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ABSTRACT

Porphyry copper deposits (PCD) are economically significant sources of Cu and Mo, formed when metal-rich fluids precipitate at shallow levels, exsolving from underlying magmatic reservoirs at depth. However, the origin and evolution of these metal-rich fluids, whether through episodic enrichment from multiple pulses or a single continuous fluid-release event, remain a subject of controversy. To gain deeper insights into these processes, data on cathodoluminescence (CL) imaging, in-situ trace elements, and Sr isotopes of newly discovered scheelite (Sch 1, Sch 2, and Sch 3) found in three generations of vein types within the giant Qulong porphyry Cu-Mo mineralization system are presented. The anhedral Sch 1 occurs in quartz + magnetite + anhydrite + chalcopyrite veins, exhibiting no obvious zoning in the CL image. These scheelite samples show high concentrations of Mo, Nb, Ta, and ^{87}Sr/^{86}Sr ratios ranging from 0.70688 to 0.71109. Moreover, they demonstrate enriched rare earth elements (REE) and negative Eu anomalies in the chondrite-normalized pattern, indicative of their formation in relatively oxidized metal-rich fluids during the early high-temperature alteration stage. Among the discovered scheelite varieties, the most volumetrically significant is the subhedral Sch2, which occurs in veins composed of quartz + pyrite + chalcopyrite. In its central region (Sch 2a), Cu-rich cores are dispersed, surrounded by an oscillatory Cu-poor mantle and rim (Sch 2b and 2c), as observed in the CL image. When compared to Sch 1, Sch 2 exhibits lower levels of REE, Nb, Ta, Mo, and ^{87}Sr/^{86}Sr ratios (ranging from 0.70502 to 0.70578), but higher Cu concentration and positive Eu anomalies. The gradual decrease in Cu content from the core to rim in Sch2, along with its rim's intergrowth with sulfide, suggests the precipitation of Cu during the second pulse of fluids. Euhedral Sch 3 is found in relatively moderate-temperature mineral assemblages within quartz + galena+ sphalerite + molybdenite veins. It displays an oscillatory pattern with a Mo-rich core (Sch 3a), an extremely Mo-rich mantle (Sch 3b), and a Mo-poor rim (Sch 3c) in the CL image. Sch 3 shows lower REE, Cu, and Pb contents but variable Mo concentrations in different domains, while consistently recording ^{87}Sr/^{86}Sr ratios

52   ranging from 0.70498 to 0.70542. These characteristics indicate the precipitation

53   process of Mo and Pb during the third pulse of fluid evolution. The observed shift in

54   mineral assemblages, metal contents, and Sr isotopic components from Sch 1 to Sch 3

55   reflects the occurrence of different fluid pulses within a cooling porphyry Cu-Mo

56   mineralization system. Overall, the three generations of scheelite found at the Qulong

57   porphyry Cu-Mo deposit indicate the occurrence of multiple pulsed flows of

58   magmatic fluids, revealing a more complex fluid evolution for PCD than previously

59   recognized. Notably, Sch 1 exhibits relatively high $^{87}Sr/^{86}Sr$ ratios, similar to the

60   post-ore mafic porphyries, which are higher compared to Sch 2 and Sch 3, showing

61    $^{87}Sr/^{86}Sr$ ratios similar to the pre- and syn-ore host granite and porphyry. This result

62   implies that mafic magma has significantly contributed to the formation of the first

63   pulse of magmatic fluids, whereas syn-ore granitic magma contributed to the ore

64   fluids responsible for forming the veins containing Sch 2 and Sch 3 in the later stage.

65   Therefore, we propose that volatiles from mafic magma, injected into the porphyry

66   metallogenic system, play a crucial role in the formation of PCD. Additionally, for the

67   first time, the presence of Cu-Mo-W metal endowment in the PCD of the Gangdese

68   magmatic belt is identified, providing valuable new insights into the metallogeny of

69   PCD and offering promising opportunities for tungsten exploration in the collision

70   zone.

71   **Keywords**: Scheelite; PCD; Cu-Mo-W mineralization; In-situ Sr isotope;

72   Cathodoluminescence imaging; Recharge of mafic magma; Gangdese

73

74 **INTRODUCTION**

75   The formation of porphyry Cu deposits (PCD) through magmatic-hydrothermal

76   processes has been well-established, supported by geologic, geochemical, and isotopic

77   studies (Seedorff et al., 2005; Sillitoe, 2010; Buret et al., 2017). These studies have

78   revealed that metals are released from magmatic fluids (>600 °C), driven by heat

79   exsolved from deep-seated sub-volcanic intrusions at a paleodepth of 5–10 km.

80   Eventually, these metals precipitate as sulfides of chalcopyrite and molybdenite in the

81   shallow crust at depths of 1-3 km (Heinrich, 2007; Sillitoe, 2010; Kouzmanov and

82   Pokrovski, 2012). However, despite this understanding, the source, mechanism, and

83   dimensions of fluid evolution remain largely unclear. Specifically, the deciphering of

84   the source and evolution processes of the metal-rich fluids, whether as a series of

85   superimposed processes involving pulsed fluids or a single and continuous

86   fluid-release event, is crucial for comprehending the formation of PCD.

87   Previous studies have established that both single and continuous metal-rich fluid

88   release and precipitation play significant roles in the formation of

89   magmatic-hydrothermal mineralization systems, often resulting in extensive

90   hydrothermal alteration haloes or spatial zoning of high- to low-temperature metallic

91   elements in various ore clusters or deposits (Sillitoe, 2010). Studies involving fluid

92   inclusions have further revealed that magmatic-hydrothermal mineralization systems,

93   such as PCD, are generally produced by a single fluid evolution process, characterized

94   by a two-phase fluid of brine and low-density vapor. This fluid is either directly

95   exsolved from the silicate melt (Shinohara, 1994) or, more likely, separated from a

96   single-phase supercritical fluid (Burnham, 1979; Cline and Bodnar, 1991). On the

97   other hand, high-precision CA-ID-TIMS U-Pb zircon and Re-Os molybdenite dating

98   have documented episodic magmatic-hydrothermal activities in certain areas. This

99   episodic behavior can be attributed to multiple veins and alterations development,

100   overprinting, or the episodic growth of fertile porphyries (Spencer et al., 2015; Buret

101   et al., 2016; Tapster et al., 2016; Li et al., 2017; Zhao et al., 2021). Recently, oxygen

102   isotope studies on mineralized quartz veins from porphyry-skarn deposits have led to

103   similar conclusions (Li et al., 2018, 2022). However, evaluating the presence of

104   multiple pulses of metal-rich fluids in PCD is challenging. The intense hydrothermal

105   alteration that often occurs can modify or alter primary mineral assemblages.

106   Additionally, evidence of multistage fluids is commonly overprinted or erased by

107   late-stage fluid-rock interactions. Therefore, the main challenge lies in three aspects:

108   (1) identifying multistage-growth domains of hydrothermal minerals that formed

109   throughout magmatic-hydrothermal systems, (2) using these minerals to trace the

110   different stages of exsolved hydrothermal fluids from a vast and long-lived magmatic

111   chamber, and (3) determining how these geochemical changes resulted in different

112   metal mineralization. By clarifying the composition, source, and evolution of

113   multistage fluids that led to metal mineralization, a better understanding of the

114   hydrothermal mineralization processes can be gained, whether they occurred as

115   pulsed events or single and continuous fluid-release events.

116   Scheelite, an important ore mineral, is found across a wide range of pressure,

117   temperature, and chemical (P-T-X) conditions in various types of ore deposits,

118   including skarns, quartz veins, greisen, and orogenic Au deposits (Robert and Brown

119   1986; Ghaderi et al. 1999; Nie et al., 2023). Its distinct textures and zonation patterns

120   can be clearly distinguished using cathodoluminescence (CL) imaging, revealing

121   changes in physical-chemical conditions, dissolution, and replacement during its

122   growth (Wang et al., 2022; Han et al., 2020). Scheelite can form in hydrothermal

123   fluids and incorporate numerous variable valence metals (Fe, Mo, Eu), metal elements

124   (Cu, Pb), and REE (Ghaderi et al. 1999; Brugger et al. 2000; Poulin et al. 2018; Zhao

125   et al. 2018). Due to its complex crystal structure, scheelite can accommodate a large

126   number of major and trace elements, making it valuable in providing information

127   about the nature of the fluids from which it formed (Sciuba et al., 2019). Moreover, its

128   Sr isotopic composition can be used to study fluid origins and fluid-related processes

129   (Darbyshire et al. 1996; Han et al., 2020). Therefore, combining the trace element

130   chemistry of scheelite with its Sr isotope composition can be used to trace the

131   hydrothermal mineralization processes of PCD.

132   In an effort to decipher the source and evolution of ore-forming fluids as either a

133   pulsed phenomenon or a continuous fluid-release event, recently discovered

134   multistage scheelites found in three different classes of mineralization veins within

135   the world-class Qulong porphyry Cu-Mo deposit have been investigated. In this study,

136   cathodoluminescence (CL) images, trace element geochemistry, and Sr isotopic

137   composition of scheelite were utilized as proxies to demonstrate the composition,

138   source, and evolution of the multistage fluids originating from a cooling magma

139   chamber over time. The new findings propose an alternative model for the formation

140   of the Qulong porphyry Cu-Mo mineralization system and provide fresh insights into

141   the metal endowment potential in collision-related PCD.

142   **GEOLOGICAL SETTING**

143   **Geological background**

144   The Lhasa terrane is situated between the Bangong-Nujiang suture zone (BNSZ) to

145   the north and the Indus-Yarlung Zangbo suture zone (IYZSZ) to the south, and it is

146   commonly subdivided into the northern, central, and southern Lhasa terrane (Fig. 1).

