Multiple fluids involved in granite-related W-Sn deposits from the world-class Jiangxi province (China)

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1 **Revision 2**

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24   **Abstract**

25

26   This paper aims at providing new insights into W-Sn ore-forming processes within one of the

27   largest granitic provinces in the world (Nanling Range, South China), which was emplaced

28   during the Jurassic-Cretaceous period. The origin, composition and pressure-temperature

29   conditions of fluids involved in the W-Sn ore-forming processes have been investigated by

30   microthermometry, Raman spectroscopy, LA-ICPMS, hydrogen isotope analyses of fluid

31   inclusions and oxygen isotope analyses of minerals from the Maoping and Piaotang W-Sn

32   deposits. For each deposit, pre- (quartz), syn- (wolframite and cassiterite) and post-ore

33   (quartz, topaz and fluorite) minerals were studied.

34   In both deposits, the vast majority of fluid inclusions are aqueous with salinities between 0.0

35   and 12.6 wt. % equiv. NaCl and homogenization temperatures between 136 and 349 °C. A

36   minor proportion (~5%) of inclusions observed in the ore-stage quartz from Maoping have

37   aquo-carbonic compositions. For both deposits, four compositional groups are defined. Early

38   quartz fluid inclusions are characterized by salinities between 0.4 and 9.0 wt. % equiv. NaCl,

39   trapping temperatures between 150 and 350 °C, and pressures between 20 and 150 MPa. LA-

40   ICPMS analyses of these fluid inclusions reveal a wide range of Na, K and Li concentrations,

41   as well as relatively low metal contents (W < 40 ppm). Values of $\delta^{18}O$ in quartz range from -

42   3.6 to 5.3 ‰ VSMOW while δD values of the fluid inclusions range from -59 to -51 ‰

43   VSMOW. The salinity of fluid inclusions in wolframite, cassiterite, topaz and fluorite is

44   between 2.4 and 11.2 wt. % equiv. NaCl, trapping temperatures are between 200 and 600 °C,

45   and pressures range from 20 to 250 MPa. LA-ICPMS analyses of these fluid inclusions reveal

46   higher concentrations of Na, K and Li as well as Cs and metals (*e.g.* between 10 and 220 ppm

47   W). Values of $\delta^{18}O$ in wolframite, cassiterite, topaz and fluorite crystals range from -3.0 to 3.3

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‰ VSMOW while δD values of fluid inclusions in these mineral phases range from -78 to -72 ‰ VSMOW.

At Piaotang, fluid inclusions in wolframite as well as in post-ore quartz and fluorite have salinities of 5.6 to 12.6 wt.% eq. NaCl, trapping temperatures between 150 and 400 °C and pressures of 20 to 150 MPa. LA-ICPMS analyses of these fluid inclusions reveal similar compositions to early quartz fluid inclusions. Values of $\delta^{18}O$ in wolframite and quartz crystals range from -0.8 to 5.2 ‰ VSMOW, while the δD values of fluid inclusions range from -66 to -62 ‰ VSMOW.

Collectively, the data suggest the involvement of four aqueous fluid end-members, mixed episodically in the mineralization process: (A) a low-salinity, low-temperature, metal-poor, low-$\delta^{18}O$, low-δD fluid derived from meteoric water; (B) a high-salinity, high-temperature, metal-poor, high-$\delta^{18}O$, low-δD fluid derived from a differentiated peraluminous granitic magma; (C) a high-salinity, high-temperature, metal-rich, lower δD magmatic fluid derived from a more differentiated peraluminous granitic magma; and (D) a high-salinity, high-temperature, metal-rich, high-$\delta^{18}O$, low-δD magmatic fluid.

This study shows that multiple fluids with distinct magmatic and meteoric origins were involved in the formation of these W-Sn deposits and that the dilution of metal-bearing magmatic fluids by meteoric fluids was probably the main driver for ore deposition. The common fluid history of the two deposits studied, as well as similarities with other deposits in the Jiangxi province, points towards common ore-forming processes at the regional scale.

1. Introduction

In granite-related W-Sn deposits, the world's main W and Sn resource, magmatic and hydrothermal activity are thought to have promoted the formation of ore minerals in and around peraluminous granitic plutons (Burnham, 1979; Candela, 1997; Audétat *et al.,* 2000; Mao *et al.,* 2007; Xi *et al.,* 2007; Pirajno, 2009; Zhou *et al.,* 2010). However, the nature and the origin of the ore-forming fluids appear to be variable and are still debated (*e.g.,* Marignac and Cathelineau, 2009). Most models involve (i) high-salinity magmatic-hydrothermal fluids exsolved from the granitic magmas (Audétat *et al.,* 2000; Kamenetsky *et al.,* 2004; Thomas *et al.,* 2005; Korges *et al.*, 2017; Lecumberri-Sanchez *et al.*, 2017), and/or (ii) "external" hydrothermal fluids of deep-seated or surficial origin, characterized by variable volatile and salt contents and equilibrated to variable degrees with the granites and their metamorphic hosts (Weisbrod 1988; Wilkinson 1990; Blamart 1991; Noronha *et al.,* 1992; Smith *et al.,* 1996; Bebout *et al.,* 1999; Polya *et al.,* 2000; Burnard and Polya 2004; Cai *et al.,* 2007).

In the present study, two W-Sn deposits (Maoping and Piaotang) were targeted as representativse of the Jiangxi province, which forms part of the world's richest W and Sn province, the Nanling Range in China (USGS, 2017). The Nanling Range is a metallogenic province in which multiple and diverse mineral deposits (W, Sn, Cu, Pb-Zn, etc.) are associated with one of the largest granitic provinces in the world (100,000 km²), emplaced during Jurassic-Cretaceous times (Zaw *et al.*, 2007).

Several fluid inclusion (FI) studies have already been carried out in W-Sn deposits from the Nanling Range, involving microthermometry (in transparent and opaque minerals), Raman spectroscopy, stable isotope (O, H, S, C) analyses and noble gas isotope (He, Ar) analyses (Giuliani *et al.,* 1988; Xuexin *et al.,* 1990; Zeng *et al.,* 2002; Xi *et al.,* 2008; Cao *et al.,* 2009; Wang *et al.,* 2009; Feng *et al.,* 2012; Gong *et al.,* 2015; Hu *et al.,* 2012; Wang *et al.,* 2012;

98   Wei *et al.,* 2012; Zhang *et al.,* 2012; Ni *et al.,* 2015; Xiong *et al.,* 2017; Chen *et al.*, 2018). All

99   of these studies point to mixing between a magmatic fluid exsolved from a peraluminous

100   granitic magma and a meteoric fluid as being responsible for ore mineral precipitation.

101   However, detailed petrographic and mineralogical studies coupled with Fe-Li-mica

102   geochemistry in the Maoping and Piaotang deposits suggest that three to four types of fluid,

103   mixed to variable degrees, were involved (Legros *et al.* 2016 and 2018). Motivated by the

104   possibility that multiple types of fluid were involved, in contrast with the single-fluid or two-

105   fluid models mentioned above, we decided to undertake the first-ever detailed

106   characterization of the fluids by microthermometry (pression-temperature-composition

107   properties of FIs), Raman spectroscopy (volatile content of the FIs), stable isotope analysis (H

108   and O isotopic compositions of FIs and host minerals, respectively), and LA-ICPMS (major

109   and trace element compositions of FIs). Economic minerals (wolframite, cassiterite) and

110   gangue minerals (quartz, topaz, and fluorite) were studied in order to investigate, for the first

111   time, the evolution of the fluids from the pre-ore to the post-ore stage using multiple

112   analytical methods.

113

114   **2. Geological setting and previous fluid inclusion studies**

115

116   2.1 The southern Jiangxi metallogenic province (Nanling Range)

117

118   The southern Jiangxi province contains 90% of China's tungsten resources (Zeng *et al.* 2007),

119   including 429 deposits with total reserves of 1.7 Mt WO_3. The province is located within the

120   Nanling Range, in the Cathaysia Block of the South China Craton (SCC).

121   The SCC formed during the late Proterozoic Jiangnan (or Sibao) orogeny by the suturing of

122   the Yangtze Block to the north and the Cathaysia Block to the south (Fig. 1; Charvet 2013 and

123 references therein). The Sibao orogeny, dated to between 1040 and 900 Ma by U-Pb (zircon)

124 and $^{40}Ar/^{39}Ar$ (muscovite) methods, formed as a result of diachronous closure of the ocean

125 between the Cathaysia and Yangtze Blocks during the assembly of Rodinia (Li *et al.* 2007).

126 The boundary between these two blocks, bordering the orogenic belt to the south-east, is

127 generally considered to be marked by the Jiangshan-Shaoxi fault zone, which marked by a

128 drop in the depth of the Moho of several Kilometers in this zone (Wang *et al.,* 2013 and

129 references therein).

130 From the late Neoproterozoic onwards, the South China Craton was strongly reworked and

131 progressively meta-cratonized by multiple intracontinental episodes, starting with the major

132 aborted Nanhua rifting episode (Wang *et al.,* 2006). The latter was followed by the bivergent

133 NE-trending Kwangsian orogeny (Ordovician-Devonian), which resulted from inversion of

134 the Nanhua rift (Charvet *et al.,* 2010 and 2013), and multiple metamorphic events that peaked

135 at 720 °C and 1030 kbar at around 450 Ma.

136 The Indosinian (Permian-Triassic) orogeny then overprinted the Proterozoic deformations of

137 the Jiangnan belt in the Cathaysia. This orogeny was marked by extensive granitic

138 magmatism that spanned more than 60 Myr (265-205 Ma; Mao *et al.,* 2012 and references

139 therein) and covered a 14,300 km^2 area (Sun *et al.,* 2012).

140 Finally, the Yanshanian orogeny (Jurassic-Cretaceous) generated the most extensive and

141 intense magmatic activity (mainly granitic and rhyolitic) in the region (Li *et al.,* 2014). Three

142 major metallogenic periods are associated with the Yanshanian orogeny: magmatic-related

143 Cu, Pb-Zn and polymetallic mineralization (Jiangxi and southeastern Hunan) between 180

144 and 170 Ma; rare-metal mineralization (W-Sn, Nb, Ta) related to S-type granitoids from 160

145 to 139 Ma; and magmatism-related Sn, U, and Au-Cu-Pb-Zn-Ag mineralizations in the

146 Nanling Range and southeast coastal zone (Hua *et al.,* 2005), between 125 and 98 Ma. The

147 W-Sn deposits occur almost exclusively within the outer contact zones of S-type Jurassic

148   granites, as is the case for the Maoping and Piaotang W-Sn deposits as well as other numerous

149   large W-Sn deposits in the Dayu district of the southern Jiangxi province, dated between 160

150   and 150 Ma, such as the Xihuashan deposit (Giuliani *et al.,* 1988; Guo *et al.,* 2012; Fig. 1).

151

152   **2.2.** Geology of the Maoping and Piaotang deposits

153

154   2.2.1 Maoping deposit

155

156   The Maoping deposit is associated with a buried peraluminous granite (*ca*. 300 m deep)

157   whose contact with the surrounding Cambrian quartzite and schists can only be observed in

158   drill cores. Two types of mineralization associated with this granite have been described:

159   wolframite-cassiterite-quartz veins and disseminated wolframite in the greisen body. A

160   drillcore-based cross-section of the Maoping deposit is presented in Figures 2A and B and

161   shows the greisen orebody at the top of the granitic intrusion and a network of radial, sub-

162   vertical ore-bearing veins, rooted to the top of the granite and mostly developed in the

163   Cambrian host rocks (Feng *et al.,* 2011). More than 400 W-Sn-bearing quartz-dominated

164   veins, 5 cm to a few meters in thickness and up to 400 m in length, have been identified (Feng

165   *et al.,* 2011). It is worth noting that even though only one level in the mine galleries (level -5,

166   *ca.* 200 m depth) was investigated in the present study, all of the veins appeared to be

167   shallow-dipping in the mine gallery, contrary to the cross-section proposed by Feng *et al.*

168   (2011). The granite was emplaced during the Jurassic at 151.8 ± 2.9 Ma (SHRIMP U-Pb

169   zircon dating; Feng *et al.,* 2011), and the greisen and the veins have been dated to 155.3 ± 2.8

170   and 150.2 ± 2.8 Ma, respectively (Re-Os on molybdenite; Feng *et al.,* 2011). The Maoping

171   deposit is estimated to contain 63 kt WO_3 and 15 kt Sn, with average grades of 0.93 % and 0.3

172   %, respectively (Feng *et al.,* 2011), and is considered one of the largest W-Sn deposits in the

173   Nanling Range.

174   A detailed petrographic study of the Maoping deposit was carried out by Legros *et al.* (2016)

175   and the paragenetic succession that was established is summarized here. Four types of vein

176   and seven successive paragenetic stages (I to VII) were identified from petrographic

177   observations and cross-cutting relationships in the mine galleries (Fig. 3). Hereafter, the

178   mineral nomenclature used here refers to (i) the recommended IMA mineral abbreviations, (ii)

179   the generation number (1 to 4, from the oldest to the youngest), and (iii) the stage to which the

180   mineral belongs (I to VII from the earliest to the latest). For example, in Figure 3, $Wf_{1\text{-}III}$

181   refers to the first time wolframite crystallized in the system, which was during stage III (the

182   W-Sn stage).

183   The first stage in the paragenetic sequence, Stage (I), is marked by cm-sized microcline and

184   smaller quartz and Fe-Li-micas that form the earliest veins. These veins were interpreted to be

185   magmatic in origin by Legros *et al.* (2016). The small size of the quartz crystals meant that FI

186   analysis was not possible for this vein type. The second stage (II) is characterized by

187   hydrothermal veins filled with Fe-Li-mica only. Stages III to VI correspond to W-Sn and

188   banded-quartz veins and involved the successive crystallization of various minerals that are

189   suitable for FI study, as described in more detail below.

190   Stage III corresponds to the formation of the ore-bearing veins (Fig. 4A). During Stage III,

191   quartz ($Qtz_{2,3\text{-}III}$), topaz ($Toz_{2\text{-}III}$), wolframite ($Wf_{1\text{-}III}$), cassiterite ($Cst_{1\text{-}III}$), Fe-Li-micas (Fe-Li-

192   $mca_{3\text{-}III}$), molybdenite ($Mlb_{1\text{-}III}$), Li-Fe muscovite ($Li\text{-}Fe\text{-}ms_{1\text{-}III}$) and Fe-Mn hydroxides were

193   successively deposited. Quartz and topaz are abundant in the veins and form geodic crystals

194   with no apparent zoning (Fig. 4B). Wolframite and cassiterite crystallized next, as euhedral

195   and well-zoned crystals (Fig. 4C and 4D). Evidence for ductile deformation during this stage

196   allows two successive episodes (syn-deformation IIIa and post-deformation IIIb) to be

197 distinguished. The deformation is particularly well-developed in quartz and topaz minerals,

198 where undulose extinction and elongated subgrains are observed. Wolframite and cassiterite

199 also show marked evidence for plastic deformation, with folded crystals but no signs of

200 recrystallization. Stage IIIb is characterised by the presence of undeformed Li-Fe-ms$_{1-III}$ and

201 Fe-Mn hydroxides.

202 Stage IV corresponds to the emplacement of banded quartz veins (Fig. 4E). Four types of

203 undeformed quartz can be distinguished. The banding was formed by a repeated sequence of

204 (1) quartz corrosion, (2) the accumulation of minerals (feldspars, micas and quartz),

205 interpreted to be relics of minerals from previous stages, together with precipitation of

206 disseminated Nb-Ta and REE minerals and Qtz$_{4a-IV}$, (3) deposition of Qtz$_{4b-IV}$, and (4)

207 deposition of laminated Qtz$_{4c-IV}$. A final generation of subhedral Qtz$_{4d-IV}$ overprints the quartz

208 banding (Fig. 4F). Given the similar results obtained for FIs in Qtz$_{4a-IV}$, Qtz$_{4b-IV}$, Qtz$_{4c-IV}$ and

209 Qtz$_{4d-IV}$, these four types are grouped together as Qtz$_{4-IV}$ and will no longer be distinguished.

210 Stage V is marked by rare and very small quartz grains (< 0.1 mm), Li-muscovite, and

211 sulphides and does not contain any mineral of interest for this FI study.

