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ABSTRACT

Skarn-type tungsten deposits are widely distributed all over the world, and contribute more than 70% of the world’s W supply. The temporal relation between the W mineralization and causative intrusions, and the evolution of ore-forming fluids are matters of ongoing debate. In this study, we combine in situ LA-ICP-MS U-Pb dating and trace element compositions of scheelite from Zhuxi, the world’s largest W deposit, and compare them with literature data to address the above issues. Three primary ore stages exist at Zhuxi: prograde skarn, retrograde skarn and quartz-sulfide stages. Most scheelite occurs in the retrograde skarn stage and is further subdivided into three generations: Sch A, B and C.

The obtained LA-ICP-MS U-Pb ages for three scheelite generations in the Zhuxi deposit are 154.0 ± 2.8, 150.3 ± 3.5 and 150.4 ± 6.3 Ma, respectively, indicating that the entire W mineralization is closely related to the emplacement of the nearby Late Jurassic granites (~154 to 150 Ma, zircon U-Pb ages). In situ LA-ICP-MS trace element results demonstrate that Sch A shows the highest Mo content (mean=1002 ppm), where those for Sch B and Sch C are 109 and 45 ppm, respectively. These, combined with the gradually increasing trend of Ce contents and δCe values, indicate a shift from oxidizing to reducing conditions for the ore-forming fluid. All three scheelite generations yield significant positive δEu anomalies, which are considered to be unrelated to the redox state, but caused by the addition of Eu (e.g., feldspar dissolution). The high Y/Ho ratio of scheelite and a good correlation between Y/Ho ratio and δEu (R² = 0.96) suggest that intense fluid-rock interactions between ore fluids and the Shuangqiaoshan Group metasedimentary rocks as well as earlier-formed skarns drove fluid evolution. This study demonstrates that scheelite U-Pb geochronology is a useful technique when identifying the temporal link between hydrothermal W mineralization and the causative intrusion. The results of this study also highlight that the reactions of the ore fluids with wall rocks and earlier-formed skarns significantly
modify the primary fluid compositions.

**Keywords:** Scheelite LA-ICP-MS U-Pb dating, trace element, skarn W mineralization, Zhuxi, South China

**INTRODUCTION**

Skarn deposits are one of the most abundant ore deposit types in the earth’s crust and have been the subject of numerous studies since their discovery (Kwik 1987; Meinert et al. 2005; Romer et al. 2005; Chang et al. 2019). Metal sources for skarn mineralization are critical for establishing robust genetic models for these ore deposits. The close spatial relationship between skarn deposits and plutons indicates a magmatic origin for metals (Audétat et al. 2000; Webster et al. 2004; Thomas et al. 2005; Song et al. 2019). In contrast, some others suggest that the metals originated from the surrounding rocks (Linnen and Williams-Jones 1995; Sun et al. 2019).

To address this issue, scheelite, which is dominant in skarn-type W deposits (Meinert et al. 2005; Song et al. 2014; Sun et al. 2019), can be adopted as an ideal mineral to constrain the compositions and sources of the fluids and the origins of the metals (Song et al. 2014; Poulin et al. 2018; Choi et al. 2020; Han et al. 2020; Su et al. 2021). Scheelite (CaWO₄) commonly accommodates significant amounts of rare earth elements (REE), Y, Mo, and Sr in substitution for Ca or W (Nassau and Loiacono 1963; Ghaderi et al. 1999), which provide insights into the ore-forming processes, including the origin and physicochemical conditions of the ore-forming fluids (Brugger et al. 2002; Song et al. 2014; Hazarika et al. 2016; Cao et al. 2021). Meanwhile, developments in U-Pb geochronology permit direct dating of the ore minerals (e.g., scheelite, cassiterite and wolframite), thus constraining the timing of the mineralizing events (Yuan et al. 2008; Wintzer et al. 2016; Harlaux et al. 2018). Hence, the combination of geochronology and trace element geochemistry of scheelite will shed new light on understanding the genetic relationship between the W mineralization and the causative intrusions. Here, we present in situ laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U-Pb ages and trace element compositions of
scheelite from the world’s largest skarn-type W deposit to constrain the W mineralization age, reconstruct the redox state of mineralizing fluids, and identify the metal sources.

**GEOLOGICAL SETTING**

The Zhuxi W deposit is located in Jiangxi Province, South China, within the Jiangnan Orogen, which is adjacent to the Cathaysia block to the south and the Yangtze block to the north (Mao et al. 2017; Fig. 1a, b). The 1500 km long and ENE-trending Jiangnan Orogen was formed by subduction-collision between the Yangtze and Cathaysia blocks at ~970 Ma (Li and McCulloch 1996; Zhang et al. 2021). The rocks exposed in this region comprise a Precambrian basement and Phanerozoic rocks (Song et al. 2019; Fig. 1c). The Precambrian basement is subdivided into the lower Shuangqiaoshan Group, which is slate, phyllite and metavolcaniclastic rocks, and the upper Neoproterozoic sedimentary rocks comprising sandstone, slate, conglomerate with lesser carbonate, metabasite and volcaniclastic rocks (Zhao et al. 2011; Zhang et al. 2021). The cover Phanerozoic rocks surrounding the Jiangnan Orogen include Silurian to Early Triassic marine clastic and carbonate rocks, Middle Triassic to Early Jurassic clastic rocks, Middle to Late Jurassic sedimentary and volcanic rocks, and Cretaceous red-bed sandstone, which occur within a series of NE-trending continental basins (Mao et al. 2017, 2020).