147   These regions are separated by the Shiquan River-Nam Tso melange zone (SNMZ)

148   and the Luobadui-Milashan fault (LMF) from north to south (Yin and Harrison, 2000;

149   Zhu et al., 2011; Hou et al., 2015a, 2015b). The northern Lhasa subterrane is

150   characterized by juvenile crust containing early Cretaceous medium-K calc-alkaline

151   arc volcanic rocks and granitoids, overlain by Middle Triassic to Cretaceous

152   sedimentary rocks (Zhu et al., 2013; Hou et al., 2015a). On the other hand, the central

153   Lhasa terrane represents a possible microcontinent, which experienced multiple

154   metamorphic events during the Neoproterozoic (Guynn et al., 2012). The southern

155   Lhasa terrane within the Gangdese magmatic belt consists of Mesozoic to Cenozoic

156   granitoids and is predominantly composed of juvenile crust with depleted mantle-like

157   Nd-Hf isotopic signatures. This region is covered by the Paleogene Linzizong

158   volcanic succession, along with thin successions of sedimentary rocks (Mo et al.,

159   2007, 2008; Ji et al., 2009; Zhu et al., 2011, 2013; Ma et al., 2018). The southern

160   Lhasa terrane has undergone complex structural evolution, including late

161   Triassic-Middle Jurassic Neo-Tethys ocean subduction, subsequent continental

162   collision from the early Eocene Indo-Eurasian to the late Oligocene-Miocene, and a

163   post-extension setting (23–12 Ma) along with Miocene N-S rifts (Yin and Harrison,

164   2000; Hou and Cook, 2009; Zhu et al., 2011; Chen et al., 2020; Fan et al., 2023). In

165   this region, the major metallogenic events can be categorized into the

166   Triassic-Jurassic porphyry Cu-Au and the Miocene–Oligocene porphyry-skarn

167   Cu-Mo(-Au) mineralization (Lang et al., 2014; Hou et al., 2015; Chen et al., 2020).

168   The Miocene–Oligocene porphyry-skarn related mineralization is of particular

169   significance and is regarded as one of the most important porphyry-type deposits in

170   China. It encompasses a series of large PCDs, including Jiama, Qulong, Chongjiang,

171   Tinggong, Beimulang, and Zhunuo from east to west (Fig. 1; Hou et al., 2009, 2015a,

172   2015b; Zheng et al., 2004, 2014; Sun et al., 2021; Liu et al., 2022Wu et al., 2022).

Ore deposit geology

174   The giant Qulong porphyry Cu-Mo deposit (29°36′–29°40′ N, 91°33′–91°37′E)

175   is situated in the eastern part of the Gangdese magmatic belt (Fig. 2) and boasts

176   substantial ore-proven reserves of 2200 Mt Cu @ 0.5% and 500 Mt Mo @ 0.04%

177   (Zheng et al., 2004; Li et al., 2017). The deposit's formation involved the intrusion of

178   pre-ore Rongmucuola intrusions and ore-related monzogranitic porphyries into the

179   Mesozoic Yeba Formation, which comprises a series of rhyolite, dacite-rhyolite

180   porphyry, and volcanic-sedimentary rocks (Fig. 2; Zheng et al., 2004). The pre-ore

181   Rongmucuola intrusions consist of biotite monzogranite (17.4 ± 0.6 Ma) in the center,

182   surrounded by granodiorite (17.9 ± 0.5 Ma) (Zhao et al., 2016). Meanwhile, the

183   syn-ore porphyries mainly comprise monzogranitic porphyries (16.9 ± 0.5 Ma) in the

184   central area (Yang et al., 2009; Zhao et al., 2016). As for the post-ore lithology, the

185   dioritic porphyries (15.7 ± 0.2 Ma) form dikes intruding into the rocks located above

186   (Yang et al., 2015). The alteration zones exhibit a typical concentric alteration pattern,

187   featuring potassic alteration overprinted by late phyllic and argillic alteration to

188   varying degrees, extending to the outer propylitic zone (Yang et al., 2009). Potassic

189   alteration assemblages, characterized by secondary K-feldspar, magnetite, anhydrite,

190   and biotite, dominate in the deep sections of the monzogranitic porphyry and

191   granodiorite porphyry. An intruding hydrothermal breccia pipe displays potassic

192   alteration, with an abundance of biotite and magnetite, subsequently overprinted by

193   late phyllic alteration (Fig. 2; Yang et al., 2009; Li et al., 2017; Yu et al., 2022). The

194   phyllic alteration zone is located in the monzogranitic porphyries and the peripheral

195   biotite monzogranite, surrounding and superimposing the potassic alteration zone

196   (Zheng et al., 2004). The Cu-Mo orebodies are primarily hosted in the biotite

197   monzogranite, monzogranite porphyry, and central hydrothermal breccia pipe (Fig. 2;

198   Zheng et al., 2004; Yang et al., 2009). The deposits consist of multiple stock veins,

199   ranging from early-stage veinlets associated with biotite + quartz + anhydrite +

200   magnetite + scheelite (Fig. 3a-b), quartz + magnetite + pyrite + chalcopyrite veins

201   (Fig. 3c), and K-feldspar + quartz veins to late-stage pyrite + chalcopyrite + scheelite

202   veins (Fig. 3d-h) and quartz + galena + Ag-rich tetrahedrite + sphalerite +

203   molybdenite + scheelite veins (Fig. 3i-k) with Cu-Fe-Mo sulfide minerals. Copper

204   mineralization is predominantly linked to potassic and phyllic alteration (Yang et al.,

205   2009; Li et al., 2017). The orebodies exhibit stockwork and disseminated

206   mineralization, primarily composed of chalcopyrite, molybdenite, pyrite, and scheelite

207   (Fig. 3; Zheng et al., 2004; Yang et al., 2009).

SAMPLING AND METHODOLOGY

Samples

210   Representative samples containing scheelite were selected from drilled holes

211   (ZK307, ZK303, ZK407, and ZK1412) at the Qulong deposit (Fig. 2). The

212   distribution of scheelite in these drilled holes was examined using an ultraviolet

213   fluorescent lamp. Approximately 25 scheelite-bearing samples were then prepared as

214   40-50 μm thick thin sections for observation under reflected and transmitted light

215   microscopy to characterize their paragenetic relationships. Scheelite is primarily

216   found in magnetite-bearing veins (sample ZK303-915), chalcopyrite-bearing veins

217   (sample ZK407-689), and galena-sphalerite-molybdenite-bearing veins (ZK307-974).

218   As a result, scheelite samples extracted from these three types of veins were subjected

219   to scanning electron microscope (SEM) cathodoluminescence, major and trace

220   elements, and Sr isotope analysis.

221   **SEM cathodoluminescence of scheelite**

222   In order to decipher the distinct textures and zonation patterns, SEM CL images of

223   scheelite were recorded using an Analytical Scanning Electron Microscope coupled

224   with a GATAN MINICL system. The applied acceleration voltage and current were

225   approximately 10-13 kV and ca. 80-85 nA, respectively.

226   **Major and trace element composition of scheelite**

227   The major and trace element concentrations of scheelite were determined at the

228   Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. Laser

229   sampling was performed using a GeolasPro laser ablation system, which consists of a

230   COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of

231   200 mJ) along with a MicroLas optical system. To acquire ion-signal intensities, an

232   Agilent 7700e ICP-MS instrument was employed. During the ablation process, helium

233   was used as the carrier gas. Each spot analysis incorporated approximately 30s of

234   background acquisition, followed by 40s of data acquisition from the sample. A spot

235   size of 32 μm was used together with a repetition rate of 8 Hz, and an energy density

236   of 5.5 J*cm^{-2}. After every 8-10 sample analyses, several analyses of external reference

237   materials were conducted. For quality control (QC) purposes, NIST SRM 610 was

238   utilized as the reference material to correct the instrumental time-dependent

239   sensitivity drift. External calibration was carried out using multiple external standards,

240   namely NIST 610, BHVO-2G, BCR-2G, BIR-1G, and GSE-1G. The preferred

241   concentrations for the reference glasses were obtained from the GeoReM database

242   (http://georem.mpch-mainz.gwdg.de/). To process the data, off-line selection and

243   integration of background and analyte signals, time drift correction, and quantitative

244   calibration were performed using ICPMSDataCal 10.9 (Liu et al., 2008). The

245   time-resolved signals for each analyzed spot were thoroughly reviewed. The

246   analytical precisions for most measured elements were better than 8%, and the results

247   were found to agree with their reference values within ±10%. The major and trace

248   element data for minerals determined using LA-ICP-MS are listed in Appendix Table

249   A1.

250   **In situ LA–MC–ICP–MS Sr isotopes of scheelite**

251   The Sr isotope ratios of scheelite were analyzed using a Neptune Plus

252   MC-ICP-MS (Thermo-Scientific) coupled with a RESOlution M-50 193 nm laser

253   ablation system at the State Key Laboratory of Isotope Geochemistry, Guangzhou

254   Institute of Geochemistry, Chinese Academy of Sciences. For each single laser spot

255   ablation, the spot diameter ranged from 112 to 180 μm, depending on the Sr signal

256   intensity. The pulse frequency was set at 6 Hz, while the laser fluence remained

257   constant at approximately 4 J*cm^{-2}. To correct for ^{87}Rb, the measured natural

258   ^{85}Rb/^{87}Rb value of 2.593 (Catanzaro et al., 1966) was used. The mass bias of ^{87}Sr/^{86}Sr

259   was normalized to ^{86}Sr/^{88}Sr = 0.1194 with an exponential law. For in situ Sr isotope

260   analysis of scheelite, a natural sample of plagioclase, PZHPl, was used as the

261   (unknown) sample. The detailed data reduction procedure was previously reported by

262   Zhang et al. (2018).

263   **RESULTS**

264   **Scheelite distribution and classification**

265   Based on vein type, mineral assemblage, and CL images, three generations of

266   scheelite (Sch 1, Sch 2, and Sch 3) associated with mineralization can be

267   distinguished (Fig. 3 and 4). Sch 1 is mainly distributed in the quartz + magnetite +

268   anhydrite + chalcopyrite veins as disseminations (Fig. 4a-b). It is characterized by

269   weak oscillation zoning in the CL image (Fig. 4c), with no obvious compositional

270   zoning. Sch 2 is the most commonly found stage associated with Cu ore and occurs as

271   quartz ± chalcopyrite ± pyrite veinlets (Fig. 4d). According to the CL image, Sch 2

272   displays homogeneity and dispersal in the core (Sch 2a), along with oscillatory zoning

273   in the bright mantle (Sch 2b) and dark rim (Sch 2c) (Fig. 4e-f). Sch 3 occurs as veins

274   intergrown with quartz, galena, sphalerite, and molybdenite (Fig. 4g-h) and can be

275   categorized into three sub-types based on the CL image (Fig. 4i). Sch 3a exhibits a

276   homogeneous texture and bright color in the core, while Sch 3b displays a grey color

277   without zoning in the mantle. Sch 3c is brighter than Sch 3b and displays

278   well-developed oscillatory zoning texture (Fig. 4i).