212 Stage VI consists of a succession of fluorite (Fl$_{1-VI}$), kaolinite (Kln$_{1-VI}$) and late porous fluorite

213 (Fl$_{2-VI}$) that fills the cavities of the W-Sn and banded quartz veins (Fig. 4G). Dissolution

214 cavities in Toz$_{2-III}$ are filled by Kln$_{1-VI}$ and have rims composed of euhedral and zoned Toz$_{4-VI}$

215 crystals (more than 100 μm in size) (Fig. 4H). The last generation of topaz was selected for

216 the FI study. The first generation of fluorite (Fl$_{1-VI}$) is euhedral, mineral inclusion-free and is

217 coeval with the kaolinite. The second generation (Fl$_{2-VI}$) postdates the kaolinite and is

218 anhedral and zoned. The zoning is associated with variation in the yttrium content, kaolinite

219 inclusions, REE mineral inclusions (phosphates, fluorides and carbonates) and porosity. Both

220 generations of fluorite were selected for the FI study.

221   Stage VII displays sulphides (*e.g.* bismuthinite and pyrite) that were not considered for the FI

222   study.

223

224   2.2.2 Piaotang deposit

225

226   The Piaotang deposit is associated with a hidden biotite granite intrusion (*ca.* 400 m deep), the

227   contact of which with the surrounding metasedimentary rocks can only be observed in drill

228   cores. Two types of mineralization are described: wolframite-cassiterite-quartz veins and

229   disseminated wolframite in the greisen. The polymetallic W-Sn-(Nb) Piaotang deposit,

230   located near the Xihuashan deposit, is one of the largest W-Sn deposits in the Nanling Range

231   (Fig. 2C). The Piaotang mine produces 1.5 kt WO_3 per year and ranks eighth largest of

232   China's reserves with 47 kt WO_3 (MB Company database: www.metalbulletin.com). A

233   drillcore-based cross-section of the Piaotang deposit has been established and shows steeply-

234   dipping sub-parallel veins rooted in the buried granitic intrusion and hosted in the

235   metasedimentary rocks (Ni *et al.*, 2015). The greisen cupola was not captured in the original

236   cross-section of Ni *et al.* (2015), and it was not possible to precisely document the extent of

237   the greisen and its relationship with the granite in the present study (Fig. 2D). The granite was

238   emplaced during the Jurassic (159.8 ± 0.3 Ma, U-Pb dating on zircon; Zhang *et al.*, 2017).

239   The greisen has not yet been dated but an age of 159.5 ± 1.5 Ma has been determined for the

240   veins (U-Pb dating on cassiterite; Zhang *et al.*, 2017).

241   One type of vein with heterogeneous ore infilling was identified in the mine galleries of the

242   Piaotang deposit by Legros *et al.* (2018). The thickness of this vein type decreases from the

243   top to the bottom of the vein system, from a few centimetres at 556m depth to more than one

244   meter at 268m depth. Based on petrographic observations, Legros *et al.* (2018) distinguished

245   four paragenetic stages (I to IV) at the Piaotang deposit (Fig. 5).

246 Stage I corresponds to the precipitation of the ore-minerals (Fig. 6A and 6B): wolframite

247 (Wf$_{1-I}$), quartz (Qtz$_{1-I}$), cassiterite (Cst$_{1-I}$), Fe-Li-micas (Fe-Li-mca$_{1-I \text{ to } 3-I}$), topaz (Toz$_{1-I}$) and

248 molybdenite (Mlb$_{1-I}$). Quartz is the most abundant mineral in the vein and is present as cm-

249 sized euhedral crystals that do not exhibit the chemical zoning observed in cassiterite (Fig. 6C

250 and 6D). All three minerals were selected for the FI study. Topaz is almost completely altered

251 into clay minerals and no FIs were observed.

252 Plastic deformation occurred during Stage I. As described in Legros *et al.* (2018), this

253 deformation is particularly evident within quartz, topaz and micas, which show low intensity

254 kinking and the formation of sub-grains, and to a lesser extent in wolframite, which presents

255 slightly folded crystals (Fig. 6C).

256 Stage II corresponds to the replacement of Wf$_{1-I}$ by scheelite (Sch$_{1-II}$) and the crystallization

257 of chlorite (Chl$_{1-II}$), columbo-tantalite (Clb$_{1-II}$) and fluorite (Fl$_{1-II}$). The fluorite forms euhedral

258 cm-sized crystals that exhibit no zonation, mineral inclusions or plastic deformation (Fig. 6B),

259 and was selected for the FI study.

260 Stages III and IV were characterized by significant sulphide precipitation together with new

261 generations of wolframite, cassiterite, Fe-Li-micas, chlorite and fluorite. Minerals from Stages

262 III and IV are all too small for FI analysis.

263

264 2.3. Previous fluid inclusion studies of W-Sn deposits in the Nanling Range

265

266 Several vein-type granite-related W-Sn deposits in the Nanling Range, and more precisely

267 within the southern Jiangxi and Hunan provinces, have been the subject of FI studies:

268 Xihuashan (Giuliani *et al.,* 1988; Wei *et al.,* 2012), Maoping (Chen *et al.*, 2018),

269 Yaogangxian (Hu *et al.,* 2012), Dajishan, Dangping, Piaotang, Pangushan (Ni *et al.,* 2015),

270 Taoxikeng (Wang *et al.,* 2012), Shimenshi (Gong *et al.,* 2015; Wei *et al.,* 2017), Baxiannao

271   (Feng *et al.,* 2012), Shizhuyuan and Yejiwei (Xuexin *et al.,* 1990). Fluid inclusion studies

272   have been carried out on various transparent and opaque minerals from the vein systems,

273   including beryl, quartz, wolframite, cassiterite, fluorite, and tourmaline. Fluids are dominantly

274   aqueous, but CO_2-rich FIs are sometimes observed in quartz and very rarely in wolframite.

275   Vapor-dominated CO_2-rich FIs that coexist with liquid-dominated aqueous FIs are commonly

276   observed in quartz and have been interpreted as being related to boiling and/or immiscibility

277   (Wei *et al.,* 2012; Giuliani *et al.,* 1988; Ni *et al.,* 2015). Nevertheless, most inclusions

278   observed in wolframite and cassiterite are aqueous and can be used to unravel differences in

279   the fluid conditions of ore and gangue minerals (Piaotang, Dangping, Dajishan, Pangushan,

280   Ni *et al.,* 2015; Xihuashan, Wei *et al.,* 2012). Microthermometry data indicate

281   homogenization temperatures (T_h) of 150 to 300 °C for the gangue minerals, significantly

282   lower than those of wolframite (250 and 400 °C). Similarly, FIs in gangue minerals have a

283   lower salinity (0.5 to 9.0 wt.% equiv. NaCl) than those in wolframite (3.0 to 14.0 wt.% equiv.

284   NaCl) (Xihuashan, Giuliani *et al.,* 1988; Maoping, Chen *et al.*, 2018; Shizhuyuan, Yejiwie,

285   Xuexin *et al.,* 1990; Piaotang, Zeng *et al.,* 2002, Wang *et al.,* 2009; Dajishan, Xi *et al.,* 2008;

286   Yaogangxian, Cao *et al.,* 2009; Baxiannao, Feng *et al.,* 2012; Taoxikeng, Wang *et al.,* 2012;

287   Dangping, Pangushan, Ni *et al.,* 2015; Shimenshi, Wei *et al.,* 2017). Within single deposits,

288   wolframite FIs usually display a continuum between a high-salinity, high-temperature end-

289   member and a low-salinity, low-temperature end-member, interpreted as a mixing trend. A

290   combination of mixing and cooling processes has been considered decisive for ore mineral

291   precipitation (Wei *et al.,* 2012; Ni *et al.,* 2015; Chen *et al.*, 2018). Estimated P-T conditions of

292   FI entrapment in the Xihuashan, Dajishan and Taoxikeng deposits, assuming hydrostatic

293   pressure conditions and a geothermal gradient of around 50°C/km, range from 40 to 130 MPa

294   and 320 to 400 °C (Wei *et al.,* 2012; Xi *et al.,* 2008; Wang *et al.,* 2012). Pressure estimates

295   define depths of emplacement of between 1 and 4 km (Xuexin *et al.,* 1990; Wang *et al.,*

296 2012). Stable isotope analyses (O-H-S) have been performed on quartz, wolframite and

297 sulphide minerals, and also on quartz-hosted FIs from the Xihuashan, Taoxikeng, Shimenshi

298 and Baxiannao deposits and on a few wolframite-hosted FIs from the Maoping deposit. In all

299 deposits, $\delta^{18}O$ values of quartz and wolframite range from -8.8 to 14.3 ‰ and 4.1 to 6.0 ‰

300 VSMOW, respectively, δD values of quartz- and wolframite-hosted FIs range from -83 to 108

301 ‰ and -64 to -49 ‰, respectively, and $\delta^{34}S$ values of late sulfides range from -1.6 to 0.1 ‰

302 (Feng *et al.,* 2012; Liu *et al.,* 2002; Wang *et al.,* 2012; Wei *et al.,* 2012; Gong *et al.,* 2015;

303 Wei *et al.,* 2017). Helium and argon isotope compositions of wolframite- and sulfide-hosted

304 inclusions from the Piaotang and Yaogangxian deposits ($^{3}He/^{4}He$ = 0.2–0.8 R/R_A and

305 $^{40}Ar/^{36}Ar$ = 350–590; Wang *et al.,* 2009; Hu *et al.,* 2012).

306 In summary, taken together, the previous FI studies of vein-type granite-related W-Sn

307 deposits in the Nanling Range point to compositions and conditions that can be interpreted as

308 reflecting either mixing of two fluids (magmatic dominant and meteoric minor) or cooling of

309 a single fluid (magmatic), either of which could have led to the precipitation of the ore

310 minerals.

311

312 **3. Samples and analytical methods**

313

314 3.1 Fluid inclusion petrography and microthermometry

315

316 Double-polished thick sections (110 to 200 µm thick) of quartz, cassiterite, wolframite,

317 fluorite and topaz samples were prepared at the GeoRessources laboratory (Nancy, France).

318 Sections were made from multiple samples from each deposit (Maoping deposit (Stages III,

319 IV and VI): Qtz_{2-III} = 3 samples, Wf_{1-III} = 6 samples, Cst_{1-III} = 3 samples, Qtz_{4-IV} = 4 samples,

320 Fl_{1-VI} = 3 samples, Toz_{4-VI} = 3 samples, Fl_{2-VI} = 1 sample. Piaotang deposit (Stages I and II):

321   Qtz$_{1-I}$ = 4 samples, Wf$_{1-I}$ = 1 sample, Cst$_{1-I}$ = 3 samples, and Fl$_{1-II}$ = 3 samples). Petrographic

322   examinations were performed on transparent and semi-opaque minerals (quartz, cassiterite,

323   fluorite and topaz) using an Olympus BX-51 optical microscope at GeoRessources laboratory

324   (Nancy, France) and on opaque minerals (wolframite) using an Olympus BH-51 microscope,

325   equipped with an Olympus XM-10 infrared camera at the University of Geneva (Switzerland).

326   Petrographic observations were made at the scale of the entire crystal in order to compare FIs

327   in different growth zones and/or subgrains of the crystals. Cathodoluminescence (CL)

328   imaging was also conducted, using a CITL cold cathode instrument CL8200 Mk4 (15 kV and

329   400 mA) at the Georessources laboratory (Nancy, France).

330   Microthermometry was performed on quartz-, fluorite- and topaz-hosted FIs using a Linkam

331   THMSG600 heating-cooling stage mounted on an Olympus BX-51 microscope at the

332   GeoRessources laboratory (Nancy, France). The stage was calibrated with in-house and

333   certified standards by measuring the temperatures of the final melting of pure water in a silica

334   glass capillary (0.0 °C), the triple point of $CO_2 \pm$ Ar in a synthetic FI (−56.9 °C), and the

335   liquid + vapor → liquid homogenization of a natural FI at 165 °C. In aqueous FIs, the

336   temperatures of two phase changes were recorded: final ice melting (T_m(ice)) and liquid +

337   vapor → liquid total homogenization (T_h). For aquo-carbonic FIs, temperatures of final

338   clathrate melting (T_m(cla)) and liquid + vapor → vapor homogenization of the CO_2-dominated

339   carbonic phase ($T_h(CO_2)$) were also measured. The temperatures of the phase transitions are

340   reported with an accuracy of about ±0.1 °C for T_m(ice), T_m(cla) and $T_h(CO_2)$, and ±1 °C for T_h.

341   Microthermometry of wolframite-hosted FIs was carried out at the University of Geneva

342   (Switzerland) using a Linkam FTIR 600 stage mounted on an Olympus BH-51 microscope

343   equipped with an Olympus XM-10 infrared camera (Ortelli *et al.,* accepted). An oriented

344   section of a single prismatic crystal cut perpendicular to the cleavage was used. It has been

345   demonstrated that the visible light absorbed by opaque minerals is partially converted into

346 heat in proportion to the opacity, and this could potentially preclude accurate

347 microthermometric measurements (Moritz, 2006). To avoid this problem, a voltmeter was

348 connected directly to the lamp of the microscope to control the power of the incident light.

349 Sample heating is not high enough to affect microthermometric measurements if a 90% closed

350 diaphragm, a condenser at 0.3, and a power of 0 to 4 V depending on the transparency of the

351 different zones of the crystals are used (Casanova *et al.,* accepted).

352 Since cassiterite is a semi-opaque mineral, the same protocol as that used for opaque minerals

353 was applied under transparent light at the GeoRessources laboratory (Nancy, France). Sample

354 heating due to visible light absorption was negligible compared to wolframite. Analyses were

355 performed with a fully open diaphragm and condenser, and within a range of 0 to 6 V

356 depending on the transparency of the different zones in the crystals.