There are two groups of granites in the Jiangnan Orogen: Neoproterozoic granites that formed during the Jinning orogeny (Li 1999; Wu et al. 2006; Wang et al. 2014) and Late Mesozoic granites that formed during the Yanshanian orogeny (Song et al. 2012; Huang and Jiang 2014; Mao et al. 2017; Zhao et al. 2017; Dai et al. 2018). The Yanshanian granitic intrusions can be further subdivided into two groups. The first group (153-136 Ma) consists of monzonitic granite and some granodiorite and alkali granite. The second group (129-102 Ma) is represented by monzonitic granite with peraluminous geochemical signatures (Song et al. 2021).

In the past decade, a dozen porphyry-skarn W polymetallic deposits have been
discovered in the Jiangnan porphyry-skarn tungsten belt (JNB) in south China (Fig. 1c): the Dahutang (1.07 Mt WO₃ at 0.15 wt.%; Mao et al. 2015) and the Dongyuan porphyry deposits (0.14 Mt WO₃ at 0.12 wt.%; Zhou et al. 2011), the Xianglushan (0.22 Mt WO₃ at 0.64 wt.%; Dai et al. 2018) and the Zhuxi skarn deposits (4.22 Mt WO₃ at 0.5 wt.%; Chen et al. 2012, 2015; No. 912 Geological Team 2020). Collectively, these surpass the Nanling W belt (Song et al., 2019), making the JNB the world’s largest W belt (up to 6 Mt of WO₃; Mao et al. 2017, 2020). Previous geochronological data revealed that most of the W-bearing deposits in the JNB were related to the first group intrusions (153-135 Ma, e.g., Song et al. 2012; Huang and Jiang 2014; Mao et al. 2017; Pan et al. 2018; Su et al. 2018), while only minor W mineralization was caused by the second group (129-102 Ma, e.g., the Xianglushan skarn deposit, ~125 Ma; Dai et al. 2018).

ORE DEPOSIT GEOLOGY

The exposed rocks in the Zhuxi deposit include the Neoproterozoic Shuangqiaoshan Group and the Carboniferous-Permian sedimentary rocks (Chen et al. 2012). The greenschist-facies Shuangqiaoshan Group mainly consists of slate and phyllite (Wang et al. 2007). It is unconformably overlain by the Carboniferous-Permian rocks, which include the Huanglong, Chuanshan, Changxing, Leping, Maokou and Xixia Formations from older to younger (Yuan et al. 2019; Figs. 2a). They mostly comprise shallow marine carbonate rocks (dolomite and limestone) with minor clastic sedimentary rocks (e.g., siltstone, sandstone) (Chen et al. 2012; Sun et al. 2019). These rocks are fractured by NE-trending faults (F1, F2 and F3), and cut by the later NW-trending fault (F4) (Fig. 2a).

Detailed core drillings identified three intrusions in the deep part of the deposit: biotite granite, muscovite granite, and granite porphyry (Song et al. 2019; Fig. 2b, c). They occur as dikes and/or stocks intruding into the Neoproterozoic Shuangqiaoshan Group slate and phyllite as well as Carboniferous-Permian carbonates (Chen et al. 2012). Recently, Zhang et al. (2021) noted that the granite porphyry caused...
mineralization. Several lamprophyre dikes in the north of the deposit intruded carbonates (Fig. 2a; Pan et al. 2017), and their zircon U-Pb dating results indicate an emplacement age of ~160 Ma (Liu et al. 2014), which is earlier than the formation age of the Zhuxi deposit.

From granites to carbonates, the alteration spatially transforms from greisen, skarn to marble zones (Pan et al. 2018; Yuan et al. 2019). Most W mineralization occurs within the skarn zone (Fig. 3a, b), and minor mineralization also formed in the greisen and marble zones (Fig. 3c) and granites (Yuan et al. 2019; He et al. 2022). The orebodies are stratiform, stratabound or lenticular (Song et al. 2019), and are 750 m long and extend more than 2000 m in depths (Fig. 2b). From the intrusion outwards, the mineralized zones vary from W, W-Cu to Cu-(Pb-Zn) at elevations from -2000 to -200 m (He et al. 2022).

The mineralization can be subdivided into three stages: prograde skarn, retrograde skarn, and quartz-sulfide stages; most scheelite was precipitated in the retrograde stage. The prograde stage predominantly consists of anhydrous minerals, such as garnet (Figs. 3d, e and 4a-c), wollastonite (Figs. 3d and 4a), and pyroxene, with minor quartz and vesuvianite (Sun et al. 2019). From core to rim, the skarn veins (several to tens of centimeters in width) exhibit mineral zonation of garnet, pyroxene, vesuvianite and wollastonite, and cut the marble (Pan et al. 2017; Figs. 3d and 4a). This reflects a time sequence with the rim bordering to the carbonates being the oldest one and the axial being the youngest one (Yardley and Lloyd 1995; Heinrich 2007; Xu et al. 2022).

Minor scheelite (Sch A) is found in this stage (Figs. 4a-c and 5a) and generally occurs as dissemination in the center of the garnet-wollastonite veins (Fig. 3d) and garnet skarn (Fig. 3e). Most Sch A replaced garnet (Fig. 4b, c) and diopside (Pan et al. 2017) in this stage. The retrograde skarn stage is characterized by the mineral assemblage of abundant tremolite (Fig. 3b), serpentine, muscovite (Figs. 3c and 4d), actinolite, chlorite, fluorite, talc, epidote and quartz (Song et al. 2019). Scheelite (Sch B) in this stage is commonly disseminated (200-1000 μm in diameter) (Figs. 4d, e and 5b), and
coexists with quartz, muscovite (Fig. 4d), tremolite and actinolite (He et al. 2022).

