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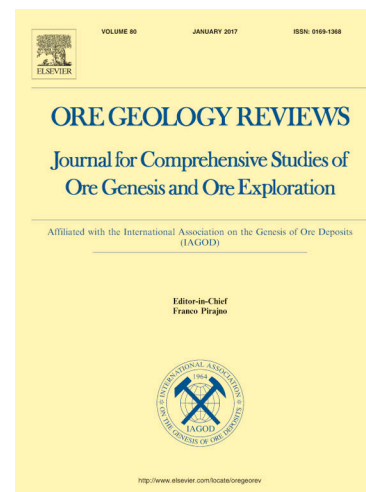
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1 **Garnet and scheelite chemistry of the Weijia tungsten deposit, South China: Implications**
2 **for fluid evolution and W skarn mineralization in F-rich ore system**

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15
16 **Abstract**

17 Fluid evolution is an essential subject in the studies of hydrothermal ore-forming processes.
18 Garnet and scheelite prevail in W-bearing skarn deposits and record plentiful information on W
19 skarn mineralization. In-situ LA-ICP-MS trace element analyses have been carried out on the
20 garnet and scheelite from the F-rich Weijia W deposit in South China to constrain the processes
21 of fluid evolution and W skarn mineralization. The Weijia W deposit mainly consists of calcic
22 and magnesian skarns and was formed through six stages of alteration and mineralization. Two
23 stages of fluid exsolution are recognized in the magmatic-hydrothermal system. The earlier
24 exsolved fluids are Cl-rich with rightward-sloping REE patterns and result in pre-ore

25 skarnization. The later exsolved fluids are F-rich with relatively flat REE patterns and are
26 responsible for W mineralization. The pre-ore garnets are LREE-enriched and HREE-depleted
27 whereas the syn-ore garnets are LREE-depleted and HREE-enriched with lower δEu values than
28 the former, denoting a transition from wall rock-controlled to magmatic fluid-dominated
29 fluid-rock interaction. Combined with the skarn occurrences, mineral assemblages, and garnet
30 textures, it is revealed that the mechanism of skarn formation shifts from more diffusive
31 metasomatism under lower water/rock ratios to more advective metasomatism at higher
32 water/rock ratios. The advective metasomatism with a high flux of ore-forming fluids is
33 hydrodynamically favorable for the consequent W mineralization. The earliest-formed scheelite
34 is akin to the host granite porphyry in REE patterns and can reflect the features of initial
35 mineralizing fluids. It has high ΣREE (1255–5059 ppm), Y (616–1416 ppm), Nb (585–2629
36 ppm), Ta (14–248 ppm), Mn (up to 1977 ppm) and low Mo (mostly < 1000 ppm) contents,
37 indicating that the primary F-rich magmatic fluids are reduced and enriched in REEs, Y, Nb, and
38 Ta. The contents of ΣREE , Y, Nb, and Ta in scheelite are decreasing with the evolution of the
39 F-rich mineralizing fluids. The latest-formed scheelites have distinctly lower ΣREE (2.9–140
40 ppm), Y (0.01–4.1 ppm), Nb (1.7–77 ppm), and Ta (0.04–0.19 ppm) contents and higher
41 $(\text{La}/\text{Yb})_{\text{N}}$ ratios and δEu values. They show 1:1 positive correlation of Eu_{N} vs. Eu^*_{N} and have
42 high Mo (up to 129466 ppm) and low Mn (as low as 3.4 ppm) contents, implying involvement of
43 meteoric waters in the evolved ore-forming fluids and an oxidizing condition. Fluid-rock
44 interaction, mineral precipitation, and fluid mixing largely control the process of fluid evolution.
45 Fluorine consumption due to the formation of fluorite and the other F-rich minerals is vital for the
46 compositional evolution of F-rich mineralizing fluids. The decrease of F concentration in fluids
47 will depress the solubilities of REEs, Y, Nb, and Ta and enhance the LREE/HREE fractionation.
48 Greisenization and skarnization induced the neutralization of the acidic W-bearing fluids and the

49 liberation of Ca from the granite porphyry and carbonate strata and then triggered the scheelite
50 precipitation. The carbonate strata contain abundant Ca and the granite porphyry is poor in Ca,
51 and thus the economic W mineralization dominantly occurs in the skarns.

52 **Keywords:** F-rich ore system, fluid exsolution, fluid-rock interaction, metasomatism mechanism,
53 fluid evolution, scheelite precipitation

54

55 1. Introduction

56 The compositions and physicochemical conditions of hydrothermal fluids exsolved from
57 crystallizing magmas have a crucial effect on fluid-melt element partitioning and subsequent
58 ore-forming processes (Hedenquist and Lowenstern, 1994; Heinrich and Candela, 2014). Large
59 tungsten deposits are dominantly related to highly fractionated F-rich granites (Černý et al., 2005;
60 Wang et al., 2021). Skarn is one of the most important types of W mineralization (Einaudi et al.,
61 1981; Meinert et al., 2005). Aksyuk (2000) quantitatively evaluated the fluid F activities of
62 various mineralized skarn systems by biotite and phlogopite fluorimeters and proved that the
63 F-enriched signature is typical of rare metal leucogranites, Li-F granites and pegmatites, and
64 related W, Be, U, Th, rare earth element (REE), Ta, Nb, Li, and Sn skarn deposits. The
65 widespread W skarn deposits in South China (Zhao et al., 2017; Mao et al., 2019) provide
66 excellent examples for studying the characteristics and evolution of magmatic fluids in F-rich ore
67 systems.

68 The trace element compositions of ore and gangue minerals from hydrothermal deposits
69 preserve abundant vestiges of ore-forming processes and are powerful tools to decipher the origin
70 and evolution of mineralizing fluids (e.g., Song et al., 2014; Sun and Chen, 2017; Legros et al.,
71 2018; Xiao et al., 2018; Zhang et al., 2018; Chen et al., 2020a; Xu et al., 2020). Especially, the
72 application of in-situ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

73 analytical technique combined with backscattered electron (BSE) and/or cathodoluminescence
74 (CL) imaging provide us with a more detailed view into the ore-forming processes (e.g., [Ding et al., 2018](#);
75 [Li et al., 2018](#); [Zhao et al., 2018](#); [Park et al., 2019](#); [Tian et al., 2019](#); [Han et al., 2020](#);
76 [Carocci et al., 2021](#)).

77 Garnet and scheelite are common in W-bearing skarn deposits. Garnet is mostly isometrical
78 with a general chemical formula of $X_3Y_2Z_3O_{12}$, where X, Y, and Z successively refer to divalent
79 cations (Ca, Mg, Mn, or Fe^{2+}) in dodecahedral site, trivalent cations (Fe^{3+} , Al, and Cr) in
80 octahedral site, and dominantly Si in tetrahedral site ([Gaspar et al., 2008](#); [Grew et al., 2013](#)).
81 Scheelite ($CaWO_4$) has a tetragonally symmetric crystal structure constructed by tetrahedral
82 $[WO_4]^{2-}$ groups and irregular dodecahedral $[CaO_8]^{14-}$ groups ([Ghaderi et al., 1999](#); [Brugger et al.,](#)
83 [2000](#)). Considerable amounts of trace elements, such as REEs, Y, Sr, and Na, can substitute for
84 Ca in both of them on account of the comparable ionic radii and valencies ([Ghaderi et al., 1999](#);
85 [Gaspar et al., 2008](#)). Likewise, substantial Mo and Nb can be incorporated into scheelite by
86 occupying the position of W (e.g., [Zhao et al., 2018](#); [Li et al., 2019](#)). The trace element variations
87 of scheelite and garnet are largely controlled by the substitution mechanisms, the sources,
88 compositions and physicochemical conditions of associated fluids, the dynamics of hydrothermal
89 system (including fluid-rock interaction and mineral precipitation), and the kinetics of mineral
90 growth ([Ghaderi et al., 1999](#); [Brugger et al., 2000](#); [Smith et al., 2004](#); [Gaspar et al., 2008](#)).

91 The Weijia W deposit in the Nanling Range of South China is a recently discovered large
92 scheelite skarn deposit that comprises primary magnesian W skarn (240 kt WO_3 at 0.18 wt%) and
93 subordinate calcic W skarn (60 kt WO_3 at 0.24 wt%). It is genetically linked to highly
94 fractionated granite porphyry ([Zhao et al., 2016](#); [Huang et al., 2017](#)) and is characterized by
95 extreme enrichment of fluorine with general CaF_2 grades of 5–18 wt%. In this publication, we
96 present a combined study on garnet and scheelite mineralogy of the Weijia W skarn deposit,

97 including textures as well as in-situ trace element compositions, aiming to reveal the processes of
98 fluid evolution and W skarn mineralization in a F-rich ore system. Our achievements highlight
99 the significance of mineral trace element geochemistry in elucidating complex ore-forming
100 processes.

101 **2. Geological setting**

102 South China is the most important W metallogenic province around the world and holds the
103 world's largest W production (Zhao et al., 2017; Mao et al., 2019). The Yangtze and Cathaysia
104 Blocks were amalgamated together along the Jiangnan Orogen into a unified South China Block
105 (Fig. 1a) during Neoproterozoic (Wang et al., 2007). Since then, South China has undergone
106 Neoproterozoic, Silurian, Triassic, Jurassic, and Cretaceous tectonic-magmatic events and
107 associated W-Sn mineralization (Chen et al., 2013; Mao et al., 2013, 2019; Shu et al., 2015;
108 Zhang et al., 2019). The stable neritic-bathyal clastic deposition from Neoproterozoic to
109 Ordovician and littoral-neritic carbonate deposition from Devonian to Triassic were responsible
110 for the formation of regionally important ore-hosting strata for subsequent Mesozoic mineral
111 deposits. Most W-Sn deposits in South China were formed during Late Mesozoic and are
112 genetically closely related to contemporaneous granites (Chen et al., 2013; Mao et al., 2013,
113 2019; Zhao et al., 2017). The Late Mesozoic explosive granitic magmatism and concomitant
114 W-Sn mineralization were geodynamically linked to the subduction and roll-back of
115 paleo-Pacific plate which induced asthenosphere upwelling and basaltic magma underplating
116 (Zhou and Li, 2000; Li and Li, 2007). It is widely accepted that the underplated basaltic magmas
117 provided the necessary heat to trigger extensive crustal melting and generation of voluminous
118 felsic magmas (Zhou and Li, 2000; Zhou et al., 2006).

119 The Nanling Range situated in the central Cathaysia Block (Fig. 1a) is one of the 21 key
120 metallogenic belts in China. It possesses numerous W-Sn deposits that were predominantly

121 formed in Late Jurassic (Mao et al., 2007, 2013, 2019). The W-bearing granites are generally
122 multi-facies mainly consisting of biotite, two-mica, and muscovite granites, which show evident
123 highly fractionated features (Chen et al., 2008; Zhang et al., 2017). Wolframite quartz vein and
124 greisen and scheelite skarn constitute the majority of W deposits in the Nanling Range (Chen et
125 al., 2008; Zhao et al., 2017; Mao et al., 2019). Topaz and fluorite are frequently observed in these
126 W deposits, indicating F-rich magmatic-hydrothermal environments (e.g., Legros et al., 2018;
127 Chen et al., 2020a). Wall-rock compositions apparently control the styles of W mineralization.
128 The wolframite quartz vein and greisen deposits occur principally in the eastern Nanling Range
129 where the strata are dominated by Neoproterozoic to Ordovician clastic metasedimentary rocks
130 (e.g., Xihuashan, Piaotang, and Maoping, Mao et al., 2007), while the scheelite skarn deposits are
131 largely distributed in the western Nanling Range where the Devonian to Triassic carbonate strata
132 are well developed (e.g., Xintianling, Shizhuyuan, and Yaogangxian, Mao et al., 2007). The
133 Weijia W deposit is one of these scheelite skarn deposits (Fig. 1a). Huang et al. (2017) reported a
134 zircon U-Pb age of 158.3 ± 2.2 Ma for the Weijia granite porphyry. Molybdenite Re-Os dating
135 revealed that this deposit was formed at 159.0 ± 5.6 Ma (Zhao et al., 2016), manifesting a genetic
136 linkage between the Weijia W skarn deposit and granite porphyry.

137 3. Deposit geology

138 The exposed strata in the Weijia W skarn deposit are mainly Middle–Late Devonian
139 carbonate rocks that include the Middle Devonian Qiziqiao Formation and Upper Devonian
140 Shetianqiao and Xikuangshan Formations (Fig. 1b). The Qiziqiao Formation is composed of a
141 lower member of limestone, a middle member of dolostone with intercalated dolomitic limestone,
142 and an upper member of limestone locally with intercalated dolomitic limestone and lenticular
143 dolostone (Figs. 1b and 2). Both the Shetianqiao and Xikuangshan Formations principally

144 comprise limestone and dolomitic limestone. These carbonate strata are slightly folded and
145 broadly strike NNW–SSE and dip 5–35° to SWW (Figs. 1b and 2).

146 The magmatic rocks associated with the Weijia W skarn deposit are granite porphyry which
147 was dominantly emplaced as scattered bosses, ductoliths, and dykes, with a total exposure area of
148 ca. 1.3 km² (Figs. 1b and 2). The granite porphyry has light red to off-white color and shows a
149 typical subvolcanic porphyritic texture (Figs. 3a and 4a). It contains 30–50 vol% of fine- to
150 medium-grained phenocrysts and 50–70 vol% of felsitic to fine-grained matrix. Rock-forming
151 minerals are K-feldspar (ca. 37 vol%), quartz (ca. 35 vol%), albite (ca. 25 vol%, An < 5), and
152 minor muscovite (ca. 2 vol%) and biotite (ca. 1 vol%). The majority of phenocrysts consist of
153 quartz, K-feldspar, albite, and biotite (Fig. 4a) and muscovite mostly occurs in the matrix (Fig.
154 4b). Accessory minerals include zircon, thorite, apatite, ilmenite, rutile, fluorite, scheelite,
155 monazite, xenotime, niobite, samarskite, fergusonite, and parisite.