357 The salinities of CO_2-rich FIs were calculated using the equation of state of Duan *et al.,*

358 (1992) in the Q2 programs of Bakker (1997, 2003). The first ice melting temperature (*e.g.* the

359 eutectic temperature) could not be precisely observed, but the range of the likely transition (-

360 25 to -15 °C) encompasses the eutectic temperatures of the H_2O-NaCl and H_2O-KCl-NaCl

361 systems (-21.2 °C and -23.5 °C, respectively). In addition to sodium, potassium was identified

362 by LA-ICPMS in almost all FIs. However, FI compositions cannot be reconstructed in the

363 H_2O-NaCl-KCl system in the absence of halite and sylvite at room temperature (Bodnar

364 2003). Nevertheless, the maximum error in the calculated salinity induced by assuming a

365 single-salt H_2O-NaCl system would be *ca.* 1 wt.% equiv. NaCl. Similarly, calcium was

366 detected by LA-ICPMS in significant amounts in some FIs, sometimes at an even higher

367 concentration than Na and K. Due to the high limits of detection for calcium in LA-ICPMS

368 analyses, we cannot exclude the possibility that all of the analyzed FIs contain significant

369 amounts of calcium. However, no hydrohalite was observed during the microthermometry

370 runs and the composition of the fluid inclusions cannot therefore be interpreted in the H_2O-

371 NaCl-CaCl$_2$ system. The salinity of aqueous FIs were therefore calculated in the H$_2$O-NaCl

372 system using the Archer (1992) equation of state and the Bulk program of Bakker (1997,

373 2003). Isochores were calculated for aqueous FIs using the ISOC program (Bakker, 1993) and

374 the empirical equations of state of Bodnar and Vityk (1994). All isochores were constructed to

375 reflect hydrostatic conditions and a depth of emplacement of between 5 and 10 km. Evidence

376 for plastic deformation during the main ore event is observed in both deposits and could be

377 indicative of lithostatic conditions. However, the pressure variation that would be associated

378 with the change from lithostatic to hydrostatic conditions does not seem realistic. Moreover,

379 most vein systems are interpreted in terms of hydrostatic conditions.

380

381 3.2 Raman spectroscopy

382

383 Raman spectroscopy of the liquid phase of one-phase liquid aqueous inclusions and of the gas

384 phases of two-phase aqueous incusions and three-phase (liquid H$_2$O + liquid CO$_2$ + vapor

385 CO$_2$) inclusions was performed at the GeoRessources laboratory (Nancy, France) in order to

386 detect possible gases and determine their nature. Raman spectra were recorded using a

387 LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with a 600 gr.mm^{-1} grating and an

388 edge filter. The confocal hole aperture was 500 µm and the slit aperture was 100 µm. The

389 excitation beam was provided by a Stabilite 2017 Ar$^+$ laser (Spectra Physics, Newport

390 Corporation) at 514.53 nm and a power of 200 mW, focused on the sample using a 100x

391 objective (Olympus). The acquisition time and number of accumulations were chosen in such

392 a way as to optimize the signal-to-noise ratio (S/N) (ideally lower than 1 %). Neither limits of

393 detection nor absolute concentrations of trace gases could be determined with precision,

394 however the relative proportions of the gas species could be estimated qualitatively using the

395   peak area, acquisition time, and the specific scattering cross-section of each peak with

396   LabSpec software (Schrotter and Klockner, 1979) as defined by Burke (2001).

397

398   3.3 LA-ICPMS analysis

399

400   Selected major, minor and trace elements were measured in FIs in quartz, cassiterite, topaz

401   and fluorite using the LA-ICPMS instrumental setup at the GeoRessources laboratory (Nancy,

402   France), which is similar to that described in Leisen *et al.* (2012) and Lach *et al.* (2013). LA-

403   ICPMS analyses were performed on the same fluid inclusions as those used for the

404   microthermometry. The instrument comprises a GeoLas excimer laser (ArF, 193 nm,

405   Microlas, Göttingen, Germany) (Günther *et al.,* 1997) and an Agilent 7500c quadrupole ICP-

406   MS. The laser beam is focused onto the sample within a small-volume lozenge-shaped

407   ablation cell dedicated to FI analysis using a Schwarzschild reflective objective

408   (magnification 25x; numerical aperture 0.4) mounted on an optical microscope (Olympus

409   BX41) equipped with an X-Y motorized stage and a CCD camera. The NIST610 glass

410   (Jochum *et al.,* 2011) was chosen as an external standard (analytical accuracy verified with

411   the NIST612 external standard; Longerich *et al.,* 1990). Analyses were performed under the

412   following operating conditions: a laser fluence of 8 J/cm² and a laser shot frequency of 5 Hz;

413   He = 0.5 L.min^{-1} as a carrier gas mixed with Ar = 0.7 L.min^{-1} *via* a cyclone mixer prior to

414   entering the ICP torch; spot sizes of 44 µm; and an ablation duration of 40 s. The following

415   isotopes were analyzed: ^{7}Li, ^{23}Na, ^{24}Mg, ^{39}K, ^{43}Ca (instead of ^{40}Ca to avoid interference with

416   ^{40}Ar^{+}), ^{55}Mn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{93}Nb, ^{95}Mo, ^{118}Sn, ^{133}Cs, ^{138}Ba, ^{181}Ta, and ^{182}W, with an

417   integration time of 0.01 s per mass channel. These elements were selected as they were

418   suspected to be present in the fluids based on the compositions of the successive minerals in

419   the paragenetic successions and/or because they are usually enriched in magmatic-

420   hydrothermal fluids in this context (*e.g.*, Na, K, Cs, and Rb). Calibration and signal-

421   integration were performed with the Matlab®-based SILLS program (Guillong *et al.,* 2008).

422   Absolute element concentrations were calculated from the ratios of the analysed elements to

423   Na. The sodium concentrations were obtained from the salinities estimated from the

424   microthermometry analyses (in wt. % equiv. NaCl) using the charge-balance technique (Allan

425   *et al.,* 2005). By using the analyzed elemental ratios of the major cationic species to Na, the

426   amount of Na (as determined from the wt. % equiv. NaCl) could be corrected for

427   contributions from other chloride salts. Each ablation spectrum was examined before further

428   processing. Spectra were only selected if the fluid inclusion was reached after ablating the

429   crystal surface (*e.g.* when the FI peak was completely detached from the surface

430   contamination peak). During processing, three sectors were defined on the spectra: the

431   background, the matrix and the FI signal. Spectra showing contamination by solid inclusions

432   in the matrix or by crystals accidentally trapped in the FIs were discarded. A matrix correction

433   was applied when the elements measured in the fluid inclusions were also present as trace

434   elements in the ablated crystal. For cassiterite and fluorite-hosted inclusions, a matrix

435   correction was applied using the SILLS program and using Sn and Ca, respectively, as

436   internal standards (determined stochiometrically). Consequently, Sn and Ca were not

437   determined for fluorite- and cassiterite-hosted FIs. The matrix signal was generally constant

438   and showed no evidence of local chemical variation. Limits of detection (LODs) were

439   calculated using the 3σ criterion (Longerich *et al.,* 1996). The analytical precision of most

440   elements is within 15 % relative standard deviation (RSD). The analytical precision of the

441   other elements is typically better than 30 % RSD (Allan *et al.,* 2005).

442

443   3.4 Isotopic measurements

444

445   3.4.1 Oxygen isotopes of minerals and fluids

446

447   Oxygen isotope analyses of quartz, Fe-Li-micas, topaz and wolframite were carried out at the

448   Stable Isotope Laboratory at the University of Lausanne, Switzerland, using a CO_2-laser

449   fluorination line coupled to a Finnigan MAT 253 mass spectrometer. Pure mineral separates

450   were hand-picked under a binocular microscope and crushed in an agate mortar. For each

451   analysis, between 1.16 and 3.15 mg of sample was loaded in the cell with the LS-1 reference

452   material. The chamber was evacuated overnight and maintained under a vacuum better than

453   10^{-4} mbar before fluorination. Samples were heated with a CO_2-laser in the presence of F_2 and

454   liberated oxygen gas was purified on overheated KCl salt within the extraction line. Oxygen

455   was absorbed on a molecular sieve (13x) held at liquid nitrogen temperature, which was then

456   heated to liberate the O_2 and release it into the mass spectrometer. The results for each

457   acquisition are reported in per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean

458   Water) and are normalized to the LS-1 quartz standard (reference value: $\delta^{18}O$ = 18.1 ‰

459   VSMOW). The precision, based on replicate analyses of the samples (when possible) and of

460   the standard run with the samples, was generally better than 0.2 ‰. The values shown in

461   Table 3 do not include replicate analyses. The oxygen isotope compositions of fluids at

462   estimated FI trapping temperatures were calculated using the fractionation equations of Zheng

463   (1993a) for Fe-Li-micas (lepidolite in this case), Zheng (1993b) for quartz, Zheng (1991) for

464   wolframite, and Zheng (1993a) for topaz. The results obtained with these equations are

465   consistent (within 0.1 ‰) with experimental calibrations in the 150–400 °C temperature range

466   considered (wolframite: Zhang *et al.*, 1994; quartz: Sharp *et al.*, 2016). It was not possible to

467   perform oxygen isotope analyses on cassiterite crystals because of the thin zoning.

468

469   3.4.2 Hydrogen isotopes of fluid inclusions

470

471 The hydrogen isotope compositions of FIs were measured at the CRPG laboratory (Nancy,

472 France). Between 2 and 4 g of pure separates of quartz, wolframite and cassiterite were hand-

473 picked and inserted into steel reaction vessels. Duplicates of each mineral from each deposit,

474 were run in order to monitor the within-batch precision (*e.g.* the analytical precision). To

475 release H_2O molecules adsorbed on the mineral surface, the vessels were connected to a

476 vacuum extraction line and heated overnight at 120 °C (Dublyansky and Spötl, 2009).

477 Microthermometric tests were conducted before extraction to ensure that the FIs would not

478 decrepitate nor stretch at temperatures below 200 °C. The vessels were then crushed under

479 vacuum to release all fluids hosted in the crystals. Incondensable gases were directly removed

480 from the extraction line so that only H_2O (and possibly CO_2) was collected on a liquid

481 nitrogen cold trap. As amounts of CO_2 were always too low to be analyzed, CO_2 was

482 therefore removed from the line. Metal reduction was chosen as the method to prepare gas

483 samples for hydrogen isotope ratio analysis because of the small amount of sample (< 1 μl)

484 needed (Wong *et al.,* 1984). H_2O was reduced into H_2 by passing it through a uranium reactor

485 heated to 800 °C (Bigeleisen *et al.*, 1952). Isotopes were analyzed using a VG 602D mass

486 spectrometer. To ensure the accuracy of isotopic measurements, three in-house standards were

487 also crushed and analyzed. Values of δD are reported in per mil (‰) relative to VSMOW.

488 The same reagent was used for the reduction of consecutive water samples. Because water

489 adheres to the internal surfaces of the uranium reactor, hydrogen isotope analyses may show a

490 memory effect. The magnitude of this memory effect depends on the difference in the isotopic

491 compositions and the amount of water reduced for two successive samples (Blaise *et al.,*

492 2015). The δD values obtained from the first extraction of a sample were therefore discarded

493 as they may have been affected by this memory effect. Isotope measurements were performed

494 one to three times for each host mineral, depending on the amount of material available. The

495   deviance in δD between each isotopic measurement of the same sample was less than ± 5 ‰

496   and was also less than the standard error.

497

498   **4. Results**

499

500   4.1 Fluid inclusion petrography

501

502   For both the Maoping and Piaotang deposits, fluid inclusions (FIs) were investigated in quartz

503   (Fig. 7A, B, C, F, J and K), wolframite (Fig. 7E and L), cassiterite (Fig. 7D and M) and

504   fluorite (Fig. 7G, I and N). Topaz was only investigated in the Maoping deposit (Fig. 7H).

505   These minerals belong to pre-, syn- and post-ore stages and were used to reconstruct fluid

506   evolution over time. Unfortunately, no FIs were found in Stages I and II minerals of the

507   Maoping deposit. Petrographic descriptions of the FIs are summarized in Table 1. The high

508   abundance of FIs in quartz gives the crystals a milky appearance that makes petrographic

509   description of the FIs difficult. Other minerals contain fewer FIs and are therefore more

510   translucent, making petrographic characterization of the FIs much easier. According to the

511   criteria of Roedder (1984), the FIs selected in this study are either pseudosecondary (*e.g.*

512   distributed along intragranular FI planes (FIPs)) or presumably primary (isolated, randomly

513   distributed or clustered or aligned and/or elongated along growth zones). In all of the samples

514   studied, there was no visible compositional difference between the pseudosecondary and the

515   presumably primary two-phase FIs and thus these two FI types will not be further

516   distinguished. The application of the FI assemblage (FIA) concept (Goldstein and Reynolds,

517   1994) is limited in this study either by the milky appearance of the quartz and/or the relatively

518   small number of FIs over 5 µm in size. The vast majority of FIs that were analyzed show two

519   phases (liquid + vapor) at room temperature and typically range from 5 to 40 µm in size. Fluid

520　inclusions display round, elongate, irregular or negative-crystal shapes, regardless of their

521　location. A visual estimate of the volumetric fraction of the vapor phase relative to the entire

522　inclusion at room temperature (φ_{vap}) was deduced from the area fraction of the vapor bubble at

523　room temperature ( ) and ranged from 10 to 50 %. values are always distributed randomly in

524　single crystals and in possible FIAs. Apparent variation in values can result, however, from

525　two-dimensional projection of the FIs under the petrographic microscope. Any apparent

526　variation in φ_{vap} should therefore be considered with caution (Bakker and Diamond, 2006).

527　Rare (< 10 %) one-phase (liquid) FIs were randomly observed in $Qtz_{2\text{-}III}$ and $Qtz_{1\text{-}I}$ from both

528　the Maoping and the Piaotang deposits. One-phase FIs were usually either isolated or

529　distributed randomly among two-phase FIs. One-phase and two-phase FIs show similar

530　salinities (0.5 - 1.0 wt.% equiv. NaCl). One-phase FIs could therefore represent metastable

531　two-phase inclusions whose bubbles had not nucleated (measured by Raman spectroscopy;

532　Tarantola and Caumon, 2015). In addition, very rare (< 5 %) three-phase (liquid H_2O + liquid

533　CO_2 + vapor CO_2) inclusions were observed as isolated clusters in $Qtz_{2\text{-}III}$ of the Maoping

534　deposit. These three-phase aquo-carbonic inclusions were only observed in this early quartz

535　and therefore seem to be representative of the crystallization conditions of this mineral. No

536　apparent relationships with two-phase inclusions were identified and there was no

537　petrographic evidence for heterogeneous trapping of different fluids within individual FIAs.

538　The two-phase and three-phase inclusions are therefore thought to represent two distinct non-

539　coeval fluids. Despite evidence of ductile deformation in early $Qtz_{2\text{-}III}$ of the Maoping deposit

540　and $Qtz_{1\text{-}I}$ of the Piaotang deposit, the FIs do not show any signs of stretching or necking-

541　down. Fluid inclusions are organized into intragranular trails that crosscut subgrain

542　boundaries. These FIs are therefore assumed to have been unaffected by, and thus to postdate,

543　the early quartz plastic deformation. Selected FIs do not display halos of small FIs that could

544　reflect either decrepitation or crystal-recovery processes (Lambrecht and Diamond, 2014).

545 Moreover, φ_{vap} variations observed in FIs are always randomly distributed among grains,

546 subgrains and possible FIAs. Following the criteria of Bakker (2017) and given the

547 descriptive features above, no evidence for post-entrapment modification of FIs due to

548 diffusion or preferential H_2O loss was identified. Cathodoluminescence imaging was used to

549 identify any particular FI arrangements associated with textural or growth features that were

550 not visible by optical microscope. No dark patchy halos (attributed to FIs or micropores) were

551 observed by cathodoluminescence nor was any evidence for recrystallization found. The

552 cathodoluminescence did however highlight the growth zoning in topaz, cassiterite and

553 fluorite that had already been observed in transmitted light.

554

555 4.2 Microthermometry

556

557 The microthermometric data of the Maoping and Piaotang FIs are summarized in Table 1 and

558 Figure 8. The T_h and salinity data are plotted in binary diagrams for two-phase aqueous

559 inclusions (Fig. 8).

