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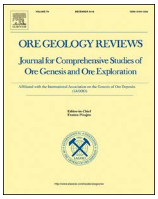

# Garnet and scheelite as indicators of multi-stage tungsten mineralization in the Huangshaping deposit, southern Hunan province, China

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## ABSTRACT

The Huangshaping W–Mo–Pb–Zn deposit in southern Hunan province, south China, contains multiple generations of garnet and scheelite in skarn and sulfide–carbonate altered rocks. Optical characteristics and chondrite-normalized rare earth element ($REE_N$) patterns obtained by in situ laser ablation–inductively coupled plasma–mass spectrometry analysis were used to distinguish different generations of garnet and scheelite. These data show a clear correspondence of garnet $REE_N$ patterns to major element zonation, with HREEs (e.g., Gd–Lu) being depleted overall. Coarse-grained garnets in the Huangshaping deposit have extreme HREE depletions and significant LREE (e.g., La–Eu) enrichment, particularly for Ce, Pr, and Nd. This indicates that REEs in these garnets are the result of coupled substitutions: $[Ca^{2+}]^{VIII}_{-1}[REE^{3+}]^{VIII}_{+1}$ and $[Fe^{2+}]IV_{+1}[Al^{3+}]IV_{-1}$. Medium-grained garnets have $REE_N$ patterns showing significant LREE enrichment and depleted HREEs, with high Sn contents. This suggests that substitution of REEs in these garnets occurs as $[Ca^{2+}]^{VIII}_{-1}[REE^{3+}]^{VIII}_{+1}[Sn^{4+}]IV_{-1}[Al^{3+}]IV_{+1}$. The fact that medium-grained garnets have high Sn contents indicates mineralizing fluids were oxidizing, which is consistent with significant positive Eu anomalies. However, hump-shaped $REE_N$ patterns for garnet rims suggest substitution by: $[Ca^{2+}]^{VIII}_{-2}[Na^{+}]^{VIII}_{+1}[REE^{3+}]^{VIII}_{+1}$, where Nd–Tb are preferentially incorporated into the garnet lattice over other REEs.

Group-1a scheelite has black cores in cathodoluminescence images, and $REE_N$ patterns showing extreme LREE enrichment and HREE depletion. Group-1b scheelite has cores with fine oscillatory zoning and enriched LREEs with depleted HREEs, similar to the $REE_N$ patterns of Group-2a scheelite that occur as rims with bright CL surrounding both Group-1a and 1b scheelite. The substitution mechanism for REEs in these three types of scheelite is: $[Ca^{2+}]^{VIII}_{-3}[\ ]^{VIII}_{+1}[REE^{3+}]^{VIII}_{+2}$, with [ ] being a Ca site vacancy. The influence of REE speciation in the hydrothermal fluid dominates the $REE_N$ patterns of these types of scheelite. However, for Group-2b bright rims of scheelite, REEs are incorporated as: $[Ca^{2+}]^{VIII}_{-2}[Na^{+}]^{VIII}_{+1}[REE^{3+}]^{VIII}_{+1}$, similar to the garnet rims. Finally, scheelite Mo contents and δEu values that decrease from Group-1a to 2b support a temporal decrease in oxygen fugacity of the mineralizing fluids.

Ratios of Y/Ho and Mo contents that decrease from Group-1a and 1b to Group-2a and 2b scheelites are similar to those in porphyry-related skarn W (Mo) and quartz vein Au–W deposits, respectively. Our studies also suggest that all these scheelites in this deposit formed from magmatic fluids. At the Huangshaping deposit, medium-grained garnets associated with Group-1a scheelite precipitated from evolved magmatic fluids during prograde metamorphism, as indicated by their complementary Y/Ho ratios. Paragentically younger scheelite, particularly Group-2b, may have formed from dilute magmatic fluids that underwent large-scale hydrothermal circulation. The characteristics of Group-1b and 2a scheelite likely reflect a transitional environment and fluid mixing during tungsten mineralization in the polymetallic Huangshaping deposit.