156 At the apex of the Weijia granite porphyry, there are some late-magmatic to hydrothermal
157 veins with a vertically upward zonation from K-feldspar-quartz pegmatite veins and
158 (K-feldspar)-quartz veins to stockwork quartz veinlets (Fig. 3b) (Huang, 2018). The stockwork
159 quartz veinlets contain fluorite and muscovite and are associated with weak greisenization that
160 occurs as interstitial muscovite and muscovite-fluorite aggregates in the granite matrix (Fig. 4b).
161 They contain a few scheelite grains (Fig. 4c) but are of no economic significance. Economic
162 calcic and magnesian W skarns are distributed along the contact zones between the granite
163 porphyry and the upper and middle members of the Qiziqiao Formation, respectively (Fig. 2).
164 The former is developed as massive at depth shallower than 300 m and is partially exposed on the
165 surface, while the latter is stratiform with buried depth of 200–900 m (Fig. 2). The calcic skarn is
166 characterized by earlier disseminated garnet (yellow-brown) and pyroxene (light-green) and later
167 stockwork garnet (red-brown) followed by stockwork pyroxene (dark-green) (Fig. 3c and d).

168 Scheelite mostly intimately coexists with the stockwork garnet and pyroxene (Fig. 5a–d). The
169 magnesian skarn generally appears as green-colored stockwork veinlets in the fissures of
170 dolostone and primarily comprises phlogopite and serpentine (Fig. 3e and f) occasionally with a
171 few earlier garnet and pyroxene. Scheelite dominantly occurs within the stockwork magnesian
172 skarn veinlets (Fig. 5e–g).

173 We have detailedly investigated the petrographic relationships, mineral assemblages, and the
174 textures and compositions of garnets and scheelites, and thus six stages of alteration and
175 mineralization are established in the Weijia W skarn deposit. The pre-ore stage 1 is characterized
176 by disseminated and stockwork skarnization in the limestone and dolostone, respectively (Fig.
177 3c–f). In this stage, the calcic skarn developed garnet ($\text{Grt}_C 1$), pyroxene ($\text{Px}_C 1$), and magnetite
178 (Fig. 5a) and the magnesian skarn generated garnet ($\text{Grt}_M 1$), pyroxene ($\text{Px}_M 1$), and marialite
179 ($\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$, Fig. 5h). The $\text{Grt}_C 1$ encloses the $\text{Px}_C 1$ and is replaced by fluorite (Fig. 5b). The
180 stockwork quartz veinlets associated with weak greisenization were formed during the stage 2
181 within the granite porphyry (Fig. 3b). The minerals in the stockwork quartz veinlets include
182 quartz, fluorite, muscovite, and a few scheelite grains ($\text{Sch}_Q 2$) (Fig. 4c). In the stage 3, the calcic
183 skarn is dominated by wollastonite, stockwork garnet ($\text{Grt}_C 3$), scheelite ($\text{Sch}_C 3$), vesuvianite,
184 and fluorite (Figs. 3c–d and 5c) and the stockwork magnesian skarn by garnet ($\text{Grt}_M 3$), scheelite
185 ($\text{Sch}_M 3$), chondrodite, and fluorite (Fig. 5e). The stage 4 is developed as stockwork pyroxene
186 ($\text{Px}_C 4$), scheelite ($\text{Sch}_C 4$), and fluorite with minor chlorite in the calcic skarn (Figs. 3c–d and 5d)
187 and chlorite, sericite, and calcite in the adjacent granite porphyry. In this stage, the stockwork
188 magnesian skarn in the dolostone is featured by the formation of phlogopite, serpentine, scheelite
189 ($\text{Sch}_M 4$), and fluorite with a few sellaite, talc, and chlorite (Figs. 3e–f and 5e–h) and the adjacent
190 granite porphyry was altered by serpentine, phlogopite, sericite, and calcite with scheelite
191 mineralization. Sporadically disseminated pyrite, pyrrhotite, arsenopyrite, chalcopyrite,

192 sphalerite, and galena were formed during the stage 5 and overprint the earlier skarn minerals
193 (Huang, 2018). The post-ore stage 6 is presented as barren (K-feldspar)-quartz, fluorite, and
194 calcite veinlets cutting the earlier skarn and sulfide minerals (Fig. 3c–f).

195 **4. Sampling and analytical methods**

196 **4.1. Sample collection**

197 We have systematically collected the samples of the granite porphyry and its stockwork
198 quartz veinlets, calcic skarn, and magnesian skarn from surface outcrops and drill cores in the
199 Weijia W deposit. The drill core locations and sampling depths are shown in Fig. 1b and listed in
200 Supplementary Tables S1–S4, respectively. These samples were prepared as polished thin
201 sections firstly for petrographic and mineral textural studies and then for mineral compositional
202 analyses.

203 **4.2. BSE and CL imaging**

204 BSE imaging of garnet and scheelite was conducted through a ZEISS MERLIN Compact
205 scanning electron microscope (SEM) equipped with a Bruker XFlash 6 | 30 silicon drift detector
206 at Institut des Sciences de la Terre d'Orléans (ISTO), France. The analytical conditions included
207 an accelerating voltage of 15 kV, a current up to 100 nA with resolution up to 0.8 nm, and a
208 working distance of 10 mm.

209 CL imaging of scheelite was performed by a TESCAN MIRA 3 LMH field emission SEM
210 equipped with a TESCAN A75c CL detector at Nanjing Hongchuang Geological Exploration
211 Technology Service Co., Ltd., China. The analytical conditions included an accelerating voltage
212 of 7 kV, an emission current of 0.15 mA and a specimen current of 2 nA, and a working distance
213 of 18–19 mm.

214 **4.3. Electron microprobe analyses**

215 Major element analyses of garnet and pyroxene were accomplished by a CAMECA SX50
216 electron microprobe at ISTO, France. The operating conditions included an accelerating voltage
217 of 15 kV, a beam current of 10 nA with diameter of 1 μm , and counting times of 10 s for each
218 element and 5 s for background. Natural albite ($\text{SiK}\alpha$ and $\text{NaK}\alpha$), andradite ($\text{CaK}\alpha$), orthoclase
219 ($\text{KK}\alpha$), and topaz ($\text{FK}\alpha$) and synthetic MnTiO_3 ($\text{TiK}\alpha$ and $\text{MnK}\alpha$), Al_2O_3 ($\text{AlK}\alpha$), Fe_2O_3 ($\text{FeK}\alpha$),
220 and MgO ($\text{MgK}\alpha$) were used as standards. The detection limits are better than 0.1 wt% for Si, Al,
221 Mg, Ca, and Na, 0.15 wt% for Ti and K, 0.3 wt% for Mn, 0.35 wt% for Fe, and 0.5 wt% for F.
222 All data were corrected with standard ZAF correction procedures.

223 4.4. In-situ LA-ICP-MS analyses

224 In-situ trace element analyses of garnet and scheelite were carried out through an Agilent
225 7700 \times ICP-MS coupled to an Excite 193 nm Photon Machines laser ablation system at Nanjing
226 FocuMS Technology Co., Ltd., China. Helium gas was used as the carrier to efficiently transport
227 aerosol and mix with argon gas via a T-connector before entering the ICP-MS. The instrument
228 settings were optimized by ablating the NIST SRM 610 synthetic glass to obtain maximum signal
229 intensities and keeping low ThO/Th ratios ($< 0.3\%$) to reduce the oxide and doubly charged ion
230 interferences. Each sample analysis was conducted by a 25–50- μm ablating spot at 5–8 Hz
231 repetition rate with fluence of 6.06 J/cm^2 for 40 s after measuring the gas blank for 15 s. After
232 every 8–10 sample analyses, the external standards (garnet: NIST SRM 612, 610 and USGS
233 BIR-1G, BHVO-2G, BCR-2G; scheelite: NIST SRM 612, 610) were measured once to correct
234 the time-dependent sensitivity drift and mass discrimination. The off-line data processing was
235 performed by the ICPMSDataCal software using 100%-normalization strategy without applying
236 an internal standard (Liu et al., 2008).

237 5. Results

238 5.1. Garnet and scheelite textures

239 The disseminated Grt_C 1 usually has millimeter-scale grain sizes and is euhedral to subhedral
 240 and oscillatorily zoned with the band width of a dozen to dozens of microns (Figs. 5a–b and 6a),
 241 while the stockwork Grt_C 3 is anhedral without obvious zonation (Figs. 5c and 6a–b). The Grt_C 3
 242 cuts the Grt_C 1 (Fig. 6a) and coexists with the Sch_C 3 (Fig. 6b). The Grt_M 1 is coarser, subhedral,
 243 and relatively homogeneous whereas the Grt_M 3 is finer, anhedral, and distinctly heterogeneous
 244 (Fig. 6c–e). The Grt_M 3 replaces the Grt_M 1 (Fig. 6c) and coexists with the Sch_M 3 (Fig. 6d and e).
 245 In light of the BSE images, both the Grt_M 1 and Grt_M 3 can be subdivided into two
 246 subgenerations, i.e., the darker Grt_M 1A and Grt_M 3A and the brighter Grt_M 1B and Grt_M 3B (Fig.
 247 6d–f). The Grt_M 1A shows micron-scale oscillatory zonation whereas the other three
 248 subgenerations do not (Fig. 6d–f). The boundary between the Grt_M 3A and Grt_M 3B is rather
 249 chaotic (Fig. 6f).

250 The Weijia scheelite grains are mostly 50–400 μm in size (Figs. 5 and 7). They are generally
 251 anhedral (Figs. 5 and 7) and some of the earliest-formed ones (Sch_Q 2) are subhedral (Fig. 7a).
 252 The Sch_Q 2 coexists with molybdenite and is oscillatorily zoned with the band width of several to
 253 a dozen microns (Fig. 7a). The Sch_C 3 and Sch_M 3 show conspicuous micron-scale oscillatory
 254 zonation, while the Sch_C 4 and Sch_M 4 are relatively homogeneous (Fig. 7b–g). The Sch_C 4 cuts
 255 the Sch_C 3 in the stockwork garnet veinlets (Fig. 7b and c) and the Sch_M 4 replaces the Sch_M 3
 256 (Fig. 7f).

257 5.2. Garnet and pyroxene major elements

258 The in-situ major and trace element analytical results of different generations of garnets,
 259 pyroxenes, and scheelites from the Weijia W skarn deposit are listed in Supplementary Tables
 260 S1–S4. The Grt_C 1 has andraditic compositions (Grs_{1–14}Adr_{81–93}), while the Grt_C 3 belongs to
 261 intermediate grandite (Grs_{38–63}Adr_{33–57}) (Fig. 8a). Both the Grt_M 1 and Grt_M 3 are grossularitic
 262 garnet (Grs_{67–84}Adr_{10–22}, Fig. 8b) and contain more MgO (mostly 1.5–2.6 wt%) than the Grt_C 1

263 and Grt_C 3 (< 0.54 wt%) (Table S1). These garnets are F-bearing. In the same stage, the garnet in
 264 the magnesian skarn is richer in F (Grt_M 1: 0.51–2.8 wt%; Grt_M 3: 2.7–4.1 wt%) than that in the
 265 calcic skarn (Grt_C 1: < 0.77 wt%; Grt_C 3: < 1.4 wt%) (Table S1). The stage-3 garnet has higher F
 266 contents than the stage-1 garnet whether in the calcic or magnesian skarn (Table S1). The Px_C 1 is
 267 diopsidic pyroxene (Di_{68–99}Hd_{0–27}) whereas the Px_C 4 has hedenbergitic compositions (Di_{0–}
 268 ₁₆Hd_{78–95}) (Fig. 8c). The Px_M 1 is almost pure diopside (Di_{98–100}Hd₀, Fig. 8d).

269 5.3. Garnet trace element compositions

270 The Grt_C 1 shows slightly rightward-sloping chondrite-normalized REE patterns without
 271 obvious Eu anomalies (Fig. 9a), while the Grt_C 3 exhibits light REE (LREE)-depleted [(La/Sm)_N
 272 = 0.05–0.16] and heavy REE (HREE)-enriched REE patterns with apparent Eu negative
 273 anomalies ($\delta\text{Eu} = 0.12\text{--}0.21$) (Figs. 9b and 10a). The Grt_M 1 displays LREE-enriched and HREE-
 274 and Eu-depleted REE patterns whereas the Grt_M 3 is significantly richer in HREEs and more
 275 depleted in Eu than the former (Fig. 9c and d). The Grt_M 1B has higher REE (especially LREE)
 276 contents and stronger Eu negative anomalies than the Grt_M 1A (Fig. 9c). The Grt_M 3A presents
 277 relatively flat and strongly Eu-depleted ($\delta\text{Eu} = 0.007\text{--}0.02$) REE patterns and the Grt_M 3B is
 278 distinguished from the former by striking depletions of LREEs [(La/Sm)_N = 0.001–0.005] (Figs.
 279 9d and 10a). Notably, all the REE patterns of the Grt_M 1 and Grt_M 3 are Tm-Yb-Lu-upwarped
 280 (Fig. 9c and d).

281 The Grt_C 1 and Grt_C 3 have higher Ti, V, Cr and lower Na, Zn, Sr contents than the Grt_M 1
 282 and Grt_M 3 on the whole (Table S3). The Grt_C 1 contains more W (7.1–1181 ppm) and less Nb
 283 (0.25–8.6 ppm) than the Grt_C 3 (5.6–168 ppm W, 2.3–21 ppm Nb) (Table S3). The Grt_M 1 and
 284 Grt_M 3 have comparable W contents (Grt_M 1: 0.42–3.1 ppm; Grt_M 3: 0.40–5.4 ppm) and Nb
 285 contents (Grt_M 1: 1.4–74 ppm; Grt_M 3: 6.3–26 ppm) (Table S3). The Ta contents of these garnets
 286 are low (0.01–0.42 ppm, Table S3).