560 Salinity values display a continuum in both deposits: 0.0 to 12.6 wt.% equiv. NaCl for the

561 Maoping deposit and 0.4 to 8.3 wt.% equiv. NaCl for the Piaotang deposit. Within a single

562 mineral, salinity varies by 2 to 8 wt.% equiv. NaCl. Two groups of T_h values can be

563 distinguished in the two deposits: a low-T_h group (150 to 250 °C) and a higher T_h group (300

564 to 350 °C) (Fig. 8). It was not possible to associate the observed variations in salinity and T_h

565 with any particular petrographic feature, such as shape, φ_{vap}, or the spatial arrangement of FIs

566 within a crystal.

567 A number of similarities between the two deposits can be observed. Fluid inclusions in quartz

568 that formed during the main mineralizing events (Qtz$_{2-III}$ at Maoping and Qtz$_{1-I}$ at Piaotang)

569 have distinctly lower salinities than FIs in other minerals (0.0–6 wt.% equiv. NaCl), as well as

570   very late fluorite from both deposits have lower T_h values. Fluid inclusions in wolframite and

571   cassiterite are characterized by high salinities (twice the salinity of quartz). At Maoping, Wf_{1-III}-

572   and Cst_{1-III}-hosted FIs both display a narrow range of high T_h. At Piaotang, Cst_{1-I}-hosted

573   FIs show a similarly narrow range high of T_h but the Wf_{1-I}-hosted FIs display much lower

574   temperatures (180–230 °C) close to those of Qtz_{1-I} (150–180 °C). In late-stage minerals (Qtz_{4-IV},

575   Fl_{1-VI} and Toz_{4-VI} at Maoping and Fl_{1-II} at Piaotang), salinities are generally comparable to

576   those of cassiterite- and wolframite-hosted FIs and in the Qtz_{4-IV} at Maoping are sometimes

577   even higher. Fluid inclusions in late-stage minerals at Maoping can be divided into two

578   groups: Qtz_{4-IV}- and Fl_{2-VI}-hosted FIs, which display a similar range of T_h as the Qtz_{2-III} and

579   Fl_{1-VI} FIs; and Toz_{4-VI}-hosted FIs, which, like the Wf_{1-III}- and Cst_{1-III} FIs, show a narrow range

580   of T_h. For the aquo-carbonic FIs, $T_m(cla)$ ranges from 7.7 to 8.1 °C and $T_h(CO_2)$ ranges from

581   29.4 to 30.6 °C to the vapor phase. Total density is homogeneous among FIs (0.39 to 0.44),

582   and compositions range from 38 to 42 % H_2O and 56 to 60 % CO_2. The total salinity of rare

583   three-phase aquo-carbonic FIs (around 0.5 wt.% NaCl equiv.) is lower than that of most two-

584   phase aqueous FIs.

585

586   4.3 Raman spectroscopy

587

588   Raman spectroscopy data (Table 1 and Fig. 8C) were acquired from the same FIs used for

589   microthermometry analyses. Traces of CO_2, CH_4 and N_2 gases were detected by Raman

590   spectroscopy in the vapor phase of two-phase aqueous FIs in Qtz_{2-III}, Cst_{1-III}, Qtz_{4-IV}, Toz_{4-VI}

591   in Maoping and Cst_{1-I} in Piaotang, but no associated phase transitions were observed during

592   microthermometry analyses (Fig. 8C).

593   In the case of the Qtz_{4-IV} and Toz_{4-VI} FIs, CO_2 was the only gas detected in the vapor phase

594   and was present in every FI. In cassiterite and Qtz_{2-III} FIs, the gas phase showed trace but

595   variable amounts of CO_2, CH_4 and N_2 (Fig. 8C). In the case of cassiterite, the proportions of

596   CO_2, CH_4 and N_2 varied from one FI to another but all three gases were detected in each FI.

597   The average compositions of FI bubbles for the two deposits were 61 to 75 mol% CO_2, 22 to

598   25 mol% CH_4, and 3 to 15 mol% N_2 (Fig. 8C). In contrast, while CO_2, CH_4 and N_2 gases were

599   detected in the gas phase in Maoping Qtz_{2-III} FIs, individual analyses contained none, one, two

600   or all three of the gas species, in highly variable proportions. The FIs mainly contained

601   bubbles filled with CO_2 + CH_4 (15 % of FIs), $CH_4 \pm N_2$ (50 % of FIs) or pure H_2O (33 % of

602   FIs). CH_4 was the most frequently detected gas because of its elevated Raman cross-section.

603   No dissolved gases were detected in the one-phase aqueous liquid FIs from the Maoping

604   deposit.

605

606   4.4 Element compositions

607

608   Two-phase aqueous FIs from the Maoping and Piaotang deposits were selected for LA-

609   ICPMS analyses if they met the following criteria: (i) previous characterization by optical

610   microscopy and microthermometry, (ii) relatively large in size (10-30 μm), and (iii) located

611   an appropriate distance from the polished thick section surface (< 15 μm). From Maoping, a

612   total of thirty-two FIs were selected from quartz (N = 11), cassiterite (N = 7), fluorite (N = 4)

613   and topaz (N = 10). From Piaotang, a total of twenty-nine FIs were selected from quartz (N =

614   8), cassiterite (N = 11) and fluorite (N = 10). Element concentrations in FIs are reported in

615   Table 2 and Figures 10 and 11. Since similar results were obtained for FIs in equivalent host

616   minerals in Maoping and Piaotang, the LA-ICPMS data will hereafter be described without

617   making any distinction between the two deposits.

618   Due to the relatively small size of the FIs and their relatively low salinities, data from many

619   analyses were lower than the limit of detection (LOD). Generally speaking, LODs vary from

620 one analysis to another as a function of the amount of the given element in the matrix, and the

621 ratio between the signal intensity of the inclusion and the background. In this study, the

622 proportions of analyses above the LOD values were: Na (100%), Cs (92%), Li (90%), K

623 (87%), Rb (85%), Mn (64%), Sn (54%), Mg (48%), W (48%), Sr (25%), Ba (25%), Mo

624 (20%), Ta (20%), Nb (18%), Y (16%) and Ca (13%). Calcium LODs are particularly high due

625 to analysis of the isotope ^{43}Ca, which is often too low in concentration to be detected. For FIs

626 with concentrations <LOD, the LODs show a similar range of concentrations to those

627 measured in other inclusions from the same mineral.

628 In all FIs, the two main cations were Na and K, which range in concentration from 960 to

629 37700 ppm and from 110 to 36000 ppm, respectively. Calcium is present in high

630 concentrations (1200 to 20000 ppm) but could only be measured in a few quartz-hosted FIs

631 from both deposits ($N = 8$).

632 In the Na-Li-K ternary diagram (Fig. 11A), quartz- and fluorite-hosted FIs have overlapping

633 compositions, while cassiterite- and topaz-hosted FIs plot in two distinct fields. In Na *vs*. Li

634 and Na *vs*. K diagrams, fluid inclusion compositions are scattered between a Na-K-Li-rich

635 end-member (high salinity associated with cassiterite, fluorite and topaz; Na > 5000 ppm, K >

636 1000 ppm and Li > 100 ppm except for one outlying value in fluorite) and a Na-K-Li-poor

637 end-member (low-salinity associated with quartz; Na = 900–11000 ppm, K = 900–10000 ppm

638 and Li = 10–500 ppm) (Figs. 11B and C).

639 The following systematics are observed: FIs in early Qtz_{2-III} and Qtz_{1-I} are more depleted in

640 Rb, Cs (< 150 ppm) and Li (< 400 ppm) than FIs in other minerals. The Cst_{1-III}- and Cst_{1-I}-

641 hosted FIs from both deposits show the highest concentrations of Li (> 1600 ppm) and Nb

642 (15-70 ppm) as well as high amounts of Cs (> 400 ppm) and W (up to 220 ppm when

643 detected). The Fl_{1-VI}- and Fl_{1-II}-hosted FIs show the highest concentrations of Sr (> 370 ppm).

644 At Maoping, Qtz_{4-IV}-hosted FIs show high Li (90-2200 ppm), Sn (120-450 ppm), W (160-300

645 ppm) contents and the highest concentrations of Mg and Mn (450-9900 ppm for both). $Toz_{4\text{-}VI}$-hosted FIs show the highest K concentrations (> 8200 ppm) and the lowest detected Mg

647 contents (< 120 ppm).

648 Fluid inclusions in quartz from both deposits have high K/Rb (20 to 420) and low Cs

649 concentrations (< 26 ppm), while fluorite and topaz have low K/Rb and intermediate Cs

650 contents and cassiterite has a low K/Rb (5 to 35) and high Cs content (400 to 1000 ppm; Fig.

651 11D).

652

653 4.5 Oxygen and hydrogen stable isotopes

654

655 Oxygen and hydrogen isotopic compositions of minerals and fluids from the Maoping and

656 Piaotang deposits are presented in Table 3 and Figure 12.

657 At the Maoping deposit, oxygen stable isotope analyses were performed on crystals of Fe-Li-

658 $micas_{2\text{-}II}$, $Qtz_{2\text{-}III}$, $Wf_{1\text{-}III}$, $Cst_{1\text{-}III}$, Fe-Li-$micas_{3\text{-}III}$, $Qtz_{4\text{-}IV}$ and $Toz_{4\text{-}VI}$. At the Piaotang deposit,

659 oxygen stable isotope analyses were performed on crystals of $Qtz_{1\text{-}I}$, $Wf_{1\text{-}I}$ and $Cst_{1\text{-}I}$. The $\delta^{18}O$

660 values of Fe-Li-micas and topaz from the Maoping deposit are 8.3 - 8.7 ‰ VSMOW and 8.4

661 ‰ VSMOW, respectively. Quartz and wolframite from both deposits have $\delta^{18}O$ values of

662 10.8 - 11.6 ‰ VSMOW and -3.0 - 0.5 ‰ VSMOW, respectively.

663 At the Maoping deposit, hydrogen isotope analyses were performed on FIs hosted by $Qtz_{2\text{-}III}$,

664 $Wf_{1\text{-}III}$, $Cst_{1\text{-}III}$ and $Qtz_{4\text{-}IV}$. At the Piaotang deposit, hydrogen isotope analyses were performed

665 on FIs in $Qtz_{1\text{-}I}$, $Wf_{1\text{-}I}$ and $Cst_{1\text{-}I}$ (Fig. 12B). Based on our data obtained from

666 microthermometry and LA-ICP-MS analyses, each mineral seems to host one specific fluid

667 composition. The δD values of bulk fluid inclusion contents recovered from crushing cannot

668 therefore result from mixing of several fluid inclusion populations. All δD values are between

669 -78 and -51 ‰ VSMOW. At the deposit scale, δD values range from -78 to -55 ‰ VSMOW

670   at Maoping and from -70 to -51 ‰ VSMOW at Piaotang. The following systematics are

671   observed in both deposits: δD values between -59 and -51 ‰ VSMOW in fluids from $Qtz_{2\text{-}III}$

672   and $Qtz_{1\text{-}I}$, δD values between -78 and -76 ‰ VSMOW in fluids from $Wf_{1\text{-}III}$ and $Wf_{1\text{-}I}$ and

673   intermediate δD values, between -72 and -58 ‰ VSMOW, in fluids from $Cst_{1\text{-}III}$ and $Cst_{1\text{-}I}$. In

674   addition, fluids in the post-ore $Qtz_{4\text{-}IV}$ from the Maoping deposit display intermediate values,

675   between -66 and -62 ‰ VSMOW.

676

677   **5. Discussion**

678

679   5.1 Identification of the fluid end-members

680

681   At both deposits, microthermometric data as well as elemental and isotopic compositions of

682   FIs show specific fluid compositions for each host mineral and show compositional variations

683   that point to four fluid reservoirs and mixing processes associated with successive episodes of

684   mineral crystallization. These end-members were identified primarily from

685   microthermometric data and then from elemental and isotopic compositions.

686   Variations in T_h and salinity (Figs. 8A and B) suggest a low-salinity, low-temperature end-

687   member (**A**), an intermediate-salinity high-temperature end-member (**B**), a high-salinity high-

688   temperature end-member (**C**), and a high-salinity low-temperature end-member (**D**). The

689   continuum of data between the possible end-members suggests mixing trends between (**A**)

690   and (**B**)-(**C**)-(**D**) at Maoping and between (**A**) and (**D**), and (**B**) and (**C**) at Piaotang.

691   End-member (**A**) is found in early quartz and fluorite from both deposits. It is characterized

692   by low salinity (< 6 wt.% NaCl equiv.) and T_h between 100 and 250 °C (Fig. 8). Trapping

693   conditions deduced from isochores (Fig. 9) indicate temperatures of 170 to 360 °C with

694   associated pressures of 60 to 120 MPa, assuming hydrostatic conditions (assumed depth of

695 granite emplacement between 5 and 10 km). According to LA-ICPMS data, this fluid end-

696 member is associated with low Li/Na and K/Na ratios and low Na (< 1000 ppm), Li (< 10

697 ppm) and K (< 100 ppm) contents. End-member (**A**) also tends to be depleted in most

698 incompatible elements, such as Cs (< 26 ppm) and rare metals (W < 40 ppm), and displays a

699 high K/Rb ratio of around 400. In agreement with the microthermometric and LA-ICPMS

700 data, the stable isotope data suggest that end-member (A) is close in composition to local

701 meteoric water. The isotopic composition of the meteoric-derived component suggested from

702 mixing scenarios at the Xihuashan deposit, located a few kilometers away from the Maoping

703 and Piaotang deposits, is consistent with this study (Wei *et al.*, 2012).

704 Fluid end-members (**B**) and (**C**) are mostly associated with the precipitation of ore minerals

705 and define the trends in FI microthermometric data for wolframite, cassiterite, topaz and

706 fluorite. These trends are characterized by a very narrow range of T_h (270-350 °C) that is

707 higher than the T_h of end-member (**A**) (Fig. 8). End-members (**B**) and (**C**) are characterized by

708 distinct salinities, with end-member (**B)** representing a low-salinity high-temperature fluid

709 end-member (less than 2.0 wt.% equiv. NaCl) and end-member (**C**) representing a high-

710 salinity high-temperature fluid end-member (more than 7.0 wt.% equiv. NaCl) (Fig. 8). As

711 these variations in salinity do not significantly influence the slopes of the isochores, the

712 trapping conditions of the two fluids are similar, with pressures similar to end-member (**A**)

713 and temperatures between 320 and 470 °C (assuming a depth of 5–10 km and a hydrostatic

714 gradient) (Fig. 9). Both end-members are characterized by relatively high Li/Na and K/Na

715 ratios (> 7000, 100 and 1000 ppm for Na, Li and K respectively). Additionally, these two end-

716 members show very low K/Rb ratios (> 50) as well as a relative enrichment in incompatible

717 elements, such as rare metals (W > 100 ppm) and Cs (> 400 ppm), compared to end-member

718 (**A**).

719　The fluid end-member (**D**) is trapped in quartz at Maoping (Qtz_{4-IV}) and in wolframite and

720　fluorite at Piaotang. This end-member is characterized by T_h values comparable to the Qtz_{1-I},

721　Qtz_{2-III} and Fl_{2-VI} data that define end-member (**A**) and a salinity similar to the ore mineral FIs

722　that characterize end-member (**C**) (Fig. 8). Fluid (**D**) was trapped at 180-380 °C and 60-120

723　MPa (Fig. 9). End-member (**D**) has intermediate Li/Na and K/Na ratios and moderate

724　concentrations of incompatible elements (W, Sn, Cs, etc.) compared to end-members (**A**) and

725　**(B)-(C)** (Fig. 11).

