emplacement age as the Taojiang pluton (HBGMR, 1988). The Sanxianba granitic porphyry stock is exposed over a small area and is associated with W mineralization in the Muguayuan deposit.

3. Ore deposit geology

The main strata in the Muguayuan W deposit are the Neoproterozoic Lengjiaxi Group, the Madiyi Formation of the Banxi Group, and Quaternary sediments (Fig. 2a). The Lengjiaxi Group comprises silty slate and sericite slate with a thickness of 649 m. The Madiyi Formation consists of gray to green silty slate, with sandstone and arkosic rocks near the base of the formation. The main structure is the Huaqiaogang syncline in the southern part of the deposit (Fig. 2a). The main faults are the WNW-ESE-trending Fault I and NE-SW-trending Fault II. Fault I dips steeply to the northeast and controlls the emplacement of the Sanxianba granitic porphyry stock.

Tungsten mineralization developed in the Sanxianba granitic porphyry stock. The stock has an elongate surface exposure along Fault I, with a length of ~200 m and width of ~45 m (Fig. 2a). The stock has a porphyritic texture (20–60 vol% phenocrysts) and massive structure. Phenocrysts with grain sizes of 0.2–3.0 mm comprise quartz (30–40 vol %), K-feldspar (30–40 vol%), plagioclase (20–30 vol%; An = 30–40), and minor biotite (< 5 vol%) (Fig. 3a–c). The matrix is composed of microcrystalline feldspar, quartz, and mica (Fig. 3a). Accessory minerals include zircon, apatite, ilmenite, and monazite (Fig. 3c). In the east of the ore district, there are several NW-SE-trending granitic porphyry dikes (Fig. 2a) that have similar mineral assemblages to the Sanxianba stock, but do not host W mineralization (No. 418 Geological Team, unpublished report).

The Sanxianba stock is strongly altered, including albitization, greisenization, phyllic alteration, and silicification, amongst which greisenization and phyllic alteration are the most common. Albite occurs as overgrowth rims on plagioclase, or within K-feldspar forming a perthitic texture (Fig. 3b). Greisenization is characterized by the pervasive and micro-veinlet replacement of primary minerals by muscovite and quartz. The pervasive replacement resulted in the formation of sparsely distributed to abundant muscovite produced by the alteration of biotite (Fig. 3d) and feldspar (Fig. 3e). Micro-veinlet replacement is characterized by the development of quartz and muscovite micro-veinlets that cut the granitic rocks (Fig. 3f). Greisenization is always overprinted by phyllic alteration, in which sericite may replace muscovite (Fig. 3g). Phyllic alteration resulted in the formation of sericite-quartz micro-veinlets (Fig. 3h). In some cases, nearly all the primary rock-forming silicates have been replaced by sericite, with quartz being the only primary mineral remaining (Fig. 3i).

Three major ore shoots have been delineated based on W grades (Fig. 2b–c). The total W reserve (WO_3) is 23,300 metric tons (No. 418 Geological Team, unpublished report). The ore minerals are mainly scheelite and minor wolframite, molybdenite, pyrite, and arsenopyrite. Gangue minerals include quartz, muscovite, sericite, and minor ankerite and apatite. Scheelite is present in disseminated form in the altered granitic porphyry, or as aggregates in veinlets (Fig. 4).

Based on crosscutting relationships and mineral assemblages, the following stages of mineralization and veining are recognized.