287 5.4. Scheelite trace element compositions

288 The Sch_Q 2 shows flat chondrite-normalized REE patterns [(La/Yb)_N = 0.29–2.7] with strong
 289 Eu negative anomalies ($\delta\text{Eu} = 0.006\text{--}0.06$) and contains the highest ΣREE (1255–5059 ppm), Y
 290 (616–1416 ppm), Nb (585–2629 ppm), Ta (14–248 ppm) and lowest Mo (mostly < 1000 ppm)
 291 contents among all generations of scheelites (Figs. 11a and 12). The Sch_C 3 exhibits slightly
 292 rightward-sloping [(La/Yb)_N = 4.0–67] and Eu-depleted ($\delta\text{Eu} = 0.03\text{--}0.36$) REE patterns (Figs.
 293 11b and 12a), while the Sch_C 4 is LREE-enriched and HREE-depleted [(La/Yb)_N = 338–4332]
 294 with negligible Eu anomalies ($\delta\text{Eu} = 0.81\text{--}2.5$) (Figs. 11c and 12a). The Sch_M 3 displays mildly
 295 HREE-enriched to HREE-depleted [(La/Yb)_N = 0.07–17] and strongly Eu-depleted ($\delta\text{Eu} =$
 296 0.001–0.13) REE patterns (Figs. 11d and 12a) whereas the Sch_M 4 is enriched in LREEs and
 297 depleted in HREEs [(La/Yb)_N = 22–238] with weak Eu anomalies ($\delta\text{Eu} = 0.58\text{--}4.9$) (Figs. 11e
 298 and 12a). The (La/Yb)_N ratios of the Sch_C 3 and Sch_C 4 are higher than those of the Sch_M 3 and
 299 Sch_M 4, respectively (Fig. 12a). The Mg contents of the Sch_C 3 (12–96 ppm) and Sch_C 4 (2.6–13
 300 ppm) are distinctly lower than those of the Sch_M 3 (up to 16729 ppm) and Sch_M 4 (up to 13565
 301 ppm) (Table S4). The Sch_C 4 and Sch_M 4 contain significantly less ΣREE , Y, Nb, and Ta than the
 302 Sch_C 3 and Sch_M 3 (Fig. 12b and c). Notably, the scheelite Mn content is negatively correlated to
 303 the scheelite Mo content (Fig. 12d).

304 6. Discussion

305 6.1. REE substitution mechanisms

306 The substitution mechanisms of REEs in skarn garnets mainly include (1) $\text{X}^{2+} + \text{Si}^{4+} =$
 307 $\text{REE}^{3+} + \text{Z}^{3+}$; (2) $\text{X}^{2+} + \text{Y}^{3+} = \text{REE}^{3+} + \text{Y}^{2+}$; (3) $2\text{X}^{2+} = \text{REE}^{3+} + \text{X}^{+}$; and (4) $3\text{X}^{2+} = 2\text{REE}^{3+} +$
 308 \square_{X} , where X^{+} , X^{2+} , Y^{2+} , Y^{3+} , Z^{3+} are essentially Na^{+} , Ca^{2+} , Mg^{2+} or Fe^{2+} , Fe^{3+} or Al^{3+} , Al^{3+} ,
 309 respectively, and \square_{X} represents a X-site vacancy (Ismail et al., 2014; Fei et al., 2019; Tian et al.,

310 2019). There is no correlation between the Na and $\Sigma\text{REE-Eu+Y}$ contents of the Weijia garnets
 311 (Table S3), suggesting that the incorporation of REEs did not follow the Eq. (3). The positive
 312 $\Sigma\text{REE-Eu+Y}$ vs. Mg correlation of the Grt_C 1 ($\text{Ca}^{2+} + \text{Fe}^{3+} = \text{REE}^{3+} + \text{Mg}^{2+}$, Fig. 13a) and
 313 negative $\Sigma\text{REE-Eu+Y}$ vs. Al correlation of the Grt_C 3 ($\text{Ca}^{2+} + \text{Al}^{3+} = \text{REE}^{3+} + \text{Fe}^{2+}$, Fig. 13b) are
 314 indicative of the mechanism (2), i.e., the menzerite-type substitution (Grew et al., 2010). The
 315 mechanism (1), i.e., the yttr garnet (YAG)-type substitution, is common for Al-rich garnets (e.g.,
 316 Jaffe, 1951; Røhr et al., 2007; Yang et al., 2013) and favors incorporating HREEs. Tm (0.994 Å),
 317 Yb (0.985 Å), and Lu (0.977 Å) have almost the ideal REE³⁺ radius (0.99 Å) for this type of
 318 substitution (Ding et al., 2018; ionic radii from Shannon, 1976, the same below). The
 319 Tm-Yb-Lu-upwarped REE patterns (Fig. 9c and d) and grossularitic compositions (Fig. 8b) of the
 320 Grt_M 1 and Grt_M 3 accord with the YAG-type substitution. The \square_{X} -involved substitution
 321 mechanism is difficult to evaluate but cannot be absolutely excluded (Gaspar et al., 2008; Fei et
 322 al., 2019).

323 The substitution of REEs into scheelite is dominated by the following three mechanisms: (1)
 324 $\text{Ca}^{2+} + \text{W}^{6+} = \text{REE}^{3+} + \text{Nb}^{5+}$; (2) $2\text{Ca}^{2+} = \text{REE}^{3+} + \text{Na}^{+}$; (3) $3\text{Ca}^{2+} = 2\text{REE}^{3+} + \square_{\text{Ca}}$, where \square_{Ca} is
 325 a Ca-site vacancy (Ghaderi et al., 1999; Song et al., 2014; Sun and Chen, 2017). The correlational
 326 plots of Nb+Ta and Na vs. $\Sigma\text{REE-Eu+Y}$ contents (Fig. 14a and b) reveal that the incorporation of
 327 REEs into the Sch_Q 2, Sch_C 3, and Sch_M 3 followed principally the Eq. (1) and subordinately the
 328 Eq. (2), while the Sch_C 4 and Sch_M 4 accommodated REEs only through the mechanism (1). Both
 329 the 1:1 atomic ratios of Nb+Ta+Na to $\Sigma\text{REE-Eu+Y}$ of the Sch_Q 2, Sch_C 3, and Sch_M 3 (Fig. 14c)
 330 and Nb+Ta to $\Sigma\text{REE-Eu+Y}$ of the Sch_C 4 and Sch_M 4 (Fig. 14a) preclude the possibility of the
 331 \square_{Ca} -involved substitution.

332 6.2. Two-stage fluid exsolution during magmatic evolution

333 Experiments on the fluid-melt distribution of F and Cl show that F is relatively concentrated
334 in granitic melts and that Cl strongly partitions into aqueous fluids (London et al., 1988; Webster
335 and Holloway, 1988, 1990; Webster, 1992). Therefore, in a F- and Cl-bearing
336 magmatic-hydrothermal system, the Cl-rich fluids tend to exsolve earlier than the F-rich fluids
337 during magmatic evolution. According to the variations of biotite Cl/F ratios and fluorite REE
338 tetrad effects, Berni et al. (2017) recognized an earlier Cl-rich fluid exsolution at the transition
339 from less evolved porphyritic granite to more evolved equigranular granite and a later F-rich fluid
340 exsolution at the stage of equigranular granite and stockscheider pegmatite in the Kymi topaz
341 granite stock, south Finland. Audétat et al. (2000) carried out in-situ compositional analyses of
342 melt and fluid inclusions and Rayleigh fractionation modeling to constrain the late magmatic to
343 early hydrothermal evolution of the Sn-W-F-mineralized Mole granite, eastern Australia. They
344 propounded that in the fractionating Mole granite the earlier exsolved fluids are Cl-rich and more
345 enriched in Sn whereas the later exsolved fluids are F-rich and more enriched in W.

346 The occurrence of abundant fluorite and the other F-rich minerals including sellaite, garnet
347 (Table S1), vesuvianite, phlogopite (Table S6), and serpentine in the Weijia W skarn deposit
348 (Huang, 2018) evidently demonstrates that the ore-forming fluids are F-enriched and were
349 exsolved from F-rich granitic magmas. To quantitatively evaluate the F activities of ore-forming
350 fluids, the compositions of biotite in the Weijia granite porphyry are used to calculate the fluid
351 HF concentrations by the biotite fluorimeter of Aksyuk (2000). There are two types of biotites in
352 the granite porphyry, one is relatively fresh (Fig. 4a) and the other is altered (Fig. 4d). The fresh
353 biotite has F contents of 2.42–4.84 wt% (Table S6) and yields fluid HF concentrations of $10^{-1.3}$ to
354 $10^{-1.0}$ mol/L that are comparable to those of the F-rich Aqshatau and Qysylrai leucogranites,
355 Central Kazakhstan (Aksyuk, 2000). The F contents of the altered biotite are 0.32–1.95 wt%

356 (Table S6) and the corresponding fluid HF concentrations are $10^{-2.3}$ to $10^{-1.5}$ mol/L which
357 resemble those of the F-rich Grenvillian pegmatites, Canada (Aksyuk, 2000).

358 Fluorine will dramatically reduce the viscosity and minimum liquidus temperature of silicate
359 melts (Manning, 1981; Dingwell et al., 1985) and protract the process of fractional crystallization
360 and then facilitate W enrichment in the residual melts (Keppler and Wyllie, 1991; Audétat et al.,
361 2000). The Weijia granite porphyry exhibits obvious variations of major and trace element
362 compositions, for example, the Mg/(Mg+Fe) ratio varies from 0.07 to 0.64 and the Rb/Sr ratio
363 varies from 8.8 to 22.4 (Fig. 15). The increasing Rb/Sr ratio with decreasing Mg/(Mg+Fe) ratio
364 denotes a magmatic evolutionary trend and manifests that the Weijia granite porphyry is a
365 fractionated granite (Fig. 15).

366 The replacement of the Grt_C 1 and Px_C 1 by fluorite (Fig. 5b) suggests that the stage-1 skarn
367 minerals were formed earlier than the influx of F-rich magmatic-hydrothermal fluids. Whether in
368 the calcic or magnesian skarn, the stage-1 garnet contains less F than the stage-3 garnet (Table
369 S1), implying relatively F-poor compositions of the stage-1 fluids. Significantly, the occurrence
370 of Cl-rich marialite in the stage-1 magnesian skarn (Fig. 5h) indicates that the stage-1 fluids are
371 probably Cl-rich. Analyses of trace elements in fluid inclusions have revealed that the Cl-rich
372 magmatic-hydrothermal fluids are normally LREE-enriched and HREE-depleted with negative
373 Eu anomalies (e.g., Norman et al., 1989; Ghazi et al., 1993; Banks et al., 1994). The Grt_M 1
374 shows rightward-sloping and Eu-depleted REE patterns and has distinctly higher LREE/HREE
375 ratios than both the granite porphyry and host dolostone (Fig. 9c), supporting that the stage-1
376 skarnization was induced by the input of Cl-rich hydrothermal fluids which were exsolved earlier
377 than the F-rich hydrothermal fluids from the evolved granitic magmas.

378 The REE characteristics of F-rich hydrothermal fluids that are intimately associated with
379 highly fractionated granites (e.g., Audétat et al., 2000; Berni et al., 2017) remain poorly

380 understood. The earliest-crystallized scheelites in various magmatic-hydrothermal deposits
381 frequently exhibit comparable REE patterns to the associated granitoids and record the
382 information of initial ore-forming fluids (e.g., [Sun and Chen, 2017](#); [Li et al., 2018](#); [Su et al.,](#)
383 [2019](#); [Sun et al., 2019](#)). The earliest-formed Sch_Q 2 that coexists with fluorite in the Weijia W
384 skarn deposit shows flat REE patterns without obvious LREE/HREE fractionation and is strongly
385 depleted in Eu ([Fig. 11a](#)). These signatures are identical to those of the host granite porphyry
386 ([Fig. 11a](#)). Compared with the stage-3 and stage-4 scheelites ([Fig. 11b–e](#)), the Sch_Q 2 might have
387 reflected the features of primary F-rich mineralizing fluids.

388 Experimental data for the partition coefficients of REEs between scheelite and hydrothermal
389 fluids (DSch/fluid REEs) are not available. [Brugger et al. \(2000\)](#) estimated apparent DSch/fluid
390 REEs values for the scheelite involving Na-coupled REE substitution in orogenic gold deposits.
391 The ideal REE³⁺ radius for the Nb-coupled substitution (1.06 Å, [Sun et al., 2019](#)) is the same as
392 that for the Na-coupled substitution (1.06 Å, [Ghaderi et al., 1999](#)). Thus, it can be speculated that
393 these two mechanisms of REE substitution will bring about comparable variation trends of
394 DSch/fluid REEs from La to Lu. Using the minimum (model 1) and maximum (model 2)
395 DSch/fluid REEs values of [Brugger et al. \(2000\)](#), the REE compositions of primary F-rich
396 magmatic fluids in equilibrium with the Sch_Q 2 are calculated with presumed fluid Eu²⁺/Eu³⁺
397 ratios of 0.4, 4, and 40 (Table S7). As shown in [Fig. 11f](#), the primary F-rich magmatic fluids are
398 inferred to have similar LREE/HREE fractionation to the granite porphyry but with overall higher
399 ΣREE concentrations.

400 Alternatively, the REE compositions of primary F-rich magmatic fluids can also be acquired
401 based on the compositions of granitic melts and the DFluid/melt REEs. However, most
402 DFluid/melt REEs data are applicable to Cl-rich hydrothermal fluids (e.g., [Flynn and Burnham,](#)
403 [1978](#); [Kravchuk et al., 1995](#); [Reed et al., 2000](#)). Considering that the primary mineralizing fluids

404 mimic the fluoride hydrosaline melts in F- and W-enriched signatures (Veksler, 2005), the
405 minimum liquid-liquid DFluoride/silicate REEs values of Veksler et al. (2012) are adopted as the
406 DFluid/melt REEs. Because both LREE-enriched minerals (e.g., monazite, parisite, and apatite)
407 and HREE-enriched minerals (e.g., xenotime, samarskite, and fergusonite) were crystallized
408 probably before the exsolution of F-rich fluids, the REE compositions of granitic melts in
409 equilibrium with exsolving F-rich fluids are calculated by subtracting hypothetical proportions of
410 10%, 50%, and 80% REEs from the granite porphyry (Table S7). As a consequence, the inferred
411 F-rich magmatic-hydrothermal fluids (model 3) show similar REE patterns to the granite
412 porphyry but with higher Σ REE concentrations as well (Fig. 11f).