279   **Major and trace element geochemistry**

280   A total of 60 major and trace elements were analyzed using LA-ICP-MS for

281   three generations of scheelite at the Qulong deposit (Appendix Table A1). These

282   scheelite grains exhibit similar major element compositions, with WO_3 ranging from

283   74.82% to 81.06% and CaO ranging from 15.60% to 19.55%. However, they display

284   variable abundances of trace elements such as Sr, Y, Zr, Nb, Ta, Mo, U, Pb, and rare

285   earth elements (REEs). The positive correlation between Na and REEs (Fig. 5a) in

286   scheelite suggests that the REEs are likely incorporated into the scheelite structure

287   through a Na substitution mechanism (Ghaderi et al. 1999).

288   Among the three generations of scheelite, Sch 1 shows the highest REE content,

289   ranging from 1244 to 2664 ppm (Fig. 6a). It is high in Y (345-1179 ppm), Sr (342-519

290   ppm), Pb (17.0-27.3 ppm), Nb (3.70-74.4 ppm), Ta (0.07-2.46), Th (5.37-14.1), and

291   Mo (2328-3824 ppm) (Fig. 5b; Appendix Table A1). Sch 1 exhibits flat REE

292   distribution patterns with a negative Eu anomaly (Eu/Eu*=0.65-0.94) (Fig. 5b and

293   6a).

294   Sch 2 displays relatively low REE concentrations, ranging from 76.7 to 1789

295   ppm, compared to Sch 1 (Fig. 6b). It shows variable abundances of U (0-403 ppm),

296   Pb (4.84-196 ppm), Nb (1.63-9.45 ppm), Ta (0.02-0.09 ppm), Mo (1.91-336 ppm), Sr

297   (326-959 ppm), Cu (0-16914 ppm), FeO (0-1.42 wt%) (Fig. 5b; Appendix Table A1).

298   It exhibits a MREE-enriched pattern, with strong positive chondrite-normalized Eu

299   anomalies (Fig. 6b). Notably, significant differences in REE content exist among

300   different domains of Sch 2, with the lowest concentration in the mantle (Sch 2b) and

301   the highest in the rim (Sch 2c) (Fig. 6b). The Eu anomalies of Sch 2 demonstrate a

302   negative correlation with Mo contents (Fig. 5b). In comparison, Sch 2a stands out

303   with its high Cu and Fe content when compared to Sch 2b and Sch 2c, and there is a

304   positive correlation between Fe and Cu contents (Fig. 5c).

305   Sch 3 grains were analyzed and found to exhibit mainly positive Eu anomalies

306   (ranging from 0.75 to 6.92) and the lowest total REE contents (ranging from 13.5 to

307   610 ppm) among all the samples analyzed (Fig. 6c). They display low concentrations

308   of U (0-4.41 ppm), Pb (0.66-9.71 ppm), and Cu (0-0.51 ppm), while Mo (0.68-6724

309   ppm) and Sr (195-1110 ppm) contents vary (Fig. 5b; Appendix Table A1). Based on

310   the difference in Mo content, Sch 3 can be divided into three types: Mo-rich Sch 3a

311   core (78.2-397 ppm), extremely Mo-rich Sch 3b mantle (1052-6724 ppm), and

312   Mo-poor Sch 3c rim (0.67-207 ppm) (Fig. 5d). Sch 3a and Sch 3b have relatively low

313   REE contents compared to Sch 3c (Fig. 5c). Additionally, the Eu anomalies of Sch 3

314   show a positive correlation with Mo contents (Fig. 5b).

315   **In situ Sr isotopes of scheelite**

316   The in situ Sr isotopes of three generations of scheelite are presented in Appendix

317   Table A2 and Fig. 7. The $^{87}Sr/^{86}Sr$ ratios of anhedral Sch 1 found in the quartz +

318   magnetite + anhydrite + chalcopyrite veins exhibit a wide variation, ranging from

319   0.70688 to 0.71109. In contrast, Sch 2 shows a lower $^{87}Sr/^{86}Sr$ ratio (ranging from

320   0.70502 to 0.70578) compared to Sch 1, and these ratios do not vary along the profiles

321   from core to rim within individual scheelite grains. The $^{87}Sr/^{86}Sr$ ratios of Sch 3

322   demonstrate little variation and are similar to Sch 2, ranging from 0.70498 to 0.70542.

323   **DISCUSSION**

324   **Evidence of multistage pulses of fluids**

325   Scheelite CL images, trace-element, and Sr isotope analyses of three generations

326   of mineralization veins (quartz + magnetite + anhydrite + chalcopyrite veins, quartz +

327   pyrite + chalcopyrite veins, and quartz + galena + sphalerite + molybdenite veins) not

328   only provide direct evidence for scheelite formation related to different mineralization

329   stages but also yield valuable information about the source and evolution of ore fluids.

330   The presence of three generations of scheelite in these veins, along with hydrothermal

331   magnetite, chalcopyrite, and molybdenite, strongly suggests their derivation from

332   hydrothermal fluids. Consequently, the cross-cutting nature of these three generations

333   of mineralization veins, displaying poly-cyclic growth scheelite zoning, indicates the

334   crystallization of these veins may be a result of multistage pulsed fluids, recording at

335   least three stages of fluid activities.

336   Anhedral Sch 1 occurs in quartz + magnetite + anhydrite + chalcopyrite veins,

337   displaying no zoning in the CL image (Fig. 4a-c). It exhibits high concentrations of

338   Mo, Nb, Ta, and an enriched pattern of REEs in comparison to chondrites along with

339   negative Eu anomalies (Fig. 5b and 6a). These veins, characterized by early

340   magnetite-bearing veinlets, exhibit varied alteration halos containing albite,

341   K-feldspar, biotite, and anhydrite, with features typical of potassic alteration stage

342   (Fig. 3a-c and 4a-c). Studies of fluid inclusions by Li et al. (2017) show that the early

343   fluids in the potassic alteration stage from the Qulong porphyry system are indicative

344   of high temperatures (~425 °C). These features suggest that they may represent

345   high-temperature fluids exsolved from an upper-crustal magma chamber during the

346   early stages (Richards, 2003; Cooke et al., 2005). The Mo-rich scheelite found in the

347   early veins of the Qulong deposit is intergrown with anhydrite and magnetite (Fig.

348   3a-c and 4a-c), indicating its formation in an oxidized hydrothermal system. Such

349   conditions are conducive to the enrichment and migration of Cu-Mo and other metal

350   elements. This observation is further supported by the presence of a negative Eu

351   anomaly and high Mo contents in Sch 1 (Fig. 5b). The incorporation of Mo (Mo^{6+})

352   into scheelite by substituting for W^{6+} is facilitated in an oxidized setting (Ghaderi et al.

353   1999; Elbaz-Poulichet et al. 2005; Zhao et al. 2018), making Mo a redox-sensitive

354   element. Additionally, a negative Eu anomaly is typically associated with relatively

355   oxidizing conditions, indicating an enrichment of Eu^{3+} compared to Eu^{2+}, while a

356   positive Eu anomaly suggests more reducing conditions (Ghaderi et al. 1999; Brugger

357   et al. 2000; Poulin et al. 2018; Zhao et al. 2018). These findings collectively indicate

358   that Sch 1 likely represents the early-stage pulse of relatively oxidized metal-rich

359   fluids during the high-temperature alteration stage.

360   Subhedral Sch 2 is found in quartz + pyrite + chalcopyrite veins (Fig. 3d-h and

361   4d), which are widely distributed and partially intersect with the early

362   magnetite-bearing veins. The presence of large amounts of chalcopyrite within these

363   quartz-pyrite veins and their associated phyllic alteration haloes suggests that the

364   ore-forming hydrothermal fluids were enriched with reducing S^{2-} and Cu. Li et al.

365   (2017) determined trapping temperatures of 340 and 280 °C in the phyllic alteration

366   stage using liquid–vapor two-phase fluid inclusions, indicating that the subhedral Sch

367   2 formed in moderate-temperature aqueous fluids. Furthermore, the clear negative

368   linear correlation between positive Eu anomalies and low Mo concentration (Fig. 5b)

369   points to the presence of relatively reduced metal-rich fluids during the mineralization

370   process (Ghaderi et al. 1999; Brugger et al. 2000; Elbaz-Poulichet et al. 2005). The

371   CL image reveals conspicuous growth zoning in Sch 2 (Fig. 4e-f), which has

372   remained unaltered by subsequent hydrothermal fluids, making it capable of

373   preserving primary features and the physical-chemical conditions of its formation

374   (Han et al., 2020). Sch 2 exhibits a dispersed Cu-rich core (Sch 2a) and an oscillatory

375   Cu-poor mantle and rim (Sch 2b and 2c) in the CL image (Fig. 4c). The decrease in

376   Cu concentration from Sch 2a to Sch 2b and 2c, along with its rim's intergrowth with

377   sulfide, indicates the precipitation of Cu in a moderate-temperature fluid environment.

378   Consequently, Sch 2 displays lower REE, Nb, Ta, Mo, and $^{87}Sr/^{86}Sr$ ratios (ranging

379   from 0.70498 to 0.70542) (Fig. 7), but higher Cu concentration and positive Eu

380   anomalies compared to Sch 1. These characteristics suggest that this stage represents

381   Cu-rich ore fluid pulses responsible for Cu ore formation under middle-temperature

382   conditions.

383   Euhedral Sch 3 is found in mineral assemblages characterized by relatively low

384   temperatures, specifically in quartz + galena + Ag-rich tetrahedrite + sphalerite +

385   molybdenite veins (Fig. 3i-k). Ag-rich tetrahedrite is a common middle- and

386   low-temperature mineral in hydrothermal deposits (Gallego and Akasaka, 2010). Thus,

387   the mineral assemblage of Sch 3 with Ag-rich tetrahedrite, galena and sphalerite,

388   indicates the formation of Sch 3 under middle- to low-temperature conditions. In the

389   CL image (Fig. 4i), Sch 3 displays an oscillatory Mo-rich core (Sch 3a), an extremely

390   Mo-rich mantle (Sch 3b), and a Mo-poor rim (Sch 3c) (Fig. 5d). This arrangement

391   provides insights into the precipitation process of Mo and Pb during fluid evolution.

392   Despite variations in different domains, Sch 3 consistently demonstrates lower levels

393   of REEs, Cu, and Pb, along with variable Mo content. The recorded $^{87}Sr/^{86}Sr$ ratios

394   (ranging from 0.70502 to 0.70578) (Fig. 7) remain constant, reflecting the fluid

395   evolution. Notably, a significant positive linear correlation between Eu anomalies and

396   Mo contents (Fig. 5b) suggests that Mo enrichment might be influenced by the Mo

397   content in the fluid rather than the oxygen fugacity of hydrothermal fluids.

