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26   **ABSTRACT**

27   Skarn-type tungsten deposits are widely distributed all over the world, and

28   contribute more than 70% of the world's W supply. The temporal relation between the

29   W mineralization and causative intrusions, and the evolution of ore-forming fluids are

30   matters of ongoing debate. In this study, we combine in situ LA-ICP-MS U-Pb dating

31   and trace element compositions of scheelite from Zhuxi, the world's largest W deposit,

32   and compare them with literature data to address the above issues. Three primary ore

33   stages exist at Zhuxi: prograde skarn, retrograde skarn and quartz-sulfide stages. Most

34   scheelite occurs in the retrograde skarn stage and is further subdivided into three

35   generations: Sch A, B and C.

36   The obtained LA-ICP-MS U-Pb ages for three scheelite generations in the Zhuxi

37   deposit are 154.0 ± 2.8, 150.3 ± 3.5 and 150.4 ± 6.3 Ma, respectively, indicating that

38   the entire W mineralization is closely related to the emplacement of the nearby Late

39   Jurassic granites (~154 to 150 Ma, zircon U-Pb ages). In situ LA-ICP-MS trace

40   element results demonstrate that Sch A shows the highest Mo content (mean=1002

41   ppm), where those for Sch B and Sch C are 109 and 45 ppm, respectively. These,

42   combined with the gradually increasing trend of Ce contents and δCe values, indicate

43   a shift from oxidizing to reducing conditions for the ore-forming fluid. All three

44   scheelite generations yield significant positive δEu anomalies, which are considered to

45   be unrelated to the redox state, but caused by the addition of Eu (e.g., feldspar

46   dissolution). The high Y/Ho ratio of scheelite and a good correlation between Y/Ho

47   ratio and δEu ($R^2 = 0.96$) suggest that intense fluid-rock interactions between ore fluids

48   and the Shuangqiaoshan Group metasedimentary rocks as well as earlier-formed skarns

49   drove fluid evolution. This study demonstrates that scheelite U-Pb geochronology is a

50   useful technique when identifying the temporal link between hydrothermal W

51   mineralization and the causative intrusion. The results of this study also highlight that

52   the reactions of the ore fluids with wall rocks and earlier-formed skarns significantly

53   modify the primary fluid compositions.

54   **Keywords:** Scheelite LA-ICP-MS U-Pb dating, trace element, skarn W

55   mineralization, Zhuxi, South China

INTRODUCTION

57   Skarn deposits are one of the most abundant ore deposit types in the earth's crust

58   and have been the subject of numerous studies since their discovery (Kwak 1987;

59   Meinert et al. 2005; Romer et al. 2005; Chang et al. 2019). Metal sources for skarn

60   mineralization are critical for establishing robust genetic models for these ore deposits.

61   The close spatial relationship between skarn deposits and plutons indicates a

62   magmatic origin for metals (Audétat et al. 2000; Webster et al. 2004; Thomas et al.

63   2005; Song et al. 2019). In contrast, some others suggest that the metals originated

64   from the surrounding rocks (Linnen and Williams-Jones 1995; Sun et al. 2019).

65   To address this issue, scheelite, which is dominant in skarn-type W deposits

66   (Meinert et al. 2005; Song et al. 2014; Sun et al. 2019), can be adopted as an ideal

67   mineral to constrain the compositions and sources of the fluids and the origins of the

68   metals (Song et al. 2014; Poulin et al. 2018; Choi et al. 2020; Han et al. 2020; Su et al.

69   2021). Scheelite ($CaWO_4$) commonly accommodates significant amounts of rare earth

70   elements (REE), Y, Mo, and Sr in substitution for Ca or W (Nassau and Loiacono 1963;

71   Ghaderi et al. 1999), which provide insights into the ore-forming processes, including

72   the origin and physicochemical conditions of the ore-forming fluids (Brugger et al.

73   2002; Song et al. 2014; Hazarika et al. 2016; Cao et al. 2021). Meanwhile,

74   developments in U-Pb geochronology permit direct dating of the ore minerals (e.g.,

75   scheelite, cassiterite and wolframite), thus constraining the timing of the mineralizing

76   events (Yuan et al. 2008; Wintzer et al. 2016; Harlaux et al. 2018). Hence, the

77   combination of geochronology and trace element geochemistry of scheelite will shed

78   new light on understanding the genetic relationship between the W mineralization and

79   the causative intrusions. Here, we present in situ laser ablation inductively coupled

80   plasma mass spectrometry (LA-ICP-MS) U-Pb ages and trace element compositions of

81   scheelite from the world's largest skarn-type W deposit to constrain the W

82   mineralization age, reconstruct the redox state of mineralizing fluids, and identify the

83   metal sources.

84   **GEOLOGICAL SETTING**

85   The Zhuxi W deposit is located in Jiangxi Province, South China, within the

86   Jiangnan Orogen, which is adjacent to the Cathaysia block to the south and the

87   Yangtze block to the north (Mao et al. 2017; Fig. 1a, b). The 1500 km long and

88   ENE-trending Jiangnan Orogen was formed by subduction-collision between the

89   Yangtze and Cathaysia blocks at ~970 Ma (Li and McCulloch 1996; Zhang et al.

90   2021). The rocks exposed in this region comprise a Precambrian basement and

91   Phanerozoic rocks (Song et al. 2019; Fig. 1c). The Precambrian basement is

92   subdivided into the lower Shuangqiaoshan Group, which is slate, phyllite and

93   metavolcaniclastic rocks, and the upper Neoproterozoic sedimentary rocks comprising

94   sandstone, slate, conglomerate with lesser carbonate, metabasite and volcaniclastic

95   rocks (Zhao et al. 2011; Zhang et al. 2021). The cover Phanerozoic rocks surrounding

96   the Jiangnan Orogen include Silurian to Early Triassic marine clastic and carbonate

97   rocks, Middle Triassic to Early Jurassic clastic rocks, Middle to Late Jurassic

98   sedimentary and volcanic rocks, and Cretaceous red-bed sandstone, which occur

99   within a series of NE-trending continental basins (Mao et al. 2017, 2020).