413 Theoretical prediction advocates that in aqueous solutions the chloride complexes of LREEs
414 are more stable than those of HREEs whereas the fluoride complexes of HREEs are more stable
415 than those of LREEs (Wood, 1990; Haas et al., 1995). The experimental study of Tsay et al.
416 (2014) also has revealed that the Cl-rich and F-rich aqueous fluids prefer to dissolve LREEs and
417 HREEs, respectively. The Cl-rich fluids have higher DFluid/melt LREEs and lower DFluid/melt
418 HREEs (Flynn and Burnham, 1978; Kravchuk et al., 1995; Reed et al., 2000) and generally
419 exhibit stronger LREE/HREE fractionation than the related granitoids (e.g., Banks et al., 1994).
420 The F-rich fluids tend to have lower LREE/HREE ratios than the Cl-rich fluids and display
421 similar REE patterns to the associated granites. Therefore, it can be concluded that in the Weijia
422 W skarn deposit the earlier exsolved Cl-rich fluids are LREE-enriched and HREE-depleted
423 whereas the later exsolved F-rich fluids have relatively flat REE patterns without obvious
424 LREE/HREE fractionation.

425 **6.3. Diffusive vs. advective metasomatism and skarn formation**

426 The formation of a skarn deposit generally includes the following four stages: (1) wall-rock
427 metamorphism; (2) wall rock-controlled reaction skarn/skarnoid by metamorphic recrystallization

428 and diffusive metasomatism; (3) magmatic fluid-controlled metasomatic skarn by advective
429 metasomatism; (4) retrograde alteration of the metamorphic and metasomatic calc-silicate
430 assemblages possibly involving exotic fluids (Einaudi et al., 1981; Meinert et al., 2005). The
431 diffusive metasomatism is driven by the chemical potential gradients in pore solutions under low
432 water/rock (W/R) ratios and is inefficient in the transport of components, while the advective
433 metasomatism is characterized by pressure gradient-forced fluid flow along percolation paths
434 under high W/R ratios and can efficiently transport the chemical components (Korzhinskii, 1968;
435 Joesten, 1977; Norton, 1987; Zharikov and Rusinov, 1998). Fracturing of rocks at depth in the
436 crust will generate elevated permeability and facilitate the high fluid flux necessary to produce
437 mineralized skarn system by advective metasomatism (Cox, 2005; Rubenach, 2013). The change
438 in hydrothermal dynamics during fluid-rock interaction will result in significant compositional
439 variation of skarn minerals (e.g., Gaspar et al., 2008; Wen et al., 2020).

440 The Grt_C 1 from the Weijia W deposit shows mildly LREE-enriched and HREE-depleted
441 REE patterns without obvious Eu anomalies (Fig. 9a). These signatures are identical to those of
442 the host limestone (Fig. 9a). The Grt_C 1 is also akin to the host limestone in Σ REE contents
443 although some grains are slightly richer in REEs (Fig. 9a). It is evident that the stage-1 calcic
444 skarn is dominantly controlled by wall-rock compositions. The distinctly higher W contents of
445 the Grt_C 1 than those of the host limestone (Fig. 10b) and the slightly higher Σ REE contents of
446 some Grt_C 1 grains (Fig. 9a) support an input of magmatic fluids, but the W/R ratio should be
447 low. Combined with the disseminated occurrence of the Grt_C 1 (Fig. 3c and d), it is concluded
448 that the stage-1 calcic skarnization was facilitated by diffusive metasomatism.

449 Compared with the host dolostone, the Grt_M 1A has distinctly higher LREE contents and
450 clearer Eu depletions but similar HREE (Gd–Er) contents except for the upward convex of
451 Tm–Yb–Lu (Fig. 9c) which is ascribed to the YAG-type REE substitution, indicating involvement

452 of more Cl-rich magmatic fluids during the formation of the Grt_M 1A relative to the Grt_C 1. The
453 generation of cracks in wall rocks will cause a drop of fluid pressure which in turn lead to the
454 infiltration of magmatic fluids along the cracks down pressure gradient with higher W/R ratios.
455 The Grt_M 1A is distributed within the stockwork veinlets that are favorable for the influx of
456 magmatic fluids. The increasing Σ REE contents and intensifying Eu negative anomalies from the
457 Grt_M 1A to the Grt_M 1B (Fig. 9c) are symptomatic of an elevating W/R ratio. From the host
458 dolostone through the Grt_M 1A to the Grt_M 1B, the greater increase of LREEs relative to that of
459 HREEs (Fig. 9c) signifies that the REEs entering the Grt_M 1 retain the LREE-enriched and
460 HREE-depleted features of the Cl-rich magmatic fluids. This likely reflects a disequilibrium state
461 between the Grt_M 1 and Cl-rich fluids because the grossularitic garnet equilibrated with fluids can
462 be theoretically predicted to display smaller increase in LREEs than that in HREEs owing to the
463 strikingly lower DGr_s/fluid LREEs and higher DGr_s/fluid HREEs (Smith et al., 2004; Gaspar et
464 al., 2008; Xu et al., 2020). The disequilibrium crystallization was probably induced by rapid
465 growth of garnet which will commonly result in oscillatory zonation, such as those observed in
466 the Grt_C 1 and Grt_M 1A (Fig. 6a and e), on account of the dynamic interaction between the
467 growing garnet and the surface layer (Smith et al., 2004; Gaspar et al., 2008; Park et al., 2017;
468 Xiao et al., 2018; Fei et al., 2019).

469 In contrast to the host limestone and dolostone, the Grt_C 3 and Grt_M 3 exhibit distinctly
470 higher HREE contents and stronger Eu depletions (Fig. 9b and d) which are apparently affinitive
471 with the F-rich magmatic fluids (Fig. 11f), manifesting a dominant control of magmatic fluids on
472 the formation of the stage-3 skarns. Combined with the stockwork occurrence of the Grt_C 3 (Fig.
473 3c and d) and the inside-stockwork distribution of the Grt_M 3, it is evident that the stage-3
474 skarnization was promoted by advective metasomatism in fluid-dominant environments with high
475 W/R ratios. The chaotic boundary between the Grt_M 3A and Grt_M 3B (Fig. 6f) is suggestive of a

476 turbulent hydrothermal dynamic state, supporting fluid advection as well. The Grt_M 3A replaces
477 the Grt_M 1B (Fig. 6d and e) and thus the high contents of LREEs in the Grt_M 3A (Fig. 9d) are in
478 all probability inherited from the Grt_M 1B (Fig. 9c). The REE patterns of the Grt_M 3B and Grt_C 3
479 present striking depletions of LREEs with low (La/Sm)_N ratios and relatively flat HREE shapes
480 (Figs. 9b, d and 10a). They are consistent with the variation trends of DGrt/fluid REEs from La to
481 Lu for Al-rich to intermediate grandite (Smith et al., 2004; Gaspar et al., 2008; Xu et al., 2020),
482 indicating an equilibrium state between the Grt_C 3 and Grt_M 3B and the F-rich magmatic fluids.
483 The absence of oscillatorily zoned texture in the Grt_C 3 and Grt_M 3B (Fig. 6b and f) is possibly
484 reflective of relatively low growth rates that are beneficial to the equilibrium with fluids. The
485 lower (La/Sm)_N ratios and higher HREE contents of the grossularitic Grt_M 3B than those of the
486 less Al-rich Grt_C 3 (Figs. 9b, d and 10a) can be well explained by the steeper increase of
487 DGrt/fluid LREEs from La to Sm and higher DGrt/fluid HREEs for more Al-rich grandite (Smith
488 et al., 2004; Xu et al., 2020).

489 The stage-4 skarnization is mainly presented as stockwork pyroxene in the calcic skarn (Fig.
490 3c and d) and stockwork phlogopite and serpentine in the magnesian skarn (Fig. 3e and f) and is
491 much more extensive than the stage-3 skarnization (Fig. 3d–f). The stage-4 skarns contain much
492 more hydrous minerals (phlogopite, serpentine, and chlorite, etc.) than the stage-3 skarns. These
493 differences evidently manifest that the stage-4 skarns were formed through more intense
494 fluid-rock interaction by advective metasomatism. Remarkably, the magnesian skarn is more
495 enriched in volatiles relative to the calcic skarn. The magnesian skarn garnet is richer in F than
496 the calcic skarn garnet in the same stage (Table S1) and the stage-4 magnesian skarn contains
497 much more hydrous minerals (phlogopite and serpentine, Fig. 5e–h) than the stage-4 calcic skarn
498 (chlorite, Fig. 5d), implying a higher W/R ratio for the magnesian skarnization relative to the

499 calcic skarnization. This is probably related to the greater depth of the magnesian skarn (Fig. 2)
500 and thus the volatile components are more difficult to escape under elevated pressure conditions.

501 **6.4. Fluid evolution and W skarn mineralization**

502 Numerous previous studies have revealed that the changes in fluid compositions and
503 physicochemical conditions (e.g., P, T, f_{O_2} , and pH) by fluid-rock interaction, mineral
504 precipitation, fluid mixing, natural cooling, and structural depressurization essentially control the
505 process of skarn mineralization (e.g., Baker et al., 2004; Ismail et al., 2014; Xiao et al., 2018;
506 Ryan-Davis et al., 2019; Tian et al., 2019; Chen et al., 2020b). Probably multi-stage fluid
507 exsolution is another critical factor affecting the skarn ore-forming process. Experimental
508 investigations show that W partitions in favor of the melts with high F concentrations (Manning
509 and Henderson, 1984; Keppler and Wyllie, 1991) and the addition of Cl will not change the
510 DFluid/melt W (Wood and Vlassopoulos, 1989; Keppler and Wyllie, 1991). Recently, Wang et
511 al. (2021) found that W is dissolved predominantly as H_3WO_4F-2 in F-rich aqueous solutions.
512 Hence, the W concentration in the residual melts would not be reduced until the extensive
513 exsolution of F-rich fluids. The earlier exsolved Cl-rich fluids is generally relatively poor in W
514 and are not beneficial to W mineralization (e.g., Audétat et al., 2000). The high contents of W in
515 the Grt_C 1 (up to 1181 ppm, Fig. 10b) are attributed to its andraditic compositions instead of
516 reflecting a high W concentration in the Cl-rich fluids. The W and andradite contents of the
517 Weijia garnets display a clear positive correlation (Fig. 10b). Such positive correlation is also
518 frequently observed in other skarn deposits (e.g., Park et al., 2017; Ding et al., 2018; Fei et al.,
519 2019; Chen et al., 2020b). The grossularitic Grt_M 1 has very low W contents (as low as 0.42 ppm,
520 Fig. 10b). Thus, in the Weijia W skarn deposit, the earlier exsolution of Cl-rich magmatic fluids

521 had not led to the precipitation of scheelite and the W mineralization dominantly followed the
522 later exsolution of F-rich magmatic fluids.

523 The existence of fluorine in magmatic-hydrothermal fluids has a significant effect on the
524 fluid nature. Fluorine is a hard base (ligand) in the Pearson classification and prefers to bond
525 electrostatically to form aqueous complexes with hard acids, such as REEs, Y, Nb, and Ta,
526 thereby raising the solubilities of these elements in aqueous solutions (Wood, 1990; Haas et al.,
527 1995; Zaraisky et al., 2010; Linnen et al., 2014; Tsay et al., 2014; Timofeev et al., 2015, 2017).
528 Therefore, REEs, Y, Nb, and Ta will partition considerably into the fluid phase during the
529 exsolution of F-rich hydrothermal fluids. The Sch_Q 2 has remarkably higher Σ REE, Y, Nb, and Ta
530 contents than the stage-3 and stage-4 scheelites (Fig. 12b and c) and also most scheelites from
531 other magmatic-hydrothermal deposits (e.g., Li et al., 2018; Poulin et al., 2018; Zhang et al.,
532 2018; Zhao et al., 2018; Sun et al., 2019), corroborating that the primary F-rich mineralizing
533 fluids are enriched in these trace elements.

534 The low Ce^{4+}/Ce^{3+} ratios (0.94–10) and δEu values (0.02–0.55) of zircon from the Weijia
535 granite porphyry manifest a low magmatic oxygen fugacity (f_{O_2}) (Zhao et al., 2016). The Mo
536 content of scheelite is an effective redox proxy and the low scheelite Mo contents indicate
537 relatively reducing conditions since oxidized Mo (Mo^{6+} , 0.41 Å) tends to enter the scheelite
538 lattice by substituting for W^{6+} (0.42 Å) whereas reduced Mo (Mo^{4+} , 0.65 Å) does not (Song et al.,
539 2014; Poulin et al., 2018; Han et al., 2020). The Mo contents of the Sch_Q 2 (mostly < 1000 ppm,
540 Fig. 12d) are much lower than those formed under oxidizing conditions (e.g., King Island) and
541 are similar to those formed under reducing conditions (e.g., Shimensi) (Fig. 6 in Sun and Chen,
542 2017), suggesting a reducing condition. Manganese is a redox-sensitive element and Mn^{2+} (0.96
543 Å) is readily to substitute for Ca^{2+} (1.12 Å) in scheelite (Poulin et al., 2018). The negative

544 correlation between the Mn and Mo contents of the Weijia scheelites (Fig. 12d) implies that the
545 Mn content of scheelite is a potential redox proxy, with high scheelite Mn contents pointing to
546 relatively reducing conditions, just as the Mn-in-apatite oxybarometer (Miles et al., 2014). The
547 Sch_Q 2 contains up to 1977 ppm Mn (Fig. 12d) which is distinctly higher than the scheelite Mn
548 contents of various deposit types (< 100 ppm) compiled by Poulin et al. (2018), supporting a
549 reducing condition as well. In combination with the coexistence between the Sch_Q 2 and
550 molybdenite (Mo⁴⁺) (Fig. 7a), it is concluded that the primary F-rich magmatic fluids are
551 reduced.