Notably, coarse-grained massive scheelite (Sch C, up to 0.5 cm in diameter; Figs. 3b, 4f, 5c and 5d) is also found in this stage, which may be associated with the dissolution of early disseminated scheelite (Sch A and B) and its re-precipitation at late sequence (Song et al. 2019). Finally, the later quartz-sulfide stage is dominated by the mineral assemblage of chalcopyrite (Fig. 4g, h), sphalerite, molybdenite, bismuthinite, native bismuth (Fig. 4h), pyrrhotite, arsenopyrite, and galena with quartz, fluorite and calcite (Song et al. 2019; Yuan et al. 2019). Both the quartz-sulfide and calcite veins cut the early formed skarns (Figs. 3f and 4i).

SAMPLES AND ANALYTICAL METHODS

Scheelite samples

All the scheelite-bearing specimens were collected from drill core (ZK3001 and ZK3004) along line 30 at depths of -1400 to -1800 m in the Zhuxi deposit (Fig. 2b). These samples were prepared as polished sections for microprobe and LA-ICP-MS analysis. Before analysis, all thin sections were finely polished and coated with carbon, and cathodoluminescence (CL) imaging was carried out in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences Beijing (CUGB).

Major elements analysis

Major element compositions of scheelite were determined by electron microprobe analysis using a Shimadzu Electron Probe Microscope Analyzer (EMPA 1720H) at the Key Laboratory of Geoscience Big Data and Deep Resource of Zhejiang Province, Zhejiang University. Operating conditions included an acceleration voltage of 20 kV, a beam current of 20 nA, and an electron beam diameter of 5 μm. Analysis used natural and synthetic minerals as calibration standards, and all data were corrected using a ZAF procedure. The precision of all analyzed elements was better than 1.5%.

LA-ICP-MS U-Pb dating and trace element analyses

The U-Pb dating of scheelite was performed on an Analytik Jena PlasmaQuant MS
quadrupole ICP-MS with a 193 nm NWR193 Ar-F excimer laser at Yanduzhongshi Geological Analysis Laboratories Ltd. Scheelite material ZS-Sch (in-house scheelite standard, 228 ± 2 Ma; Li et al., 2022) was used as the standard to calibrate the U-Pb age. Instrument drift, mass bias and fractionation of the U-Pb ratio are corrected with a standard-sample bracketing method. Isotopes measured were $^{44}$Ca, $^{206}$Pb, $^{207}$Pb, $^{208}$Pb, $^{232}$Th, $^{235}$U and $^{238}$U. The dwell time was set to 8 ms for $^{44}$Ca, 30 ms for $^{206}$Pb, 35 ms for $^{207}$Pb, 15 ms for $^{208}$Pb, 10 ms for $^{232}$Th, 15 ms for $^{235}$U, 25 ms for $^{238}$U.

Each analysis on the scheelite began with a 15 second blank gas measurement followed by a further 40 seconds of analysis time when the laser was switched on. Scheelites were sampled on 40-micron spots using the laser at 8 Hz and a density of approximately 4.0 J/cm². A flow of He carrier gas at a rate of 0.6 L/min carried particles ablated by the laser out of the chamber to be mixed with Ar gas and carried to the plasma torch. The raw data were corrected offline employing ICPMSDataCal software (Liu et al. 2010) and ZSkits software (Cai et al. 2020). Common Pb was corrected using the $^{207}$Pb-based correction method outlined in detail by Chew et al. (2014). Isoplot 4.15 was used to calculate U-Pb ages in the Tera-Wasserburg diagram (Ludwig 2012), which is particularly useful in systems with high common Pb abundance (Chew et al. 2011, 2014).

Trace element measurements of scheelite were separately performed from U-Pb dating using the same instrument conditions. The concentrations of trace elements were quantified using SRM610 as external standard and $^{44}$Ca as the internal standard element assuming a stochiometric scheelite composition.

RESULTS

Major element compositions

The major element compositions of scheelites are listed in Table 1. The WO₃ and CaO contents for scheelites range from 79.9 to 81.3 wt.% and 18.6 to 19.9 wt.%, respectively. The MoO₃ content is up to 0.2 wt.%. In addition to these elements, most other components are negligible and below the detection limit, especially for Nd, Nb
and Ta (Table 1).

LA-ICP-MS trace element compositions

The summarized results of LA-ICP-MS trace element analyses of scheelites are given in Table 2 and detailed data can be found in Appendix Table A1, and the chondrite-normalized REE patterns are shown in Figure 6. Chemically, Sch A contains relatively higher concentrations of Mo (557-1680 ppm) and lower contents of Sr (7.6-16.4 ppm) and rare earth elements (REE; 0.3-11 ppm) compared to Sch B and Sch C (Table 2). The mean contents of Mo, Sr and REE for Sch B and C are 109, 39, 90 ppm, and 45, 58, 364 ppm, respectively (Table 2), showing systematically lower Mo contents and increasingly higher Sr and REE from Sch A to Sch C (Fig. 7a and 7b). The contents of Mn show no significant variation in the three scheelite generations, ranging from 31 to 138 ppm, 27 to 74 ppm and 40 to 103 ppm, respectively (Appendix Table A1).

The three generations of scheelite show different chondrite-normalized REE patterns (Fig. 6a-c). The majority of Sch A are characterized by LREE-enriched patterns, and the LREE/HREE ratios of Sch A vary from 1.9 to 164 with a mean value of 35. The LREE/HREE ratios of Sch B and Sch C, however, are much lower, ranging from 1.7 to 8.7 (mean = 4.5) and 2.7 to 6.7 (mean = 4.7), respectively (Table 2). Notably, almost all of the scheelite spots have positive Eu anomalies and the patterns show depleted MREE relative to LREE and HREE. Among them, some points in Sch C show negative Eu anomalies with significantly higher MREE contents, and the differentiation between LREE and HREE is not obvious (Fig. 6c).