100   There are two groups of granites in the Jiangnan Orogen: Neoproterozoic granites

101   that formed during the Jinning orogeny (Li 1999; Wu et al. 2006; Wang et al. 2014)

102   and Late Mesozoic granites that formed during the Yanshanian orogeny (Song et al.

103   2012; Huang and Jiang 2014; Mao et al. 2017; Zhao et al. 2017; Dai et al. 2018). The

104   Yanshanian granitic intrusions can be further subdivided into two groups. The first

105   group (153-136 Ma) consists of monzonitic granite and some granodiorite and alkali

106   granite. The second group (129-102 Ma) is represented by monzonitic granite with

107   peraluminous geochemical signatures (Song et al. 2021).

108   In the past decade, a dozen porphyry-skarn W polymetallic deposits have been

109   discovered in the Jiangnan porphyry-skarn tungsten belt (JNB) in south China (Fig.

110   1c): the Dahutang (1.07 Mt WO_3 at 0.15 wt.%; Mao et al. 2015) and the Dongyuan

111   porphyry deposits (0.14 Mt WO_3 at 0.12 wt.%; Zhou et al. 2011), the Xianglushan

112   (0.22 Mt WO_3 at 0.64 wt.%; Dai et al. 2018) and the Zhuxi skarn deposits (4.22 Mt

113   WO_3 at 0.5 wt.%; Chen et al. 2012, 2015; No. 912 Geological Team 2020).

114   Collectively, these surpass the Nanling W belt (Song et al., 2019), making the JNB the

115   world's largest W belt (up to 6 Mt of WO_3; Mao et al. 2017, 2020). Previous

116   geochronological data revealed that most of the W-bearing deposits in the JNB were

117   related to the first group intrusions (153-135 Ma, e.g., Song et al. 2012; Huang and

118   Jiang 2014; Mao et al. 2017; Pan et al. 2018; Su et al. 2018), while only minor W

119   mineralization was caused by the second group (129-102 Ma, e.g., the Xianglushan

120   skarn deposit, ~125 Ma; Dai et al. 2018).

121   **ORE DEPOSIT GEOLOGY**

122   The   exposed   rocks   in   the   Zhuxi   deposit   include   the   Neoproterozoic

123   Shuangqiaoshan Group and the Carboniferous-Permian sedimentary rocks (Chen et al.

124   2012). The greenschist-facies Shuangqiaoshan Group mainly consists of slate and

125   phyllite   (Wang   et   al.   2007).   It   is   unconformably   overlain   by   the

126   Carboniferous-Permian rocks, which include the Huanglong, Chuanshan, Changxing,

127   Leping, Maokou and Xixia Formations from older to younger (Yuan et al. 2019; Figs.

128   2a). They mostly comprise shallow marine carbonate rocks (dolomite and limestone)

129   with minor clastic sedimentary rocks (e.g., siltstone, sandstone) (Chen et al. 2012;

130   Sun et al. 2019). These rocks are fractured by NE-trending faults (F1, F2 and F3), and

131   cut by the later NW-trending fault (F4) (Fig. 2a).

132   Detailed core drillings identified three intrusions in the deep part of the deposit:

133   biotite granite, muscovite granite, and granite porphyry (Song et al. 2019; Fig. 2b, c).

134   They occur as dikes and/or stocks intruding into the Neoproterozoic Shuangqiaoshan

135   Group slate and phyllite as well as Carboniferous-Permian carbonates (Chen et al.

136   2012). Recently, Zhang et al. (2021) noted that the granite porphyry caused

137   mineralization. Several lamprophyre dikes in the north of the deposit intruded

138   carbonates (Fig. 2a; Pan et al. 2017), and their zircon U-Pb dating results indicate an

139   emplacement age of ~160 Ma (Liu et al. 2014), which is earlier than the formation

140   age of the Zhuxi deposit.

141   From granites to carbonates, the alteration spatially transforms from greisen, skarn

142   to marble zones (Pan et al. 2018; Yuan et al. 2019). Most W mineralization occurs

143   within the skarn zone (Fig. 3a, b), and minor mineralization also formed in the greisen

144   and marble zones (Fig. 3c) and granites (Yuan et al. 2019; He et al. 2022). The

145   orebodies are stratiform, stratabound or lenticular (Song et al. 2019), and are 750 m

146   long and extend more than 2000 m in depths (Fig. 2b). From the intrusion outwards,

147   the mineralized zones vary from W, W-Cu to Cu-(Pb-Zn) at elevations from -2000 to

148   -200 m (He et al. 2022).

149   The mineralization can be subdivided into three stages: prograde skarn, retrograde

150   skarn, and quartz-sulfide stages; most scheelite was precipitated in the retrograde

151   stage. The prograde stage predominantly consists of anhydrous minerals, such as

152   garnet (Figs. 3d, e and 4a-c), wollastonite (Figs. 3d and 4a), and pyroxene, with minor

153   quartz and vesuvianite (Sun et al. 2019). From core to rim, the skarn veins (several to

154   tens of centimeters in width) exhibit mineral zonation of garnet, pyroxene, vesuvianite

155   and wollastonite, and cut the marble (Pan et al. 2017; Figs. 3d and 4a). This reflects a

156   time sequence with the rim bordering to the carbonates being the oldest one and the

157   axial being the youngest one (Yardley and Lloyd 1995; Heinrich 2007; Xu et al. 2022).