726　The hypothesis of an evolving magmatic fluid reservoir for end-members **(B)**, **(C)** and **(D)** is

727　consistent with their observed high salinities, high temperatures, and incompatible element

728　(Li, Cs, W, etc.) contents, as well as with the trend in their isotopic compositions toward the

729　magmatic box (Fig. 12D). Though the Maoping and Piaotang deposits do not display the

730　higher temperatures (> 600 °C) and salinities (> 20 wt.% equiv. NaCl) sometimes observed

731　in magma-derived fluids (Audétat *et al.*, 2000; Webster *et al.*, 2004; Rickers *et al.*, 2006),

732　given that the data reflect the P-T-x composition of a mixture containing meteoric fluids (end-

733　member(**A**)), a magmatic origin for end-members **(B)**, **(C)** and **(D)** is still consistent.

734

735　5.2 P-T-x evolution

736

737　In both deposits, pre-ore quartz-hosted FIs define intragranular trails and crosscut subgrain

738　boundaries. These fluid inclusions therefore post-date the ductile deformation of quartz and

739　could have been trapped during any post-crystallization fluid event. Furthermore, these FIs

740　have low-salinities, contain CO_2-CH_4-N_2 gases, contain less than 400 ppm Li and less than

741　150 ppm Rb and Cs, and have low-δD, *e.g.* conditions that are only seen in pre-ore quartz.

742　Two hypotheses can therefore be put forward: (i) early quartz FI entrapment postdates quartz

743　crystallization and deformation but predates any subsequent mineral crystallization (in this

744 case, wolframite and cassiterite); or (ii) early quartz FI entrapment postdates the

745 crystallization of other minerals that did not register this event. Given that (i) the wolframite

746 at Piaotang was deformed under the same P-T conditions as the early quartz (based on

747 isochore interpretations), (ii) post-ore fluid stages are characterized by FIs in quartz and

748 fluorite (minerals that can deform under the same P-T conditions as the early quartz), and (iii)

749 none of these minerals contain FIs that show similar P-T-x conditions to the early quartz FIs,

750 then the first hypothesis is the more likely of the two.

751 Crystallization of early quartz in both deposits and of wolframite in Piaotang, through mixing

752 of the meteoric (**A**) and magmatic (**B**) (at Maoping) or (**D**) (at Piaotang) reservoirs, occurred

753 under hydrostatic conditions (Fig. 9). The salinity resulting from this mixing ranges from

754 essentially zero to 6 wt.% equiv. NaCl. Furthermore, wolframite and cassiterite display a

755 higher salinity and a higher temperature. The magmatic end-member therefore seems to have

756 become more predominant after conditions of ore crystallization were reached.

757 Like quartz, wolframite and cassiterite from Maoping and cassiterite from Piaotang appear to

758 have crystallized under hydrostatic conditions (Fig. 9) and from mixing between the meteoric

759 (**A**) and highly differentiated magmatic (**C**) reservoirs. During this stage, the temperature

760 stabilized whereas salinity fluctuated between 5 and 12 wt.% equiv. NaCl (Fig. 8A and 8B),

761 and the metal stock in the fluid mixture increased until saturation and the precipitation of ore

762 minerals.

763 Differences between the quartz- and ore mineral-crystallizing fluids might be explained by

764 differentiation of the granite. An increasing degree of differentiation can be traced by the

765 decrease in the K/Rb fluid ratio (Shaw, 1968; Klemm *et al.*, 2008; Lüders *et al.*, 2009), and

766 we observe here that the K/Rb ratio of quartz-hosted FIs is indeed significantly higher (75–

767 414) than the ratio observed in ore-hosted FIs (7–36). Moreover, FIs in ore minerals contain

768 higher concentrations of incompatible elements such as Cs (> 410 ppm) and rare metals such

769　as W (2 - 220 ppm, which are enriched in the residual melt during differentiation (Fig. 10 and

770　11).

771　Quartz and ore mineral FIs also display significantly different δD values (-59 to -51 ‰ and -

772　78 to -58 ‰ VSMOW, respectively). This difference cannot be explained by the

773　differentiation process itself but some studies have demonstrated that degassing of water from

774　the magma through fractional distillation can lead to such a decrease (Taylor *et al.*, 1983;

775　France-Lanord *et al.*, 1988, Hedenquist and Lowenstern, 1994).

776　To confirm the validity of the processes proposed, T-x parameters were tested using the

777　mixing proportions determined from the stable isotope contents of pre-ore quartz and ore

778　minerals in both deposits shown in Fig. 12D. According to Fig. 12D, the proportions of

779　mixing between the meteoric and magmatic reservoirs (expected to lie in the felsic magmatic

780　water box) are $Qtz_{2-III\ MP}$, 30%; $Qtz_{1-I\ PT}$, 50%; $Wf_{1-III\ MP}$, 25%; and $Wf_{1-I\ PT}$, 60% (where the

781　percentage indicates the proportion of the meteoric component).

782　For the magmatic end-member defined by the quartz FI values, the temperature would be

783　between 260 and 500 °C, while it would be between 470 and 750 °C if the wolframite FI

784　values were used (calculated using the minimum and maximum values determined from

785　isochores). If we assume that the temperature of the exsolved magmatic fluid did not change

786　over time, then the actual initial temperature must have been around 500 °C, which is

787　consistent with current understanding (Rickers *et al.*, 2006; Thomas *et al.*, 2012; Hulsbosch *et*

788　*al.*, 2016). Using the same dilution proportions, the magmatic end-member involved during

789　quartz crystallization would have had a salinity of around 5 wt.% equiv. NaCl, while it would

790　have had a salinity between 12 and 17 wt.% during wolframite crystallization. This variation

791　can be explained by the degree of differentiation of the source (Audétat *et al.*, 2008).

792　According to the LA-ICPMS data, the quartz crystallization involved mixing of a magmatic

793　fluid containing between 10 and 100 ppm of dissolved tungsten while during wolframite

794 crystallization the magmatic fluid contained around 400 ppm W (still based on the measured

795 mixing proportions). These values are consistent with the models of Hulsbosch *et al.* (2016)

796 for evolving tungsten contents in fluids during differentiation of the source and indicate much

797 higher mass fractionation of the melt in the case of wolframite crystallization.

798

799 5.3 Regional and global implications for granite-related W-Sn deposits

800

801 FI studies have been performed on eleven W-Sn deposits from the Jiangxi and Hunan

802 provinces in the Nanling Range and on many other W-Sn deposits worldwide (*e.g.* Norohna *et*

803 *al.*, 1992; Lüders *et al.*, 2009; Ni *et al.*, 2015; Lecumberri-Sanchez *et al.*, 2017; Korges *et al.*,

804 2017; Fig. 13). In previous FI studies of the Maoping and Piaotang deposits, distinct

805 microthermometric characteristics were observed in quartz- and wolframite-hosted FIs (Ni *et*

806 *al.*, 2015; Chen *et al.*, 2018). While the petrographic and microthermometric data they

807 obtained from FIs in quartz were similar to our data, both Ni *et al* (2018) and Chen *et al.*

808 (2018) suggested that simple cooling was the main process responsible for wolframite

809 crystallization. Their interpretation was based on the assumption of constant salinity over

810 time, however the salinities they report are comparable to the results of the present study (4 to

811 9 wt.% equiv. NaCl). Both studies invoked a magmatic and meteoric fluid, as deduced mainly

812 from the microthermometry data, although one of the studies (Chen *et al.*, 2018) used only

813 stable isotope data. The stable isotope data of Chen *et al.* (2018) plot between the magmatic

814 box and the meteoric water line, but lie closer to the magmatic box than the data from this

815 study. This difference is mainly an artefact of the temperature used to calculate the actual

816 $\delta^{18}O$ value of the fluid. In the case of Chen *et al.* (2018), $\delta^{18}O$ values were calculated using T_h

817 values without any correction for pressure, while our study used the complete range of

818 possible temperatures determined from the isochores.

In W-Sn deposits in general, the inclusions observed are predominantly aqueous but early quartz FIs are often found to contain varying amounts of gas (CH_4 and N_2 in addition to CO_2) (*e.g.,* Norohna *et al.*, 1992; Wei *et al.*, 2012; Ni *et al.*, 2015; Chicharro *et al.*, 2016; Lecumberri-Sanchez *et al.*, 2017; Appendix A), as we observed here. In the other studies, these FIs often showed variable proportions of the vapor fraction, the presence of which could be indicative of boiling, but this was not observed in our study.

Microthermometric data from previous studies and the present study point to different trapping conditions for gangue and ore minerals (Wei *et al.*, 2012; Ni *et al.*, 2015), with higher trapping temperatures and higher salinities associated with ore fluids. Moreover, the temperatures and salinities determined in our study are similar to those found for W-Sn deposits in South China and worldwide (Fig. 13). Mineralization occurred at temperatures between 150 and 400 °C and salinities of 0 to 15 wt.% equiv. NaCl for the syn-ore fluids (Fig. 13). However, some studies show higher salinities, above 15 wt.% equiv. NaCl (*e.g.* Audétat *et al.*, 2000; Carruzzo *et al.*, 2000; Harlaux *et al.*, 2017). In the present study, we also demonstrate that the conditions and mixing process are maintained during post-mineralizing stages, when tungsten is still present in the fluids but is not precipitating.

Our stable isotope data (oxygen and hydrogen) are consistent with the involvement of magmatic and meteoric fluids (see Beuchat *et al.*, 2004; Carruzzo *et al.*, 2004; Wei *et al.*, 2012; Liu *et al.*, 2002; Wang *et al.*, 2012; Gong *et al.*, 2015; Feng *et al.*, 2012), which is a common interpretation despite the wide range of isotopic values reported in the literature (Fig. 12D).

The K, Rb and Cs contents of fluids indicate magma differentiation as the process responsible for generating higher W-Sn concentrations in the fluid (cf. Audétat *et al.*, 2000; Lüders *et al.*, 2009; Hulsbosch *et al.*, 2016). Recent trace element studies include Korges *et al.* (2017) and Lecumberri-Sanchez *et al.* (2017), for example. The amount of tungsten detected in our study

844   is comparable to that reported in the Lecumberri-Sanchez *et al.* (2017) study of the Variscan

845   W-Sn Panasqueira deposit. However, the Korges *et al.* (2017) study was conducted on CO_2-

846   rich FIs and brines and the trace element contents cannot therefore be compared to our study

847   due to the very distinct properties of the fluid.

848   Regarding the mechanism of wolframite mineralization, Lecumberri-Sanchez *et al.* (2017)

849   and Korges *et al.* (2017) invoke a single magmatic fluid undergoing fluid-rock interaction,

850   cooling, depressurization, and/or boiling. In the present study, temperature fluctuations are

851   linked to variable degrees of mixing between magmatic and meteoric fluids. No

852   depressurization or associated boiling is identified. The occasional detection of high calcium

853   abundances in some FIs could be indicative of local fluid-rock interaction between magmatic

854   fluids and the host rocks.

855

856

857   **6. Conclusions**

858

859   By combining microthermometry, Raman spectroscopy, LA-ICPMS and oxygen and

860   hydrogen isotope analyses of fluid inclusions and their host minerals, we have been able to

861   identify the different ore-forming processes involved in the formation of the Maoping and

862   Piaotang W-Sn deposits in the Nanling Range in China:

863   -   Quartz and ore minerals (wolframite and cassiterite) that precipitated during the

864   mineralizing stages suggest mixing between a magmatic fluid exsolved from the

865   associated peraluminous granite and a meteoric fluid. During the barren post-

866   mineralizing stages, conditions were the same but did not lead to crystallization of ore

867   minerals.

868   -   The timing of ore mineral crystallization depended on the degree of differentiation of

869   the granite. Fluids that crystallized quartz were more depleted in metals than later

870   fluids, which were exsolved from a more differentiated melt and were enriched in

871   incompatible elements, including metals. Quartz-forming fluids do not therefore

872   reflect ore-forming fluids.

873   -   In both deposits, wolframite precipitation resulted from mixing of a meteoric fluid and

874   a highly evolved magmatic fluid. However, the mixing in each deposit occurred under

875   different temperature conditions (350 to 450 °C at Maoping and 200 to 300 °C at

876   Piaotang).

877   -   Tungsten was still present in the fluid during these later stages, but did not precipitate

878   wolframite.

879   -   Similar mineral associations and fluid inclusion compositions are observed in all W-

880   Sn deposits of the Nanling Range at 160-150 Ma.

881

894

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1290 **Figure captions**

1291

1292 Figure 1: Geological and geographical context of the Maoping and Piaotang deposits
1293   (modified after Legros *et al.,* 2016). (A) Locations of mineral deposits and
1294   Cretaceous and Jurassic granitoids of the Cathaysia Block. Most W-Sn deposits from
1295   the Cathaysia Block are located in the Nanling Metallogenic Belt, here indicated in
1296   orange, and associated with Jurassic and Cretaceous granitoids. The southern Jiangxi
1297   Province is outlined in red (B) Location of mining districts, associated mineral
1298   deposits and Cretaceous and Jurassic granitoids from the southern part of the
1299   Southern Jiangxi province. The Southern Jiangxi province is the richest part of the
1300   Nanling Metallogenic Belt in terms of W-Sn resources. The Maoping and Piaotang
1301   deposits are located in the Dayu district in the western part of the Southern Jiangxi
1302   province.

1303

1304   Figure 2: Location, schematic cross-sections and sampling levels of the studied deposits

1305   showing the relationships between the deep Jurassic granites, Cambrian host rocks,

1306   and W-Sn quartz veins. (A) and (B) Maoping deposit (Modified after Feng *et al.*,

1307   2011 and Legros *et al.,* 2016), located near the Tiangmenshan granite. The Maoping

1308   granite is thought to be the north-plunging extension of this granite (Feng *et al.*,

1309   2011). (C) and (D) Piaotang deposit (Modified after Ni *et al.*, 2015 and Legros *et al.*,

1310   2017), located near the Xihuashan deposit. Like the Maoping deposit, the Piaotang

1311   deposit also exhibits a greisen cupola in the field but it could not be defined well

1312   enough in this study to modify the cross-section of Ni *et al.*, (2015).

1313

1314   Figure 3: Paragenetic sequence of the Maoping W-Sn deposit based on samples from the mine

1315   gallery at level -5 (e.g. -200 m; the only level drawn on the cross-section in Fig. 2A)

1316   modified after Legros *et al.* (2016). Details of the different stages and petrographic

1317   descriptions are provided in Legros *et al.* (2016). Minerals indicated in color (here,

1318   quartz, wolframite, cassiterite, fluorite and topaz) were chosen for this FI study.

1319   Colors are in accordance with Figures 8 to 12.

1320

1321   Figure 4: Textural characterization of minerals from the Maoping deposit selected for FI

1322   study, according to their respective stages. Modified after Legros *et al.* (2016). (A)

1323   W-Sn vein (Stage III). (B) Association of $Qtz_{2\text{-III}}$ with $Cst_{1\text{-III}}$ and $Fe\text{-}Li\text{-}mca_{3\text{-III}}$

1324   (Stage III) (cross polars). (C) Complex growth-zones in the Mn-rich wolframite $Wf_{1\text{-III}}$

1325   (Stage III) (natural light). (D) Complex growth zones in cassiterite $Cst_{1\text{-III}}$ of stage

1326   III (natural light). (E) Banded quartz vein (Stage IV) showing the centimeter-scale

1327   banding of quartz and Fe-Li-micas. (F) Stage IV banded quartz (thick section

1328   observed under crossed polars). (G) Two generations of fluorite ($Fl_{1\text{-VI}}$ and $Fl_{2\text{-VI}}$)

from Stage VI (observed by cathodoluminescence). (H) Overgrowth and growth-zone textures in Toz_{4-VI} and Wf_{1-III} in contact with kaolinite (Kln_{1-VI}) (crossed polars). Abbreviations according to the IMA: cst = cassiterite, fl = fluorite, kln = kaolinite, mca = mica, qtz = quartz, toz = topaz, wf = wolframite.