## 1. Introduction

The concentrations of trace elements in hydrothermal minerals can help constrain the composition and source(s) of mineralizing fluids. Scheelite ($CaWO_4$) is an abundant tungstate mineral in skarn-type and porphyry-type W polymetallic deposits (Meinert et al., 2005; Lentz and McFarlane, 2014). Scheelite is also an accessory mineral in quartz vein Au–W deposits, hosted by metamorphic rocks in Archean and

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Neoproterozoic gold deposits (Voicu et al., 2000; Brugger et al., 2002; Peng et al., 2006; Dostal et al., 2009). The tetragonal symmetry of scheelite allows for substitution of trace elements with large ionic radii into cation sites, including strontium (Sr), barium (Ba), uranium (U), lead (Pb), and rare earth elements (REEs) (Ghaderi et al., 1999; Brugger et al., 2000). Hexavalent molybdenum substitutes for tungsten to form the solid solution series scheelite ($CaWO_4$)–powellite ($CaMoO_4$) (Huang et al., 1989; Klein and Hurlbut, 1993). Previous studies determined that the precipitation of scheelite can pre-date or be contemporaneous with gold mineralization in hydrothermal quartz vein Au–W deposits (Uspensky et al., 1998). Therefore, the REE composition of scheelite can be a useful indicator of the source(s) of ore-forming fluids and metals. This is evident in hydrothermal Au–W deposits, where the chondrite-normalized rare earth element ($REE_N$) patterns vary as a smooth function of ionic radii in scheelite (Cottrant, 1981; Peng et al., 2005; Xiong et al., 2006; Liu et al., 2007; Ren et al., 2010; Wang et al., 2010).

Research utilizing in situ laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) shows how individual scheelite grains contain compositional heterogeneities (Sylvester and Ghaderi, 1997; Peng et al., 2010; Zhang et al., 2012; Fu et al., 2013). Distinct $REE_N$ patterns of scheelite can reflect cation speciation (e.g., $Ca^{2+}$ or $Na^{+}$) in a hydrothermal fluid (Ghaderi et al., 1999; Brugger et al., 2000), and the strength of Eu anomalies (e.g., $\delta Eu = 2*Eu_N/(Sm_N + Gd_N)$) relates to redox state because δEu values are dominated by the $Eu^{3+}/Eu^{2+}$ ratios of the hydrothermal fluid (Ghaderi et al., 1999; Brugger et al., 2008). This makes scheelite a sensitive proxy for the environment of formation. The Mo concentration of scheelite is also an indicator of redox state, with higher Mo values indicating formation from an oxidizing fluid (Ghaderi et al., 1999; Song et al., 2014). As most researchers have studied scheelite from quartz vein Au–W deposits associated with Archean or Neoproterozoic gold deposits, there are few data for scheelite from skarn-type W–Mo deposits associated with igneous rocks (Song et al., 2014).

Scheelite in hydrothermal systems is commonly accompanied by garnet, with a general chemical formula of $X_3Y_2Z_3O_{12}$. Where X is a divalent cation (e.g., Ca, Mg, Mn, or Fe) in eightfold coordination, Y is a trivalent cation (e.g., Fe, Al, and Cr) in octahedral coordination and Z is dominantly Si in tetrahedral coordination (Menzer, 1926; Gaspar et al., 2008). Numerous trace elements can substitute into the structure of garnet via cation sites, including Y, Zn, Sn, Na, Ti, and REEs. Although the geochemical behavior of these elements in garnet and their partitioning between garnet and hydrothermal fluid is still debated, researchers use this suite of trace elements and $REE_N$ patterns to decipher fluid source(s), redox states, and the degree of water–rock interaction (Chen et al., 1992; Fedorowich et al., 1995; Ganguly et al., 1998; Wang et al., 2003; Carlson, 2006; Wilbur and Ague, 2006; Yu et al., 2008; Li et al., 2012). Such studies document how garnets from metamorphic and magmatic rocks are Al-rich (e.g., pyrope, almandine, spessartine, and grossular) and fractionate heavy rare earth elements (HREEs) from light rare earth elements (LREEs), producing HREE-enrichment patterns and high Sm/Nd and Lu/Hf ratios (Zong et al., 2006; Dahlquist et al., 2007; Li et al., 2012; Yang et al., 2013; Zhu et al., 2014). However, few studies have examined garnets from mineralized skarn, which commonly have andraditic (e.g., $Fe^{3+}$) compositions (Chen et al., 1992; Smith et al., 2004; Gaspar et al., 2008).