398   Consequently, the third generation of fluids is interpreted as representing a Mo-rich

399   fluid pulse originating from the cooling magma chamber.

400   **The source and evolution of pulsed fluids**

401   Based on the preceding discussion, scheelite from three generations of vein types

402   exhibits intricate growth zoning patterns. This suggests that these scheelite samples

403   can serve as indicators of the primary physicochemical conditions during their growth.

404   Notably, $^{87}Rb/^{86}Sr$ ratios in scheelite are typically quite low, ranging from 0 to 0.17.

405   As a result, the measured $^{87}Sr/^{86}Sr$ ratios can directly reflect the initial Sr isotope

406   composition of the fluid from which scheelite crystallized (Chugaev et al., 2010). The

407   high-temperature fluid exsolution would not alter the Sr-Nd isotope signatures in

408   magmatic systems (Xu et al., 2015; Cao et al., 2021). Therefore, Sr-Nd isotope ratios

409   of hydrothermal scheelite can be used to constrain the source of hydrothermal fluids

410   and their parent magma. Previous studies have established a close connection between

411   the Qulong porphyry Cu-Mo mineralization and the syn-ore monzonitic porphyries

412   (Zheng et al., 2004; Yang et al., 2009; Zhao et al., 2016; Li et al., 2017). However, the

413   newly identified $^{87}Sr/^{86}Sr$ values (ranging from 0.70688 to 0.71109) of Sch 1 are

414   higher than those of the pre- and syn-ore host granite and porphyry (($^{87}Sr/^{86}Sr)_i$:

415   0.704847–0.705237; Fig. 7; Yang et al., 2015). These values align more closely with

416   those from post-ore mafic porphyries (($^{87}Sr/^{86}Sr)_i$: 0.707004–0.707198; Yang et al.,

417   2015) and postcollisional ultrapotassic rocks from southern Tibet (Yang et al., 2016).

418   This similarity implies that volatile components from more radiogenic mafic and

419   ultrapotassic magma might have significantly contributed to the formation of

420   Mo-W-rich magmatic fluids. Sch 2 and Sch 3, characterized by chalcopyrite and

421   molybdenite mineralization, exhibit a comparable Sr isotope composition. This

422   composition is akin to that of the pre- and syn-ore host granite and porphyry. Such

423   similarity suggests that the primary metal-enriched fluids likely originated from either

424   the syn-ore granitic magma or from an interaction between fluids emanating from the

425   radiogenic mafic magma and exsolved hydrothermal fluids from the monzonitic

426   porphyries. Consequently, the variations in isotopic ratios observed in scheelite across

427   the three generations of vein types could potentially signify the involvement of

428   multiple fluid and metal sources in the formation of the collision-related PCD.

429   The formation of three generations of scheelite and veins offers a record of the

430   progressive evolution of exsolved fluids within a cooling porphyry metallogenic

431   system. Initial fluids from the porphyry system are enriched in metals and sulfur,

432   representing an oxidizing nature. The subsequent two fluid generations, which might

433   represent evolved fluids originating from the magmatic chamber, exhibit relatively

434   different oxidation states, creating favorable conditions for the late stage precipitation

435   of Cu and Mo enrichment. The sequential exsolution of Cu- and Mo-rich fluids at

436   distinct time intervals from the magmatic chamber could potentially result in their

437   spatial separation. Consequently, the pulsed evolution of fluids and the gradual

438   cooling process significantly contribute to the precipitation of Cu, Mo, and W.

A modified genetic model for the world-class Qulong porphyry deposit

440   As discussed earlier, the following modified model is presented to elucidate the

441   formation of the W-bearing world-class Qulong porphyry deposit through the

442   hydrothermal evolution involving multiple stages of scheelite formation (Fig. 8). The

443   initial stage is linked to pre-ore magmatic processes, resulting in the development of

444   the Rongmucuola granite host (Fig. 8a; Zhao et al., 2016; Li et al., 2017). This

445   granitic magma exhibited relatively low volatile content, which did not give rise to

446   significant Cu mineralization or alteration. Subsequently, it is presumed that the felsic

447   magma reservoir underwent enrichment through the exsolution of volatiles from the

448   underlying mafic magma into the overlying felsic mush (Fig. 8b). Supporting

449   evidence comes from Sch-1 found in the quartz + magnetite + anhydrite + pyrite veins,

450   exhibiting $^{87}Sr/^{86}Sr$ ratios comparable to those of high-Mg dioritic porphyries and

451   postcollisional ultrapotassic rocks in southern Tibet (Yang et al., 2015, 2016). Yang et

452   al. (2015) and Sun et al. (2018) proposed that mantle-derived high-Mg dioritic and

453   postcollisional ultrapotassic magmas would increase water content through

454   differentiation, influencing the Cu ore-forming fertility of porphyry intrusions.

455   Additionally, previous research has demonstrated that mafic magmas derived from

456   metasomatized mantle contain elevated volatile components and metals, including Cu

457   and S (Hattori and Keith, 2001; Halter et al., 2005; Seedorff et al., 2005), which were

458   repeatedly injected into the felsic magma chamber (Hollings et al., 2011; Cao et al.,

459   2018). This injection likely introduced a substantial amount of ore-forming elements

460   (Hattori, 1993; Hattori and Keith, 2001; Cao et al., 2018), as supported by examples

461   such as Bingham and Black Mountain (Hattori and Keith, 2001; Zhang and Audétat,

462   2017; Cao et al., 2018, 2019), reinforcing the validity of this model. Hence,

463   high-temperature fluid exsolution from the mafic melt is likely to have higher

464   concentrations of volatiles such as water and S compared to the fluids exsolved from

465   the overlying felsic mush, leading to the localized formation of early stage

466   independent quartz + magnetite + anhydrite + chalcopyrite veins. These

467   high-temperature fluids might further migrate, blend with lower-temperature fluids

468   originating from the overlying felsic mush, and potentially engage with host rocks.

469   This could trigger subsequent fluid pulses, marked by the precipitation of Sch-2 and

470   Sch-3 during the process of fluid evolution and cooling. Volatiles released from the

471   mafic melt can also induce alterations in the morphology and structure of minerals

472   (Blundy et al., 2015). For instance, zircons exhibiting dark CL zoning in the

473   Alumbrera Au-rich PCD signify their origin from the mafic melt infusion into the

474   magma chamber. The subsequent release of volatile matter during growth can lead to

475   uneven crystallization of zircons (Buret et al., 2016). Additionally, the influence of

476   high-temperature volatiles, coupled with the mafic melt input, can result in the

477   development of disequilibrium phenocryst zoning, embayed quartz crystals, and

478   cumulate clots (Wark et al., 2007; Cao et al., 2018, 2021). In light of this, both

479   petrographic and chemical evidence from scheelite suggests that the influx of fluids

480   through a mafic recharge event introduced substantial quantities of volatiles into the

481   porphyry system. This process assumes vital importance in the formation of

482   collision-related PCD.

483   **IMPLICATIONS**

484   The synthesis of currently available data encompassing petrography, CL analyses,

485   in-situ trace element, and Sr isotope data of scheelite derived from three generations

486   of vein types at the Qulong PCD reveals a record of temporal and spatial overlap of

487   multiple hydrothermal events. The distinctive characteristics of these three

488   generations of scheelite, including varied metal compositions, REE patterns, and

489    $^{87}Sr/^{86}Sr$ values, suggest that the fluid influx was marked by superimposed, episodic

490   hydrothermal pulses. This contrasts with the notion of a singular, continuous release

491   of metal-rich fluids. The first generations of scheelite, characterized by high

492   concentrations of Mo, Nb, Ta, elevated $^{87}Sr/^{86}Sr$ values, and high REEs along with

493   negative Eu anomalies in the chondrite-normalized pattern, indicates its formation

494   within relatively oxidized metal-rich fluids during the early high-temperature

495   alteration stage. The second and third generations of scheelite, found within distinct

496   temperature mineral assemblages, display varying concentrations of Cu and Mo. This

497   discrepancy suggests the occurrence of separate Cu-rich and Mo-rich ore fluid pulses,

498   potentially leading to local decoupling of Cu-Mo mineralization. Therefore, the rapid

499   and episodic release of such fluids offers an explanation for the presence of multiple

500   mutually intersecting vein types and the widespread overlay of extensive multipulsed

501   alteration and mineralization phenomena. These fluids could have undergone

502   migration, intermixing with other fluid types, and interaction with host rocks,

503   consequently triggering metal precipitation throughout the course of fluid evolution

504   and cooling. The duration and timing intervals of fluid pulses directly influence the

505   efficiency of fluid exsolution and metal precipitation. Rapid and multi-stage fluid

506   pulsing is particularly conducive to the expansion of mineral deposit scales. Moreover,

507   Sch-1 exhibits relatively high $^{87}Sr/^{86}Sr$ ratios, akin to those of the post-ore mafic

508   porphyries. This contrasts with Sch-2 and Sch-3, which present similar $^{87}Sr/^{86}Sr$ ratios

509   to the pre-ore and syn-ore host granite and porphyry. These findings suggest a

510   significant contribution of mafic magma to the initiation of the first pulse of magmatic

511   fluids, whereas syn-ore granitic magma plays a role in supplying ore fluids for the

512   formation of Sch-2- and Sch-3-bearing veins in the subsequent stages. Therefore, our

513   proposition suggests that volatiles originating from mafic rocks, injected into the

514   porphyry metallogenic system, assume a pivotal role in shaping PCD formation. The

515   recent findings demonstrate that scheelite, displaying discernible internal textures

516   across various vein generations, offers essential insights into the genesis and

517   evolutionary trajectory of ore fluids. This represents a significant stride forward in

518   comprehending the intricate development of multi-stage pulsed ore fluids derived

519   from an upper-crustal magma chamber within the context of porphyry Cu-Mo

520   mineralization systems.

521   Furthermore, the co-occurrence of scheelite with quartz + pyrite+ chalcopyrite

522   veins and quartz + galena + sphalerite + molybdenite veins displays a discernible

523   spatial progression, becoming more pronounced at greater depths within the vein

524   system, culminating from 700 to 900 m at the Qulong deposit. This finding bears

525   significant implications for future exploration endeavors. The recognition of

526   Cu-Mo-W mineralization within the Qulong PCD of the Gangdese magmatic belt

527   offers valuable novel insights, shedding light on the potential for identifying

528   complementary metal endowments of W-Cu-Mo and extending the metallogenic

529   scope of PCD within collision zones. Given the Qulong PCD's status as a prototypical

530   representative of the Gangdese magmatic belt, the search for tungsten (W) potential

531   could emerge as a promising new avenue for exploration, positioning it as an

532   innovative target for collision-related PCD investigations.

