

1 **Revision 1**

2 **Word Count: 9544**

3

4 **Magnetite texture and trace-element geochemistry fingerprint of**
5 **pulsed mineralization in the Xinqiao Cu–Fe–Au deposit, Eastern**
6 **China**

7

8 YU ZHANG^{1,2}, PETE HOLLINGS³, YONGJUN SHAO^{1,2,*}, DENG FENG LI⁴,

9 HUAYONG CHEN⁵, HONGBIN LI^{1,2}

10

11 ¹ *Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment*

12 *Monitor (Central South University), Ministry of Education, Changsha 410083, China*

13 ² *School of Geosciences and Info-Physics, Central South University, Changsha 410083, China*

14 ³ *Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1,*

15 *Canada*

16 ⁴ *School of Marine Sciences, Sun Yat-sen University, Guangzhou 510006, China*

17 ⁵ *Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese*

18 *Academy of Sciences, Guangzhou 510640, China*

19

20

21 *Corresponding author: Y. SHAO (shaoyongjun@126.com)

22

ABSTRACT

23 The origin of stratabound deposits in the Middle-Lower Yangtze River Valley Metallogenic
24 Belt (MLYRB), Eastern China, is the subject of considerable debate. The Xinqiao Cu–Fe–Au
25 deposit in the Tongling ore district is a typical stratabound ore body characterized by multi-stage
26 magnetite. A total of six generations of magnetite have been identified. Mt1 is commonly replaced
27 by porous Mt2, and both are commonly trapped in the core of Mt3, which is characterized by both
28 core-rim textures and oscillatory zoning. Porous Mt4 commonly truncates the oscillatory zoning
29 of Mt3, and Mt5 is characterized by 120° triple junction texture. Mt1 to Mt5 are commonly
30 replaced by pyrite that coexists with quartz, whereas Mt6, with a fine-grained foliated and
31 needle-like texture, commonly cuts the early pyrite as veins and is replaced by pyrite that coexists
32 with calcite. The geochemistry of the magnetite suggests that they are hydrothermal in origin. The
33 microporosity of Mt2 and Mt4 magnetite, their sharp contacts with Mt1 and Mt3, and lower trace
34 element contents (e.g., Si, Ca, Mg, and Ti) than Mt1 and Mt3 suggest that they formed via coupled
35 dissolution and reprecipitation of the precursor Mt1 and Mt3 magnetite, respectively. This was
36 likely caused by high-salinity fluids derived from intensive water-rock interaction between the
37 magmatic-hydrothermal fluids associated with the Jitou stock and Late Permian metalliferous
38 black shales. The 120° triple junction texture of Mt5 suggests it is the result of fluid-assisted
39 recrystallization, whereas Mt6 formed by replacement of hematite as a result of fracturing. The
40 geochemistry of the magnetite suggests that the temperature increased from Mt2 to Mt3, and
41 implies that there were multiple pulses of fluids from a magmatic-hydrothermal system. Therefore,
42 we propose that the Xinqiao stratiform mineralization was genetically associated with multiple
43 influxes of magmatic hydrothermal fluids derived from the Early Cretaceous Jitou stock. This

44 study demonstrates that detailed texture examination and in-situ trace elements analysis under
45 robust geological and petrographic frameworks can effectively constrain the mineralization
46 processes and ore genesis.

47

48 **Keywords:** Magnetite; Stratabound mineralization; Xinqiao Cu–Fe–Au deposit;
49 Middle–Lower Yangtze River Valley Metallogenic Belt.

