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

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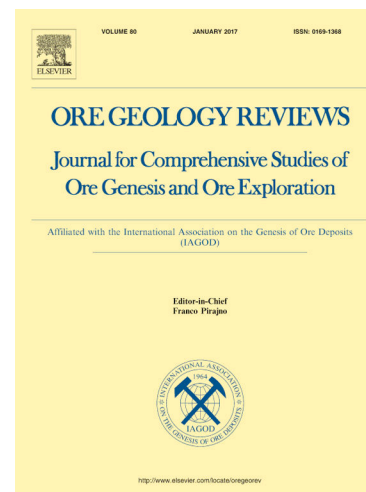
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1 **Garnet and scheelite chemistry of the Weijia tungsten deposit, South China: Implications**  
2 **for fluid evolution and W skarn mineralization in F-rich ore system**

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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  $\delta\text{Eu}$  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  $\Sigma\text{REE}$  (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  $\Sigma\text{REE}$ , 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  $\Sigma\text{REE}$  (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  $\delta\text{Eu}$  values. They show 1:1 positive correlation of  $\text{Eu}_{\text{N}}$  vs.  $\text{Eu}^*_{\text{N}}$  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  $158.3 \pm 2.2$  Ma for the Weijia granite porphyry. Molybdenite Re-Os dating  
135 revealed that this deposit was formed at  $159.0 \pm 5.6$  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 km<sup>2</sup> (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  $\mu\text{m}$ , 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  $\text{MnTiO}_3$  ( $\text{TiK}\alpha$  and  $\text{MnK}\alpha$ ),  $\text{Al}_2\text{O}_3$  ( $\text{AlK}\alpha$ ),  $\text{Fe}_2\text{O}_3$  ( $\text{FeK}\alpha$ ),  
220 and  $\text{MgO}$  ( $\text{MgK}\alpha$ ) 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- $\mu\text{m}$  ablating spot at 5–8 Hz  
231 repetition rate with fluence of 6.06  $\text{J}/\text{cm}^2$  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<sub>C</sub> 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<sub>C</sub> 3 is anhedral without obvious zonation (Figs. 5c and 6a–b). The Grt<sub>C</sub> 3  
 242 cuts the Grt<sub>C</sub> 1 (Fig. 6a) and coexists with the Sch<sub>C</sub> 3 (Fig. 6b). The Grt<sub>M</sub> 1 is coarser, subhedral,  
 243 and relatively homogeneous whereas the Grt<sub>M</sub> 3 is finer, anhedral, and distinctly heterogeneous  
 244 (Fig. 6c–e). The Grt<sub>M</sub> 3 replaces the Grt<sub>M</sub> 1 (Fig. 6c) and coexists with the Sch<sub>M</sub> 3 (Fig. 6d and e).  
 245 In light of the BSE images, both the Grt<sub>M</sub> 1 and Grt<sub>M</sub> 3 can be subdivided into two  
 246 subgenerations, i.e., the darker Grt<sub>M</sub> 1A and Grt<sub>M</sub> 3A and the brighter Grt<sub>M</sub> 1B and Grt<sub>M</sub> 3B (Fig.  
 247 6d–f). The Grt<sub>M</sub> 1A shows micron-scale oscillatory zonation whereas the other three  
 248 subgenerations do not (Fig. 6d–f). The boundary between the Grt<sub>M</sub> 3A and Grt<sub>M</sub> 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<sub>Q</sub> 2) are subhedral (Fig. 7a).  
 252 The Sch<sub>Q</sub> 2 coexists with molybdenite and is oscillatorily zoned with the band width of several to  
 253 a dozen microns (Fig. 7a). The Sch<sub>C</sub> 3 and Sch<sub>M</sub> 3 show conspicuous micron-scale oscillatory  
 254 zonation, while the Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4 are relatively homogeneous (Fig. 7b–g). The Sch<sub>C</sub> 4 cuts  
 255 the Sch<sub>C</sub> 3 in the stockwork garnet veinlets (Fig. 7b and c) and the Sch<sub>M</sub> 4 replaces the Sch<sub>M</sub> 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<sub>C</sub> 1 has andraditic compositions (Grs<sub>1–14</sub>Adr<sub>81–93</sub>), while the Grt<sub>C</sub> 3 belongs to  
 261 intermediate grandite (Grs<sub>38–63</sub>Adr<sub>33–57</sub>) (Fig. 8a). Both the Grt<sub>M</sub> 1 and Grt<sub>M</sub> 3 are grossularitic  
 262 garnet (Grs<sub>67–84</sub>Adr<sub>10–22</sub>, Fig. 8b) and contain more MgO (mostly 1.5–2.6 wt%) than the Grt<sub>C</sub> 1