158   Minor scheelite (Sch A) is found in this stage (Figs. 4a-c and 5a) and generally occurs

159   as disseminations in the center of the garnet-wollastonite veins (Fig. 3d) and garnet

160   skarn (Fig. 3e). Most Sch A replaced garnet (Fig. 4b, c) and diopside (Pan et al. 2017)

161   in this stage. The retrograde skarn stage is characterized by the mineral assemblage of

162   abundant tremolite (Fig. 3b), serpentine, muscovite (Figs. 3c and 4d), actinolite,

163   chlorite, fluorite, talc, epidote and quartz (Song et al. 2019). Scheelite (Sch B) in this

164   stage is commonly disseminated (200-1000 μm in diameter) (Figs. 4d, e and 5b), and

165   coexists with quartz, muscovite (Fig. 4d), tremolite and actinolite (He et al. 2022).

166   Notably, coarse-grained massive scheelite (Sch C, up to 0.5 cm in diameter; Figs. 3b,

167   4f, 5c and 5d) is also found in this stage, which may be associated with the dissolution

168   of early disseminated scheelite (Sch A and B) and its re-precipitation at late sequence

169   (Song et al. 2019). Finally, the later quartz-sulfide stage is dominated by the mineral

170   assemblage of chalcopyrite (Fig. 4g, h), sphalerite, molybdenite, bismuthinite, native

171   bismuth (Fig. 4h), pyrrhotite, arsenopyrite, and galena with quartz, fluorite and calcite

172   (Song et al. 2019; Yuan et al. 2019). Both the quartz-sulfide and calcite veins cut the

173   early formed skarns (Figs. 3f and 4i).

174   **SAMPLES AND ANALYTICAL METHODS**

175   **Scheelite samples**

176   All the scheelite-bearing specimens were collected from drill core (ZK3001 and

177   ZK3004) along line 30 at depths of -1400 to -1800 m in the Zhuxi deposit (Fig. 2b).

178   These samples were prepared as polished sections for microprobe and LA-ICP-MS

179   analysis. Before analysis, all thin sections were finely polished and coated with

180   carbon, and cathodoluminescence (CL) imaging was carried out in the State Key

181   Laboratory of Geological Processes and Mineral Resources, China University of

182   Geosciences Beijing (CUGB).

183   **Major elements analysis**

184   Major element compositions of scheelite were determined by electron microprobe

185   analysis using a Shimadzu Electron Probe Microscope Analyzer (EMPA 1720H) at the

186   Key Laboratory of Geoscience Big Data and Deep Resource of Zhejiang Province,

187   Zhejiang University. Operating conditions included an acceleration voltage of 20 kV,

188   a beam current of 20 nA, and an electron beam diameter of 5 μm. Analysis used

189   natural and synthetic minerals as calibration standards, and all data were corrected

190   using a ZAF procedure. The precision of all analyzed elements was better than 1.5%.

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

192   The U-Pb dating of scheelite was performed on an Analytik Jena PlasmaQuant MS

193   quadrupole ICP-MS with a 193 nm NWR193 Ar-F excimer laser at Yanduzhongshi

194   Geological Analysis Laboratories Ltd. Scheelite material ZS-Sch (in-house scheelite

195   standard, 228 ± 2 Ma; Li et al., 2022) was used as the standard to calibrate the U-Pb age.

196   Instrument drift, mass bias and fractionation of the U-Pb ratio are corrected with a

197   standard-sample bracketing method. Isotopes measured were ^{44}Ca, ^{206}Pb, ^{207}Pb, ^{208}Pb,

198   ^{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

199   ^{207}Pb, 15 ms for ^{208}Pb,10 ms for ^{232}Th, 15 ms for ^{235}U, 25 ms for ^{238}U.

200   Each analysis on the scheelite began with a 15 second blank gas measurement

201   followed by a further 40 seconds of analysis time when the laser was switched on.

202   Scheelites were sampled on 40-micron spots using the laser at 8 Hz and a density of

203   approximately 4.0 J/cm^2. A flow of He carrier gas at a rate of 0.6 L/min carried particles

204   ablated by the laser out of the chamber to be mixed with Ar gas and carried to the

205   plasma torch. The raw data were corrected offline employing ICPMSDataCal software

206   (Liu et al. 2010) and ZSkits software (Cai et al. 2020). Common Pb was corrected using

207   the ^{207}Pb-based correction method outlined in detail by Chew et al. (2014). Isoplot 4.15

208   was used to calculate U-Pb ages in the Tera-Wasserburg diagram (Ludwig 2012), which

209   is particularly useful in systems with high common Pb abundance (Chew et al. 2011,

210   2014).

211   Trace element measurements of scheelite were separately performed from U-Pb

212   dating using the same instrument conditions. The concentrations of trace elements were

213   quantified using SRM610 as external standard and ^{44}Ca as the internal standard element

214   assuming a stochiometric scheelite composition.

215   **RESULTS**

216   **Major element compositions**

217   The major element compositions of scheelites are listed in Table 1. The WO_3 and

218   CaO contents for scheelites range from 79.9 to 81.3 wt.% and 18.6 to 19.9 wt.%,

219   respectively. The MoO_3 content is up to 0.2 wt.%. In addition to these elements, most

220   other components are negligible and below the detection limit, especially for Nd, Nb

221   and Ta (Table 1).