LA-ICP-MS U-Pb ages

The U-Pb ages obtained in this study are listed in Appendix Table A2 with representative time-resolved depth profiles showing in Appendix Figure A1. For the Sch A (sample 18ZX-15), 22 scheelite grains were analyzed for their U-Pb isotopic ages, which yield an intercept age of 154 ± 2.8 Ma (MSWD = 1.02) (Fig. 8a). Though the scheelite crystals exhibit relatively high common Pb contents, the corresponding $^{206}\text{Pb}/^{238}\text{U}$ ages after $^{207}\text{Pb}$-correction range from 141.7 to 165.4 Ma (Appendix Table
A2) with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 153.7 ± 2.5 Ma (n = 22, MSWD = 0.98, 2σ) (Fig. 8b), which is within error of its intercept age (Fig. 8a). Thirty-one scheelite grains (Sch B) (sample 18ZX-21) give an intercept age of 150.2 ± 3.6 Ma (MSWD = 1.8) (Fig. 8c) with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age after $^{207}\text{Pb}$-correction of 151.1 ± 2.8 Ma (n = 31, MSWD = 1.3, 2σ) (Fig. 8d). Finally, 25 spot analyses performed on the coarse-grained scheelite (Sch C) (sample 18ZX-22) from the high-grade W ore yield an intercept age of 150.4 ± 6.3 Ma (MSWD = 0.87) (Fig. 8e) with a weighted mean age of 150.7 ± 3.8 Ma (n = 25, MSWD = 0.5, 2σ) (Fig. 8f). Because of the low U contents, the age error of Sch C is larger than that of Sch A and Sch B (Appendix Table A2).

**DISCUSSION**

**Direct time constraint of tungsten mineralization at Zhuxi**

Numerous studies have been conducted to constrain the mineralization age for the Zhuxi skarn-type W deposit (Liu et al. 2014; Chen et al. 2015). For example, Pan et al. (2017) reported muscovite 40Ar/39Ar age of 150.2 ± 0.9 Ma. Song et al. (2019) obtained titanite U-Pb ages of 149.9 ± 1.3 to 148.1 ± 7.4 Ma and Zhang et al. (2021) obtained apatite U-Pb ages of 153.7 ± 1.9 to 152.6 ± 4.6 Ma. Recently, Hong et al. (2022) reported garnet U-Pb ages of 153.0 ± 4.4 and 148.7 ± 7.9 Ma. These ages, however, are mostly reported for hydrothermal minerals (i.e., garnet, muscovite, titanite and apatite), which may not temporally coexist with W mineralization and therefore cannot directly represent W mineralization ages. To date, the only geochronology study of the Zhuxi scheelite was conducted by Liu et al. (2017), who reported an age of 144 ± 5 Ma using scheelite Sm-Nd dating method. In addition to the large error of this age, there is an obvious gap between this age and the timing of adjacent granites (recalculated ages of biotite granite, muscovite granite, and granite porphyry are 153.6 ± 0.6 Ma, n=35; 150.7 ± 1.2 Ma, n=28; and 152.7 ± 0.6 Ma, n=38; Pan et al. 2018; Zhang et al. 2020). It has been reported that Sm-Nd dating has a high potential to yield rotated mixing lines with too old or too young ages. Thus, the 144 Ma age from scheelite Sm-Nd dating method might be inaccurate. Besides,
Pan et al. (2017) reported a molybdenite Re-Os age of 145.1 ± 1.5 Ma. Considering that molybdenite belongs to the sulfide stage and obviously formed later than scheelite, the obtained molybdenite Re-Os age could not represent a primary event for scheelite precipitation. Therefore, the W mineralization age of the Zhuxi deposit requires further investigation.

Scheelite has relatively high and variable U concentrations (~10 ppm), making it an ideal mineral for U-Pb geochronology (Wintzer et al. 2016; Poitrenaud et al. 2020). The Zhuxi scheelite contains relatively high U contents (6-64 ppm). Time-resolved depth profiles show smooth curves for all the analyzed elements (Appendix Figure A1), ruling out the existence of mineral inclusion and its influence on U-Pb system. Therefore, the U content in scheelite is dominantly structural, and the obtained U-Pb ages can be interpreted as the ages of the tungsten mineralization. There is a negative correction between age error and U content (Appendix Table A2, Fig. 8), indicating that the content of U plays an important role in determining the viability of precise U-Pb dating.

Our LA-ICP-MS U-Pb results show that all three scheelite generations (Sch A, Sch B and Sch C) formed between 154.0 ± 2.8 and 150.4 ± 6.3 Ma (Fig. 8), which is consistent with the ages of other hydrothermal minerals in the Zhuxi W deposit (e.g., muscovite, titanite and apatite; Pan et al. 2017; Song et al. 2019; Zhang et al. 2021) and adjacent granites (recalculated zircon U-Pb ages from 153.6 ± 0.6 to 150.7 ± 1.2 Ma; Pan et al. 2018; Zhang et al. 2020). Compared to scheelite Sm-Nd age (144 ± 5 Ma; Liu et al. 2017), the obtained ages of Sch A to C (154-150 Ma) are more consistent with those of adjacent granites (153.6-150.7 Ma). Overall, the Zhuxi granite, garnet, apatite, muscovite and scheelite were formed almost contemporaneously from 154 to 150 Ma. The consistency of these ages supports the reliability of the scheelite U-Pb dating in identifying W mineralization. The results from this study also show that the Zhuxi tungsten mineralization is closely related to the Late Jurassic to Early Cretaceous magmatism.
Element substitution mechanism in scheelite