263 and Grt<sub>C</sub> 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<sub>M</sub> 1: 0.51–2.8 wt%; Grt<sub>M</sub> 3: 2.7–4.1 wt%) than that in the  
 265 calcic skarn (Grt<sub>C</sub> 1: < 0.77 wt%; Grt<sub>C</sub> 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<sub>C</sub> 1 is  
 267 diopsidic pyroxene (Di<sub>68–99</sub>Hd<sub>0–27</sub>) whereas the Px<sub>C</sub> 4 has hedenbergitic compositions (Di<sub>0–</sub>  
 268 <sub>16</sub>Hd<sub>78–95</sub>) (Fig. 8c). The Px<sub>M</sub> 1 is almost pure diopside (Di<sub>98–100</sub>Hd<sub>0</sub>, Fig. 8d).

### 269 5.3. Garnet trace element compositions

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

281 The Grt<sub>C</sub> 1 and Grt<sub>C</sub> 3 have higher Ti, V, Cr and lower Na, Zn, Sr contents than the Grt<sub>M</sub> 1  
 282 and Grt<sub>M</sub> 3 on the whole (Table S3). The Grt<sub>C</sub> 1 contains more W (7.1–1181 ppm) and less Nb  
 283 (0.25–8.6 ppm) than the Grt<sub>C</sub> 3 (5.6–168 ppm W, 2.3–21 ppm Nb) (Table S3). The Grt<sub>M</sub> 1 and  
 284 Grt<sub>M</sub> 3 have comparable W contents (Grt<sub>M</sub> 1: 0.42–3.1 ppm; Grt<sub>M</sub> 3: 0.40–5.4 ppm) and Nb  
 285 contents (Grt<sub>M</sub> 1: 1.4–74 ppm; Grt<sub>M</sub> 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<sub>Q</sub> 2 shows flat chondrite-normalized REE patterns [(La/Yb)<sub>N</sub> = 0.29–2.7] with strong  
 289 Eu negative anomalies ( $\delta\text{Eu} = 0.006\text{--}0.06$ ) and contains the highest  $\Sigma\text{REE}$  (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<sub>C</sub> 3 exhibits slightly  
 292 rightward-sloping [(La/Yb)<sub>N</sub> = 4.0–67] and Eu-depleted ( $\delta\text{Eu} = 0.03\text{--}0.36$ ) REE patterns (Figs.  
 293 11b and 12a), while the Sch<sub>C</sub> 4 is LREE-enriched and HREE-depleted [(La/Yb)<sub>N</sub> = 338–4332]  
 294 with negligible Eu anomalies ( $\delta\text{Eu} = 0.81\text{--}2.5$ ) (Figs. 11c and 12a). The Sch<sub>M</sub> 3 displays mildly  
 295 HREE-enriched to HREE-depleted [(La/Yb)<sub>N</sub> = 0.07–17] and strongly Eu-depleted ( $\delta\text{Eu} =$   
 296 0.001–0.13) REE patterns (Figs. 11d and 12a) whereas the Sch<sub>M</sub> 4 is enriched in LREEs and  
 297 depleted in HREEs [(La/Yb)<sub>N</sub> = 22–238] with weak Eu anomalies ( $\delta\text{Eu} = 0.58\text{--}4.9$ ) (Figs. 11e  
 298 and 12a). The (La/Yb)<sub>N</sub> ratios of the Sch<sub>C</sub> 3 and Sch<sub>C</sub> 4 are higher than those of the Sch<sub>M</sub> 3 and  
 299 Sch<sub>M</sub> 4, respectively (Fig. 12a). The Mg contents of the Sch<sub>C</sub> 3 (12–96 ppm) and Sch<sub>C</sub> 4 (2.6–13  
 300 ppm) are distinctly lower than those of the Sch<sub>M</sub> 3 (up to 16729 ppm) and Sch<sub>M</sub> 4 (up to 13565  
 301 ppm) (Table S4). The Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4 contain significantly less  $\Sigma\text{REE}$ , Y, Nb, and Ta than the  
 302 Sch<sub>C</sub> 3 and Sch<sub>M</sub> 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  $\square_{\text{X}}$ , where  $\text{X}^{+}$ ,  $\text{X}^{2+}$ ,  $\text{Y}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Z}^{3+}$  are essentially  $\text{Na}^{+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ ,  $\text{Al}^{3+}$ ,  
 309 respectively, and  $\square_{\text{X}}$  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<sub>C</sub> 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<sub>C</sub> 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 REE<sup>3+</sup> 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<sub>M</sub> 1 and Grt<sub>M</sub> 3 accord with the YAG-type substitution. The  $\square_{\text{X}}$ -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  $\square_{\text{Ca}}$  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<sub>Q</sub> 2, Sch<sub>C</sub> 3, and Sch<sub>M</sub> 3 followed principally the Eq. (1) and subordinately the  
 328 Eq. (2), while the Sch<sub>C</sub> 4 and Sch<sub>M</sub> 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<sub>Q</sub> 2, Sch<sub>C</sub> 3, and Sch<sub>M</sub> 3 (Fig. 14c)  
 330 and Nb+Ta to  $\Sigma\text{REE-Eu+Y}$  of the Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4 (Fig. 14a) preclude the possibility of the  
 331  $\square_{\text{Ca}}$ -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<sub>C</sub> 1 and Px<sub>C</sub> 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<sub>M</sub> 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<sub>Q</sub> 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<sub>Q</sub> 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 REE<sup>3+</sup> 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<sub>Q</sub> 2 are calculated with presumed fluid Eu<sup>2+</sup>/Eu<sup>3+</sup>  
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  $\Sigma$ 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<sub>C</sub> 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<sub>C</sub> 1 is also akin to the host limestone in  $\Sigma$ 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<sub>C</sub> 1 than those of the host limestone (Fig. 10b) and the slightly higher  $\Sigma$ REE contents of  
446 some Grt<sub>C</sub> 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<sub>C</sub> 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<sub>M</sub> 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<sub>M</sub> 1A relative to the Grt<sub>C</sub> 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<sub>M</sub> 1A is distributed within the stockwork veinlets that are favorable for the influx of  
456 magmatic fluids. The increasing  $\Sigma$ REE contents and intensifying Eu negative anomalies from the  
457 Grt<sub>M</sub> 1A to the Grt<sub>M</sub> 1B (Fig. 9c) are symptomatic of an elevating W/R ratio. From the host  
458 dolostone through the Grt<sub>M</sub> 1A to the Grt<sub>M</sub> 1B, the greater increase of LREEs relative to that of  
459 HREEs (Fig. 9c) signifies that the REEs entering the Grt<sub>M</sub> 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<sub>M</sub> 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<sub>s</sub>/fluid LREEs and higher DGr<sub>s</sub>/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<sub>C</sub> 1 and Grt<sub>M</sub> 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<sub>C</sub> 3 and Grt<sub>M</sub> 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<sub>C</sub> 3 (Fig.  
473 3c and d) and the inside-stockwork distribution of the Grt<sub>M</sub> 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<sub>M</sub> 3A and Grt<sub>M</sub> 3B (Fig. 6f) is suggestive of a