552 The assemblage of andraditic Grt_C 1 (Fe exists as Fe³⁺, Fig. 8a) and diopsidic Px_C 1 (Fig. 8c)
553 in the limestone implies a relatively oxidizing environment (Meinert et al., 2005). However, the
554 Cl-rich fluids derived from the reduced granitic magmas can be expected to be reduced. The Sch_C
555 3 and Sch_M 3 within the carbonate strata have higher Mo and lower Mn contents than the Sch_Q 2
556 within the granite porphyry (Fig. 12d), denoting an elevating fluid f_{O_2} during the interaction
557 between the reduced F-rich magmatic fluids and the carbonate strata. Hence, it is deduced that
558 there was a storage of oxidizing fluids in the carbonate wall rocks. In all probability, the
559 oxidizing fluids at a shallow crustal level were meteoric waters that are commonly involved in
560 the formation of skarn deposits (Einaudi et al., 1981; Meinert et al., 2005, e.g., Zhao et al., 2018;
561 Park et al., 2019; Ryan-Davis et al., 2019). The change of REE substitution mechanism from
562 $Ca^{2+} + Fe^{3+} = REE^{3+} + Mg^{2+}$ for the andraditic Grt_C 1 (Fig. 13a) to $Ca^{2+} + Al^{3+} = REE^{3+} + Fe^{2+}$ for
563 the less Fe-rich Grt_C 3 (Fig. 13b) signifies the transition of a Fe³⁺-dominant state into a
564 Fe²⁺-prevalent state of the Fe in fluids and thus a depressing fluid f_{O_2} . The fluid f_{O_2} depends on
565 the relative proportions of the reduced magmatic fluids and the oxidized meteoric waters. The

566 reduction of fluids from the stage-1 to stage-3 skarnization is consistent with the increasing influx
567 of reduced magmatic fluids as discussed above.

568 The Sch_C 3 and Sch_M 3 are comparable to the Sch_Q 2 in REE patterns (Fig. 11a–b and d) and
569 REE substitution mechanisms (Fig. 14), manifesting that the stage-3 fluids are inherited from the
570 stage-2 fluids. Nevertheless, the lower Σ REE, Y, Nb, and Ta contents of the Sch_C 3 and Sch_M 3
571 than those of the Sch_Q 2 (Fig. 12b and c) indicate that the stage-3 fluids are relatively evolved
572 than the stage-2 fluids. On the one hand, the precipitation of fluorite during the stage 2 consumed
573 a fraction of F which would depress the solubilities of REEs, Y, Nb, and Ta in fluids. On the
574 other hand, the Sch_Q 2 had taken away a certain amount of these trace elements. The Sch_C 3 and
575 Sch_M 3 coexist with the stage-3 garnets (Figs. 5c, e and 6b, d–e). The coexisting garnets that
576 contain REEs, Y, Nb, and Ta (Table S3) partly account for the lower contents of these trace
577 elements in the Sch_C 3 and Sch_M 3 relative to those in the Sch_Q 2 (Fig. 12b and c). The Grt_C 3 is
578 depleted in LREEs (Fig. 9b), therefore, the coexisting Sch_C 3 has higher (La/Yb)_N ratios than the
579 Sch_Q 2 (Figs. 11a–b and 12a). The Grt_M 3A and Grt_M 3B display relatively flat and
580 LREE-depleted REE patterns, respectively (Fig. 9d), as a result, some grains of the coexisting
581 Sch_M 3 have similar (La/Yb)_N ratios to the Sch_Q 2 and some grains show higher (La/Yb)_N ratios
582 than the Sch_Q 2 (Figs. 11a, d and 12a).

583 The Sch_C 4 and Sch_M 4 have strikingly lower Σ REE, Y, Nb, and Ta contents than the Sch_Q 2,
584 Sch_C 3, and Sch_M 3 (Fig. 12b and c). Compared with the stage-2 and stage-3 scheelites, the
585 stage-4 scheelites are strongly HREE-depleted without obvious Eu anomalies and apparently
586 deviate from the primary F-rich magmatic fluids in REE patterns (Fig. 11). These differences
587 signify that the stage-4 scheelites were crystallized from evidently evolved mineralizing fluids.
588 The scheelite precipitated from oxidized fluids will produce a diagonal Eu_N vs. Eu* N array with
589 a slope of +1 as Eu³⁺ follows Sm³⁺ and Gd³⁺, while the scheelite crystallized in reduced fluids

590 will yield a horizontal array because Eu^{2+} is decoupled from Sm^{3+} and Gd^{3+} (Ghaderi et al.,
591 1999). As clearly shown in Fig. 16, the $\text{Sch}_C 4$ and $\text{Sch}_M 4$ were formed in the fluids with $\text{Eu}^{3+} \gg$
592 Eu^{2+} , manifesting that the evolved stage-4 fluids are oxidized. The increasing Mo contents from
593 the $\text{Sch}_C 3$ to $\text{Sch}_C 4$ and the decreasing Mn contents from the $\text{Sch}_M 3$ to $\text{Sch}_M 4$ (Fig. 12d) also
594 support an elevating fluid f_{O_2} . The oxidation of fluids from the stage-3 to stage-4 skarnization
595 reflects an increasing influx of meteoric waters during the process of fluid evolution.

596 Both the Nb and Ta solubilities in fluids decrease with decreasing F concentration at high-F
597 conditions and are constant at low-F conditions, and the Ta solubility is lower than the Nb
598 solubility at the same F content and shifts into the constant state more readily than the latter with
599 decreasing F concentration (Timofeev et al., 2015, 2017). In the Weijia W deposit, the Nb and Ta
600 contents of the $\text{Sch}_Q 2$, $\text{Sch}_C 3$, and $\text{Sch}_M 3$ are concurrently decreasing, while the Ta contents of
601 the $\text{Sch}_C 4$ and $\text{Sch}_M 4$ are almost constant as the Nb contents decrease (Fig. 12c), implying that
602 the stage-4 fluids are relatively depleted in F than the stage-2 and stage-3 fluids. The phlogopite
603 in the stage-4 magnesian skarn has F contents of 2.65–6.88 wt% (Table S6). Using the phlogopite
604 fluorimeter of Aksyuk (2000), the HF concentrations of the stage-4 fluids are estimated to be 10^{-
605 3.0 to $10^{-2.6}$ mol/L and are distinctly lower than those of the primary F-rich magmatic fluids ($10^{-2.3}$
606 to $10^{-1.0}$ mol/L), revealing a decreased fluid F activity. The consumption of fluorine by the
607 formation of fluorite and the other F-rich minerals largely controls the compositional evolution of
608 the F-rich ore-forming fluids. The decrease of F concentration can depress the solubilities and
609 thus the concentrations of REEs, Y, Nb, and Ta in fluids. Moreover, the reduced F concentration
610 in fluids would lead to stronger depletions of HREEs than those of LREEs since the influence of
611 F on the solubilities of HREEs is stronger than those of LREEs (Wood, 1990; Haas et al., 1995;
612 Tsay et al., 2014).

613 The Grt_C 3, Grt_M 3, Sch_C 3, and Sch_M 3 contain considerable amounts of REEs, Y, Nb, Ta
 614 and are all obviously Eu-depleted (Figs. 9, 11, 12 and Table S3). The crystallization of the
 615 stage-3 garnets and scheelites would cause the depletions of REEs, Y, Nb, Ta and a relative
 616 enrichment of Eu in the remaining stage-4 fluids. The increasing influx of meteoric waters would
 617 dilute the mineralizing fluids and raise the DSch/fluid Eu due to the elevating fluid f_{O_2} (Brugger
 618 et al., 2000; Li et al., 2018). The relative enrichment of Eu in the stage-4 fluids and the increased
 619 DSch/fluid Eu account for the increased δEu values of the Sch_C 4 and Sch_M 4 (Fig. 12a). The
 620 HREE-depleted signature of the Sch_C 4 (Fig. 11c) is partly ascribed to its coexisting Px_C 4 owing
 621 to the lower DCpx/fluid LREEs and higher DCpx/fluid HREEs (Zhao et al., 2018; Wen et al.,
 622 2020). The existence of the Px_C 4 is also responsible for the higher (La/Yb)_N ratios of the Sch_C 4
 623 than those of the Sch_M 4 (Fig. 12a).

624 Scheelite precipitation is commonly considered as a result of fluid-rock interaction (e.g.,
 625 Song et al., 2014; Sun and Chen, 2017; Li et al., 2018; Zhang et al., 2018; Sun et al., 2019; Han
 626 et al., 2020). We propound that the neutralization of acidic magmatic fluids and the release of Ca
 627 from host rocks during fluid-rock interaction are critical for the precipitation of scheelite in the
 628 Weijia W deposit. The W-bearing magmatic-hydrothermal fluids are generally acidic (Wood and
 629 Samson, 2000). It is well known that greisen is mostly the alteration product of granitic rocks by
 630 acidic F-rich magmatic fluids (Shcherba, 1970; Burt, 1981; Štemprok, 1987; Launay et al., 2021).
 631 The Sch_Q 2 within the granite porphyry is closely associated with greisenization, implying that
 632 the primary F-rich magmatic fluids in the Weijia W deposit should be acidic. Both the
 633 transformation of feldspars to muscovite during greisenization ($3KAlSi_3O_8 + 2H^+ =$
 634 $KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+$; $3NaAlSi_3O_8 + 2H^+ + K^+ = KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 3Na^+$;
 635 $3CaAl_2Si_2O_8 + 4H^+ + 2K^+ = 2KAl_3Si_3O_{10}(OH)_2 + 3Ca^{2+}$) and the decomposition of calcite and

636 dolomite during skarnization ($\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$; $\text{CaMg}(\text{CO}_3)_2 + 4\text{H}^+ = \text{Ca}^{2+} +$
637 $\text{Mg}^{2+} + 2\text{H}_2\text{O} + 2\text{CO}_2$) are acid-consuming reactions and raise the pH value of mineralizing
638 fluids. The variation of fluid pH largely controls the dominant tungsten species and also
639 significantly affects the tungsten solubility (Wood and Samson, 2000; Wang et al., 2019, 2021).
640 The solubility of scheelite in fluids with near-neutral pH is lower than those in acidic and alkaline
641 fluids, and thus near-neutral fluid pH condition is more beneficial to scheelite precipitation
642 (Wang et al., 2019). The precipitation of scheelite took place in both reducing (Sch_Q 2) and
643 oxidizing (Sch_C 4 and Sch_M 4) environments, therefore, the change of fluid f_{O_2} is not the trigger
644 for scheelite precipitation.

645 A sufficient supply of Ca is crucial for scheelite mineralization. The Weijia granite porphyry
646 has very low CaO contents (mostly < 1 wt%, Zhao et al., 2016; Huang et al., 2017; Wu et al.,
647 2021) and the plagioclase therein is albite (An < 5). The amount of Ca released through the weak
648 greisenization of granite porphyry is small. This could be decisive for the economic
649 unimportance of the scheelite-bearing stockwork quartz veinlets in the Weijia W deposit.
650 However, Ca is oversupplied by the carbonate wall rocks during the process of skarnization even
651 though large amounts of calc-silicate minerals and fluorite are formed. Hence, the economically
652 significant W mineralization of the Weijia W deposit dominantly occurs in the calcic and
653 magnesian skarns. Additionally, the decrease of fluid pressure by stockwork fracturing promoted
654 the liberation of Ca from the carbonate wall rocks by CO₂ escape and then facilitated the
655 scheelite mineralization, although the tungsten solubility is only weakly dependent on pressure
656 (Wood and Samson, 2000).

657 7. Conclusions

658 In this study, trace element geochemistry of garnet and scheelite is applied to constrain the
659 processes of fluid evolution and W skarn mineralization in the F-rich Weijia W deposit. We
660 advocate that a combined study of multiple minerals will provide us with a more comprehensive
661 view into the ore-forming processes. The main conclusions are summarized as follows:

662 (1) An earlier exsolution of Cl-rich magmatic fluids and a later exsolution of F-rich
663 magmatic fluids are recognized in the Weijia W skarn deposit. The Cl-rich fluids are
664 LREE-enriched and HREE-depleted and bring about pre-ore skarnization, while the F-rich fluids
665 have relatively flat REE patterns without obvious LREE/HREE fractionation and are responsible
666 for W mineralization;

667 (2) The process of skarn formation in the Weijia W deposit is characterized by a shift from
668 more diffusive to more advective metasomatism with an elevating water/rock ratio. The advective
669 metasomatism with a high flux of mineralizing fluids is hydrodynamically favorable for the
670 consequent ore deposition;

671 (3) The consumption of fluorine in the ore-forming fluids decreased the Σ REE, Y, Nb, Ta
672 concentrations and enhanced the LREE/HREE fractionation. The oxygen fugacity of ore-forming
673 fluids was increased with the influx of meteoric waters. Scheelite precipitation was triggered by
674 the neutralization of acidic W-bearing fluids and the liberation of Ca from host rocks through
675 fluid-rock interaction.