The contents of Sr, Mn, and Pb of scheelite in Zhuxi are relatively high, indicating these divalent cations could directly enter the scheelite lattice to replace Ca$^{2+}$ due to the similar ionic radius (Nassau and Loiacono 1963; Ghaderi et al. 1999; Ding et al. 2018). As to REE$^{3+}$, several charge-compensating mechanisms have been proposed to maintain the charge-compensating to maintain electrostatic neutrality (Cottrant 1981; Burt 1989; Ghaderi et al. 1999; Zhao et al. 2018). The very low concentrations of Na and Nb in Zhuxi scheelite (Tables 1 and 2) and the poor correlation between Nb and REE-Eu+Y (Fig. 7c) indicate that the mechanisms (2Ca$^{2+}$ = REE$^{3+}$ + Na$^{+}$ and Ca$^{2+}$ + W$^{6+}$ = REE$^{3+}$ + Nb$^{5+}$) are insignificant for the REE accommodation. Furthermore, there is no linear relationship between Nb and Mo (Fig. 7d), which excludes the possibility of the substitution: Ca$^{2+}$ + Mo$^{6+}$ = REE$^{3+}$ + (1 − x) Mo$^{5+}$ + xNb$^{5+}$(0 ≤ x ≤ 1) (Zhao et al. 2018). Previous studies also revealed that scheelite with REE$^{3+}$ + Na$^{+}$ substitution mechanism has obvious MREE-rich (hump-shaped) patterns (Ding et al. 2018), which is not observed in the Zhuxi scheelite (Fig. 6).

The REE in skarn minerals are the combination of the REE present in the carbonates and the REE added by the fluid. As the REE are relatively immobile in most fluids (depending on the ligands available), the REE are commonly less abundant for incorporation. In the Zhuxi deposit, because the low contents of Na and Nb, the above substitution mechanisms are excluded. As a result, scheelite accommodates low concentrations of the REE, therefore there is little fractionation between fluid and scheelite. Overall, excluding the other three possibilities, the mechanism 3Ca$^{2+}$ = 2REE$^{3+}$ + [ ]Ca (where [ ]Ca represents a Ca-site vacancy; Ding et al. 2018) best explains the REE substitution in scheelite in the studied deposit.

Redox conditions during W mineralization

In the Zhuxi deposit, scheelite from all three generations show predominantly high Eu$_N$/Eu$_N^*$ ratios ($\delta$Eu) (Fig. 9a) and significant positive Eu anomalies ($\delta$Eu >1; Fig. 9b and 9c). Because Eu$^{2+}$ has the same charge as Ca$^{2+}$, Eu can substitute for Ca in scheelite
easily in reducing conditions, which could result in a positive Eu anomaly (Sun and Chen 2017; Poulin et al. 2018; Han et al. 2020). Similarly, Mo can occur in Mo$^{6+}$ and Mo$^{4+}$ states, and the former can easily substitute for W$^{6+}$ whereas the latter hardly substitutes for W$^{6+}$, leading to the high Mo contents in oxidizing conditions and low contents in reducing conditions (Yuan et al. 2019). Song et al. (2014) reported a negative correlation between Mo and Eu$_N$/Eu*$_N$ in porphyry-skarn deposits. However, there is a significant decoupling relationship between Mo content and Eu$_N$/Eu*$_N$ in the Zhuxi deposit. From Sch A to Sch C, the Mo content decreases but there is no accompanying change in Eu$_N$/Eu*$_N$ ratio (Fig. 9b). In addition to the redox state, the crystallization of early minerals may have an effect on Mo distribution in scheelite. For instance, the early crystallization of garnet may favor partition of Mo, Sn, and W into this mineral phase (Xu et al., 2016; Fei et al., 2019; Zhu et al., 2021), thus the coeval scheelite will have relatively low contents of these elements, as their source has been depleted. However, previous studies have shown that the Zhuxi garnets contain extremely low contents of Mo (<1ppm; Ouyang et al, 2020). By contrast, the coeval scheelites (Sch A) yield relatively high contents of Mo (up to 1680 ppm), ruling out the possibility of the influence from mineral crystallization. Therefore, the variation of Mo content suggests that the fluid changes from oxidizing to reducing conditions during mineralization.

In addition to Eu and Mo, Ce can also be adopted to trace redox conditions (Ding et al. 2015). Because Ce$^{3+}$ (radius of 1.14 Å) is easier to enter scheelite (Ca$^{2+}$ radius of 1.12 Å) than Ce$^{4+}$ (radius of 0.97 Å), scheelite formed by the oxidizing fluid will contain a low Ce content with negative Ce anomaly. This can be recorded from the Mo vs. Ce and Mo vs. $\delta$Ce plots (Fig. 9d and 9e), on which Ce contents and $\delta$Ce decrease with increasing Mo contents in the Zhuxi deposit. The Sch A has the highest Mo contents and lowest Ce contents with significantly negative $\delta$Ce values (0.5-1.2, mean = 0.8), suggesting an oxidized condition. The $\delta$Ce values of Sch B (0.8-1.0, mean = 0.9) and Sch C (1.0-1.3, mean = 1.0) indicate that the fluid shifted from oxidation to
reduction (Fig. 9e), and are consistent with the variations of Mo contents. The Mo, Ce and \( \delta \)Ce variations in scheelite show that the ore fluid has undergone a transition from oxidizing to more reducing conditions. However, there is no significant difference in \( \delta \)Eu values of the three scheelite generations (Fig. 9f), which may be caused by Eu\(^{2+} \) addition into the fluids (Yuan et al. 2019), partly due to the plagioclase dissolution.