222   **LA-ICP-MS trace element compositions**

223   The summarized results of LA-ICP-MS trace element analyses of scheelites are

224   given in Table 2 and detailed data can be found in Appendix Table A1, and the

225   chondrite-normalized REE patterns are shown in Figure 6. Chemically, Sch A contains

226   relatively higher concentrations of Mo (557-1680 ppm) and lower contents of Sr

227   (7.6-16.4 ppm) and rare earth elements (REE; 0.3-11 ppm) compared to Sch B and Sch

228   C (Table 2). The mean contents of Mo, Sr and REE for Sch B and C are 109, 39, 90 ppm,

229   and 45, 58, 364 ppm, respectively (Table 2), showing systematically lower Mo contents

230   and increasingly higher Sr and REE from Sch A to Sch C (Fig. 7a and 7b). The contents

231   of Mn show no significant variation in the three scheelite generations, ranging from 31

232   to 138 ppm, 27 to 74 ppm and 40 to 103 ppm, respectively (Appendix Table A1).

233   The three generations of scheelite show different chondrite-normalized REE patterns

234   (Fig. 6a-c). The majority of Sch A are characterized by LREE-enriched patterns, and

235   the LREE/HREE ratios of Sch A vary from 1.9 to 164 with a mean value of 35. The

236   LREE/HREE ratios of Sch B and Sch C, however, are much lower, ranging from 1.7 to

237   8.7 (mean =4.5) and 2.7 to 6.7 (mean = 4.7), respectively (Table 2). Notably, almost all

238   of the scheelite spots have positive Eu anomalies and the patterns show depleted MREE

239   relative to LREE and HREE. Among them, some points in Sch C show negative Eu

240   anomalies with significantly higher MREE contents, and the differentiation between

241   LREE and HREE is not obvious (Fig. 6c).

242   **LA-ICP-MS U-Pb ages**

243   The U-Pb ages obtained in this study are listed in Appendix Table A2 with

244   representative time-resolved depth profiles showing in Appendix Figure A1. For the

245   Sch A (sample 18ZX-15), 22 scheelite grains were analyzed for their U-Pb isotopic

246   ages, which yield an intercept age of 154 ± 2.8 Ma (MSWD = 1.02) (Fig. 8a). Though

247   the scheelite crystals exhibit relatively high common Pb contents, the corresponding

248    $^{206}Pb/^{238}U$ ages after ^{207}Pb-correction range from 141.7 to 165.4 Ma (Appendix Table

249   A2) with a weighted mean $^{206}Pb/^{238}U$ age of 153.7 ± 2.5 Ma (n = 22, MSWD = 0.98, 2σ)

250   (Fig. 8b), which is within error of its intercept age (Fig. 8a). Thirty-one scheelite grains

251   (Sch B) (sample 18ZX-21) give an intercept age of 150.2 ± 3.6 Ma (MSWD= 1.8) (Fig.

252   8c) with a weighted mean $^{206}Pb/^{238}U$ age after ^{207}Pb-correction of 151.1 ± 2.8 Ma (n =

253   31, MSWD = 1.3, 2σ) (Fig. 8d). Finally, 25 spot analyses performed on the

254   coarse-grained scheelite (Sch C) (sample 18ZX-22) from the high-grade W ore yield an

255   intercept age of 150.4 ± 6.3 Ma (MSWD = 0.87) (Fig. 8e) with a weighted mean age of

256   150.7 ± 3.8 Ma (n = 25, MSWD = 0.5, 2σ) (Fig. 8f). Because of the low U contents, the

257   age error of Sch C is larger than that of Sch A and Sch B (Appendix Table A2).

258   **DISCUSSION**

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

260   Numerous studies have been conducted to constrain the mineralization age for the

261   Zhuxi skarn-type W deposit (Liu et al. 2014; Chen et al. 2015). For example, Pan et al.

262   (2017) reported muscovite $^{40}Ar/^{39}Ar$ age of 150.2 ± 0.9 Ma. Song et al. (2019) obtained

263   titanite U-Pb ages of 149.9 ± 1.3 to 148.1 ± 7.4 Ma and Zhang et al. (2021) obtained

264   apatite U-Pb ages of 153.7 ± 1.9 to 152.6 ± 4.6 Ma. Recently, Hong et al. (2022)

265   reported garnet U-Pb ages of 153.0 ± 4.4 and 148.7 ± 7.9 Ma. These ages, however, are

266   mostly reported for hydrothermal minerals (i.e., garnet, muscovite, titanite and apatite),

267   which may not temporally coexist with W mineralization and therefore cannot directly

268   represent W mineralization ages.

269   To date, the only geochronology study of the Zhuxi scheelite was conducted by Liu

270   et al. (2017), who reported an age of 144 ± 5 Ma using scheelite Sm-Nd dating method.

271   In addition to the large error of this age, there is an obvious gap between this age and

272   the timing of adjacent granites (recalculated ages of biotite granite, muscovite granite,

273   and granite porphyry are 153.6 ± 0.6 Ma, n=35; 150.7 ± 1.2 Ma, n=28; and 152.7 ± 0.6

274   Ma, n=38; Pan et al. 2018; Zhang et al. 2020). It has been reported that Sm-Nd dating

275   has a high potential to yield rotated mixing lines with too old or too young ages. Thus,

276   the 144 Ma age from scheelite Sm-Nd dating method might be inaccurate. Besides,

277   Pan et al. (2017) reported a molybdenite Re-Os age of 145.1 ± 1.5 Ma. Considering

278   that molybdenite belongs to the sulfide stage and obviously formed later than

279   scheelite, the obtained molybdenite Re-Os age could not represent a primary event for

280   scheelite precipitation. Therefore, the W mineralization age of the Zhuxi deposit

281   requires further investigation.

282   Scheelite has relatively high and variable U concentrations (~10 ppm), making it an

283   ideal mineral for U-Pb geochronology (Wintzer et al. 2016; Poitrenaud et al. 2020). The

284   Zhuxi scheelite contains relatively high U contents (6-64 ppm). Time-resolved depth

285   profiles show smooth curves for all the analyzed elements (Appendix Figure A1),

286   ruling out the existence of mineral inclusion and its influence on U-Pb system.