50

INTRODUCTION

51 Magnetite is a ubiquitous mineral phase in different geological environments and represents a
52 dominant metallic mineral phase in wide variety of hydrothermal ore systems (Nadoll et al. 2014,
53 2015). Octahedral and tetrahedral coordinated positions in the magnetite structure provide host
54 sites for many trace elements (e.g., Al, Mn, Ti, V, Ni, Cr, Zn, Co, Sn, Ga, and Mg) via isovalent
55 and coupled substitutions (Dupuis and Beaudoin 2011; Nadoll et al. 2012; Deditius et al. 2018).
56 The trace-element compositions of hydrothermal magnetite are mainly governed by the
57 composition of the hydrothermal fluids, temperature, oxygen fugacity (fO_2), sulfur fugacity (fS_2),
58 co-crystallized mineral phases and fluid-rock interactions (McIntire 1963; Dare et al. 2012, 2014;
59 Nadoll et al. 2014; Knipping et al. 2015; Huang et al. 2019a, b; Liu et al. 2019; Salazar et al. 2019;
60 Sun et al. 2019). Therefore, a number of studies have focused on the trace-element geochemistry
61 of magnetite to constrain mineralization type and ore genesis (Beaudoin et al. 2007; Dupuis and
62 Beaudoin 2011; Dare et al. 2012, 2014; Nadoll et al. 2012, 2014, 2015), fingerprint the temporal
63 and/or spatial evolution of the ore-forming hydrothermal fluids (e.g., Li et al. 2019; Liu et al.
64 2019), and reconstruct the mineralization processes (e.g., Li et al. 2019; Hu et al., 2020). More
65 importantly, magnetite undergoes dissolution and reprecipitation (DRP), oxy-exsolution, and/or
66 recrystallization to reach chemical and textural re-equilibration, and consequently detailed studies
67 of internal textures are necessary before conducting trace-element analyses (Hu et al. 2014, 2015;
68 Salazar et al. 2019).

69 The Middle-Lower Yangtze River Valley Metallogenic Belt (MLYRB), Eastern China, is one
70 of the most important mining regions in China, and is characterized by abundant large stratabound
71 deposits (e.g., the Dongguashan Cu–Au deposit and the Xinqiao Cu–Fe–Au deposit; Mao et al.

72 2011). The origin of these stratabound deposits is still a matter of debate with a number of models
73 proposed including Late Paleozoic submarine exhalative processes (SEDEX, e.g., Gu et al. 2000;
74 Xu and Zhou 2001), Early Cretaceous magmatic-hydrothermal fluids (skarn-type, e.g., Pan and
75 Done 1999; Mao et al. 2009, 2011; Zhang et al. 2017b, c, 2018; Li et al. 2017, 2018a, 2019), or a
76 combination of the two (e.g., Tang et al. 1998; Zhou et al. 2010; Guo et al. 2011). The Xinqiao
77 Cu–Fe–Au deposit in the Tongling ore district has a proven reserve of 0.5 Mt Cu @ 0.71%, 24.9
78 Mt Fe @ 46%, 11.2 t Au @ 4.7g/t and 248.4 t Ag @ 248.4 g/t (Xu and Zhou 2001), and is
79 dominated by a large-scale stratiform orebody with extensive skarn alteration and unique
80 colloform pyrite (Zhang et al. 2017a). The fact that colloform pyrite in the Xinqiao stratiform
81 orebody is cut by magnetite veins is consistent with a syn-depositional origin of colloform pyrite
82 (Xiao et al. 2016). However, in-situ Sensitive High Resolution Ion Microprobe (SHRIMP) sulfur
83 isotope compositions ($\delta^{34}\text{S}_{\text{CDT}} = -0.6$ to 2.7% , Avg. 0.58% ; Zhang et al. 2017a) and Co/Ni ratios
84 (0.67 to 2.94 , Avg. 1.66 ; Zhang et al. 2017a) of the colloform pyrite, similar ages between
85 colloform pyrite (Re–Os age: 136.7 ± 4.6 Ma; Li et al. 2018a) and the quartz diorite of the Jitou
86 stock at Xinqiao (zircon U–Pb age: 139.6 ± 1.5 Ma; Zhang et al. 2017c), coupled with the fact that
87 colloform pyrite cements massive magnetite (Zhang et al. 2017a) suggests a magmatic
88 hydrothermal origin for the colloform pyrite and the occurrence of multi-stage magnetite in the
89 Xinqiao stratiform orebody. Therefore, the complex magnetite at Xinqiao offers an excellent
90 opportunity to examine the detailed paragenesis of the stratiform mineralization in MLYRB.