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685 **References**

- 686 Aksyuk, A.M., 2000. Estimation of fluorine concentrations in fluids of mineralized skarn
687 systems. *Econ. Geol.* 95, 1339–1347. <https://doi.org/10.2113/gsecongeo.95.6.1339>.
- 688 Audétat, A., Günther, D., Heinrich, C.A., 2000. Magmatic-hydrothermal evolution in a
689 fractionating granite: A microchemical study of the Sn-W-F-mineralized Mole Granite
690 (Australia). *Geochim. Cosmochim. Acta* 64, 3373–3393.
691 [https://doi.org/10.1016/S0016-7037\(00\)00428-2](https://doi.org/10.1016/S0016-7037(00)00428-2).
- 692 Baker, T., van Achterberg, E., Ryan, C.G., Lang, J.R., 2004. Composition and evolution of ore
693 fluids in a magmatic-hydrothermal skarn deposit. *Geology* 32, 117–120.
694 <https://doi.org/10.1130/G19950.1>.
- 695 Banks, D.A., Yardley, B.W.D., Campbell, A.R., Jarvis, K.E., 1994. REE composition of an
696 aqueous magmatic fluid: A fluid inclusion study from the Capitan Pluton, New Mexico,
697 U.S.A. *Chem. Geol.* 113, 259–272. [https://doi.org/10.1016/0009-2541\(94\)90070-1](https://doi.org/10.1016/0009-2541(94)90070-1).
- 698 Berni, G.V., Wagner, T., Fusswinkel, T., Wenzel, T., 2017. Magmatic-hydrothermal evolution of
699 the Kymi topaz granite stock, SE Finland: Mineral chemistry evidence for episodic fluid
700 exsolution. *Lithos* 292–293, 401–423. <https://doi.org/10.1016/j.lithos.2017.09.015>.
- 701 Boynton, W.V., 1984. Cosmochemistry of the rare earth elements: meteorite studies, in:
702 Henderson, P. (Ed.), *Rare Earth Element Geochemistry*. Elsevier, Amsterdam, pp. 63–114.
703 <https://doi.org/10.1016/B978-0-444-42148-7.50008-3>.
- 704 Brugger, J., Lahaye, Y., Costa, S., Lambert, D., Bateman, R., 2000. Inhomogeneous distribution
705 of REE in scheelite and dynamics of Archaean hydrothermal systems (Mt. Charlotte and
706 Drysdale gold deposits, Western Australia). *Contrib. Mineral. Petrol.* 139, 251–264.
707 <https://doi.org/10.1007/s004100000135>.
- 708 Burt, D.M., 1981. Acidity-salinity diagrams—application to greisen and porphyry deposits. *Econ.*

- 709 Geol. 76, 832–843. <https://doi.org/10.2113/gsecongeo.76.4.832>.
- 710 Carocci, E., Marignac, C., Cathelineau, M., Truche, L., Poujol, M., Boiron, M.-C., Pinto, F.,
711 2021. Incipient wolframite deposition at Panasqueira (Portugal): W-rutile and tourmaline
712 compositions as proxies for the early fluid composition. *Econ. Geol.* 116, 123–146.
713 <https://doi.org/10.5382/econgeo.4783>.
- 714 Černý, P., Blevin, P.L., Cuney, M., London, D., 2005. Granite-related ore deposits. *Economic*
715 *Geology 100th Anniversary Volume*, 337–370. <https://doi.org/10.5382/AV100.12>.
- 716 Chen, G.H., Gao, J.F., Lu, J.J., Zhang, R.Q., 2020a. In situ LA-ICP-MS analyses of mica and
717 wolframite from the Maoping tungsten deposit, southern Jiangxi, China. *Acta Geochim.* 39,
718 811–829. <https://doi.org/10.1007/s11631-020-00423-5>.
- 719 Chen, J., Lu, J.J., Chen, W.F., Wang, R.C., Ma, D.S., Zhu, J.C., Zhang, W.L., Ji, J.F., 2008.
720 W-Sn-Nb-Ta-bearing granites in the Nanling Range and their relationship to
721 metallogensis. *Geol. J. China Univ.* 14, 459–473 (in Chinese with English abstract).
722 <https://doi.org/10.3969/j.issn.1006-7493.2008.04.001>.
- 723 Chen, J., Wang, R.C., Zhu, J.C., Lu, J.J., Ma, D.S., 2013. Multiple-aged granitoids and related
724 tungsten-tin mineralization in the Nanling Range, South China. *Sci. China Earth Sci.* 56,
725 2045–2055. <https://doi.org/10.1007/s11430-013-4736-9>.
- 726 Chen, L., Qin, K.Z., Li, G.M., Li, J.X., Xiao, B., Zhao, J.X., 2020b. In situ major and trace
727 elements of garnet and scheelite in the Nuri Cu-W-Mo deposit, South Gangdese, Tibet:
728 Implications for mineral genesis and ore-forming fluid records. *Ore Geol. Rev.* 122, 103549.
729 <https://doi.org/10.1016/j.oregeorev.2020.103549>.
- 730 Cox, S.F., 2005. Coupling between deformation, fluid pressures, and fluid flow in ore-producing
731 hydrothermal systems at depth in the crust. *Economic Geology 100th Anniversary Volume*,
732 39–75. <https://doi.org/10.5382/AV100.04>.

- 733 Ding, T., Ma, D.S., Lu, J.J., Zhang, R.Q., 2018. Garnet and scheelite as indicators of multi-stage
734 tungsten mineralization in the Huangshaping deposit, southern Hunan province, China. *Ore*
735 *Geol. Rev.* 94, 193–211. <https://doi.org/10.1016/j.oregeorev.2018.01.029>.
- 736 Dingwell, D.B., Scarfe, C.M., Cronin, D.J., 1985. The effect of fluorine on viscosities in the
737 system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$: implications for phonolites, trachytes and rhyolites. *Am. Mineral.*
738 70, 80–87.
- 739 Einaudi, M.T., Meinert, L.D., Newberry, R.J., 1981. Skarn deposits. *Economic Geology* 75th
740 Anniversary Volume, 317–391. <https://doi.org/10.5382/AV75.11>.
- 741 Fei, X.H., Zhang, Z.C., Cheng, Z.G., Santosh, M., 2019. Factors controlling the crystal
742 morphology and chemistry of garnet in skarn deposits: A case study from the Cuihongshan
743 polymetallic deposit, Lesser Xing'an Range, NE China. *Am. Mineral.* 104, 1455–1468.
744 <https://doi.org/10.2138/am-2019-6968>.
- 745 Flynn, R.T., Burnham, C.W., 1978. An experimental determination of rare earth partition
746 coefficients between a chloride containing vapour phase and silicate melts. *Geochim.*
747 *Cosmochim. Acta* 42, 685–701. [https://doi.org/10.1016/0016-7037\(78\)90087-X](https://doi.org/10.1016/0016-7037(78)90087-X).
- 748 Gaspar, M., Knaack, C., Meinert, L.D., Moretti, R., 2008. REE in skarn systems: A LA-ICP-MS
749 study of garnets from the Crown Jewel gold deposit. *Geochim. Cosmochim. Acta* 72, 185–
750 205. <https://doi.org/10.1016/j.gca.2007.09.033>.
- 751 Ghaderi, M., Palin, J.M., Campbell, I.H., Sylvester, P.J., 1999. Rare earth element systematics in
752 scheelite from hydrothermal gold deposits in the Kalgoorlie-Norseman region, Western
753 Australia. *Econ. Geol.* 94, 423–437. <https://doi.org/10.2113/gsecongeo.94.3.423>.
- 754 Ghazi, A.M., Vanko, D.A., Roedder, E., Seeley, R.C., 1993. Determination of rare earth elements
755 in fluid inclusions by inductively coupled plasma-mass spectrometry (ICP-MS). *Geochim.*
756 *Cosmochim. Acta* 57, 4513–4516. [https://doi.org/10.1016/0016-7037\(93\)90500-V](https://doi.org/10.1016/0016-7037(93)90500-V).

- 757 Grew, E.S., Locock, A.J., Mills, S.J., Galuskina, I.O., Galuskin, E.V., Hålenius, U., 2013.
758 Nomenclature of the garnet supergroup. *Am. Mineral.* 98, 785–811.
759 <https://doi.org/10.2138/am.2013.4201>.
- 760 Grew, E.S., Marsh, J.H., Yates, M.G., Lazic, B., Armbruster, T., Locock, A., Bell, S.W., Dyar,
761 M.D., Bernhardt, H.-J., Medenbach, O., 2010. Menzerite-(Y), a new species,
762 $\{(Y,REE)(Ca,Fe^{2+})_2\}[(Mg,Fe^{2+})(Fe^{3+},Al)](Si_3)O_{12}$, from a felsic granulite, Parry Sound,
763 Ontario, and a new garnet end-member, $\{Y_2Ca\}[Mg_2](Si_3)O_{12}$. *Can. Mineral.* 48, 1171–
764 1193. <https://doi.org/10.3749/canmin.48.5.1171>.
- 765 Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare earth elements in hydrothermal systems:
766 Estimates of standard partial molal thermodynamic properties of aqueous complexes of the
767 rare earth elements at high pressures and temperatures. *Geochim. Cosmochim. Acta* 59,
768 4329–4350. [https://doi.org/10.1016/0016-7037\(95\)00314-P](https://doi.org/10.1016/0016-7037(95)00314-P).
- 769 Han, J.S., Chen, H.Y., Hong, W., Hollings, P., Chu, G.B., Zhang, L., Sun, S.Q., 2020. Texture
770 and geochemistry of multi-stage hydrothermal scheelite in the Tongshankou porphyry-skarn
771 Cu-Mo(-W) deposit, eastern China: Implications for ore-forming process and fluid
772 metasomatism. *Am. Mineral.* 105, 945–954. <https://doi.org/10.2138/am-2020-7194>.
- 773 Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magmas in the formation of hydrothermal
774 ore deposits. *Nature* 370, 519–527. <https://doi.org/10.1038/370519a0>.
- 775 Heinrich, C.A., Candela, P.A., 2014. Fluids and ore formation in the Earth's crust, in: Holland,
776 H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*, second ed. Elsevier, Amsterdam,
777 vol. 13, pp. 1–28. <https://doi.org/10.1016/B978-0-08-095975-7.01101-3>.
- 778 Huang, X.D., 2018. Middle-Late Jurassic Cu-Pb-Zn-bearing and W-bearing granitoids and their
779 skarn mineralization in the Nanling Range, South China: the Tongshanling and Weijia
780 deposits (Ph.D. thesis). Nanjing University, Nanjing, pp. 1–330.

- 781 <https://doi.org/10.27235/d.cnki.gnjiu.2018.000946>.
- 782 Huang, X.D., Lu, J.J., Sizaret, S., Wang, R.C., Ma, D.S., Zhang, R.Q., Zhao, X., Wu, J.W., 2017.
783 Petrogenetic differences between the Middle-Late Jurassic Cu-Pb-Zn-bearing and
784 W-bearing granites in the Nanling Range, South China: A case study of the Tongshanling
785 and Weijia deposits in southern Hunan Province. *Sci. China Earth Sci.* 60, 1220–1236.
786 <https://doi.org/10.1007/s11430-016-9044-5>.
- 787 Ismail, R., Ciobanu, C.L., Cook, N.J., Teale, G.S., Giles, D., Schmidt Mumm, A., Wade, B.,
788 2014. Rare earths and other trace elements in minerals from skarn assemblages, Hillside iron
789 oxide-copper-gold deposit, Yorke Peninsula, South Australia. *Lithos* 184–187, 456–477.
790 <https://doi.org/10.1016/j.lithos.2013.07.023>.
- 791 Jaffe, H.W., 1951. The role of yttrium and other minor elements in the garnet group. *Am.*
792 *Mineral.* 36, 133–155.
- 793 Joesten, R., 1977. Evolution of mineral assemblage zoning in diffusion metasomatism. *Geochim.*
794 *Cosmochim. Acta* 41, 649–670. [https://doi.org/10.1016/0016-7037\(77\)90303-9](https://doi.org/10.1016/0016-7037(77)90303-9).
- 795 Keppler, H., Wyllie, P.J., 1991. Partitioning of Cu, Sn, Mo, W, U, and Th between melt and
796 aqueous fluid in the systems haplogranite-H₂O–HCl and haplogranite-H₂O–HF. *Contrib.*
797 *Mineral. Petrol.* 109, 139–150. <https://doi.org/10.1007/BF00306474>.
- 798 Korzhinskii, D.S., 1968. The theory of metasomatic zoning. *Miner. Depos.* 3, 222–231.
799 <https://doi.org/10.1007/BF00207435>.
- 800 Kravchuk, I.F., Ivanova, G.F., Varezhkina, N.S., Malinin, S.D., 1995. REE fractionation in acid
801 fluid-magma systems. *Geochem. Int.* 32, 60–68.
- 802 Launay, G., Sizaret, S., Lach, P., Melleton, J., Gloaguen, É., Poujol, M., 2021. Genetic
803 relationship between greisenization and Sn-W mineralizations in vein and greisen deposits:
804 Insights from the Panasqueira deposit (Portugal). *BSGF-Earth Sci. Bull.* 192, 2.

- 805 <https://doi.org/10.1051/bsgf/2020046>.
- 806 Legros, H., Marignac, C., Tabary, T., Mercadier, J., Richard, A., Cuney, M., Wang, R.C.,
807 Charles, N., Lespinasse, M.-Y., 2018. The ore-forming magmatic-hydrothermal system of
808 the Piaotang W-Sn deposit (Jiangxi, China) as seen from Li-mica geochemistry. *Am.*
809 *Mineral.* 103, 39–54. <https://doi.org/10.2138/am-2018-6196>.
- 810 Li, J.D., Li, X.F., Xiao, R., 2019. Multiple-stage tungsten mineralization in the Silurian Jiepai W
811 skarn deposit, South China: Insights from cathodoluminescence images, trace elements, and
812 fluid inclusions of scheelite. *J. Asian Earth Sci.* 181, 103898.
813 <https://doi.org/10.1016/j.jseaes.2019.103898>.
- 814 Li, X.Y., Gao, J.F., Zhang, R.Q., Lu, J.J., Chen, W.H., Wu, J.W., 2018. Origin of the Muguayuan
815 veinlet-disseminated tungsten deposit, South China: Constraints from in-situ trace element
816 analyses of scheelite. *Ore Geol. Rev.* 99, 180–194.
817 <https://doi.org/10.1016/j.oregeorev.2018.06.005>.
- 818 Li, Z.X., Li, X.H., 2007. Formation of the 1300-km-wide intracontinental orogen and
819 postorogenic magmatic province in Mesozoic South China: A flat-slab subduction model.
820 *Geology* 35, 179–182. <https://doi.org/10.1130/G23193A.1>.
- 821 Linnen, R.L., Samson, I.M., Williams-Jones, A.E., Chakhmouradian, A.R., 2014. Geochemistry
822 of the rare-earth element, Nb, Ta, Hf, and Zr deposits, in: Holland, H.D., Turekian, K.K.
823 (Eds.), *Treatise on Geochemistry*, second ed. Elsevier, Amsterdam, vol. 13, pp. 543–568.
824 <https://doi.org/10.1016/B978-0-08-095975-7.01124-4>.
- 825 Liu, Y.S., Hu, Z.C., Gao, S., Günther, D., Xu, J., Gao, C.G., Chen, H.H., 2008. In situ analysis of
826 major and trace elements of anhydrous minerals by LA-ICP-MS without applying an
827 internal standard. *Chem. Geol.* 257, 34–43. <https://doi.org/10.1016/j.chemgeo.2008.08.004>.
- 828 London, D., Hervig, R.L., Morgan, G.B. VI, 1988. Melt-vapor solubilities and elemental