533   **Acknowledgments**

542

543   **References**

544   Blundy, J., Mavrogenes, J., Tattitch, B., Sparks, S., and Gilmer, A. (2015). Generation

545   of porphyry copper deposits by gas–brine reaction in volcanic arcs. Nature

546   Geoscience, 8(3), 235-240.

547   Burnham, C. W. (1979). Magmas and hydrothermal fluids. Geochemistry of

548   hydrothermal ore deposits, 71-136.

549   Brugger, J., Bettiol, A. A., Costa, S., Lahaye, Y., Bateman, R., Lambert, D. D., and

550   Jamieson, D. N. (2000). Mapping REE distribution in scheelite using

551   luminescence. Mineralogical Magazine, 64(5), 891-903.

552   Buret, Y., von Quadt, A., Heinrich, C., Selby, D., Wälle, M., and Peytcheva, I. (2016).

553   From a long-lived upper-crustal magma chamber to rapid porphyry copper

554   emplacement: Reading the geochemistry of zircon crystals at Bajo de la

555   Alumbrera (NW Argentina). Earth and Planetary Science Letters, 450, 120-131.

556   Buret, Y., Wotzlaw, J. F., Roozen, S., Guillong, M., von Quadt, A., and Heinrich, C. A.

557   (2017). Zircon petrochronological evidence for a plutonic-volcanic connection in

558   porphyry copper deposits. Geology, 45(7), 623-626.

559   Cao, M., Hollings, P., Cooke, D. R., Evans, N. J., McInnes, B. I., Qin, K., and Baker,

560   M. (2018). Physicochemical processes in the magma chamber under the Black

561   Mountain porphyry Cu-Au deposit, Philippines: Insights from mineral chemistry

562   and implications for mineralization. Economic Geology, 113(1), 63-82.

563   Cao, M., Evans, N. J., Hollings, P., Cooke, D. R., McInnes, B. I., and Qin, K. (2021).

564   Apatite texture, composition, and O-Sr-Nd isotope signatures record magmatic

565   and hydrothermal fluid characteristics at the Black Mountain porphyry deposit,

566   Philippines. Economic Geology, 116(5), 1189-1207.

567   Cao, K., Yang, Z. M., White, N. C., and Hou, Z. Q. (2022). Generation of the giant

568   porphyry Cu-Au deposit by repeated recharge of mafic magmas at Pulang in

569   eastern Tibet. Economic Geology, 117(1), 57-90.

570   Cao, K., Yang, Z. M., Mavrogenes, J., White, N. C., Xu, J. F., Li, Y., and Li, W. K.

571   (2019). Geology and genesis of the giant Pulang porphyry Cu-Au district,

572   Yunnan, Southwest China. Economic Geology, 114(2), 275-301.

573   Catanzaro, E.J., Murphy, T.J., Garner, E.L., and Shields, W.R. (1966) Absolute

574   isotopic abundance ratio and atomic weight of terrestrial rubidium. Journal of

575   Research of the National Bureau of Standards, 73, 511–516.

576   Chen, X., Zheng, Y., Gao, S., Wu, S., Jiang, X., Jiang, J., and Lin, C. (2020a). Ages

577   and petrogenesis of the late Triassic andesitic rocks at the Luerma porphyry Cu

578   deposit, western Gangdese, and implications for regional metallogeny.

579   Gondwana Research, 85, 103-123.

580   Chen, H., Cui, H., Zhong, R., Xie, Y., Yu, C., Li, Z., and Ling, Y. (2020b). Solubility

581   of Na_2SO_4 in silica-saturated solutions: Implications for REE mineralization.

582   American Mineralogist, 105(11), 1686-1694.

583   Chugaev, A. V., Chernyshov, I. V., Gamyanin, G. N., Bortnikov, N. S., and Baranova,

584   A. N. (2010). Rb-Sr isotopic systematic of hydrothermal minerals, age, and

585   matter sources of the Nezhdaninskoe gold deposit (Yakutia). In Doklady Earth

586   Sciences (Vol. 434, No. 2, p. 1337). Springer Nature BV.

587   Cline, J. S., and Bodnar, R. J. (1991). Can economic porphyry copper mineralization
588   be generated by a typical calc-alkaline melt? Journal of Geophysical Research:
589   Solid Earth, 96, 8113-8126.

590   Cui, H., Zhong, R., Xie, Y., Wang, X., and Chen, H. (2021). Melt–fluid and fluid–
591   fluid immiscibility in a Na_2SO_4–SiO_2–H_2O system and implications for the
592   formation of rare earth deposits. Acta Geologica Sinica-English Edition, 95(5),
593   1604-1610.

594   Darbyshire, D. P. F., Pitfield, P. E. J., and Campbell, S. D. G. (1996). Late Archean
595   and Early Proterozoic gold-tungsten mineralization in the Zimbabwe Archean
596   craton: Rb-Sr and Sm-Nd isotope constraints. Geology, 24(1), 19-22.

597   Elbaz-Poulichet, F., Seidel, J. L., Jézéquel, D., Metzger, E., Prévot, F., Simonucci, C.,
598   and Radakovitch, O. (2005). Sedimentary record of redox-sensitive elements (U,
599   Mn, Mo) in a transitory anoxic basin (the Thau lagoon, France). Marine
600   Chemistry, 95(3-4), 271-281.

601   Fan, J. J., Zhang, X. Z., Ma, L., Wang, Q., Jiang, Z. Q., Xia, X. P., Wei, G., Wang, Z.,
602   Zhou, J., Li, Q., Liu, X., Huang, T., Zhang, M., Liu, J. H. (2023). Formation of
603   Eocene− Miocene felsic magmatic rocks along NS− trending
604   Yardoi-Kongbugang mountain ranges in the eastern Himalaya: New insights into
605   surface uplift and the initiation of EW extension in southern Tibet. Geological
606   Society of America Bulletin. https://doi.org/10.1130/B36617.1

607   Gallego Hernández, A. N., Akasaka, M. (2010). Ag-rich Tetrahedrite in the El
608   Zancudo Deposit, Colombia: Occurrence, Chemical Compositions and Genetic
609   Temperatures. Resource geology, 60(3), 218-233.

610   Ghaderi, M., Palin, J. M., Campbell, I. H., and Sylvester, P. J. (1999). Rare earth
611   element systematics in scheelite from hydrothermal gold deposits in the
612   Kalgoorlie-Norseman region, Western Australia. Economic Geology, 94(3),
613   423-437.

614   Guynn, J., Kapp, P., Gehrels, G. E., and Ding, L. (2012). U–Pb geochronology of
615   basement rocks in central Tibet and paleogeographic implications. Journal of

616   Asian Earth Sciences, 43(1), 23-50.

617 Hattori, K. H., and Keith, J. D. (2001). Contribution of mafic melt to porphyry copper

618   mineralization: evidence from Mount Pinatubo, Philippines, and Bingham

619   Canyon, Utah, USA. Mineralium Deposita, 36, 799-806.

620 Halter, W. E., Heinrich, C. A., and Pettke, T. (2005). Magma evolution and the

621   formation of porphyry Cu–Au ore fluids: evidence from silicate and sulfide melt

622   inclusions. Mineralium Deposita, 39, 845-863.

623 Hattori, K. (1993). High-sulfur magma, a product of fluid discharge from underlying

624   mafic magma: evidence from Mount Pinatubo, Philippines. Geology, 21(12),

625   1083-1086.

626 Han, J., Chen, H., Hong, W., Hollings, P., Chu, G., Zhang, L., and Sun, S. (2020).

627   Texture and geochemistry of multi-stage hydrothermal scheelite in the

628   Tongshankou porphyry-skarn Cu-Mo (-W) deposit, eastern China: Implications

629   for ore-forming process and fluid metasomatism. American Mineralogist, 105(6),

630   945-954.

631 Heinrich, C. A. (2007). Fluid-fluid interactions in magmatic-hydrothermal ore

632   formation. Reviews in Mineralogy and Geochemistry, 65(1), 363-387.

633 Hollings, P., Cooke, D. R., Waters, P. J., and Cousens, B. (2011). Igneous

634   geochemistry of mineralized rocks of the Baguio district, Philippines:

635   Implications for tectonic evolution and the genesis of porphyry-style

636   mineralization. Economic Geology, 106(8), 1317-1333.

637 Hou, Z., Duan, L., Lu, Y., Zheng, Y., Zhu, D., Yang, Z., and McCuaig, T. C. (2015a).

638   Lithospheric architecture of the Lhasa terrane and its control on ore deposits in

639   the Himalayan-Tibetan orogen. Economic Geology, 110(6), 1541-1575.

640 Hou, Z., Yang, Z., Lu, Y., Kemp, A., Zheng, Y., Li, Q., Tang, J., Yang, Z., and Duan, L.

641   (2015b). A genetic linkage between subduction- and collision-related porphyry

642   Cu deposits in continental collision zones. Geology, 43, 247-250.

643 Hou, Z., and Cook, N. J. (2009). Metallogenesis of the Tibetan collisional orogen: A

644   review and introduction to the special issue. Ore Geology Reviews, 36(1-3),

645   2-24.

646   Hu, Y. B., Liu, J. Q., Ling, M. X., Ding, W., Liu, Y., Zartman, R. E., and Sun, W. D.

647   (2015). The formation of Qulong adakites and their relationship with porphyry

648   copper deposit: geochemical constraints. Lithos, 220, 60-80.

649   Ji, W. Q., Wu, F. Y., Chung, S. L., Li, J. X., and Liu, C. Z. (2009). Zircon U–Pb

650   geochronology and Hf isotopic constraints on petrogenesis of the Gangdese

651   batholith, southern Tibet. Chemical Geology, 262(3-4), 229-245.

652   Lang, X., Tang, J., Li, Z., Huang, Y., Ding, F., Yang, H., Zhou, Y. (2014). U–Pb and

653   Re–Os geochronological evidence for the Jurassic porphyry metallogenic event

654   of the Xiongcun district in the Gangdese porphyry copper belt, southern Tibet,

655   PRC. Journal of Asian Earth Sciences, 79, 608-622.

656   Li, Y., Selby, D., Condon, D., and Tapster, S. (2017). Cyclic magmatic-hydrothermal

657   evolution in porphyry systems: High-precision U-Pb and Re-Os geochronology

658   constraints on the Tibetan Qulong porphyry Cu-Mo deposit. Economic Geology,

659   112(6), 1419-1440.