Southern Hunan province is within a structurally complex area where the Shi-Hang Zone and Nanling Belt overlap (Fig. 1a). Numerous pollymetallic ore deposits formed in this region during the late Mesozoic in association with coeval intrusive and volcanic rocks (Fig. 1a; Zhou et al., 2006; Hua et al., 2007; Mao et al., 2013; Ding et al., 2015; Zhang et al., 2015). The polymetallic Huangshaping deposit occurs in southern Hunan province, on the northwest side of the Qitianling granite pluton (Fig. 1b), and is unique for its metals combination of W–Mo–Pb–Zn and the occurrence of significant reserves of all these metals in this area, containing 152.9 Kt $WO_3$ grading 0.2%, 43.2 Kt Mo grading 0.2%, 761.3 Kt Pb grading 3.55%, and 1.5291 Mt Zn grading 7.13% (Ding et al., 2016a). Scheelite and molybdenite are disseminated within a proximal skarn zone between granite porphyry and Carboniferous neritic marine sedimentary–carbonate rocks. Sulfide ores of galena, sphalerite, pyrrhotite, and pyrite occur as distal carbonate-hosted stratiform orebodies (Tong, 1986; Yao et al., 2007). As the W–Mo mineralization has a close temporal (~155 Ma) and spatial relationship with granite porphyry (155.2 ± 0.4 Ma) in the Huangshaping deposit, previous studies assumed a genetic relationship (Ma et al., 2007; Yao et al., 2007; Lei et al., 2010; Qi et al., 2012; Zhu et al., 2012; Huang et al., 2013). However, the validity of that assumption is questioned because a cathodoluminescence (CL) study of scheelite from the Huangshaping deposit reveals many crystals have dark cores surrounded by a bright rim. Coexisting garnet in the Huangshaping skarn can be divided into different generations based on optical characteristics and crystal morphology, indicating multiple stages of both garnet and scheelite mineralization. The purpose of this paper is to develop a genetic model for the Huangshaping W–Mo–Pb–Zn pollymetallic deposit using the geochemistry and REE signatures of scheelite and garnet to identify the source(s) and evolution of mineralizing fluids, and further to figure out whether the compositions of these minerals can be the proxies to indicate the ore forming processes in other skarn tungsten deposits, since garnet and scheelite are generally the representative minerals in these deposits.

## 2. Tectonic setting

Southern Hunan province lies within the Cathaysia Block (Fig. 1a), which collided with the Yangtze Block during the ~970 Ma Jinning orogenic event (Li and McCulloch, 1996). Basement rocks of the Cathaysia Block are dominated by Paleo- to Mesoproterozoic metamorphic rocks, possibly with Neoarchean rocks at depth (Yu et al., 2006; Zheng et al., 2006). Widespread arc magmatism along the Yangtze Block margin suggests the accretion of continental crust during the Neoproterozoic (Li 1999, 2003; Zhou et al., 2002a, 2002b), which likely affected the geology of southern Hunan province (Xie et al., 2013; Zhang et al., 2014). Metamorphic basement rocks of the Cathaysia Block are overlain by Neoproterozoic–Paleozoic continental and neritic marine sediments related to collision of the Indian and Huanan plates (Fig. 1b; Wang et al., 2003a,b).

Intense Mesozoic igneous activity during the Jurassic–Cretaceous occurs in a distinct belt, with ages decreasing towards the coast (Fig. 1a; Zhou et al., 2006), and this is a dominant feature of the Cathaysia Block (Gilder et al., 1991, 1996; Charvet et al., 1994; Li et al., 2007; Jiang et al., 2009). Igneous rocks in the belt are both intrusive and extrusive, with granites having high Sm (> 8 ppm) and Nd (> 45 ppm) concentrations, $\varepsilon_{Nd}(t)$ values greater than −8, and young Nd model ages ($T_{DM} < 1.5$ Ga; Gilder et al. 1996). The granite intrusions form a chain that approximately parallels two NE–SW trending Mesozoic grabens between Hangzhou, Zhejiang province, and Shiwandashan, Guangxi province, known as the Shi-Hang Zone (Fig. 1a).

Polymetallic W–Sn–Cu–Pb–Zn deposits associated with granitoids occur in an area encompassing parts of Guangxi, Hunan, Jiangxi, and Guangdong provinces, known as the Nanling belt (Fig. 1a; Mao et al. 2013). The Huangshaping deposit occurs where the Shi-Hang Zone and Nanling Belt intersect in southern Hunan province (Fig. 1a). Polymetallic mineralization (e.g., W, Sn, Pb, Zn, and Cu) within Devonian and Carboniferous carbonate rocks is coeval with Mesozoic magmatism in this region (Fig. 1b; Zhou et al., 2006; Hua et al., 2007; Mao et al., 2013; Zuo et al., 2014; Cai et al., 2015; Ding et al., 2015; Zhang et al., 2015). Mesozoic granitic rocks are subdivided into two groups: early granodiorite porphyries (~160 Ma) associated with Cu–Pb–Zn mineralization, and later granites (~155 Ma) related to W–Sn mineralization (Ding et al., 2015 and references therein). The granodiorite porphyries formed by partial melting of Paleoproterozoic basement in the lower crust, with input from coeval basaltic magma. In contrast, partial melting of crustal metamorphic rocks generated the granites, which