- 829 partitioning in peraluminous granite-pegmatite systems: experimental results with Macusani
830 glass at 200 MPa. *Contrib. Mineral. Petrol.* 99, 360–373.
831 <https://doi.org/10.1007/BF00375368>.
- 832 Manning, D.A.C., 1981. The effect of fluorine on liquidus phase relationships in the system
833 Qz-Ab-Or with excess water at 1kb. *Contrib. Mineral. Petrol.* 76, 206–215.
834 <https://doi.org/10.1007/BF00371960>.
- 835 Manning, D.A.C., Henderson, P., 1984. The behaviour of tungsten in granitic melt-vapour
836 systems. *Contrib. Mineral. Petrol.* 86, 286–293. <https://doi.org/10.1007/BF00373674>.
- 837 Mao, J.W., Cheng, Y.B., Chen, M.H., Pirajno, F., 2013. Major types and time-space distribution
838 of Mesozoic ore deposits in South China and their geodynamic settings. *Miner. Depos.* 48,
839 267–294. <https://doi.org/10.1007/s00126-012-0446-z>.
- 840 Mao, J.W., Ouyang, H.G., Song, S.W., Santosh, M., Yuan, S.D., Zhou, Z.H., Zheng, W., Liu, H.,
841 Liu, P., Cheng, Y.B., Chen, M.H., 2019. Geology and metallogeny of tungsten and tin
842 deposits in China. *Society of Economic Geologists Special Publication* 22, 411–482.
843 <https://doi.org/10.5382/SP.22.10>.
- 844 Mao, J.W., Xie, G.Q., Guo, C.L., Chen, Y.C., 2007. Large-scale tungsten-tin mineralization in
845 the Nanling region, South China: Metallogenic ages and corresponding geodynamic
846 processes. *Acta Petrol. Sin.* 23, 2329–2338 (in Chinese with English abstract).
847 <https://doi.org/10.3969/j.issn.1000-0569.2007.10.002>.
- 848 Meinert, L.D., Dipple, G.M., Nicolescu, S., 2005. World skarn deposits. *Economic Geology*
849 100th Anniversary Volume, 299–336. <https://doi.org/10.5382/AV100.11>.
- 850 Miles, A.J., Graham, C.M., Hawkesworth, C.J., Gillespie, M.R., Hinton, R.W., Bromiley, G.D.,
851 EMMAC, 2014. Apatite: A new redox proxy for silicic magmas? *Geochim. Cosmochim.*
852 *Acta* 132, 101–119. <https://doi.org/10.1016/j.gca.2014.01.040>.

- 853 Norman, D.I., Kyle, P.R., Baron, C., 1989. Analysis of trace elements including rare earth
854 elements in fluid inclusion liquids. *Econ. Geol.* 84, 162–166.
855 <https://doi.org/10.2113/gsecongeo.84.1.162>.
- 856 Norton, D.L., 1987. Advective metasomatism, in: Helgeson, H.C. (Ed.), *Chemical Transport in*
857 *Metasomatic Processes*. D. Reidel Publishing Company, Dordrecht, pp. 123–132.
858 https://doi.org/10.1007/978-94-009-4013-0_5.
- 859 Park, C., Choi, W., Kim, H., Park, M.-H., Kang, I.-M., Lee, H.-S., Song, Y., 2017. Oscillatory
860 zoning in skarn garnet: Implications for tungsten ore exploration. *Ore Geol. Rev.* 89, 1006–
861 1018. <https://doi.org/10.1016/j.oregeorev.2017.08.003>.
- 862 Park, C., Park, C., Song, Y., Choi, S.-G., 2019. Sequential trace element analysis of zoned skarn
863 garnet: Implications for multi-stage fluxing and flow of magmatic fluid into a skarn system.
864 *Lithos* 350–351, 105213. <https://doi.org/10.1016/j.lithos.2019.105213>.
- 865 Poulin, R.S., Kontak, D.J., McDonald, A., McClenaghan, M.B., 2018. Assessing scheelite as an
866 ore-deposit discriminator using its trace-element and REE chemistry. *Can. Mineral.* 56,
867 265–302. <https://doi.org/10.3749/canmin.1800005>.
- 868 Reed, M.J., Candela, P.A., Piccoli, P.M., 2000. The distribution of rare earth elements between
869 monzogranitic melt and the aqueous volatile phase in experimental investigations at 800 °C
870 and 200 MPa. *Contrib. Mineral. Petrol.* 140, 251–262.
871 <https://doi.org/10.1007/s004100000182>.
- 872 Røhr, T.S., Austrheim, H., Erambert, M., 2007. Stress-induced redistribution of yttrium and
873 heavy rare-earth elements (HREE) in garnet during high-grade polymetamorphism. *Am.*
874 *Mineral.* 92, 1276–1287. <https://doi.org/10.2138/am.2007.2479>.
- 875 Rubenach, M., 2013. Structural controls of metasomatism on a regional scale, in: Harlov, D.E.,
876 Austrheim, H. (Eds.), *Metasomatism and the Chemical Transformation of Rock*. Springer,

- 877 Berlin, pp. 93–140. https://doi.org/10.1007/978-3-642-28394-9_4.
- 878 Ryan-Davis, J., Lackey, J.S., Gevedon, M., Barnes, J.D., Lee, C.-T.A., Kitajima, K., Valley,
879 J.W., 2019. Andradite skarn garnet records of exceptionally low $\delta^{18}\text{O}$ values within an Early
880 Cretaceous hydrothermal system, Sierra Nevada, CA. *Contrib. Mineral. Petrol.* 174, 68.
881 <https://doi.org/10.1007/s00410-019-1602-6>.
- 882 Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic
883 distances in halides and chalcogenides. *Acta Crystallogr.* A32, 751–767.
884 <https://doi.org/10.1107/S0567739476001551>.
- 885 Shcherba, G.N., 1970. *Greisens. Int. Geol. Rev.* 12, 114–150 & 239–255.
886 <https://doi.org/10.1080/00206817009475216>.
- 887 Shu, L.S., Wang, B., Cawood, P.A., Santosh, M., Xu, Z.Q., 2015. Early Paleozoic and Early
888 Mesozoic intraplate tectonic and magmatic events in the Cathaysia Block, South China.
889 *Tectonics* 34, 1600–1621. <https://doi.org/10.1002/2015TC003835>.
- 890 Smith, M.P., Henderson, P., Jeffries, T.E.R., Long, J., Williams, C.T., 2004. The rare earth
891 elements and uranium in garnets from the Beinn an Dubhaich aureole, Skye, Scotland, UK:
892 Constraints on processes in a dynamic hydrothermal system. *J. Petrol.* 45, 457–484.
893 <https://doi.org/10.1093/petrology/egg087>.
- 894 Song, G.X., Qin, K.Z., Li, G.M., Evans, N.J., Chen, L., 2014. Scheelite elemental and isotopic
895 signatures: Implications for the genesis of skarn-type W-Mo deposits in the Chizhou Area,
896 Anhui Province, Eastern China. *Am. Mineral.* 99, 303–317.
897 <https://doi.org/10.2138/am.2014.4431>.
- 898 Štemprok, M., 1987. Greisenization (a review). *Geol. Rundsch.* 76, 169–175.
899 <https://doi.org/10.1007/BF01820580>.
- 900 Su, S.Q., Qin, K.Z., Li, G.M., Olin, P., Thompson, J., 2019. Cathodoluminescence and trace

- 901 elements of scheelite: Constraints on ore-forming processes of the Dabaoshan porphyry
902 Mo-W deposit, South China. *Ore Geol. Rev.* 115, 103183.
903 <https://doi.org/10.1016/j.oregeorev.2019.103183>.
- 904 Sun, K.K., Chen, B., 2017. Trace elements and Sr-Nd isotopes of scheelite: Implications for the
905 W-Cu-Mo polymetallic mineralization of the Shimensi deposit, South China. *Am. Mineral.*
906 102, 1114–1128. <https://doi.org/10.2138/am-2017-5654>.
- 907 Sun, K.K., Chen, B., Deng, J., 2019. Ore genesis of the Zhuxi supergiant W-Cu skarn
908 polymetallic deposit, South China: Evidence from scheelite geochemistry. *Ore Geol. Rev.*
909 107, 14–29. <https://doi.org/10.1016/j.oregeorev.2019.02.017>.
- 910 Tian, Z.D., Leng, C.B., Zhang, X.C., Zafar, T., Zhang, L.J., Hong, W., Lai, C.-K., 2019.
911 Chemical composition, genesis and exploration implication of garnet from the Hongshan
912 Cu-Mo skarn deposit, SW China. *Ore Geol. Rev.* 112, 103016.
913 <https://doi.org/10.1016/j.oregeorev.2019.103016>.
- 914 Timofeev, A., Migdisov, A.A., Williams-Jones, A.E., 2015. An experimental study of the
915 solubility and speciation of niobium in fluoride-bearing aqueous solutions at elevated
916 temperature. *Geochim. Cosmochim. Acta* 158, 103–111.
917 <https://doi.org/10.1016/j.gca.2015.02.015>.
- 918 Timofeev, A., Migdisov, A.A., Williams-Jones, A.E., 2017. An experimental study of the
919 solubility and speciation of tantalum in fluoride-bearing aqueous solutions at elevated
920 temperature. *Geochim. Cosmochim. Acta* 197, 294–304.
921 <https://doi.org/10.1016/j.gca.2016.10.027>.
- 922 Tsay, A., Zajacz, Z., Sanchez-Valle, C., 2014. Efficient mobilization and fractionation of
923 rare-earth elements by aqueous fluids upon slab dehydration. *Earth Planet. Sci. Lett.* 398,
924 101–112. <https://doi.org/10.1016/j.epsl.2014.04.042>.

- 925 Veksler, I.V., 2005. Element enrichment and fractionation by magmatic aqueous fluids:
926 Experimental constraints on fluid-melt immiscibility and element partitioning, in: Linnen,
927 R.L., Samson, I.M. (Eds.), *Rare-Element Geochemistry and Mineral Deposits*. Geological
928 Association of Canada, Short Course Notes, vol. 17, pp. 69–85.
- 929 Veksler, I.V., Dorfman, A.M., Dulski, P., Kamenetsky, V.S., Danyushevsky, L.V., Jeffries, T.,
930 Dingwell, D.B., 2012. Partitioning of elements between silicate melt and immiscible
931 fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of
932 natrocarbonatite. *Geochim. Cosmochim. Acta* 79, 20–40.
933 <https://doi.org/10.1016/j.gca.2011.11.035>.
- 934 Wang, X.L., Zhou, J.C., Griffin, W.L., Wang, R.C., Qiu, J.S., O'Reilly, S.Y., Xu, X.S., Liu,
935 X.M., Zhang, G.L., 2007. Detrital zircon geochronology of Precambrian basement
936 sequences in the Jiangnan orogen: Dating the assembly of the Yangtze and Cathaysia
937 Blocks. *Precambrian Res.* 159, 117–131. <https://doi.org/10.1016/j.precamres.2007.06.005>.
- 938 Wang, X.S., Timofeev, A., Williams-Jones, A.E., Shang, L.B., Bi, X.W., 2019. An experimental
939 study of the solubility and speciation of tungsten in NaCl-bearing aqueous solutions at 250,
940 300, and 350 °C. *Geochim. Cosmochim. Acta* 265, 313–329.
941 <https://doi.org/10.1016/j.gca.2019.09.013>.
- 942 Wang, X.S., Williams-Jones, A.E., Hu, R.Z., Shang, L.B., Bi, X.W., 2021. The role of fluorine in
943 granite-related hydrothermal tungsten ore genesis: Results of experiments and modeling.
944 *Geochim. Cosmochim. Acta* 292, 170–187. <https://doi.org/10.1016/j.gca.2020.09.032>.
- 945 Webster, J.D., 1992. Water solubility and chlorine partitioning in Cl-rich granitic systems:
946 Effects of melt composition at 2 kbar and 800 °C. *Geochim. Cosmochim. Acta* 56, 679–687.
947 [https://doi.org/10.1016/0016-7037\(92\)90089-2](https://doi.org/10.1016/0016-7037(92)90089-2).
- 948 Webster, J.D., Holloway, J.R., 1988. Experimental constraints on the partitioning of Cl between

- 949 topaz rhyolite melt and H₂O and H₂O + CO₂ fluids: New implications for granitic
950 differentiation and ore deposition. *Geochim. Cosmochim. Acta* 52, 2091–2105.
951 [https://doi.org/10.1016/0016-7037\(88\)90189-5](https://doi.org/10.1016/0016-7037(88)90189-5).
- 952 Webster, J.D., Holloway, J.R., 1990. Partitioning of F and Cl between magmatic hydrothermal
953 fluids and highly evolved granitic magmas, in: Stein, H.J., Hannah, J.L. (Eds.), *Ore-bearing*
954 *Granite Systems; Petrogenesis and Mineralizing Processes*. Geological Society of America,
955 Special Paper, vol. 246, pp. 21–34. <https://doi.org/10.1130/SPE246-p21>.
- 956 Wen, G., Li, J.W., Hofstra, A.H., Koenig, A.E., Cui, B.Z., 2020. Textures and compositions of
957 clinopyroxene in an Fe skarn with implications for ore-fluid evolution and mineral-fluid
958 REE partitioning. *Geochim. Cosmochim. Acta* 290, 104–123.
959 <https://doi.org/10.1016/j.gca.2020.08.020>.
- 960 Wood, S.A., 1990. The aqueous geochemistry of the rare-earth elements and yttrium: 1. Review
961 of available low-temperature data for inorganic complexes and the inorganic REE speciation
962 of natural waters. *Chem. Geol.* 82, 159–186.
963 [https://doi.org/10.1016/0009-2541\(90\)90080-Q](https://doi.org/10.1016/0009-2541(90)90080-Q).
- 964 Wood, S.A., Samson, I.M., 2000. The hydrothermal geochemistry of tungsten in granitoid
965 environments: I. Relative solubilities of ferberite and scheelite as a function of T, P, pH, and
966 m_{NaCl} . *Econ. Geol.* 95, 143–182. <https://doi.org/10.2113/gsecongeo.95.1.143>.
- 967 Wood, S.A., Vlassopoulos, D., 1989. Experimental determination of the hydrothermal solubility
968 and speciation of tungsten at 500 °C and 1 kbar. *Geochim. Cosmochim. Acta* 53, 303–312.
969 [https://doi.org/10.1016/0016-7037\(89\)90382-7](https://doi.org/10.1016/0016-7037(89)90382-7).
- 970 Wu, J.H., Kong, H., Li, H., Algeo, T.J., Yonezu, K., Liu, B., Wu, Q.H., Zhu, D.P., Jiang, H.,
971 2021. Multiple metal sources of coupled Cu-Sn deposits: Insights from the Tongshanling
972 polymetallic deposit in the Nanling Range, South China. *Ore Geol. Rev.* 139, 104521.