In recent years, several studies have also found that there are limitations in using \( \delta \)Eu to constrain redox state not only in skarn deposits but also in porphyry-related and/or orogenic deposits. For example, all types of scheelite in the Nui Phao W deposit from Vietnam are characterized by negative Eu anomalies (Nguyen et al. 2020), suggesting that it is necessary to consider the effects of fluid compositions and mineral crystallization. Sciuba et al. (2020) noted that strong positive Eu anomalies are predominantly related to flat REE patterns with low REE contents in scheelite, whereas weakly positive to negative Eu anomalies are characteristic of scheelite with higher REE contents in orogenic deposits. Europium anomalies likely reflect initial fluid Eu\(^{2+}/\)Eu\(^{3+} \) ratios, redox state, temperature, as well as the Na activity during crystallization (Ghaderi et al. 1999; Sciuba et al. 2020). Therefore, it is difficult to define the redox state by \( \delta \)Eu alone, and it is necessary to make a comprehensive consideration to judge the evolution history of fluid and its redox state variation for different kinds of ore deposits.

**Reaction between fluid and rock during fluid evolution**

As stated above, the consistent ages of scheelite and granitic intrusions (ca. 154-150 Ma) suggest that the Zhuxi W mineralization is closely related to the intrusions. All the Zhuxi scheelites demonstrate an obvious positive correlation between Y and Ho contents (Fig. 10a), which are consistent with previously obtained data (Fig. 10b; Yuan et al. 2019; Sun et al. 2019). However, these ratios of scheelite are significantly higher than the chondrite Y/Ho ratio of 28, and also higher than those of the related intrusions (from 16 to 42, mean = 23; Pan et al. 2018; Zhang et al. 2020) and the Shuangqiaoshan Group slate (from 20 to 39, mean = 29; Zhang et al. 2012).
It has been suggested that, due to the similar ionic radii and ionic charge, Y and Ho display a similar geochemical behavior during various geological processes with a consistent chondritic Y/Ho ratio of 28 for most igneous rocks and clastic sediments (Bau 1996; Ding et al. 2018). However, previous studies have also shown that the Y/Ho ratio in scheelite can be affected by fluid mixing (Liu et al. 2019) or Y-(Ho)-rich minerals precipitation (e.g., garnet is a Y-enriched mineral, the Y/Ho ratio of fluid will decrease after garnet precipitation; Ding et al. 2018). Therefore, though it may be difficult to distinguish fluid sources using Y/Ho ratios, significantly different ratios could be useful tracers of the evolution of ore-forming fluid (Bau 1996; Sun et al. 2019).

The Sch A is characterized by low REE contents, indicating a REE-depleted fluid, which may be caused by the crystallization of REE-rich minerals (e.g., apatite, up to 1000 ppm REE; Song et al., 2021). Meanwhile, we consider that the high Y/Ho ratios in Sch A most likely originate from Y released from garnet instead of the residual fluid after garnet crystallization, as the Sch A usually coexists and replaces the early-formed garnet. The REE are not highly enriched in garnet, so this mineral could not have singly provided the REE in Sch A, the excess Y produced by its dissolution can still increase the Y/Ho ratio of the REE-depleted fluids.

Moreover, there is a very good correlation ($R^2 = 0.96, n = 20$) between the Y/Ho ratio and $\delta$Eu value of the coarse-grained Sch C (Fig. 10b). The core of the scheelite (with dark CL image; Figs. 5c and 10b) contains extremely high Y/Ho ratio (up to 213) and $\delta$Eu value (up to 36.2), which may be caused by the dissolution of garnet and plagioclase. The Y/Ho ratio gradually decreases from core to rim, to values close to those of granite and Shuangqiaoshan Group metasedimentary rocks (Fig. 10b), consistent with intense fluid-rock interactions. The Sch C is characterized by high Sr contents (mean = 58 ppm), which are higher than those of adjacent granites (mean = 6 ppm, Zhang et al. 2020). In contrast, a previous study noted that the Shuangqiaoshan Group metasedimentary rocks have high Sr contents (mean = 120, Zhang et al. 2012).
Thus, the linear relationship between the Y/Ho ratio and $\delta$Eu for Sch C is plausibly explained by reaction between the ore-forming fluid and the Shuangqiaoshan Group rocks. Overall, the ore-forming fluid exsolved from magma has experienced intense interactions with surrounding rocks and/or earlier-formed skarns (e.g., garnet), leading to distinctive variations in the trace element composition of these fluids.

**IMPLICATIONS**

This study presents U-Pb ages and trace element data of scheelite with the aim to constrain the mineralizing event and fluid evolution for a skarn ore system. We firstly report scheelite U-Pb data from the world’s largest skarn W deposit at Zhuxi, which yield mineralizing ages from 154.0 ± 2.8 to 150.4 ± 6.3 Ma. These results are consistent with the age of adjacent granite and thus support a close genetic relationship between W mineralization and granitic magmatism. We highlight that scheelite LA-ICP-MS U-Pb dating is a useful technique to determine the mineralization age of a skarn-type W deposit, which will be also useful for understanding the timing of various types of mineralization associated with scheelite formation.

The relationships among Y/Ho ratios and metal contents of granite, scheelite and garnet at Zhuxi indicate that the reaction between ore fluids and early-formed garnet could lead to a high Y/Ho ratio for the evolved ore-forming fluid, and the lower Y/Ho ratios and $\delta$Eu values could be caused by the reaction between ore-forming fluid and the Shuangqiaoshan Group rocks. Therefore, the results from this study contribute to a better understanding of the fluid evolution for the skarn-type ore deposits using Y/Ho ratios.