660   Li, Y., Li, X. H., Selby, D., and Li, J. W. (2018). Pulsed magmatic fluid release for the

661   formation of porphyry deposits: Tracing fluid evolution in absolute time from the

662   Tibetan Qulong Cu-Mo deposit. Geology, 46(1), 7-10.

663   Li, Y., Allen, M. B., and Li, X. H. (2022). Millennial pulses of ore formation and an

664   extra-high Tibetan Plateau. Geology, 50(6), 665-669.

665   Liu, Y., Hu, Z., Gao, S., Günther, D., Xu, J., Gao, C. and Chen, H. (2008) In situ

666   analysis of major and trace elements of anhydrous minerals by LA-ICP-MS

667   without applying an internal standard. Chemical Geology 257, 34-43.

668   Liu, P., Wu, S., Zheng, Y., Wang, X., Kang, Y., Yan, J., and Chen, L. (2022). Geology

669   and factors controlling the formation of the newly discovered Beimulang

670   porphyry Cu deposit in the western Gangdese, southern Tibet. Ore Geology

671   Reviews, 144, 104823.

672   Ma, X., Meert, J. G., Xu, Z., and Yi, Z. (2018). Late Triassic intra-oceanic arc system

673   within Neotethys: Evidence from cumulate appinite in the Gangdese belt,

674   southern Tibet. Lithosphere, 10(4), 545-565.

675   Nie, L., Wang, F., White, N. C., Zhang, D., Yan, C., and Wang, X. (2023). Scheelite

676   trace element compositions: A robust new tool for mineral exploration. Ore

677   Geology Reviews, 105338.

678   Kouzmanov, K., and Pokrovski, G.S., 2012. Hydrothermal controls on metal

679   distribution in porphyry Cu (-Mo-Au) systems. Society of Economic Geologists,

680   Special Publication, 16, 573–618.

681   Poulin, R. S., Kontak, D. J., McDonald, A., and McCLenaghan, M. B. (2018).

682   Assessing scheelite as an ore-deposit discriminator using its trace-element and

683   REE chemistry. The Canadian Mineralogist, 56(3), 265-302.

684   Richards, J. P. (2003). Tectono-magmatic precursors for porphyry Cu-(Mo-Au)

685   deposit formation. Economic geology, 98(8), 1515-1533.

686   Robert, F., and Brown, A. C. (1986). Archean gold-bearing quartz veins at the Sigma

687   Mine, Abitibi greenstone belt, Quebec; Part II, Vein paragenesis and

688   hydrothermal alteration. Economic Geology, 81(3), 593-616.

689   Seedorff, E., Dilles, J.H., Proffett, J.M., Jr., Einaudi, M.T., Zurcher, L., Stavast,

690   W.J.A., Johnson, D.A. and Barton, M.D. (2005). Porphyry Deposits:

691   Characteristics and Origin of Hypogene Features. Economic Geology, 251–298

692   (100th Anniversary Volume 1905–2005).

693   Sillitoe, R.H. (2010) Porphyry Copper Systems. Economic Geology,105, 3-41.

694   Sciuba, M., Beaudoin, G., Grzela, D., and Makvandi, S. (2020). Trace element

695   composition of scheelite in orogenic gold deposits. Mineralium Deposita, 55,

696   1149-1172.

697   Shinohara, H. (1994). Exsolution of immiscible vapor and liquid phases from a

698   crystallizing silicate melt: Implications for chlorine and metal transport.

699   Geochimica et Cosmochimica Acta, 58(23), 5215-5221.

700   Spencer, E. T., Wilkinson, J. J., Creaser, R. A., and Seguel, J. (2015). The distribution

701   and timing of molybdenite mineralization at the El Teniente Cu-Mo porphyry

702   deposit, Chile. Economic Geology, 110(2), 387-421.

703   Sun, X., Hollings, P., and Lu, Y. J. (2021). Geology and origin of the Zhunuo
704   porphyry copper deposit, Gangdese belt, southern Tibet. Mineralium Deposita,
705   56, 457-480.

706   Sun, S. S., and McDonough, W. F. (1989). Chemical and isotopic systematics of
707   oceanic basalts: implications for mantle composition and processes. Geological
708   Society, London, Special Publications, 42(1), 313-345.

709   Tapster, S., Condon, D. J., Naden, J., Noble, S. R., Petterson, M. G., Roberts, N. M.
710   W., and Smith, D. J. (2016). Rapid thermal rejuvenation of high-crystallinity
711   magma linked to porphyry copper deposit formation; evidence from the Koloula
712   Porphyry Prospect, Solomon Islands. Earth and Planetary Science Letters, 442,
713   206-217.

714   Wark, D. A., Hildreth, W., Spear, F. S., Cherniak, D. J., and Watson, E. B. (2007).
715   Pre-eruption recharge of the Bishop magma system. Geology, 35(3), 235-238.

716   Wang, M., Zhao, R., Shang, X., Wei, K., Liu, K., and An, W. (2022). REE and
717   cathodoluminescence features of scheelites from the Tongshankou Cu–Mo
718   deposit in Eastern China. Ore Geology Reviews, 147, 104998.

719   Wu, S., Zheng, Y., Xu, B., Jiang, G., Yi, J., Liu, X., and Li, L. (2022). Heterogeneous
720   mantle associated with asthenosphere and Indian slab metasomatism: Constraints
721   on fertilization of porphyry Cu mineralization in Tibetan orogen. Ore Geology
722   Reviews, 140, 104601.

723   Xu, W.G., Fan, H.R., Hu, F.F., Santosh, M., Yang, K.F., and Lan, T.G. (2015). In situ
724   chemical and Sr-Nd-O isotopic compositions of apatite from the Tongshi
725   intrusive complex in the southern part of the North China craton: Implications
726   for petrogenesis and metallogeny: Journal of Asian Earth Sciences, 105, 208–
727   222.

728   Yang, Z., Hou, Z., White, N.C., Chang, Z., Li, Z. and Song, Y. (2009). Geology of the
729   post-collisional porphyry copper–molybdenum deposit at Qulong, Tibet. Ore
730   Geology Reviews 36, 133-159.

731   Yang, Z., Lu, Y.-j., Hou, Z. and Chang, Z. (2015) High-Mg Diorite from Qulong in

732   Southern Tibet: Implications for the Genesis of Adakite-like Intrusions and

733   Associated Porphyry Cu Deposits in Collisional Orogens. Journal of Petrology

734   56, 227-254.

735 Yin, A. and Harrison, T.M. (2000) Geologic Evolution of the Himalayan-Tibetan

736   Orogen. Annual Review of Earth and Planetary Sciences, 28, 211-280.

737 Yu, K., Li, G., Zhao, J., Evans, N. J., Li, J., Jiang, G., Guo, H., 2022. Biotite

738   composition as a tracer of fluid evolution and mineralization center: A case study

739   at the Qulong porphyry Cu-Mo deposit, Tibet. Mineralium Deposita, 57(6),

740   1047-1069.

741 Zheng, Y., Xue, Y., Cheng, L., Fan, Z. and Gao, S. (2004) Finding, Characteristic and

742   significances of Qulong Superlarge porphyry Copper (Molybdenum) Deposit,

743   Tibet. Earth Science 29. 1, 103-108 (in Chinese with English abstract).

744 Zheng, Y., Sun, X., Gao, S., Zhao, Z., Zhang, G., Wu, S., You, Z., and Li, J. (2014).

745   Multiple mineralization events at the Jiru porphyry copper deposit, southern

746   Tibet: Implications for Eocene and Miocene magma sources and resource

747   potential. Journal of Asian Earth Sciences, 79, 842-857.

748 Zhang, L., Ren, Z.Y., Wu, Y.D., and Li, N. (2018) Sr isotope measurement of basaltic

749   glasses by LA-MC-ICP-MS based on a linear relationship between analytical

750   bias and Rb/Sr ratios. Rapid Communications in Mass Spectrometry, 32, 105–

751   112.

752 Zhang, D., and Audétat, A. (2017). What caused the formation of the giant Bingham

753   Canyon porphyry Cu-Mo-Au deposit? Insights from melt inclusions and

754   magmatic sulfides. Economic Geology, 112(2), 221-244.

755 Zhao, Q., Zhai, D., Mathur, R., Liu, J., Selby, D., and Williams-Jones, A. E. (2021).

756   The giant Chalukou porphyry Mo deposit, northeast China: The product of a

757   short-lived, high flux mineralizing event. Economic Geology, 116(5), 1209-1225.

758 Zhao, J., Qin, K., Xiao, B., McInnes, B., Li, G., Evans, N., and Li, J. (2016). Thermal

759   history of the giant Qulong Cu–Mo deposit, Gangdese metallogenic belt, Tibet:

760   constraints on magmatic–hydrothermal evolution and exhumation. Gondwana

761   Research, 36, 390-409.

762 Zhao, W. W., Zhou, M. F., Williams-Jones, A. E., and Zhao, Z. (2018). Constraints on

763   the uptake of REE by scheelite in the Baoshan tungsten skarn deposit, South

764   China. Chemical Geology, 477, 123-136.

765 Zhu, D. C., Zhao, Z. D., Niu, Y., Dilek, Y., and Mo, X. X. (2011). Lhasa terrane in

766   southern Tibet came from Australia. Geology, 39(8), 727-730.

767 Zhu, D.C., Zhao, Z.D., Niu, Y., Dilek, Y., Hou, Z.Q. and Mo, X.X. (2013). The origin

768   and pre-Cenozoic evolution of the Tibetan Plateau. Gondwana Research, 23,

769   1429–1454.

770   **FIGURE AND TABLE CAPTION**

771

772 **Fig. 1** Distribution of tectonic framework and Miocene porphyry copper deposits of

773   the Lhasa terrane (modified after Hou et al., 2015a). Abbreviations: BNSZ =

774   Bangong-Nujiang Suture Zone, GLZCF = Gar–Lunggar–Zhari Nam Tso–Comai

775   Fault, LMF = Luobadui-Milashan Fault, SNMZ = Shiquanhe-Nam Tso Melange

776   Zone, IYZSZ = Indus-Yarlung Zangbo Suture Zone, SLT = southern Lhasa

777   terrane, CLT = central Lhasa terrane, NLT = northern Lhasa terrane.