287   Therefore, the U content in scheelite is dominantly structural, and the obtained U-Pb

288   ages can be interpreted as the ages of the tungsten mineralization. There is a negative

289   correction between age error and U content (Appendix Table A2, Fig. 8), indicating that

290   the content of U plays an important role in determining the viability of precise U-Pb

291   dating.

292   Our LA-ICP-MS U-Pb results show that all three scheelite generations (Sch A, Sch B

293   and Sch C) formed between 154.0 ± 2.8 and 150.4 ± 6.3 Ma (Fig. 8), which is

294   consistent with the ages of other hydrothermal minerals in the Zhuxi W deposit (e.g.,

295   muscovite, titanite and apatite; Pan et al. 2017; Song et al. 2019; Zhang et al. 2021) and

296   adjacent granites (recalculated zircon U-Pb ages from 153.6 ± 0.6 to 150.7 ± 1.2 Ma;

297   Pan et al. 2018; Zhang et al. 2020). Compared to scheelite Sm-Nd age (144 ± 5 Ma; Liu

298   et al. 2017), the obtained ages of Sch A to C (154-150 Ma) are more consistent with

299   those of adjacent granites (153.6-150.7 Ma). Overall, the Zhuxi granite, garnet, apatite,

300   muscovite and scheelite were formed almost contemporaneously from 154 to 150 Ma.

301   The consistency of these ages supports the reliability of the scheelite U-Pb dating in

302   identifying W mineralization. The results from this study also show that the Zhuxi

303   tungsten mineralization is closely related to the Late Jurassic to Early Cretaceous

304   magmatism.

Element substitution mechanism in scheelite

305

306   The contents of Sr, Mn, and Pb of scheelite in Zhuxi are relatively high,

307 indicating these divalent cations could directly enter the scheelite lattice to replace Ca^{2+}

308 due to the similar ionic radius (Nassau and Loiacono 1963; Ghaderi et al. 1999; Ding et

309 al. 2018). As to REE^{3+}, several charge-compensating mechanisms have been proposed

310 to maintain the charge-compensating to maintain electrostatic neutrality (Cottrant 1981;

311 Burt 1989; Ghaderi et al. 1999; Zhao et al. 2018). The very low concentrations of Na

312 and Nb in Zhuxi scheelite (Tables 1 and 2) and the poor correlation between Nb and

313 REE-Eu+Y (Fig. 7c) indicate that the mechanisms ($2Ca^{2+} = REE^{3+} + Na^+$ and $Ca^{2+} +$

314 $W^{6+} = REE^{3+} + Nb^{5+}$) are insignificant for the REE accommodation. Furthermore, there

315 is no linear relationship between Nb and Mo (Fig. 7d), which excludes the possibility of

316 the substitution: $Ca^{2+} + Mo^{6+} = REE^{3+} + (1 - x) Mo^{5+} + xNb^{5+}(0 \le x \le 1)$ (Zhao et al.

317 2018). Previous studies also revealed that scheelite with $REE^{3+} + Na^+$ substitution

318 mechanism has obvious MREE-rich (hump-shaped) patterns (Ding et al. 2018), which

319 is not observed in the Zhuxi scheelite (Fig. 6).

320   The REE in skarn minerals are the combination of the REE present in the

321 carbonates and the REE added by the fluid. As the REE are relatively immobile in most

322 fluids (depending on the ligands available), the REE are commonly less abundant for

323 incorporation. In the Zhuxi deposit, because the low contents of Na and Nb, the above

324 substitution mechanisms are excluded. As a result, scheelite accommodates low

325 concentrations of the REE, therefore there is little fractionation between fluid and

326 scheelite. Overall, excluding the other three possibilities, the mechanism $3Ca^{2+} =$

327 $2REE^{3+} +$ [ ]Ca (where [ ]Ca represents a Ca-site vacancy; Ding et al. 2018) best

328 explains the REE substitution in scheelite in the studied deposit.

Redox conditions during W mineralization

329

330   In the Zhuxi deposit, scheelite from all three generations show predominantly high

331 $Eu_N/Eu*_N$ ratios (δEu) (Fig. 9a) and significant positive Eu anomalies ($\delta Eu > 1$; Fig. 9b

332 and 9c). Because Eu^{2+} has the same charge as Ca^{2+}, Eu can substitute for Ca in scheelite

333   easily in reducing conditions, which could result in a positive Eu anomaly (Sun and

334   Chen 2017; Poulin et al. 2018; Han et al. 2020). Similarly, Mo can occur in Mo^{6+} and

335   Mo^{4+} states, and the former can easily substitute for W^{6+} whereas the latter hardly

336   substitutes for W^{6+}, leading to the high Mo contents in oxidizing conditions and low

337   contents in reducing conditions (Yuan et al. 2019). Song et al. (2014) reported a

338   negative correlation between Mo and $Eu_N/Eu*_N$ in porphyry-skarn deposits. However,

339   there is a significant decoupling relationship between Mo content and $Eu_N/Eu*_N$ in the

340   Zhuxi deposit. From Sch A to Sch C, the Mo content decreases but there is no

341   accompanying change in $Eu_N/Eu*_N$ ratio (Fig. 9b). In addition to the redox state, the

342   crystallization of early minerals may have an effect on Mo distribution in scheelite. For

343   instance, the early crystallization of garnet may favor partition of Mo, Sn, and W into

344   this mineral phase (Xu et al., 2016; Fei et al., 2019; Zhu et al., 2021), thus the coeval

345   scheelite will have relatively low contents of these elements, as their source has been

346   depleted. However, previous studies have shown that the Zhuxi garnets contain

347   extremely low contents of Mo (<1ppm; Ouyang et al, 2020). By contrast, the coeval

348   scheelites (Sch A) yield relatively high contents of Mo (up to 1680 ppm), ruling out the

349   possibility of the influence from mineral crystallization. Therefore, the variation of Mo

350   content suggests that the fluid changes from oxidizing to reducing conditions during

351   mineralization.