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precise U–Pb age on cassiterite from the Xianghuling tin–polymetallic deposit (Hunan, South China). Mineralium Deposita, 43, 375–382.


Figure captions

Fig. 1 (a) A schematic map of the South China Craton (modified from Mao et al. 2017); (b) A tectonic map of South China showing the position of the Jiangnan Orogenic Belt (modified from Hong et al. 2022); (c) A regional geological map of the Jiangnan porphyry-skarn tungsten belt (JNB) showing the distributions of major W deposits (modified from Mao et al. 2017 and Song et al. 2021).

Fig. 2 (a) A geological map of the Zhuxi skarn deposit (modified from Yuan et al. 2019); (b-c) Representative cross-sections showing the local intrusions and W-Cu orebodies (after No. 912 Geological Team 2020).

Fig. 3 Photographs of representative hand samples showing paragenetic sequences of the Zhuxi deposit. (a) Disseminated tungsten mineralization; (b) Coarse-grained scheelite coexisting with tremolite and minor chalcopyrite; (c) Disseminated scheelite in marble cut by a scheelite-muscovite vein; (d) A vein of garnet-pyroxene-wollastonite in marble, with minor scheelite; (e) Disseminated scheelite in garnet skarn; (f) Scheelite cut by a quartz-sulfide vein. Insets (and panel f) show long-wave UV images of the samples. Abbreviations: Ccp-chalcopyrite; Grt-garnet; Mb-marble; Ms-muscovite; Pyx-pyroxene; Qz-quartz; Sch-scheelite; Tr-tremolite; Wo-wollastonite.

Fig. 4 Photomicrographs of thin sections showing the mineral assemblages of the
Zhuxi deposit. (a) A garnet-pyroxene-wollastonite vein in prograde skarn stage; (b-c) Garnet replaced by disseminated scheelite (Sch A); (d) Scheelite (Sch B) coexisting with muscovite and quartz; (e) Disseminated scheelite (Sch B) in retrograde skarn stage; (f) Coarse-grained scheelite (Sch C, up to 0.5 cm) in retrograde skarn stage; (g) Sch B replaced by chalcopyrite; (h) Chalcopyrite intergrown with sphalerite, bismuthinite, and native bismuth; (i) Sch B cut by a later calcite vein. All pictures are performed under cross-polarized light, except for panels g and h, which are reflected light. Abbreviations: Bi-native bismuth; Bmt-bismuthinite; Cal-calcite; Ccp-chalcopyrite; Grt-garnet; Ms-muscovite; Qz-quartz; Sch-scheelite; Sph-sphalerite; Wo-wollastonite.

Fig. 5 Representative cathodoluminescence (CL) images of scheelite from the Zhuxi deposit. (a) Sch A with weak oscillatory zoning; (b) Sch B with notable oscillatory zoning; (c-d) Coarse-grained Sch C showing a CL-dark core with oscillatory zoning.

Fig. 6 Chondrite-normalized REE patterns for different generations of scheelite from the Zhuxi deposit. The normalized values for chondrite are from Sun and McDonough (1989). Granite and garnet data are collected from Pan et al. (2018), Zhang et al. (2020), and Hong et al. (2022).

Fig. 7 Binary plots of (a) Sr vs. Mo; (b) REE vs. Sr; (c) REE-Eu+Y (representing REE$^{3+}$) vs. Nb; (d) Mo vs. Nb for different generations of scheelite from the Zhuxi deposit. Grey arrows schematically indicate that the Sr and REE contents increase from Sch A to Sch C, while the Mo contents decrease.

Fig. 8 Tera-Wasserburg concordia diagrams of the corresponding $^{207}\text{Pb-corrected}^{206}\text{Pb}/^{238}\text{U}$ ages for scheelites from the Zhuxi deposit. (a-b) U-Pb ages for disseminated Sch A; (c-d) U-Pb ages for disseminated Sch B; (e-f) U-Pb ages for
coarse-grained massive Sch C. The uncertainties are quoted as $2\sigma$.

Fig. 9 Discrimination diagrams for different generations of scheelite. (a) Plot of chondrite-normalized Eu concentrations ($Eu_N$) vs. calculated $Eu^*_N$ values, where $Eu^*_N = (Sm_N \times Gd_N)^{1/2}$; (b) Plot of $Eu_N/Eu^*_N$ ($\delta Eu$) vs. Mo; (c) Plot of $Eu_N/Eu^*_N$ ($\delta Eu$) vs. Sr; (d) Plot of Ce vs. Mo; (e) Plot of $\delta Ce$ vs. Mo; (f) Plot of $\delta Ce$ vs. $\delta Eu$.

Fig. 10 (a) Plot of Y vs. Ho (after Ding et al. 2018); (b) Plot of Y/Ho vs. $\delta Eu$. Data from Pan et al. (2018), Sun et al. (2019), Yuan et al. (2019), Liu et al. (2021), Zhang et al. (2020), Zhang et al. (2021) and Hong et al. (2022). Insets in b show that the core of the Sch C with dark CL image has relatively high Y/Ho and $\delta Eu$ values.

Table 1. Major element results of scheelite from the Zhuxi W deposit (wt.%)

Table 2. Summarized LA-ICP-MS trace element results of scheelite from the Zhuxi W deposit (ppm)

Appendix Figure A1. Representative time-resolved depth profiles of scheelite showing smooth curves for all the selected elements.