- 973 <https://doi.org/10.1016/j.oregeorev.2021.104521>.
- 974 Xiao, X., Zhou, T.F., White, N.C., Zhang, L.J., Fan, Y., Wang, F.Y., Chen, X.F., 2018. The
975 formation and trace elements of garnet in the skarn zone from the Xinqiao Cu-S-Fe-Au
976 deposit, Tongling ore district, Anhui Province, Eastern China. *Lithos* 302–303, 467–479.
977 <https://doi.org/10.1016/j.lithos.2018.01.023>.
- 978 Xu, J., Ciobanu, C.L., Cook, N.J., Zheng, Y.Y., Li, X.F., Wade, B.P., Verdugo-Ihl, M.R., Gao,
979 W.Y., Zhu, Q.Q., 2020. Numerical modelling of rare earth element fractionation trends in
980 garnet: a tool to monitor skarn evolution. *Contrib. Mineral. Petrol.* 175, 30.
981 <https://doi.org/10.1007/s00410-020-1670-7>.
- 982 Yang, J.H., Peng, J.T., Hu, R.Z., Bi, X.W., Zhao, J.H., Fu, Y.Z., Shen, N.P., 2013. Garnet
983 geochemistry of tungsten-mineralized Xihuashan granites in South China. *Lithos* 177, 79–
984 90. <https://doi.org/10.1016/j.lithos.2013.06.008>.
- 985 Zaraisky, G.P., Korzhinskaya, V., Kotova, N., 2010. Experimental studies of Ta₂O₅ and
986 columbite-tantalite solubility in fluoride solutions from 300 to 550 °C and 50 to 100 MPa.
987 *Miner. Petrol.* 99, 287–300. <https://doi.org/10.1007/s00710-010-0112-z>.
- 988 Zhang, Q., Zhang, R.Q., Gao, J.F., Lu, J.J., Wu, J.W., 2018. In-situ LA-ICP-MS trace element
989 analyses of scheelite and wolframite: Constraints on the genesis of veinlet-disseminated and
990 vein-type tungsten deposits, South China. *Ore Geol. Rev.* 99, 166–179.
991 <https://doi.org/10.1016/j.oregeorev.2018.06.004>.
- 992 Zhang, S.T., Zhang, R.Q., Lu, J.J., Ma, D.S., Ding, T., Gao, S.Y., Zhang, Q., 2019.
993 Neoproterozoic tin mineralization in South China: geology and cassiterite U-Pb age of the
994 Baotan tin deposit in northern Guangxi. *Miner. Depos.* 54, 1125–1142.
995 <https://doi.org/10.1007/s00126-019-00862-y>.
- 996 Zhang, Y., Yang, J.H., Chen, J.Y., Wang, H., Xiang, Y.X., 2017. Petrogenesis of Jurassic

- 997 tungsten-bearing granites in the Nanling Range, South China: Evidence from whole-rock
998 geochemistry and zircon U-Pb and Hf-O isotopes. *Lithos* 278–281, 166–180.
999 <https://doi.org/10.1016/j.lithos.2017.01.018>.
- 1000 Zhao, P.L., Yuan, S.D., Mao, J.W., Santosh, M., Li, C., Hou, K.J., 2016. Geochronological and
1001 petrogeochemical constraints on the skarn deposits in Tongshanling ore district, southern
1002 Hunan Province: Implications for Jurassic Cu and W metallogenic events in South China.
1003 *Ore Geol. Rev.* 78, 120–137. <https://doi.org/10.1016/j.oregeorev.2016.03.004>.
- 1004 Zhao, W.W., Zhou, M.F., Li, Y.H.M., Zhao, Z., Gao, J.F., 2017. Genetic types, mineralization
1005 styles, and geodynamic settings of Mesozoic tungsten deposits in South China. *J. Asian*
1006 *Earth Sci.* 137, 109–140. <https://doi.org/10.1016/j.jseaes.2016.12.047>.
- 1007 Zhao, W.W., Zhou, M.F., Williams-Jones, A.E., Zhao, Z., 2018. Constraints on the uptake of
1008 REE by scheelite in the Baoshan tungsten skarn deposit, South China. *Chem. Geol.* 477,
1009 123–136. <https://doi.org/10.1016/j.chemgeo.2017.12.020>.
- 1010 Zharikov, V.A., Rusinov, V.L., 1998. *Metasomatism and Metasomatic Rocks*. Nauchnyi Mir,
1011 Moscow (in Russian).
- 1012 Zhou, X.M., Li, W.X., 2000. Origin of Late Mesozoic igneous rocks in Southeastern China:
1013 implications for lithosphere subduction and underplating of mafic magmas. *Tectonophysics*
1014 326, 269–287. [https://doi.org/10.1016/S0040-1951\(00\)00120-7](https://doi.org/10.1016/S0040-1951(00)00120-7).
- 1015 Zhou, X.M., Sun, T., Shen, W.Z., Shu, L.S., Niu, Y.L., 2006. Petrogenesis of Mesozoic
1016 granitoids and volcanic rocks in South China: A response to tectonic evolution. *Episodes* 29,
1017 26–33. <https://doi.org/10.18814/epiugs/2006/v29i1/004>.

1018 **Figure captions**

1019 **Fig. 1.** (a) Map of South China showing the location of the Weijia W skarn deposit. (b)

1020 Geological map of the Weijia W skarn deposit.

1021 **Fig. 2.** West–east-trending geological cross section (section line shown in Fig. 1b) of the Weijia

1022 W skarn deposit.

1023 **Fig. 3.** Representative samples of the (a) granite porphyry and its (b) stockwork quartz veinlets,
1024 (c–d) calcic skarn, and (e–f) magnesian skarn from the Weijia W deposit. Mineral abbreviations:

1025 Cal = calcite, Grt = garnet, Kfs = K-feldspar, Phl = phlogopite, Px = pyroxene, Qz = quartz, Srp

1026 = serpentine, Wo = wollastonite. Subscripts C and M represent calcic and magnesian skarns,

1027 respectively, Arabic numerals denote paragenetic stages.

1028 **Fig. 4.** Petrographic photomicrographs of the granite porphyry and its stockwork quartz veinlets

1029 from the Weijia W skarn deposit. (a) Subvolcanic porphyritic texture of the granite porphyry with
1030 phenocrysts of quartz, K-feldspar, albite, and biotite (crossed-polarized light, XPL). (b)

1031 Interstitial muscovite and muscovite-fluorite aggregates in the matrix of granite porphyry (XPL).

1032 (c) Stage-2 scheelite coexisting with fluorite in the stockwork quartz veinlets hosted by weakly

1033 greisenized granite porphyry (plane-polarized light, PPL). (d) Altered biotite in the granite

1034 porphyry (XPL). Mineral abbreviations: Ab = albite, Bt = biotite, Fl = fluorite, Kfs = K-feldspar,

1035 Ms = muscovite, Qz = quartz, Sch = scheelite. Subscript Q represents stockwork quartz veinlets,

1036 Arabic numeral denotes paragenetic stage.

1037 **Fig. 5.** Petrographic photomicrographs of the calcic and magnesian skarns with different

1038 generations of garnets and scheelites from the Weijia W deposit. (a) Stage-1 disseminated garnet

1039 and pyroxene in the calcic skarn (PPL). (b) The stage-1 garnet enclosing the stage-1 pyroxene

1040 and replaced by fluorite in the calcic skarn (BSE). (c) Stage-3 stockwork garnet and associated

1041 scheelite in the calcic skarn (PPL). (d) Stage-4 stockwork pyroxene and associated scheelite in

1042 the calcic skarn (XPL). (e) Stage-3 garnet and associated scheelite in the stockwork magnesian
 1043 skarn (XPL). (f) Stage-4 scheelite coexisting with phlogopite in the stockwork magnesian skarn
 1044 (XPL). (g) Stage-4 scheelite coexisting with serpentine in the stockwork magnesian skarn (XPL).
 1045 (h) Stage-1 marialite ($\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$) in the stockwork magnesian skarn (BSE). Mineral
 1046 abbreviations: Cal = calcite, Chl = chlorite, Dol = dolomite, Fl = fluorite, Grt = garnet, Mar =
 1047 marialite, Phl = phlogopite, Px = pyroxene, Sch = scheelite, Sel = sellaite, Srp = serpentine, Wo =
 1048 wollastonite.

1049 **Fig. 6.** BSE images showing the textures of garnets in the calcic skarn (a–b) and magnesian skarn
 1050 (c–f). Mineral abbreviations: Fl = fluorite, Grt = garnet, Px = pyroxene, Sch = scheelite. A and B
 1051 denote two subgenerations of the $\text{Grt}_M 1$ and $\text{Grt}_M 3$.

1052 **Fig. 7.** (a–d) CL and (e–g) BSE images showing the textures of scheelites in the stockwork quartz
 1053 veinlets (a), calcic skarn (b–d), and magnesian skarn (e–g). Mineral abbreviations: Fl = fluorite,
 1054 Mol = molybdenite, Sch = scheelite. Subscripts Q, C, and M represent stockwork quartz veinlets,
 1055 calcic skarn, and magnesian skarn, respectively, Arabic numerals denote paragenetic stages.

1056 **Fig. 8.** Major element compositions of different generations of garnets and pyroxenes from the
 1057 Weijia W skarn deposit. End-member abbreviations: Adr = andradite, Alm = almandine, Di =
 1058 diopside, Grs = grossular, Hd = hedenbergite, Jhn = johannsenite, Prp = pyrope, Sps =
 1059 spessartine.

1060 **Fig. 9.** Chondrite-normalized (Boynton, 1984) REE patterns of different generations of garnets
 1061 from the Weijia W skarn deposit. The REE data of granite porphyry and carbonate strata are from
 1062 Huang et al. (2017) and listed in Supplementary Table S5, respectively.

1063 **Fig. 10.** (a) $(\text{La}/\text{Sm})_N - \delta\text{Eu} [\text{Eu}_N/(\text{Sm}_N \times \text{Gd}_N)^{1/2}]$ and (b) Adr (mol%)-W (ppm) binary diagrams of
 1064 the Weijia garnets. The W data of carbonate strata are listed in Supplementary Table S5.

1065 **Fig. 11.** Chondrite-normalized (Boynton, 1984) REE patterns of (a–e) different generations of

1066 scheelites and (f) model primary F-rich magmatic fluids in the Weijia W skarn deposit. The REE
 1067 data of granite porphyry and carbonate strata are from [Huang et al. \(2017\)](#) and listed in
 1068 Supplementary Table S5, respectively. The model 1 and model 2 of primary F-rich magmatic
 1069 fluids are calculated based on the mean REE compositions of Sch_Q 2 and the minimum (model 1)
 1070 and maximum (model 2) DSch/fluid REEs values from [Brugger et al. \(2000\)](#) with presumed fluid
 1071 Eu²⁺/Eu³⁺ ratios of 0.4, 4, and 40. The model 3 of primary F-rich magmatic fluids is calculated
 1072 based on the mean REE compositions of granitic melts (calculated by subtracting hypothetical
 1073 proportions of 10%, 50%, and 80% REEs in crystallized accessory minerals from the granite
 1074 porphyry) and the minimum liquid-liquid DFluoride/silicate REEs values from [Veksler et al.](#)
 1075 [\(2012\)](#). The parameters and calculated results are listed in Supplementary Table S7.

1076 **Fig. 12.** (a) (La/Yb)_N-δEu, (b) ΣREE (ppm)-Y (ppm), (c) Nb (ppm)-Ta (ppm), and (d) Mo
 1077 (ppm)-Mn (ppm) binary diagrams of the Weijia scheelites.

1078 **Fig. 13.** (a) ΣREE-Eu+Y (μmol/g) vs. Total Mg (apfu: atoms per formula unit) and (b) ΣREE-
 1079 Eu+Y (μmol/g) vs. Total Al (apfu) correlational plots of the Weijia garnets. Legend refers to [Fig.](#)
 1080 [10](#).

1081 **Fig. 14.** (a) Nb+Ta (μmol/g) vs. ΣREE-Eu+Y (μmol/g), (b) Na (μmol/g) vs. ΣREE-Eu+Y
 1082 (μmol/g), and (c) Nb+Ta+Na (μmol/g) vs. ΣREE-Eu+Y (μmol/g) correlational plots of the
 1083 Weijia scheelites. Legend refers to [Fig. 12](#).

1084 **Fig. 15.** Rb/Sr vs. Mg/(Mg+Fe) diagram of the Weijia granite porphyry. These whole-rock
 1085 geochemical data are from [Zhao et al. \(2016\)](#), [Huang et al. \(2017\)](#), and [Wu et al. \(2021\)](#).

1086 **Fig. 16.** Eu_N vs. Eu* N [(Sm_N×Gd_N)^{1/2}] diagram (after [Ghaderi et al., 1999](#)) of the Weijia
 1087 scheelites. Legend refers to [Fig. 12](#).

1088 **Highlights**

- 1089 • Two stages of fluid exsolution are recognized in the Weijia W skarn deposit.
- 1090 • F-rich magmatic fluids are enriched in REEs, Y, Nb, Ta with flat REE patterns.
- 1091 • F consumption is critical for the compositional evolution of F-rich mineralizing fluids.
- 1092 • Combined garnet and scheelite trace elements are powerful in tracking W skarn
1093 mineralization.
- 1094