352   In addition to Eu and Mo, Ce can also be adopted to trace redox conditions (Ding et

353   al. 2015). Because Ce^{3+} (radius of 1.14 Å) is easier to enter scheelite (Ca^{2+} radius of

354   1.12 Å) than Ce^{4+} (radius of 0.97 Å), scheelite formed by the oxidizing fluid will

355   contain a low Ce content with negative Ce anomaly. This can be recorded from the Mo

356   vs. Ce and Mo vs. δCe plots (Fig. 9d and 9e), on which Ce contents and δCe decrease

357   with increasing Mo contents in the Zhuxi deposit. The Sch A has the highest Mo

358   contents and lowest Ce contents with significantly negative δCe values (0.5-1.2, mean

359   = 0.8), suggesting an oxidized condition. The δCe values of Sch B (0.8-1.0, mean = 0.9)

360   and Sch C (1.0-1.3, mean = 1.0) indicate that the fluid shifted from oxidation to

361   reduction (Fig. 9e), and are consistent with the variations of Mo contents. The Mo, Ce

362   and δCe variations in scheelite show that the ore fluid has undergone a transition from

363   oxidizing to more reducing conditions. However, there is no significant difference in

364   δEu values of the three scheelite generations (Fig. 9f), which may be caused by Eu^{2+}

365   addition into the fluids (Yuan et al. 2019), partly due to the plagioclase dissolution.

366   In recent years, several studies have also found that there are limitations in using δEu

367   to constrain redox state not only in skarn deposits but also in porphyry-related and/or

368   orogenic deposits. For example, all types of scheelite in the Nui Phao W deposit from

369   Vietnam are characterized by negative Eu anomalies (Nguyen et al. 2020), suggesting

370   that it is necessary to consider the effects of fluid compositions and mineral

371   crystallization. Sciuba et al. (2020) noted that strong positive Eu anomalies are

372   predominantly related to flat REE patterns with low REE contents in scheelite, whereas

373   weakly positive to negative Eu anomalies are characteristic of scheelite with higher

374   REE contents in orogenic deposits. Europium anomalies likely reflect initial fluid

375   Eu^{2+}/Eu^{3+} ratios, redox state, temperature, as well as the Na activity during

376   crystallization (Ghaderi et al. 1999; Sciuba et al. 2020). Therefore, it is difficult to

377   define the redox state by δEu alone, and it is necessary to make a comprehensive

378   consideration to judge the evolution history of fluid and its redox state variation for

379   different kinds of ore deposits.

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

381   As stated above, the consistent ages of scheelite and granitic intrusions (ca. 154-150

382   Ma) suggest that the Zhuxi W mineralization is closely related to the intrusions. All the

383   Zhuxi scheelites demonstrate an obvious positive correlation between Y and Ho

384   contents (Fig. 10a), which are consistent with previously obtained data (Fig. 10b; Yuan

385   et al. 2019; Sun et al. 2019). However, these ratios of scheelite are significantly higher

386   than the chondrite Y/Ho ratio of 28, and also higher than those of the related intrusions

387   (from 16 to 42, mean = 23; Pan et al. 2018; Zhang et al. 2020) and the Shuangqiaoshan

388   Group slate (from 20 to 39, mean = 29; Zhang et al. 2012).

389   It has been suggested that, due to the similar ionic radii and ionic charge, Y and Ho

390   display a similar geochemical behavior during various geological processes with a

391   consistent chondritic Y/Ho ratio of 28 for most igneous rocks and clastic sediments

392   (Bau 1996; Ding et al. 2018). However, previous studies have also shown that the Y/Ho

393   ratio in scheelite can be affected by fluid mixing (Liu et al. 2019) or Y-(Ho)-rich

394   minerals precipitation (e.g., garnet is a Y-enriched mineral, the Y/Ho ratio of fluid will

395   decrease after garnet precipitation; Ding et al. 2018). Therefore, though it may be

396   difficult to distinguish fluid sources using Y/Ho ratios, significantly different ratios

397   could be useful tracers of the evolution of ore-forming fluid (Bau 1996; Sun et al.

398   2019).

399   The Sch A is characterized by low REE contents, indicating a REE-depleted fluid,

400   which may be caused by the crystallization of REE-rich minerals (e.g., apatite, up to

401   1000 ppm REE; Song et al., 2021). Meanwhile, we consider that the high Y/Ho ratios

402   in Sch A most likely originate from Y released from garnet instead of the residual fluid

403   after garnet crystallization, as the Sch A usually coexists and replaces the early-formed

404   garnet. The REE are not highly enriched in garnet, so this mineral could not have singly

405   provided the REE in Sch A, the excess Y produced by its dissolution can still increase

406   the Y/Ho ratio of the REE-depleted fluids.

407   Moreover, there is a very good correlation ($R^2 = 0.96$, n = 20) between the Y/Ho ratio

408   and δEu value of the coarse-grained Sch C (Fig. 10b). The core of the scheelite (with

409   dark CL image; Figs. 5c and 10b) contains extremely high Y/Ho ratio (up to 213) and

410   δEu value (up to 36.2), which may be caused by the dissolution of garnet and

411   plagioclase. The Y/Ho ratio gradually decreases from core to rim, to values close to

412   those of granite and Shuangqiaoshan Group metasedimentary rocks (Fig. 10b),

413   consistent with intense fluid-rock interactions. The Sch C is characterized by high Sr

414   contents (mean = 58 ppm), which are higher than those of adjacent granites (mean = 6

415   ppm, Zhang et al. 2020). In contrast, a previous study noted that the Shuangqiaoshan

416   Group metasedimentary rocks have high Sr contents (mean = 120, Zhang et al. 2012).

417   Thus, the linear relationship between the Y/Ho ratio and δEu for Sch C is plausibly

418   explained by reaction between the ore-forming fluid and the Shuangqiaoshan Group

419   rocks. Overall, the ore-forming fluid exsolved from magma has experienced intense

420   interactions with surrounding rocks and/or earlier-formed skarns (e.g., garnet), leading

421   to distinctive variations in the trace element composition of these fluids.