778 **Fig. 2** (a) Deposit geology map of the Qulong porphyry Cu-Mo deposit (modified

779   from Yang et al., 2009 and Zhao et al., 2016). (b) simplified geological condition

780   of drill hole refers to ZK-numbers and depth.

781 **Fig. 3** Hand specimen photographs of veins and alteration in the monzogranite and

782   monzonitic porphyry at the Qulong deposit. (a-c) Hydrothermal breccias with

783   early veins with mineral assemblages of quartz + magnetite + anhydrite +

784   chalcopyrite; (d-h) Monzogranite with quartz + scheelite + pyrite + chalcopyrite

785 veins and intensive phyllic alteration; (i-k) Late stage veins with mineral

786 assemblages of quartz + galena+ sphalerite + molybdenite veins intruded into the

787 monzogranite Abbreviations: Sch = Scheelite, Mag = Magnetite, Ccp =

788 Chalcopyrite, Anh = Anhydrite, Qz = Quartz, Py = Pyrite, Sp = sphalerite, Mol =

789 Molybdenite, Gn = galena. Mineral abbreviation according to Whitney and

790 Evans (2010).

791 **Fig. 4** Representative photomicrographs of three generations of scheelite at the

792 Qulong deposit. (a-b) Anhedral Sch 1 occurs in a quartz + anhydrite + magnetite

793 + chalcopyrite vein; (c) Anhedral Sch 1 with dispersive zoning in CL image; (d)

794 Subhedral Sch 2 intergrowth with quartz + pyrite + chalcopyrite + rutile veins;

795 (e-f) Sch 2 with dispersed Cu-rich core (Sch 2a) and oscillatory mantle (Sch 2b)

796 and rim (Sch 2c) in CL image; (g-h) Euhedral Sch 3 intergrowth with quartz,

797 galena, sphalerite, Ag-rich tetrahedrite, and molybdenite in the veinlet; (i) Sch 3

798 exhibits an oscillatory zone with bright core (Sch 3a), dark mantle (Sch 3b), and

799 oscillatory bright rim (Sch 3c) in the CL image. Abbreviations: Sch = Scheelite,

800 Mag = Magnetite, Ccp = Chalcopyrite, Anh = Anhydrite, Qz = Quartz, Py =

801 Pyrite, Rt = Rutile, Sp = sphalerite, Mol = Molybdenite, Gn = galena; Te =

802 tetrahedrite.

803 **Fig. 5** Selected trace elemental variation of three generations of scheelite (a) Eu/Eu*

804 vs. Mo, (b) REE+Y vs. Na, (c) Fe vs Cu, (d) Mo vs. WO_3.

805 **Fig. 6** Chondrite-normalized REE patterns of three generations of scheelite from the

806 Qulong deposit. Data are normalized by values of chondrite (Sun and

807   McDonough 1989).

808 **Fig. 7** In situ Sr isotopes for three generations of scheelite compared with whole-rock

809   Sr isotopes of the Rongmucuola pluton, monzogranitic porphyries, and High-Mg

810   diorite porphyry in the Qulong deposit. The data of Rongmucuola pluton,

811   monzogranitic porphyries, High-Mg diorite porphyry, and postcollisional

812   ultrapotassic rocks from southern Tibet are from (Yang et al., 2015, 2016; Hu et

813   al., 2015)

814 **Fig. 8** Schematic illustration showing the genetic model of the Qulong porphyry

815   Cu-Mo deposit. (a) Crystallization of pre-ore monzogranite and granodiorite with

816   weak mineralization and alteration; (b) Metal-rich volatiles from mafic rocks

817   injected in the depth into the porphyry metallogenic system and provide metals

818   and sulphurous gases for formation of syn-ore monzogranitic porphyries, sulfide,

819   and scheelite.

820 **Appendix Table A1**. LA-ICP-MS major and trace elemental data of three generations

821 of scheelite at the Qulong deposit.

822 **Appendix Table A2**. LA-MC-ICP-MS Sr isotopes of three generations of scheelite at
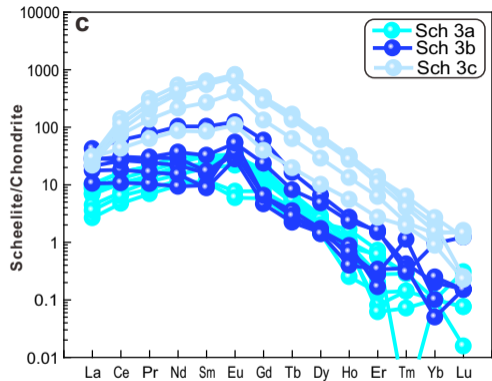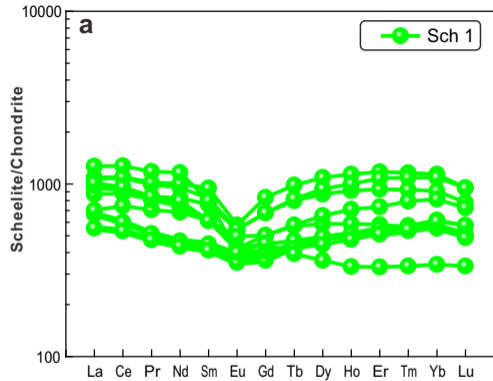
823 the Qulong deposit.