Figure 5: Paragenetic sequence of the Piaotang W-Sn deposit based on observations made on samples collected at three levels (-268, -388 and -556 m) of the mine galleries (modified after Legros *et al.* (2018)). Details of the different stages and petrographic descriptions are provided in Legros *et al.* (2018). Minerals in color (wolframite, quartz, cassiterite and fluorite) were chosen for this FI study. Colors are in accordance with Figures 8 to 12.

Figure 6: Textural characterization of the minerals from the Piaotang deposit selected for FI study, according to their respective stages. Modified after Legros *et al.* (2018). (A) Wolframite-cassiterite-quartz vein from Stage I. (B) Fluorite-cassiterite-quartz vein, where fluorite is late and belongs to Stage II. (C) Whole thin-section observed in natural light. (D) Same whole thin-section as that shown in (C) observed with crossed polars. The main minerals crystallizing in Stage I (Cst_{1-I}, Wf_{1-I}, Qtz_{1-I} and Fe-Li-mca) show complex relationships. Abbreviations according to the IMA: cst = cassiterite, fl = fluorite, mca = mica, qtz = quartz, wf = wolframite.

Figure 7: Petrography and filling phases of FIs from the Maoping and Piaotang deposits, studied at room temperature. Zooms show representative fills for each type of FI observed in isolation, within clusters or in trails. FIs from Maoping are shown in (A) to (I). FIs from Piaotang are shown in (J) to (N). (A) Two-phase liquid (L_{aq}) + vapor

1354 (V_{aq}) aqueous FI found as isolated irregular inclusions and intragranular FIPs (dotted

1355   red lines) in $Qtz_{2\text{-III}}$. (B) Intragranular FIPs (dotted red lines) of two-phase liquid

1356 (L_{aq}) + vapor (V_{aq}) aqueous FI and isolated irregular three-phase liquid H_2O (L_{aq}) +

1357   liquid CO_2 (L_{CO2}) + vapor CO_2 (V_{CO2}) aquo-carbonic FI in $Qtz_{2\text{-III}}$. (C) Intragranular

1358   FIPs of two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous FI and isolated irregular one-

1359   phase liquid (L_{aq}) aqueous FI in $Qtz_{2\text{-III}}$. (D) Two-phase liquid (L_{aq}) + vapor (V_{aq})

1360   aqueous FIs that occur as isolated regular inclusions parallel to growth zones and

1361   intragranular FIPs oblique to the growth zones in $Cst_{1\text{-III}}$. (E) Two-phase liquid (L_{aq})

1362   + vapor (V_{aq}) aqueous FI isolated irregular inclusions and intragranular FIP in $Wf_{1\text{-III}}$.

1363   (F) Two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous FI as isolated negative crystal-

1364   shape inclusions and intragranular FIP in $Qtz_{4\text{-IV}}$. (G) Two-phase liquid (L_{aq}) + vapor

1365 (V_{aq}) aqueous FI as isolated regular inclusions and intragranular FIP displayed

1366   parallel to the growth zone in $Fl_{1\text{-VI}}$. (H) Two-phase liquid (L_{aq}) + vapor (V_{aq})

1367   aqueous FI as isolated regular inclusions and intragranular FIP along $Toz_{4\text{-VI}}$ growth

1368   zones. (I) Two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous FI as isolated regular

1369   inclusions and intragranular FIP along $Fl_{2\text{-VI}}$ growth zones. (J) Two-phase liquid (L_{aq})

1370   + vapor (V_{aq}) aqueous FI as isolated irregular inclusions and intragranular FIP in

1371 $Qtz_{1\text{-I}}$. (K) One-phase liquid (L_{aq}) aqueous FI isolated irregular inclusions and

1372   intragranular FIP in $Qtz_{1\text{-I}}$. (L) Two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous FI as

1373   isolated regular inclusions observed along the $Wf_{1\text{-I}}$ c-axis and in secondary FIP

1374   crossing the $Wf_{1\text{-I}}$ c-axis. (M) Two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous FI as

1375   isolated regular inclusions displayed along a $Cst_{1\text{-I}}$ growth zones and secondary FIP

1376   crossing the $Cst_{1\text{-I}}$ growth zones. (N) Two-phase liquid (L_{aq}) + vapor (V_{aq}) aqueous

1377   FI as isolated regular inclusions and intragranular FIP in $Fl_{1\text{-II}}$. Abbreviations

1378   according to the IMA: cst = cassiterite, fl = fluorite, qtz = quartz, toz = topaz, wf =

1379   wolframite.

1380

1381   Figure 8: Microthermometric and Raman spectroscopy data on two-phase aqueous FIs for the

1382   Maoping and Piaotang deposits. (A) Binary salinity *vs.* T_h diagram for Maoping FIs

1383   at all stages in quartz, cassiterite and wolframite from the W-Sn mineralized stage

1384   III, quartz crystallized in the banded quartz veins on stage IV and fluorite and topaz

1385   in late stage VI. (B) Binary salinity *vs.* T_h diagram for Piaotang FIs at all stages in

1386   quartz, cassiterite and wolframite from the silicate-oxide mineralizing stage I and late

1387   fluorite from the carbonate stage II. For both Maoping and Piaotang data, possible

1388   fluid end-members are indicated by letters from (**A**) to (**D**). Serrated sides of the

1389   boxes indicate the direction along which the exact position of the actual end-member

1390   should be. (C) Gas concentrations obtained by Raman spectroscopy on the vapor

1391   phase of FIs hosted in Qtz_{2-III} and Cst_{1-III} at Maoping and Cst_{1-I} from stage I at

1392   Piaotang are represented in a ternary diagram showing relative molar proportions of

1393 CO_2, CH_4 and N_2.

1394

1395   Figure 9: Minimum and maximum trapping condition isochores drawn for all end-members

1396   determined from two-phase aqueous FIs from the Maoping (A) and Piaotang (B)

1397   deposits. Estimation of the PT conditions of fluid trapping requires intersecting the

1398   FI isochores by independent P or T constraints. The wet-saturated solidus of granitic

1399   magmas (Joyce and Voigt, 1994) defines the maximum PT conditions of the

1400   investigated fluids. To draw the geothermal gradients in the PT diagram, pressure

1401   conditions must be assumed to be either lithostatic or hydrostatic. The Maoping and

1402   Piaotang systems are interpreted to have formed under hydrostatic conditions

57

1403	because both deposits were formed during multiple fluid pulses that were not in
1404	equilibrium with the surrounding rocks. Geothermal gradients with values between
1405	30°C/km (normal crustal gradient) and 90°C/km (gradients typical of high
1406	temperature geothermal systems) have been drawn. The minimum and maximum
1407	pressures are also constrained by the range of common emplacement depths for the
1408	granitic pluton (5-10 km; e.g. Audétat *et al.*, 2000; Chicharro *et al.*, 2016).
1409	
1410	Figure 10: Major and trace element concentrations in FIs from the Maoping and Piaotang
1411	deposits, as determined by LA-ICPMS analysis. All concentrations are expressed in
1412	ppm. (A) Qtz_{2-III}, (B) Cst_{1-III}, (C) Qtz_{4-IV}, (D) Fl_{1-VI} and (E) Toz_{4-VI} from the Maoping
1413	deposit. (F) Qtz_{1-I}, (G) Cst_{1-I} and (H) Fl_{1-II} from the Piaotang deposit. Each symbol
1414	represents a single ablated fluid inclusion. Full symbols represent calculated values
1415	that are above the LODs. Empty symbols represent the LODs when an element was
1416	considered undetected.
1417	
1418	Figure 11: Selected element concentration relationships from LA-ICPMS analyses of fluid
1419	inclusions from the Maoping and Piaotang deposits. Each symbol represents a single
1420	ablated fluid inclusion. (A) Na-K-Li(x10) ternary diagram. The compositions are
1421	calculated as a function of their respective concentrations expressed in ppm. Lines
1422	indicating equal values for K:Na and Li:Na molar ratios (1:1 and 1:10) are in grey.
1423	(B) and (C) Na *vs.* Li and Na *vs.* K binary concentration diagrams. Lines indicate
1424	equal values for K:Na and Li:Na molar ratios (1:1 and 1:10) in grey. (D) K/Rb *vs.* Cs
1425	concentration diagram where K/Rb is expressed as a function of the respective
1426	concentrations expressed in ppm. Boxes representing the possible fluid reservoirs are

1427   shown in each binary diagram. The exact position of these reservoirs on the

1428   respective diagrams are not known and are therefore indicated by dashed lines.

1429

1430   Figure 12: Stable isotope (O, H) data for minerals and fluids from the Maoping and Piaotang

1431   deposits. (A) Oxygen isotopic compositions of minerals (empty symbols) and

1432   calculated equilibrium compositions for fluids according to temperature estimates

1433   from FI isochores. (B) Hydrogen isotopic compositions of FIs. (C) Extracted

1434   temperature estimates from isochores. Fe-Li-micas are interpreted as co-precipitating

1435   with $Qtz_{2\text{-}III}$ and $Cst_{1\text{-}III}$ at the Maoping deposit. (D) Binary δD *vs.* $\delta^{18}O$ diagram for

1436   the fluids from the Maoping and Piaotang deposits. Compositions of metamorphic

1437   waters and felsic magmatic waters are after Sheppard (1994). Boxes for the possible

1438   fluid reservoirs are shown. The exact positions of these reservoirs on the respective

1439   diagrams are not known and are therefore indicated by dashed lines. The box on the

1440   meteoric water line represents possible local meteoric water in accordance with Wei

1441   *et al.* (2012). Grey dashed lines indicate possible mixing trends between magmatic

1442   fluids and meteoric waters. The arrow illustrates the possible evolution of the

1443   magmatic fluid end-member associated to degassing according to Hedenquist and

1444   Lowenstern (1994). Grey transparent boxes in the background represent isotopic data

1445   from Chinese W-Sn deposits (dark grey with dashed edges) and worldwide deposits

1446   as synthesized/compiled in Marignac and Cathelineau, 2009 (light grey).

1447

1448   Figure 13: Compilation of fluid inclusion microthermometric data from the literature. Each

1449   data point represents one deposit. The compiled data show the T_h and salinity

1450   measured for fluids interpreted to be involved in ore-forming processes only. For

1451   homogeneity, ranges represent the minimum and maximum values acquired by the

author. For better readability, (A) shows data from deposits worldwide and (B) shows data measured for W-Sn deposits from the South China Craton only. Deposits are referred to in the figure as: [1] Brandberg, Namibia, [2] Karagwe-Ankole, Rwanda, [3] Kibaran, Rwanda, [4] Nyakabingo, Rwanda, [5] Grey River, Canada, [6] Mount Pleasant, Canada, [7] New ross area, Canada, [8] Tombstone belt, Canada, [9] Sweet home mine, USA, [10] Correas, Brazil, [11] Julcanie, Peru, [12] Pasto Buena, Peru, [13] San Cristobal, Peru, [14] Bankura, India, [15] Degana, India, [16] Ohtani and Kaneuchi, Japan, [17] Hwanggangri, Korea, [18] Kyzylto, Mongolia, [19] Triginoe, Russia, [20] Hub stock, Czech Republic, [21] Carrock fell, England, [22] Cligga Head, England, [23] Beauvoir, France, [24] Ehrenfriedersdorf, Germany, [25] Zinnwald, Germany, [26] Carris, Portugal, [27] Panasqueira, Portugal, [28] Logrosan, Spain, [29] Spanish central system, [30] Aberfoyle, Australia, [31] Herberton, Australia, [32] Mole granite, Australia, [33] Dajishan, China, [34] Dangping, China, [35] [36] Maoping, China, [37] Pangushan, China, [38] [39] Piaotang, China, [40] Shimenshi, China, [41] Taoxikeng, China, [42] Xihuashan, China, [43] Shizuyuan, China, [44] Yaogangxian, China, [45] Yejiwei, China. Associated references, host mineral and gas contents are listed in the table in Appendix A. Critical and halite saturation curves are from Wilkinson (2001). Possible fluid end-members interpreted from our study of the Maoping and Piaotang deposits are indicated by letters (**A**) to (**D**). Serrated sides of the boxes indicate the direction along which the exact position of the actual end-member should be.

1473   **Table 1 – Petrography, Raman spectroscopy and microthermometry data for fluid inclusions from the Maoping and Piaotang deposits. Values in parentheses indicate modes.**

Mineral	Phases at 25 °C (trace gases after Raman spectroscopy)	Proportion within a crystal (visual estimation)	Petrography	Morphology	Size / μm	$\alpha_{(\%)}$ (25°C)	N	T_m(ice)	T_m(cla)	T_h(CO$_2$)	T_h	Salinity / wt. % equiv. NaCl
										(to vapor)	(to liquid)	
MAOPING												
Stage III: W-Sn veins												
	L_{aq}-$V_{aq\ +\ trace\ CO2>CH4>N2}$	85%	intragranular FIP or isolated	irregular	5-30	20-50	96	-4.5 to -0.2 (-0.7)	-	-	157 to 287 (220)	0.4 to 9.0 (1.3)
Quartz$_{2-III}$	L_{aq}-L_{CO2}-V_{CO2}	5%	isolated or cluster	irregular	10-20	85-95	6	-1.7 to -0.9 (-1.2)	7.7 to 8.1 (8.0)	29.4 to 30.6 (30.3)	200 to 252 (230)	0.4 to 0.5 (0.4)
	L_{aq}	10%	intragranular FIP or isolated	irregular	5-30	20-50	c	-	-	-	-	-
Wolframite$_{1-III}$	L_{aq}-V_{aq} [a]	100%	FIP along growth zone or intragranular	regular	5-25	20-50	30	-5.2 to -3.7 (-4.4)	-	-	284 to 346 (340)	7.2 to 10.5 (8.7)
Cassiterite$_{1-III}$	L_{aq}-$V_{aq\ +\ trace\ CO2>CH4>N2}$	100%	FIP along growth zone or isolated	irregular	10-20	30-60	25	-5.5 to -3.0 (-3.8)	-	-	299 to 338 (340)	5.8 to 11.2 (7.5)
Stage IV: Banded quartz veins												
Quartz$_{4-IV}$	L_{aq}-$V_{aq\ +\ trace\ CO2}$	100%	intragranular FIP	regular	5-15	20-30	41	-6.1 to -1.3 (-4.2)	-	-	148 to 291 (240)	7.7 to 12.6 (9.0)
Stage VI: Late phases												
Fluorite$_{1-VI}$	L_{aq}-V_{aq} [b]	100%	FIP along growth zone or intragranular	regular	5-15	30-60	20	-5.4 to -4.3 (-4.5)	-	-	195 to 325 (340)	8.1 to 11.1 (9.0)
Topaz$_{4-VI}$	L_{aq}-$V_{aq\ +\ trace\ CO2}$	100%	FIP along growth zone or clusters	irregular	5-30	10-50	46	-4.2 to -3.3 (-3.9)	-	-	307 to 346 (340)	5.6 to 7.0 (6.1)
Fluorite$_{2-VI}$	L_{aq}-V_{aq} [b]	100%	FIP along growth zone	regular	5-20	10-20	15	-0.9 to -0.1 (-0.1)	-	-	136 to 292 (230)	0 to 1.6 (0.1)
PIAOTANG												
Stage I: Silicate-oxide												
	L_{aq}-V_{aq}	100%	intragranular FIP or isolated	irregular	5-15	10-30	20	-2.2 to -0.2 (-2.2)	-	-	144 to 175 (160)	0.4 to 3.8 (2.2)
Quartz$_{1-I}$	L_{aq}	10%	intragranular FIP or isolated	irregular	5-15	10-30	c	-	-	-	-	-
Wolframite$_{1-I}$	L_{aq}-V_{aq} [a]	100%	FIP along growth zone	regular	5-15	10-40	18	-5.3 to -3.1 (-4.2)	-	-	173 to 222 (210)	5.6 to 8.3 (6.5)
Cassiterite$_{1-I}$	L_{aq}-$V_{aq\ +\ trace\ CO2>CH4>N2}$	100%	FIP along growth zone or intragranular	regular	5-20	10-40	24	-3.7 to -1.4 (-3.5)	-	-	283 to 349 (340)	2.4 to 6.2 (5.8)
Stage II: Calcic stage												
Fluorite$_{1-II}$	L_{aq}-V_{aq} [b]	100%	intragranular FIP or isolated	regular	15-40	10-30	23	-5.0 to 0.0 (0)	-	-	142 to 185 (170)	0 to 7.7