422

423   **IMPLICATIONS**

424   This study presents U-Pb ages and trace element data of scheelite with the aim to

425   constrain the mineralizing event and fluid evolution for a skarn ore system. We firstly

426   report scheelite U-Pb data from the world's largest skarn W deposit at Zhuxi, which

427   yield mineralizing ages from 154.0 ± 2.8 to 150.4 ± 6.3 Ma. These results are consistent

428   with the age of adjacent granite and thus support a close genetic relationship between

429   W mineralization and granitic magmatism. We highlight that scheelite LA-ICP-MS

430   U-Pb dating is a useful technique to determine the mineralization age of a skarn-type W

431   deposit, which will be also useful for understanding the timing of various types of

432   mineralization associated with scheelite formation.

433   The relationships among Y/Ho ratios and metal contents of granite, scheelite and

434   garnet at Zhuxi indicate that the reaction between ore fluids and early-formed garnet

435   could lead to a high Y/Ho ratio for the evolved ore-forming fluid, and the lower Y/Ho

436   ratios and δEu values could be caused by the reaction between ore-forming fluid and

437   the Shuangqiaoshan Group rocks. Therefore, the results from this study contribute to a

438   better understanding of the fluid evolution for the skarn-type ore deposits using Y/Ho

439   ratios.

440

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448

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730

731 **Figure captions**

732 Fig. 1 (a) A schematic map of the South China Craton (modified from Mao et al.

733 2017); (b) A tectonic map of South China showing the position of the Jiangnan

734 Orogenic Belt (modified from Hong et al. 2022); (c) A regional geological map of the

735 Jiangnan porphyry-skarn tungsten belt (JNB) showing the distributions of major W

736 deposits (modified from Mao et al. 2017 and Song et al. 2021).

737

738 Fig. 2 (a) A geological map of the Zhuxi skarn deposit (modified from Yuan et al.

739 2019); (b-c) Representative cross-sections showing the local intrusions and W-Cu

740 orebodies (after No. 912 Geological Team 2020).

741

742 Fig. 3 Photographs of representative hand samples showing paragenetic sequences of

743 the Zhuxi deposit. (a) Disseminated tungsten mineralization; (b) Coarse-grained

744 scheelite coexisting with tremolite and minor chalcopyrite; (c) Disseminated scheelite

745 in marble cut by a scheelite-muscovite vein; (d) A vein of

746 garnet-pyroxene-wollastonite in marble, with minor scheelite; (e) Disseminated

747 scheelite in garnet skarn; (f) Scheelite cut by a quartz-sulfide vein. Insets (and panel f)

748 show long-wave UV images of the samples. Abbreviations: Ccp-chalcopyrite;

749 Grt-garnet; Mb-marble; Ms-muscovite; Pyx-pyroxene; Qz-quartz; Sch-scheelite;

750 Tr-tremolite; Wo-wollastonite.

751

752 Fig. 4 Photomicrographs of thin sections showing the mineral assemblages of the

753   Zhuxi deposit. (a) A garnet-pyroxene-wollastonite vein in prograde skarn stage; (b-c)

754   Garnet replaced by disseminated scheelite (Sch A); (d) Scheelite (Sch B) coexisting

755   with muscovite and quartz; (e) Disseminated scheelite (Sch B) in retrograde skarn

756   stage; (f) Coarse-grained scheelite (Sch C, up to 0.5 cm) in retrograde skarn stage; (g)

757   Sch B replaced by chalcopyrite; (h) Chalcopyrite intergrown with sphalerite,

758   bismuthinite, and native bismuth; (i) Sch B cut by a later calcite vein. All pictures are

759   performed under cross-polarized light, except for panels g and h, which are reflected

760   light. Abbreviations: Bi-native bismuth; Bmt-bismuthinite; Cal-calcite;

761   Ccp-chalcopyrite; Grt-garnet; Ms-muscovite; Qz-quartz; Sch-scheelite; Sph-sphalerite;

762   Wo-wollastonite.

763

764   Fig. 5 Representative cathodoluminescence (CL) images of scheelite from the Zhuxi

765   deposit. (a) Sch A with weak oscillatory zoning; (b) Sch B with notable oscillatory

766   zoning; (c-d) Coarse-grained Sch C showing a CL-dark core with oscillatory zoning.

767

768   Fig. 6 Chondrite-normalized REE patterns for different generations of scheelite from

769   the Zhuxi deposit. The normalized values for chondrite are from Sun and McDonough

770   (1989). Granite and garnet data are collected from Pan et al. (2018), Zhang et al.

771   (2020), and Hong et al. (2022).

772

773   Fig. 7 Binary plots of (a) Sr vs. Mo; (b) REE vs. Sr; (c) REE-Eu+Y (representing

774   REE^{3+}) vs. Nb; (d) Mo vs. Nb for different generations of scheelite from the Zhuxi

775   deposit. Grey arrows schematically indicate that the Sr and REE contents increase from

776   Sch A to Sch C, while the Mo contents decrease.

777

778   Fig. 7 Tera-Wasserburg concordia diagrams of the corresponding ^{207}Pb-corrected

779   ^{206}Pb/^{238}U ages for scheelites from the Zhuxi deposit. (a-b) U-Pb ages for

780   disseminated Sch A; (c-d) U-Pb ages for disseminated Sch B; (e-f) U-Pb ages for

28

781   coarse-grained massive Sch C. The uncertainties are quoted as 2σ.