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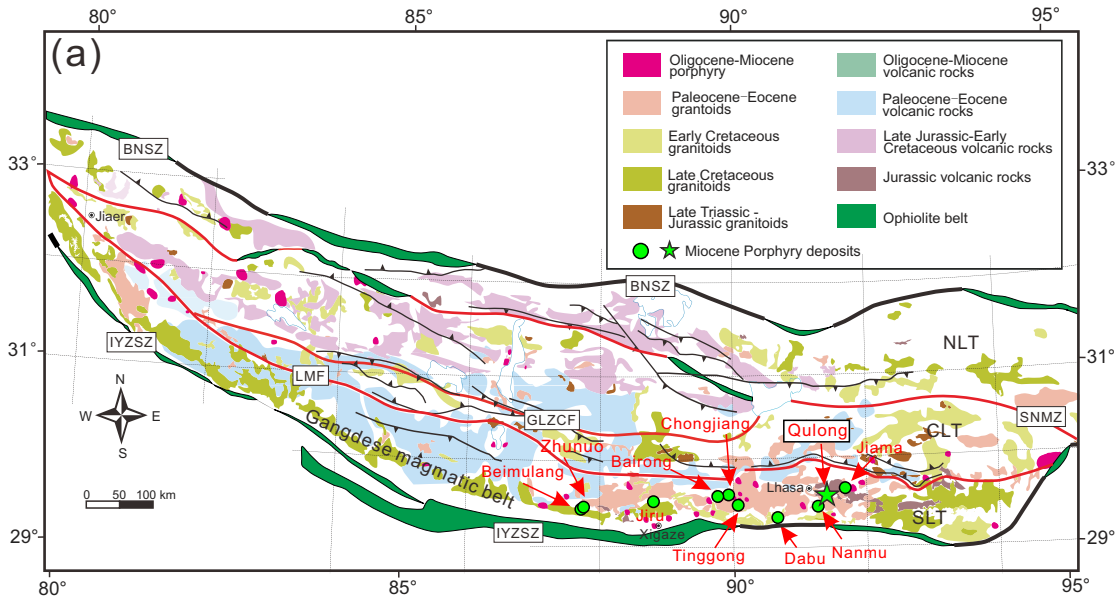
Figure 1
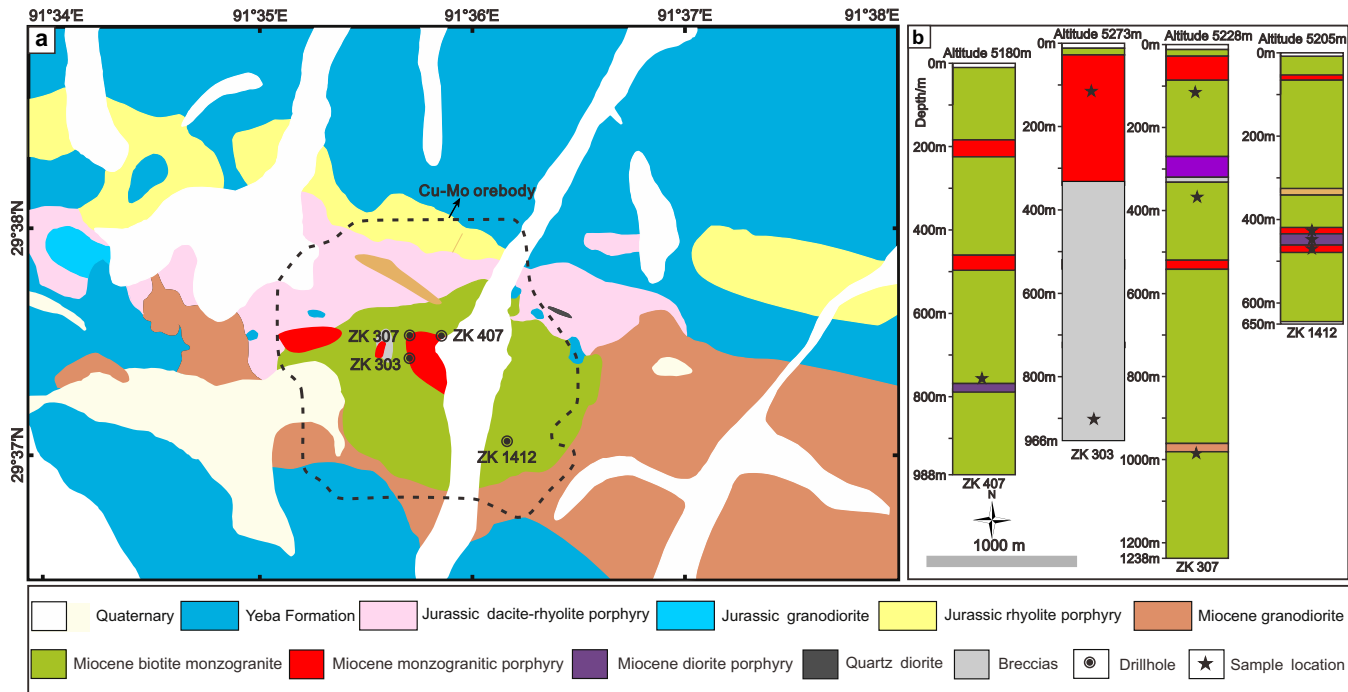
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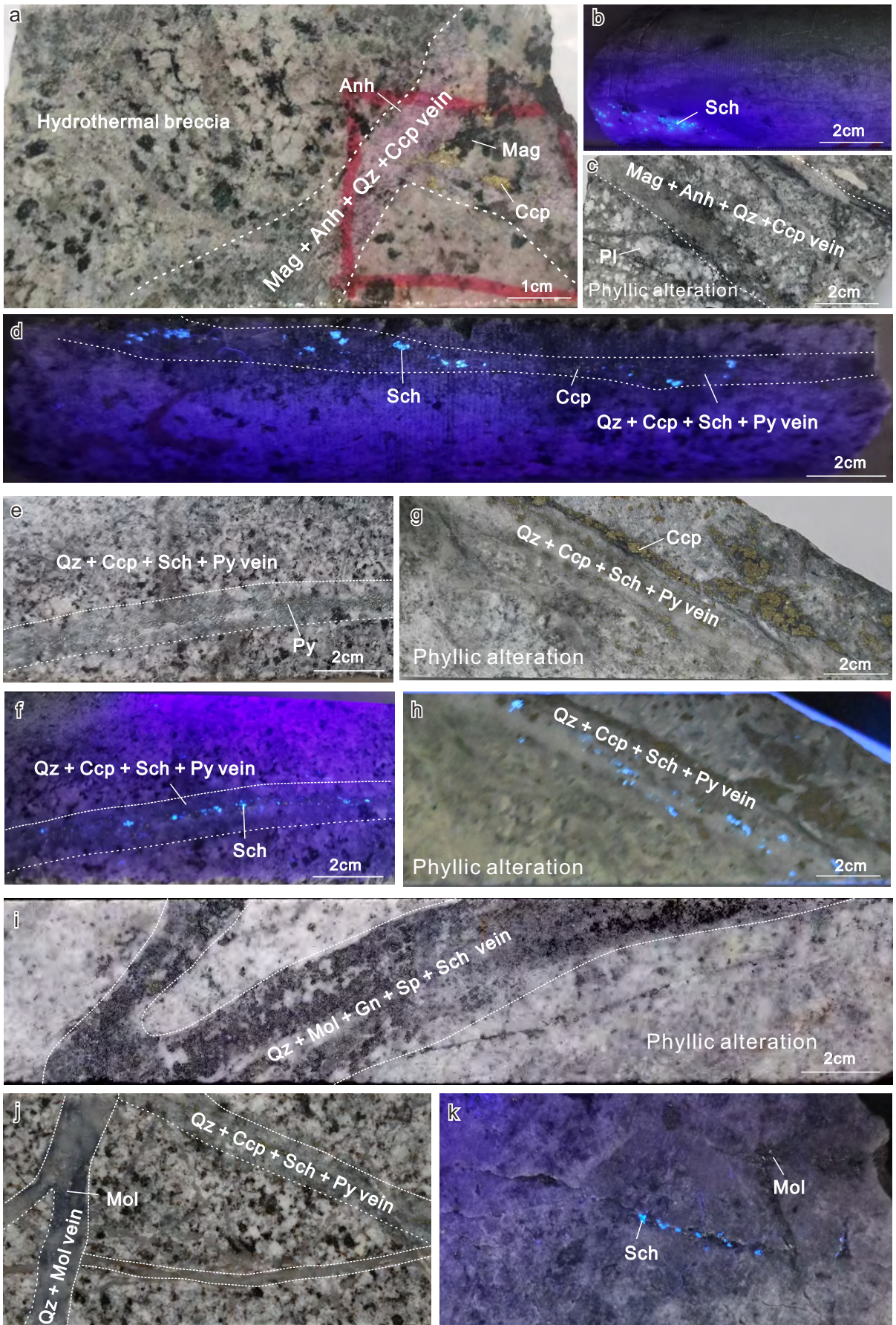
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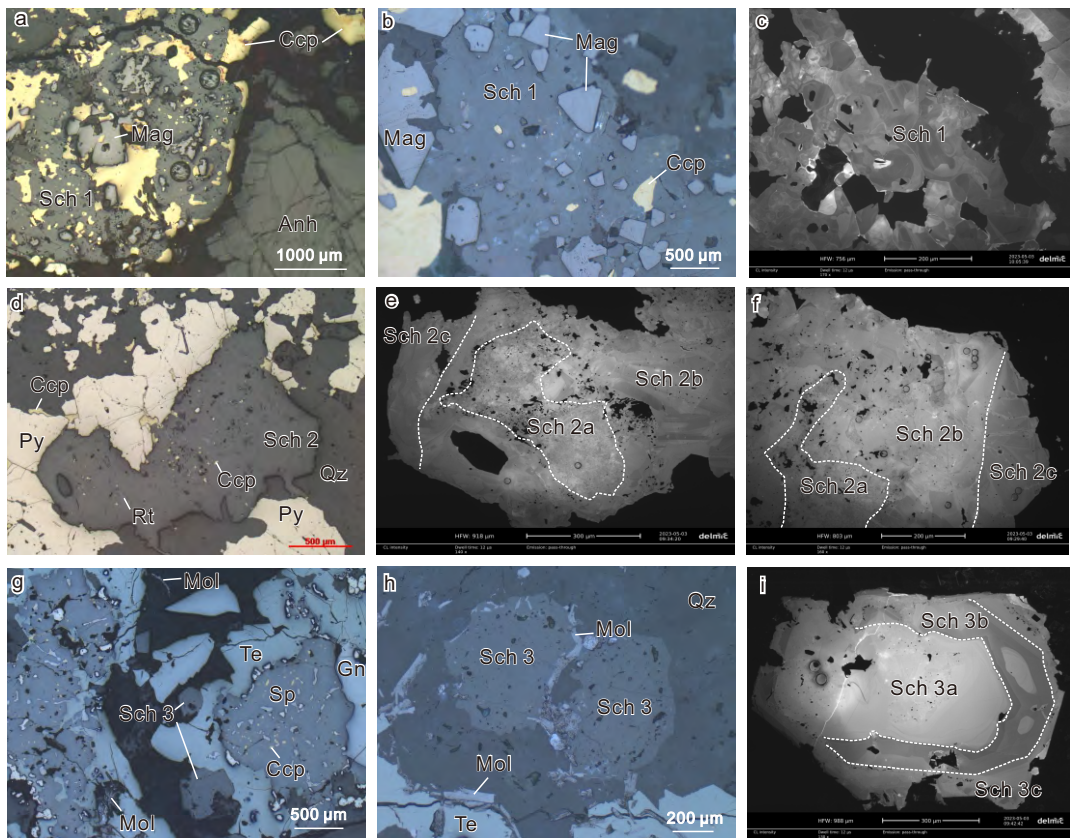
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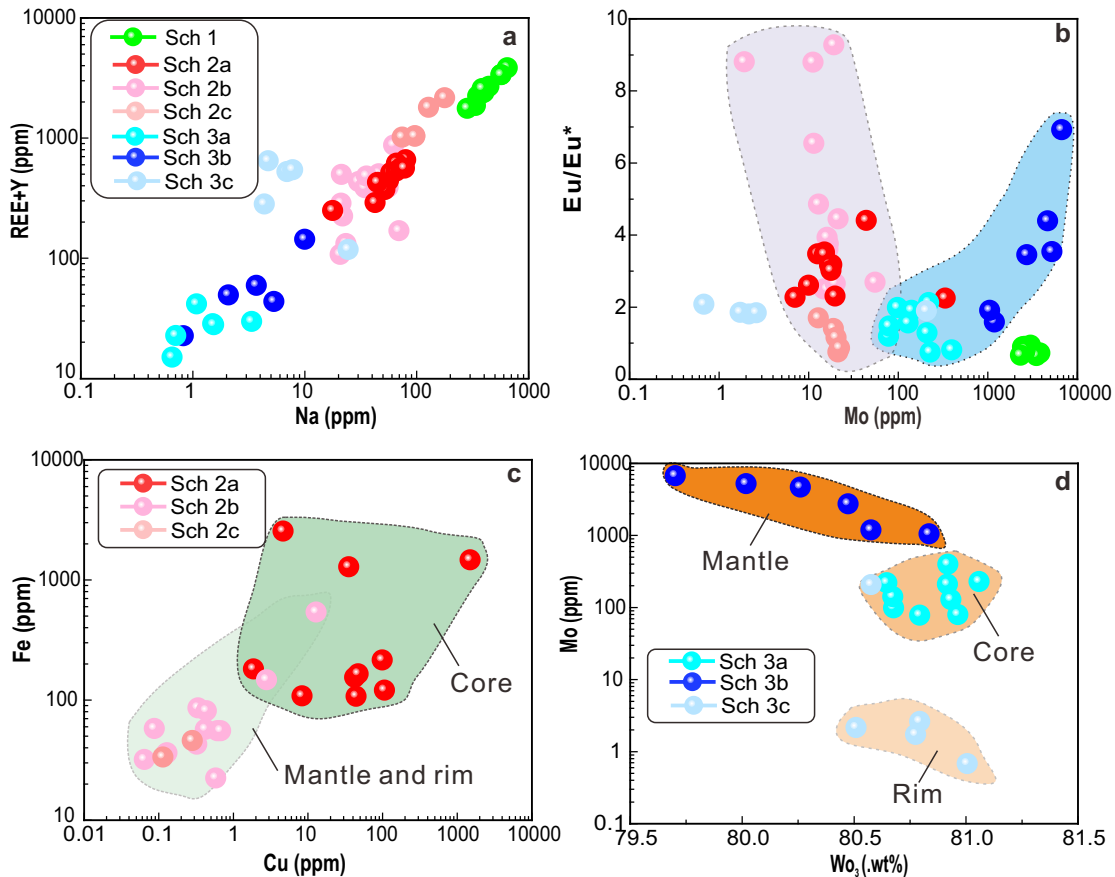
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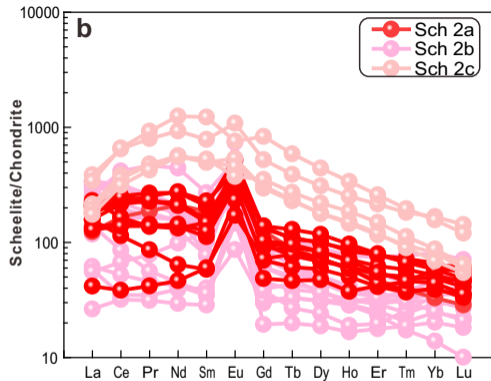
Figure 6

Figure 7

Figure 8