476 turbulent hydrothermal dynamic state, supporting fluid advection as well. The Grt<sub>M</sub> 3A replaces  
477 the Grt<sub>M</sub> 1B (Fig. 6d and e) and thus the high contents of LREEs in the Grt<sub>M</sub> 3A (Fig. 9d) are in  
478 all probability inherited from the Grt<sub>M</sub> 1B (Fig. 9c). The REE patterns of the Grt<sub>M</sub> 3B and Grt<sub>C</sub> 3  
479 present striking depletions of LREEs with low (La/Sm)<sub>N</sub> 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<sub>C</sub> 3 and Grt<sub>M</sub> 3B and the F-rich magmatic fluids.  
483 The absence of oscillatorily zoned texture in the Grt<sub>C</sub> 3 and Grt<sub>M</sub> 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)<sub>N</sub> ratios and higher HREE contents of the grossularitic Grt<sub>M</sub> 3B than those of the  
486 less Al-rich Grt<sub>C</sub> 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<sub>C</sub> 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<sub>M</sub> 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<sub>Q</sub> 2 has remarkably higher  $\Sigma$ 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  $\delta Eu$  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<sub>Q</sub> 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<sub>Q</sub> 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<sub>Q</sub> 2 and  
550 molybdenite (Mo<sup>4+</sup>) (Fig. 7a), it is concluded that the primary F-rich magmatic fluids are  
551 reduced.