[a] Wolframite is an opaque mineral and could not therefore be analyzed by Raman spectroscopy

[b] Due to fluorescence, it was impossible to observe gas peaks by Raman spectroscopy

[c] Phase transitions could not be observed in one-phase liquid inclusions

Abbreviations: α = vapor phase, L = liquid, V = vapor, aq = aqueous, FIP = fluid inclusion plane, T_m = melting temperature, T_h = homogenization temperature, cla = clathrate

1474

Table 2 - LA-ICPMS measurements made on fluid inclusions from the Maoping and Piaotang deposits. Values preceded by a < symbol stand for element concentrations below the limit of detection. N.A. = not analyzed

MAOPING	Salinity / wt.% equiv. NaCl	Li / ppm	Na / ppm	Mg / ppm	K / ppm	Ca / ppm	Mn / ppm	Rb / ppm	Sr / ppm	Y / ppm	Nb / ppm	Mo / ppm	Sn / ppm	Cs / ppm	Ba / ppm	Ta / ppm	W / ppm	Na/Li (molar ratio)	Na/K (molar ratio)	Na/Ca (molar ratio)	K/Rb (mass ratio)
Quartz2-III	1.3	37	1000	43	490	<5200	160	2	<1.5	<1.6	<1.4	<8.6	42	<1	<1.4	1.1	24	8.4	3.3	-	196
	1.5	84	1600	28	530	<4000	810	7	<1.5	<1.1	<1.4	58	18	1.8	3.0	<1	41	5.8	5.0	-	75
	0.5	41	1200	55	110	<410	74	<1	<1	<1	<1	11	4.7	2.8	8.5	<0.06	7.8	9.1	10.0	-	-
	6	360	13000	220	9000	<24000	180	22	11	<7.6	<8.5	<37	49	18	<9.2	<3.9	<21	11.3	2.5	-	414
	1.5	61	2300	32	500	2500	120	<1	<1	<1	<1	4.4	37	6.0	1.3	<1	10	11.7	10.0	1.7	-
	4.1	250	6300	180	1200	<21300	220	<11	<8.3	<7.9	<6.6	<39	73	26	<7.9	<3.7	<18	7.7	10.0	-	-
Cassiterite 1-III	8.3	2600	17000	<60	9500	<25000	1280	660	<8	<11	<65	<55	N.A.	960	<8	<61	<40	2.0	3.3	-	14
	10	3200	26000	<50	4300	<21000	<90	650	<10	<40	<35	N.A.	500	<7	<31	<34		2.4	10.0	-	7
	8.5	2300	19000	<250	8500	<96000	<420	540	<38	<20	<230	<170	N.A.	700	<21	<170	150	2.6	3.3	-	16
	8.5	1800	20000	<430	10000	<138000	1000	560	<47	<44	<200	<250	N.A.	640	<55	<190	<170	3.3	3.3	-	18
	8.5	3200	20000	<54	2400	<25000	<110	280	<7	<9	33	<45	N.A.	410	<8	<22	<28	1.9	10.0	-	9
	8.5	1600	21000	<250	10400	<91000	970	390	<31	<34	<460	<110	N.A.	460	<27	<840	<80	4.0	3.3	-	27
Quartz4-IV	9	2200	18500	<150	8700	<43000	4200	320	<16	<12	<14	110	450	60	16	<13	270	2.5	3.3	-	27
	9	<90	6000	<51	9800	20000	450	250	<6	<5	<5	57	<67	9	<4	5	160	-	1.0	0.6	39
	9	90	1400	8300	1600	<17000	500	<9	9	<5	<6	<48	140	<4	<5	<3	220	4.9	1.4	-	-
	9	260	7000	9900	2200	<12000	1400	27	10	<4	<3	83	120	40	<4	<2	300	8.1	5.0	-	82
	9	400	7300	5300	4800	<19000	760	19	7	<5	<6	87	220	23	6	<4	200	5.5	2.5	-	250
Fluorite 1-VI	8	<2200	27700	<970	<15600	N.A.	<1800	<240	1100	<2400	<130	<780	<1800	<120	<140	<75	<340	-	-	-	-
	9	<2800	34100	<1200	<19200	N.A.	<2500	<290	370	<4800	<200	<870	2800	<140	<200	<79	<430	-	-	-	-
	9.6	<890	37700	<450	<6250	N.A.	<830	<120	<82	<1700	<59	<220	<710	220	<73	<21	<150	-	-	-	-
	1	<55	3900	<26	<400	N.A.	<49	<5	<4	<85	<4	<20	<45	<3	<4	<2	<9	-	-	-	-
Topaz4-VI	6.4	230	20000	<13	<1700	<7600	79	330	<3	<2	<2	<27	200	310	<2	1	190	27.5	-	-	-
	6.4	1600	19000	<38	<18000	<23000	360	560	12	<6	<6	<100	100	660	<5	<4	<56	3.8	-	-	-
	6.4	280	3200	<1	36000	<1100	120	170	<1	1	<1	<4	7	150	<1	<1	10	3.5	0.1	-	1200
	6.4	280	6400	<7	27000	<4700	99	730	2	2	<2	<12	54	340	<1	<1	190	6.9	0.4	-	200
	6.4	1500	9400	5	12000	<3500	65	630	2	<1	<1	<8	18	420	<1	1	160	2.0	1.2	-	37
	6.4	710	10000	120	13000	<6400	380	730	4	430	5	<13	140	910	<2	5	180	4.4	1.4	-	19
	6.4	1400	6500	33	8200	<11000	580	910	<8	<28	7	<36	<66	850	<15	7	420	4.8	0.8	-	9
	6.4	1000	10000	<44	18000	<13000	440	1400	<9	<11	<10	<48	150	1000	<25	<14	240	9.3	0.5	-	13
	6.4	1200	14000	<33	10000	<8600	300	1000	62	<3	<6	<23	110	1500	<24	<6	190	11.4	1.4	-	10
	6.4	980	10000	<33	13000	<12000	660	1600	<9	34	<5	<25	<71	2300	<16	<4	160	10.2	0.8	-	8

PIAOTANG

	Salinity / wt.% equiv. NaCl	Li / ppm	Na / ppm	Mg / ppm	K / ppm	Ca / ppm	Mn / ppm	Rb / ppm	Sr / ppm	Y / ppm	Nb / ppm	Mo / ppm	Sn / ppm	Cs / ppm	Ba / ppm	Ta / ppm	W / ppm	Na/Li (molar ratio)	Na/K (molar ratio)	Na/Ca (molar ratio)	K/Rb (mass ratio)
Quartz1-I	4.9	200	2300	670	<350	13000	<38	<3	<3	<3	<2	<20	100	4	30	<2	<7	10.7	-	0.3	-
	4.7	98	5400	120	670	10000	<18	7	19	<1	<2	10	200	18	6	<1	<4	54.6	10.0	0.9	99
	4.5	<31	4100	35	1500	10000	<29	8	<3	<2	<2	<10	<22	4	19	<1	5	-	2.0	0.7	190
	4.7	400	9100	<37	2200	<14000	1000	49	<6	<4	<4	<20	<41	5	<5	<3	<10	22.8	5.0	-	45
	3.1	120	3400	100	160	6400	30	<3	<2	<1	<1	12	130	4	43	9	<850	28.5	0.0	1.0	-
	3.7	80	1530	560	1200	9200	71	9	3	<2	<2	17	330	11	<5	<1	<350	19.0	1.2	0.3	130
	5.2	180	16338	15	1200	<2800	330	150	2	<2	<1	<8	62	<400	<5	<1	<5	89.2	10.0	-	8
	0.9	10	960	430	450	1200	9	2	3	<1	<1	<1	51	1	1	<1	<1	98.4	2.0	1.4	200
Cassiterite1-I	7.9	2400	17000	<59	7400	<21000	<94	350	<8	<6	10	<40	N.A.	600	<6	<3	130	2.1	3.3	-	21
	8.3	2400	18000	<52	5700	<14000	<63	200	<5	<5	<5	<29	N.A.	430	<6	<2	<18	2.3	5.0	-	27
	9.6	2800	23000	<21	7400	<8500	<37	350	<3	<3	25	<14	N.A.	750	<2	<2	<9	2.5	5.0	-	21
	9.6	2300	23000	<80	11400	<27000	<123	420	<9	<9	<23	<49	N.A.	560	<7	<5	<37	3.1	3.3	-	27
	7.6	2400	17000	<44	8200	<16000	<72	350	<5	<6	15	<36	N.A.	800	<6	7	<22	2.2	3.3	-	23
	8	2900	18000	<50	4400	<17000	<80	220	<7	<7	71	<36	N.A.	610	<6	14	<23	1.8	10.0	-	20
	10.3	3700	23000	<12	8700	<4300	<20	240	<1	<1	<2	<7	N.A.	780	<1	1	9	1.9	5.0	-	36
	6.2	1800	13000	<41	4600	<20000	110	160	<8	<6	41	<23	N.A.	400	<8	<3	130	2.2	5.0	-	28
	9.6	3300	22000	<56	7500	<31000	<140	220	<11	<12	<14	<51	N.A.	490	<11	<6	220	2.1	5.0	-	34
	6.2	1800	15000	<90	4500	<32000	<150	200	<11	<10	<12	<63	N.A.	460	<12	<5	<40	2.6	5.0	-	23
	7.4	2200	16000	<29	7500	<12000	280	250	<5	<4	15	<24	N.A.	600	<4	<2	140	2.2	3.3	-	30
Fluorite1-II	9.6	290	18000	300	1700	N.A.	120	39	3200	27	<1	<6	340	61	15	2	16	18.5	10.0	-	44
	9.6	510	32000	690	3700	N.A.	280	93	<220	<5	<3	32	360	150	14	3	<7	19.0	10.0	-	40
	4.7	310	11000	40	1100	N.A.	<8	31	1100	20	<1	<4	12	32	2	1	<1	10.5	10.0	-	36
	4.7	21	1100	40	<78	N.A.	38	3	3300	10	<1	9	74	7	<1	1	10	15.7	-	-	-
	9.6	650	29000	390	2400	N.A.	250	100	770	<15	<15	<88	390	120	<47	<8	<42	44.2	10.0	-	30
	4.7	260	12000	1200	5200	N.A.	<320	<69	<540	<48	<35	<200	<360	70	<95	<22	<110	45.9	2.5	-	25
	9.6	300	13000	1500	1500	N.A.	110	110	3700	71	<4	<22	59	41	<15	<3	<14	44.8	10.0	-	-
	9.6	110	26000	800	1300	N.A.	63	50	1700	100	<3	<16	60	33	23	<1	<9	226.0	-	-	14
	9.6	530	24000	470	5600	N.A.	<100	130	1400	28	<10	<58	530	160	<32	<6	<33	45.7	5.0	-	26
	10	670	31000	200	2900	N.A.	62	96	720	<1	<1	<4	<8	140	2	1	<1	14.1	10.0	-	43

Table 3 – Stable isotope (O, H) results for minerals and fluids from the Maoping and Piaotang deposits.

Mineral	$\delta^{18}O$ / ‰VSMOW mineral measured	T range / °C estimated from isochores	$\delta^{18}O$ / ‰VSMOW fluid calculated	δD / ‰VSMOW fluid measured
MAOPING				(min. to max.)
Stage II: Fe-Li-mica veins				
Fe-Li-micas$_{2\text{-}II}$	8.3	180-340	2.8 to 7.5	-
Stage III: W-Sn veins				
Quartz$_{2\text{-}III}$	10.9	180-340	-2.1 to 5.1	-59 to -55 (N=3)
Wolframite$_{1\text{-}III}$	0.5	350-440	2.8 to 3.4	-78 to -77 (N=3)
Cassiterite$_{1\text{-}III}$	-	360-450	-	-72 (N=1)
Fe-Li-micas$_{3\text{-}III}$	8.7	360-450	8.2 to 9.1	-
Stage IV: Banded quartz veins				
Quartz$_{4\text{-}IV}$	10.8	180-380	-2.2 to 5.9	-66 to -62 (N=2)
Stage VI: Late phases				
Topaz$_{4\text{-}VI}$	8.4	380-440	7.4 to 8.1	-
PIAOTANG				
Stage I: Silicate-oxide				
Quartz$_{1\text{-}I}$	11.6	170-240	-2.2 to 2.2	-54 to -51 (N=2)
Wolframite$_{1\text{-}I}$	-3.0	200-290	-3.6 to -2.4	-77 to -76 (N=2)
Cassiterite$_{1\text{-}I}$	-	360-460	-	-70 to -58 (N=3)

Appendix A – Compilation of fluid inclusion data interpreted in the literature to represent ore-forming processes in W-Sn deposits