Appendix Table A1. LA-ICP-MS trace element results of scheelite from the Zhuxi W deposit (ppm)

Appendix Table A2. LA-ICP-MS U-Pb dating results for scheelite from the Zhuxi deposit
<table>
<thead>
<tr>
<th>Spot No.</th>
<th>MoO$_3$</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
<th>MnO</th>
<th>CaO</th>
<th>FeO</th>
<th>Nb$_2$O$_5$</th>
<th>Ta$_2$O$_5$</th>
<th>UO$_3$</th>
<th>WO$_3$</th>
<th>Total</th>
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<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>19.86</td>
<td>0.01</td>
<td>bd</td>
<td>bd</td>
<td>0.03</td>
<td>79.89</td>
<td>99.81</td>
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<td>0.06</td>
<td>bd</td>
<td>bd</td>
<td>0.04</td>
<td>79.11</td>
<td>99.07</td>
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<td>0.01</td>
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<td>0.01</td>
<td>bd</td>
<td>bd</td>
<td>0.04</td>
<td>78.52</td>
<td>97.09</td>
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<tr>
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<td>bd</td>
<td>19.56</td>
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<td>0.01</td>
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<td>99.43</td>
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<tr>
<td>18zx-21q1d2</td>
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<td>0.01</td>
<td>bd</td>
<td>0.02</td>
<td>20.08</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>80.55</td>
<td>100.68</td>
</tr>
</tbody>
</table>

Note: bd= below detection.
Table 2. Summarized LA-ICP-MS trace element results of scheelite from the Zhuxi W deposit (ppm)

| Sample No. | Sr  | Nb  | Mo  | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Tb  | Ho  | Er  | Tm  | Yb  | Lu  | Hf  | Ta  | Y  | ΣREE | δEu | δCe | Y/Ho |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|------|------|------|------|
| Sch A (n=20) | Mean | 10  | 87  | 1002 | 1.2 | 1.3 | 0.09 | 0.25 | 0.06 | 0.05 | 0.04 | 0.01 | 0.01 | 0.03 | 0.005 | 0.03 | 0.004 | 0.014 | 1  | 0.4 | 3.2 | 9.6 | 0.8 | 74 |
|             | S.D. | 2.70 | 293 | 1   | 1.7 | 0.08 | 0.28 | 0.09 | 0.03 | 0.06 | 0.01 | 0.08 | 0.01 | 0.04 | 0.005 | 0.03 | 0.006 | 0.036 | 0.8 | 0.4 | 2.7 | 12  | 0.1 | 43 |
|             | Min  | 8   | 23  | 557 | 0.1 | 0.1 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.001 | 0.002 | 0.0003 | 0.001 | 0.001 | 0.001 | 0.001 | 0.2 | 0.04 | 0.3 | 0.9 | 0.5 | 31 |
|             | Max  | 16  | 274 | 1680 | 3.3 | 7.5 | 0.32 | 1.13 | 0.35 | 0.11 | 0.24 | 0.05 | 0.3  | 0.05 | 0.14 | 0.02 | 0.13 | 0.02 | 0.156 | 3.3 | 1.6 | 11  | 54  | 1.2 | 207 |
| Sch B (n=20) | Mean | 39  | 23  | 109 | 22  | 30  | 2.9  | 8.4  | 2.3  | 6.4  | 2.4  | 0.5  | 3.8  | 0.7  | 2.7  | 0.6  | 6.7  | 1.1  | 0.004 | 1.6  | 56.2 | 90  | 18.4 | 0.9 | 86 |
|             | S.D. | 6   | 15  | 22  | 13  | 17  | 1.7  | 4.4  | 2.2  | 0.4  | 2.9  | 0.5  | 1.8  | 0.4  | 4.7  | 0.7  | 0.002 | 1.5  | 43   | 47  | 19  | 0.04 | 39 |
|             | Min  | 20  | 12  | 69  | 7.4 | 6.9 | 0.5  | 1.1  | 0.2  | 0.8  | 0.24 | 0.05 | 0.4  | 0.1  | 0.3  | 0.1  | 0.3  | 0.1  | 0.002 | 0.6  | 9    | 22  | 1.3 | 0.8 | 39 |
|             | Max  | 45  | 80  | 167 | 61  | 78  | 7.3  | 25.7 | 7.9  | 16.9 | 8.2  | 1.7  | 11  | 1.9  | 5.8  | 2    | 23   | 3.7  | 0.008 | 7    | 187  | 215 | 65  | 1   | 190 |
| Sch C (n=20) | Mean | 58  | 135 | 45  | 73  | 131 | 15.5 | 52   | 14.6 | 7    | 13.4 | 2.8  | 19  | 3.5  | 11.2 | 2.1  | 17.6 | 2.5  | 0.004 | 8.3  | 151  | 364 | 7   | 1   | 72 |
|             | S.D. | 10  | 204 | 13  | 52  | 103 | 16   | 65   | 21   | 4    | 20   | 4    | 25   | 4.4  | 12   | 1.7  | 12   | 1.7  | 0.002 | 14   | 116  | 313 | 9   | 0.1 | 49 |
|             | Min  | 42.4 | 10  | 25.5 | 6.3 | 19.9 | 2    | 4.3  | 0.9  | 1.4  | 0.6  | 0.2  | 1.5  | 0.3  | 1.2  | 0.3  | 2.4  | 0.3  | 0.001 | 0.4  | 21.3 | 50  | 0.4 | 1   | 27 |
|             | Max  | 72  | 619 | 74.7 | 152 | 334 | 51   | 212  | 68   | 13.1 | 66.3 | 13.1 | 83   | 14.5 | 40   | 5.7  | 34   | 5.3  | 0.01  | 41   | 403  | 1064| 36.2| 1.3 | 213 |

Note: S.D. = standard deviation values.
Fig. 6

(a) Scheelite A

(b) Scheelite B

(c) Scheelite C