552 The assemblage of andraditic Grt<sub>C</sub> 1 (Fe exists as Fe<sup>3+</sup>, Fig. 8a) and diopsidic Px<sub>C</sub> 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<sub>C</sub>  
555 3 and Sch<sub>M</sub> 3 within the carbonate strata have higher Mo and lower Mn contents than the Sch<sub>Q</sub> 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<sub>C</sub> 1 (Fig. 13a) to  $Ca^{2+} + Al^{3+} = REE^{3+} + Fe^{2+}$  for  
563 the less Fe-rich Grt<sub>C</sub> 3 (Fig. 13b) signifies the transition of a Fe<sup>3+</sup>-dominant state into a  
564 Fe<sup>2+</sup>-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<sub>C</sub> 3 and Sch<sub>M</sub> 3 are comparable to the Sch<sub>Q</sub> 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  $\Sigma$ REE, Y, Nb, and Ta contents of the Sch<sub>C</sub> 3 and Sch<sub>M</sub> 3  
571 than those of the Sch<sub>Q</sub> 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<sub>Q</sub> 2 had taken away a certain amount of these trace elements. The Sch<sub>C</sub> 3 and  
575 Sch<sub>M</sub> 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<sub>C</sub> 3 and Sch<sub>M</sub> 3 relative to those in the Sch<sub>Q</sub> 2 (Fig. 12b and c). The Grt<sub>C</sub> 3 is  
578 depleted in LREEs (Fig. 9b), therefore, the coexisting Sch<sub>C</sub> 3 has higher (La/Yb)<sub>N</sub> ratios than the  
579 Sch<sub>Q</sub> 2 (Figs. 11a–b and 12a). The Grt<sub>M</sub> 3A and Grt<sub>M</sub> 3B display relatively flat and  
580 LREE-depleted REE patterns, respectively (Fig. 9d), as a result, some grains of the coexisting  
581 Sch<sub>M</sub> 3 have similar (La/Yb)<sub>N</sub> ratios to the Sch<sub>Q</sub> 2 and some grains show higher (La/Yb)<sub>N</sub> ratios  
582 than the Sch<sub>Q</sub> 2 (Figs. 11a, d and 12a).

583 The Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4 have strikingly lower  $\Sigma$ REE, Y, Nb, and Ta contents than the Sch<sub>Q</sub> 2,  
584 Sch<sub>C</sub> 3, and Sch<sub>M</sub> 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<sub>N</sub> vs. Eu\* N array with  
589 a slope of +1 as Eu<sup>3+</sup> follows Sm<sup>3+</sup> and Gd<sup>3+</sup>, while the scheelite crystallized in reduced fluids

590 will yield a horizontal array because  $\text{Eu}^{2+}$  is decoupled from  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$  (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  $\text{Eu}^{2+}$ , 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  $f_{\text{O}_2}$ . 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<sub>C</sub> 3, Grt<sub>M</sub> 3, Sch<sub>C</sub> 3, and Sch<sub>M</sub> 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  $\delta Eu$  values of the Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4 (Fig. 12a). The  
 620 HREE-depleted signature of the Sch<sub>C</sub> 4 (Fig. 11c) is partly ascribed to its coexisting Px<sub>C</sub> 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<sub>C</sub> 4 is also responsible for the higher (La/Yb)<sub>N</sub> ratios of the Sch<sub>C</sub> 4  
 623 than those of the Sch<sub>M</sub> 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<sub>Q</sub> 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<sub>Q</sub> 2) and  
643 oxidizing (Sch<sub>C</sub> 4 and Sch<sub>M</sub> 4) environments, therefore, the change of fluid  $f_{\text{O}_2}$  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 CO<sub>2</sub> 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  $\Sigma$ 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**

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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<sub>Q</sub> 2 and the minimum (model 1)  
 1070 and maximum (model 2) DSch/fluid REEs values from [Brugger et al. \(2000\)](#) with presumed fluid  
 1071 Eu<sup>2+</sup>/Eu<sup>3+</sup> 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)<sub>N</sub>-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<sub>N</sub> vs. Eu\* N [(Sm<sub>N</sub>×Gd<sub>N</sub>)<sup>1/2</sup>] 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