782

783   Fig. 9 Discrimination diagrams for different generations of scheelite. (a) Plot of

784   chondrite-normalized Eu concentrations (Eu$_N$) vs. calculated Eu*$_N$ values, where Eu*$_N$

785   = (Sm$_N$ × Gd$_N$)$^{1/2}$; (b) Plot of Eu$_N$/Eu*$_N$ (δEu) vs. Mo; (c) Plot of Eu$_N$/Eu*$_N$ (δEu) vs. Sr;

786   (d) Plot of Ce vs. Mo; (e) Plot of δCe vs. Mo; (f) Plot of δCe vs. δEu.

787

788   Fig. 10 (a) Plot of Y vs. Ho (after Ding et al. 2018); (b) Plot of Y/Ho vs. δEu. Data from

789   Pan et al. (2018), Sun et al. (2019), Yuan et al. (2019), Liu et al. (2021), Zhang et al.

790   (2020), Zhang et al. (2021) and Hong et al. (2022). Insets in b show that the core of

791   the Sch C with dark CL image has relatively high Y/Ho and δEu values.

792

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

794

795   Table 2. Summarized LA-ICP-MS trace element results of scheelite from the Zhuxi W

796   deposit (ppm)

797

798   Appendix Figure A1. Representative time-resolved depth profiles of scheelite showing

799   smooth curves for all the selected elements.

800

801   Appendix Table A1. LA-ICP-MS trace element results of scheelite from the Zhuxi W

802   deposit (ppm)

803

804   Appendix Table A2. LA-ICP-MS U-Pb dating results for scheelite from the Zhuxi

805   deposit

806

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

Spot No.	MoO_3	Na_2O	TiO_2	MnO	CaO	FeO	Nb_2O_5	Ta_2O_5	UO_3	WO_3	Total
18zx-13q1d1	0.02	bd	bd	bd	19.86	0.01	bd	bd	0.03	79.89	99.81
18zx-14q1d1	0.18	bd	0.01	bd	19.72	bd	0.06	bd	bd	79.11	99.07
18zx-17q1d1	0.01	bd	0.01	bd	18.50	0.01	bd	bd	0.04	78.52	97.09
18zx-18q1d1	bd	bd	0.01	bd	19.56	0.03	bd	bd	0.01	80.41	100.01
18zx-21q1d1	0.05	bd	0.03	bd	18.45	0.03	bd	bd	0.01	80.86	99.43
18zx-21q1d2	0.04	0.01	bd	0.02	20.08	bd	bd	bd	bd	80.55	100.68

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	Dy	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	0.06	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	0.01	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	6	2	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	1.3	0.2	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. 1

(a) Junggar Block; Songliao Block; Tarim Block; North China Craton; Tibet; South China Craton; 1000 km; Fig. 1b

(b) North China Craton; Qinling-Dabieshan Orogenic Belt; Yangtze Block; Jiangnan Orogenic Belt; Cathaysia Block; Indosinian Block; Fig. 1c; 200 km

(c)
North China Craton
Qinling-Dabieshan Orogenic Belt
Middle-Lower Yangtze River porphyry-skarn Cu-Au-Mo-Fe ore belt(YRB)
Tancheng-Lujiang fault
Xiangfan-Guangji fault
Yangtze River
Yangxing-Changzhou fault
Yangtze Block
Jiangnan porphyry-skarn tungsten belt(JNB)

Baizhangya Re-Os 134.1±2.2Ma
Zhuxiling U-Pb(Zircon) 138.7±1.6Ma
Jitoushan Re-Os 136.6±1.5Ma
Matou Re-Os 136.6±1.5Ma
Shangjinshan
Xiaoyao Re-Os 148.7±2.3Ma
Dongyuan Re-Os 146.4±2.3Ma
Re-Os 139.3±1.7Ma
Jixia
Sanbao
Huangshan Re-Os 141.8±2.2Ma
Xianglushan Re-Os 125.5±0.7Ma
Yangchuling Re-Os 146.4±1.0Ma
Re-Os 139.2±1.0Ma
Fig. 2
Zhuxi U-Pb(Scheelite) 154.0 ± 2.8 Ma
Poyang lake
Dahutang
Shiweidong Re-Os 140.9±3.6Ma
Nanchang

0 30 60 km

Legend:
- Middle Jurassic to Cretaceous sedimentary and volcanic rocks
- Cambrian to Early Triassic marine clastic and carbonate rocks, and Middle Triassic to Early Jurassic paralic clastic rocks
- Jiangnan Orogen: Neoproteroizoic epimetamorphic and sedimentary rocks
- Cretaceous granitoids
- Jurassic granitoids
- Neoproterozoic granites
- Neoproterozoic ophiolite
- River and lake
- W deposits

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

(a) Scheelite A — Intercept at 154.0 ± 2.8 Ma, MSWD = 1.02

(b) Mean ^{207}Pb corrected age 153.7 ± 2.5 Ma, MSWD = 0.98, n = 22

(c) Scheelite B — Intercept at 150.3 ± 3.5 Ma, MSWD = 1.8

(d) Mean ^{207}Pb corrected age 151.1 ± 2.4 Ma, MSWD = 1.3, n = 31

(e) Scheelite C — Intercept at 150.4 ± 6.3 Ma, MSWD = 0.87

(f) Mean ^{207}Pb corrected age 150.8 ± 4.4 Ma, MSWD = 0.5, n = 25

Fig. 9

Fig. 10