Country	Name	Host mineral	Salinity	Th	Aqueous	CO2	CH4	N2	Halite cube	Reference	on Fig. 13
Africa											
Namibia	Brandberg	quartz	1.8-11.7	152-224	x	x			x	Macey and Harris, 2006	1
	Karagwe-Ankole	tourmaline	7.7-21.4	269-398	x	x				Hulsbosch *et al.*, 2016	2
Rwanda	Kibaran	quartz	13-17	130-300	x	x				Pohl and Günther, 1991	3
	Nyakabingo	wolframite	3.2-4.5	240-320	x	x				Dewaele *et al.*, 2016	4
America (North)											
	Grey River	scheelite	1.9-5.1	265-285	x					Higgins, 1985	5
Canada	Mount Pleasant	quartz	10-42	260-490	x				x	Davis and Williams-Jones, 1985	6
	New Ross area	quartz	0-43	80-370	x				x	Carruzzo *et al.*, 2000	7
	Tombstone belt	quartz	0.2-8	174-355		x	x		x	Baker and Lang, 2001	8
USA	Sweet Home mine	wolframite	5.7-6.3	325-355	x					Lüders *et al.*, 2009	9
America (South)											
Brazil	Correas	quartz	1-18	340-440	x	x	x			Bettencourt *et al.*, 2005	10
	Julcanie	wolframite	10.9-17.2	287-322	x					Deen *et al.*, 1994	11
Peru	Pasto Buena	various	2-17	175-290	x	x			x	Landis and Rye, 1974	12
	San Cristobal	quartz	2.1-5.1	146-257	x	x			x	Beuchat *et al.*, 2004	13
Asia											
India	Bankura	quartz	8-17	230-370	x	x			x	Mishra *et al.*, 1999	14
	Degana	quartz	8-33	118-425		x			x	Krylova *et al.*, 2012	15
Japan	Ohtani and Kaneuchi	quartz	3.7-8.2	190-530		x	x		x	Morishita *et al.*, 1991	16
Korea	Hwanggangri	various	0.5-10	285-370	x	x				So and Yun, 1994	17
Mongolia	Kyzyltau	various	2-32	113-432	x	x	x	x	x	Graupner *et al.*, 1999	18
Russia	Tigrinoe	quartz	3-7	240-420	x					Krylova *et al.*, 2012	19
Europe											
Czech Republic	Hub stock	various	0.6-3.2	330-470		x	x	x		Dolnicek *et al.*, 2012	20
England	Carrock Fell	various	6	235-335	x	x				Ball *et al.*, 1985	21

Country	Deposit	Mineral								Reference	#
	Cligga Head	cassiterite	6.5-7.9	290-370	x					Smith *et al.*, 1996	22
France	Beauvoir	quartz	1.4-48.2	305-600	x	x	x	x		Harlaux *et al.*, 2017	23
Germany	Ehrenfriedersdorf	quartz	5-50	380-480	x					Rickers *et al.*, 2006	24
	Zinnwald	wolframite	10-12	340-350	x					Korges *et al.*, 2017	25
Portugal	Carris	scheelite	3-8	230-280	x	x		x	x	Moura *et al.*, 2014	26
	Panasqueira	quartz	5-10	230-360	x		x		x	Polya *et al.*, 2000	27
Spain	Logrosan	various	0.4-11	280-400		x	x	x		Chicharro *et al.*, 2016	28
	Spanish central system	quartz	0.2-1.8	310-340		x	x			Vindel *et al.*, 1995	29
Oceania											
	Aberfoyle	various	6-45	175-400	x	x			x	Hoffman *et al.*, 1988	30
Australia	Herberton	various	0-50	13-460	x	x			x	Charoy and Polard, 1989	31
	Mole granite	quartz	2.1-40.7	350-563	x				x	Audétat *et al.*, 2000	32
South China Block											
	Dajishan	wolframite	4.3-9	240-370	x					Ni *et al.*, 2015	33
	Dangping	wolframite	6.7-8.7	284-324	x					Ni *et al.*, 2015	34
	Maoping	wolframite	4.6-8.8	292-362	x	x				Chen *et al.*, 2018	35
		wolframite	5.8-11.2	284-346	x					This study	36
Jiangxi, China	Pangushan	quartz	3.1-8	240-366	x					Ni *et al.*, 2015	37
	Piaotang	wolframite	4.6-8.9	280-390	x					Ni *et al.*, 2015	38
		wolframite	5.6-8.3	173-222						This study	39
	Shimenshi	quartz	0.5-9.5	162-363	x	x	x	x		Gong *et al.*, 2015 (in chinese)	40
	Taoxikeng	quartz	8	310-390						Wang *et al.*, 2012	41
	Xihuashan	wolframite	3.8-13.7	239-380	x					Wei *et al.*, 2012	42
	Shizhuyuan	quartz	-	230-300						Xuexin *et al.*, 1990	43
Hunan, China	Yaogangxian	quartz	4.5-15.2	212-386						Hu *et al.*, 2012	44
	Yejiwei	quartz	-	220-240						Xuexin *et al.*, 1990	45

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Figure legend:

Mineral deposits
- W (orange square)
- Cu (white diamond)
- Pb-Zn (white triangle)
- Ag (gray circle)
- Sn (green square)
- Mo (blue circle)
- Sb-(Hg) (plus sign)
- Au (white circle)

Age of Mesozoic intrusions
- Cretaceous granitoids (135-80 Ma) (dark gray)
- Jurassic granitoids (190-150 Ma) (light gray)

- Provinces (gray line)
- Southern Jiangxi province (red line)
- Districts (red dash-dot line)
- Nanling metallogenic belt (orange shading)
- Dayu district (red star)

A MAOPING DEPOSIT

N   S

100 m

	Middle Cambrian metasedimentary rocks		Jurassic porphyritic medium to fine-grained biotite granite (Tiangmeshan complex)		Greisen-type orebodies
	Lower Cambrian metasedimentary rocks		Jurassic fine-grained biotite granite (Tiangmeshan complex)		Fracture zone
	Neoproterozoic metasedimentary rocks		Deep Jurassic Maoping granite		W-Sn quartz veins
					Faults

B

N

Maoping

Jigongaiu
Changlongken

Laoanli

Dahuangli

Tiangmenshan
granite

Baxiangao

Guizibei

2 km

C

N

Piaotang

Xihuashan
granite

Xihuashan

Dayu

5 km

D PIAOTANG DEPOSIT

177°30   357°30

-268 m

50 m

1 m

-388 m

-556 m

	Quaternary red soil, alluvium		W-Sn rich quartz veins		Tungsten mines
	Upper Cambrian metasedimentary rocks		Deep Jurassic biotite granite (Xihuashan granite)		Faults
	Neoproterozoic metasedimentary rocks		Deep Jurassic Piaotang granite		Sampling levels

	Stage I	Stage II	Stage III: W-Sn veins (W-Sn-Li-Mo)		Stage IV: Banded quartz veins (Nb-Ta-Zr-REE)	Stage V (S)	Stage VI: Dissolution (F-REE)	Stage VII (Bi-S)
			a	b				
K-feldspar	1				2			
Quartz	1		2 3		4	5		
Fe-Li-micas	1	2	3		4			
Albite	1				2			
Topaz	1		2		3		recrystallization (4)	
Wolframite			1				overgrowth	
Graphite			1					
Cassiterite			1 overgrowth		2			
Molybdenite			1					
Fe-Li-muscovite				1	2			
Fe-Mn hydroxides				1				
Zircon					1			
Colombo-tantalite					1			
Emplectite					1			
Li-muscovite	1					2		
Sphalerite						1		
Chalcopyrite						1		
Stannite							1	
Fluorite							1	2
Kaolinite							1	
REE phosphates								1
REE fluorides								1
REE carbonates								1
Bismuthinite								1
Native bismuth								1
Pyrite								1

Plastic deformation

Corrosion

Panel A — Stage III. Labels: Fe-Li-mca$_{2-III}$, Host rock, Qtz$_{2-III}$, Toz$_{2-III}$, Wf$_{1-III}$, Fe-Li-mca$_{4-III}$, W-Sn vein, 20 cm.

Panel B — Stage III. Labels: Fe-Li-mca$_{3-III}$, Cst$_{1-III}$, Qtz$_{2-III}$, 0.2 mm.

Panel C — Stage III. Labels: Toz$_{2-III}$, Wf$_{1-III}$, 1 mm.

Panel D — Stage III. Labels: Wf$_{1-III}$, Cst$_{1-III}$, 0.5 cm.

Panel E — Stage IV. Labels: Qtz$_{4-IV}$, Fe-Li-mca$_{4-IV}$, Banded quartz vein, 10 cm.

Panel F — Stage IV. Labels: Qtz$_{2-III}$, Qtz$_{4-IV}$, 5 mm.

Panel G — Stage VI. Labels: Toz$_{2-III}$, Fl$_{1-VI}$, Fl$_{2-VI}$, Fl$_{2-VI}$, 0.2 mm.

Panel H — Stage VI. Labels: Toz$_{4-VI}$, Wf$_{1-III}$, Kln$_{1-VI}$, Toz$_{2-III}$, 0.2 mm.

	Stage I: Silicate-oxide *(W-Sn-Li-Mo)*	**Stage II:** Calcic stage *(Ca-W-F-Nb-Ta)*	**Stage III:** Base Metal Sulphides *(S)*	**Stage IV:** Sulphides *(S)*

Wolframite

Quartz

Beryl?

Cassiterite

Fe-Li-micas

Topaz

Molybdenite

Scheelite

Chlorite

Columbo-tantalite

Fluorite

Chalcopyrite

Phenakite

Sphalerite

Stannite

Galena

Lillianite

Pyrite

Bismuthinite

Native Bismuth

Corrosion

Brittle episode

Plastic deformation

Figure panels labeled A (Stage I), B (Stage I-II), C (Stage I), and D (Stage I).

A — Host rock, Wf_{1-I}, Cst_{1-I}, Qtz_{1-I}; scale bar 10 cm.

B — Qtz_{1-I}, Fl_{1-II}, Cst_{1-I}, Host rock; scale bar 5 cm.

C — Cst_{1-I}, Wf_{1-I}, Qtz_{1-I}; scale bar 5 mm.

D — Fe-Li-mca; scale bar 5 mm.

A — Qtz$_{2-III}$ — 50 µm — V$_{aq}$, L$_{aq}$

B — Qtz$_{2-III}$ — 50 µm — V$_{CO2}$, L$_{aq}$, L$_{CO2}$

C — Qtz$_{2-III}$ — 100 µm — L$_{aq}$

D — Cst$_{1-III}$ — 20 µm — V$_{aq}$, L$_{aq}$

E — Wf$_{1-III}$ — 100 µm — V$_{aq}$, L$_{aq}$

F — Qtz$_{4-IV}$ — 50 µm — L$_{aq}$, V$_{aq}$

G — Fl$_{1-VI}$ — 100 µm — L$_{aq}$, V$_{aq}$

H — Toz$_{4-VI}$ — 100 µm — L$_{aq}$, V$_{aq}$

I — Fl$_{2-VI}$ — 50 µm — L$_{aq}$, V$_{aq}$

J — Qtz$_{1-I}$ — 50 µm — V$_{aq}$, L$_{aq}$

K — Qtz$_{1-I}$ — 50 µm — L$_{aq}$

L — Wf$_{1-I}$ — C axis — 50 µm — V$_{aq}$, L$_{aq}$

M — Cst$_{1-I}$ — 50 µm — L$_{aq}$, V$_{aq}$

N — Fl$_{1-II}$ — 100 µm — L$_{aq}$, V$_{aq}$

Maoping deposit
Piaotang deposit
Representative zoom
Isolated or clustered FI
FIP   Growth zones

Maoping

Stage III: *W-Sn veins*
- Quartz$_{2\text{-III}}$ (N=96)
- Wolframite$_{1\text{-III}}$ (N=30)
- Cassiterite$_{1\text{-III}}$ (N=25)

Stage IV: *banded quartz veins*
- Quartz$_{4\text{-IV}}$ (N=41)

Stage VI: *late filling stages*
- Fluorite$_{1\text{-VI}}$ (N=20)
- Topaze$_{4\text{-VI}}$ (N=46)
- Fluorite$_{2\text{-VI}}$ (N=15)

Piaotang

Stage I: *oxide-silicate stage*
- Quartz$_{1\text{-I}}$ (N=20)
- Wolframite$_{1\text{-I}}$ (N=18)
- Cassiterite$_{1\text{-I}}$ (N=24)

Stage II: *calcic stage*
- Fluorite$_{1\text{-II}}$ (N=23)

A Maoping

- 30 °C/km
- 50 °C/km
- 90 °C/km
- Hydrostatic pressure
- Water-saturated granite solidus

(A) Meteoric end-member

(D) Magmatic end-member

(B) and (C) Magmatic end-member

Pressure / MPa — Temperature / °C — Depth / km (hydrostatic conditions)

B Piaotang

- 30 °C/km
- 50 °C/km
- 90 °C/km
- Hydrostatic pressure
- Water-saturated granite solidus
- Chl$_{(l)}$ thermometer (Legros et al., 2018)

(A) Meteoric end-member

(D) Magmatic end-member

(B) and (C) Magmatic end-member

Pressure / MPa — Temperature / °C — Depth / km (hydrostatic conditions)

Figure legend:

Maoping

Stage III: *W-Sn veins*
- Quartz$_{2-III}$ (N=6)
- Cassiterite$_{1-III}$ (N=7)

Stage IV: *banded quartz veins*
- Quartz$_{4-IV}$ (N=5)

Stage VI: *late filling stages*
- Fluorite$_{1-VI}$ (N=4)
- Topaz$_{4-VI}$ (N=10)

Piaotang

Stage I: *oxide-silicate stage*
- Quartz$_{1-I}$ (N=8)
- Cassiterite$_{1-I}$ (N=11)

Stage II: *calcic stage*
- Fluorite$_{1-II}$ (N=10)

values in ppm
- calculated values
- det. lim. values

Legend:

Maoping

Stage III: *W-Sn veins*
- Quartz$_{2-III}$ (N=6) — light blue circle
- Cassiterite$_{1-III}$ (N=7) — orange circle

Stage IV: *banded quartz veins*
- Quartz$_{4-IV}$ (N=5) — dark blue circle

Stage VI: *late filling stages*
- Fluorite$_{1-VI}$ (N=4) — green circle
- Topaz$_{4-VI}$ (N=10) — yellow circle

Piaotang

Stage I: *oxide-silicate stage*
- Quartz$_{1-I}$ (N=8) — light blue diamond
- Cassiterite$_{1-I}$ (N=11) — orange diamond

Stage II: *calcic stage*
- Fluorite$_{1-II}$ (N=10) — green diamond

A — δ¹⁸O / ‰ VSMOW

MAOPING | PIAOTANG

Fe-Li-Mca$_{2-II}$, Qtz$_{2-III}$, Fe-Li-Mca$_{3-III}$, Wf$_{1-III}$, Qtz$_{4-IV}$, Toz$_{4-VI}$, Qtz$_{1-I}$, Wf$_{1-I}$

□ mineral
⊢ fluid calculated value from temperature estimates

II   III   IV   VI   I

B — δD / ‰ VSMOW _fluid inclusions_

MAOPING | PIAOTANG

Qtz$_{2-III}$, Qtz$_{1-I}$, Qtz$_{4-IV}$, Cst$_{1-I}$, Cst$_{1-III}$, Wf$_{1-III}$, Wf$_{1-I}$

III   IV   I

C — T / °C estimates (from isochores)

MAOPING | PIAOTANG

Fe-Li-Mca$_{2-II}$, Qtz$_{2-III}$, Wf$_{1-III}$, Cst$_{1-III}$, Fe-Li-Mca$_{3-III}$, Qtz$_{4-IV}$, Fl$_{1-VI}$, Toz$_{4-VI}$, Fl$_{2-VI}$, Cst$_{1-I}$, Wf$_{1-I}$, Qtz$_{1-I}$

II   III   IV   VI   I

D — MP: Maoping   PT: Piaotang

δD / ‰ VSMOW   δ¹⁸O / ‰ VSMOW

meteoric waters
«metamorphic» waters
felsic magmatic waters

meteoric reservoir

Qtz$_{1-I}$ PT   Qtz$_{2-III}$ MP
Qtz$_{4-IV}$ MP
Cst$_{1-I}$ PT
Cst$_{1-III}$ MP
Wf$_{1-I}$ PT   Wf$_{1-III}$ MP

magmatic reservoir

Figure caption omitted — figure shows two cross-plots of Homogenization temperature (°C) versus Salinity (wt. % equiv. NaCl). Panel A labeled "Worldwide", Panel B labeled "South China Craton".