91 This paper reports data for a paragenetically well-constrained suite of magnetite-bearing
92 samples from the Xinqiao deposit. Using back-scattered electron (BSE) imaging of internal
93 textures combined with electron probe microanalyzer (EPMA) and laser ablation inductively

94 coupled plasma mass spectrometry (LA-ICP-MS) analysis of magnetite, the textures and
95 geochemistry of the multi-stage magnetite at Xinqiao have been documented. These results
96 provide new constraints on the origin of the Xinqiao stratiform mineralization, and the stratabound
97 deposits of the MLYRB.

98

99

GEOLOGICAL BACKGROUND

100 **Regional geology**

101 The Middle–Lower Yangtze River Valley Metallogenic Belt is located along the northern
102 margin of the Yangtze craton, which is separated from the North China craton to the north by the
103 Triassic Qinling-Dabieshan orogenic belt, and from the Cathaysian block to the south by a
104 Neoproterozoic suture (Fig. 1a; Li et al. 2014; Zhang et al. 2019). The belt hosts seven ore
105 districts, which are from west to east the Edong, Jiurui, Anqing-Guichi, Luzong, Tongling,
106 Ningwu and Ningzhen districts with more than 200 known polymetallic deposits (Fig. 1a; Ling et
107 al. 2009). The Tongling ore district, located in the central part of MLYRB (Fig. 1a), is the largest
108 Cu–Au–Fe–Mo ore district in the belt and hosts numerous skarn deposits (Tang et al. 1998; Pan
109 and Dong 1999; Lai and Chi 2007; Mao et al. 2011; Sun et al. 2019). More than 50 ore deposits
110 have been discovered in the Tongling district, clustered in five ore fields, namely Tongguanshan,
111 Shizishan, Xinqiao, Fenghuangshan and Shatanjiao, distributed from east to west (Wu et al. 2014;
112 Fig. 1b). The dominant lithologies in the Tongling district are marine and continental sedimentary
113 rocks. Marine sedimentary rocks, including clastic sedimentary rocks, carbonates and evaporites,
114 were deposited in the Silurian to Middle Triassic, with a break in the Early to Middle Devonian.
115 Continental rocks including clastic and volcanic-sedimentary rocks were deposited from the

116 Middle Jurassic to Quaternary, with a break in the Middle-Late Devonian (Wang et al. 2015; Cao
117 et al. 2017). These sedimentary rocks were deposited on a stable Precambrian basement and are
118 the host rocks for later Cu, Au, Fe, and Mo mineralization (Chang et al. 1991; Zhai et al. 1992).
119 The Lower Permian Qixia Formation and the Lower Triassic Nanlinghu Formation are dominated
120 by limestone and are important ore-hosting strata for the widespread skarn mineralization in the
121 district. The unconformity between the quartz sandstone of the Upper Devonian Wutong
122 Formation and the dolomite and limestone of the Upper Carboniferous Huanglong Formation
123 constrains the economically significant stratiform mineralization in this district, including the
124 Xinqiao and Dongguashan deposits. Structurally, the region contains NE-trending folds and NNE-
125 and NW-trending faults that have influenced the emplacement of the intrusions. Igneous rocks are
126 widely distributed in the region and are dominated by Late Jurassic – Early Cretaceous (ca. 156 to
127 137 Ma) high-K calc-alkaline granitoids (e.g., granite porphyry, granodiorite porphyry and quartz
128 monzodiorite; Fig. 1b; Mao et al. 2011; Wang et al. 2015; Cao et al. 2017). Many small plutons
129 occur as composite stocks, dikes and sills (Du et al. 2015).

130

131 **Ore deposit geology**

132 The outcropping sedimentary rocks in the mining area range from the Middle-Upper Silurian
133 sandstone and siltstone to the Lower Triassic Yinkeng Formation limestone, whereas the Lower
134 Carboniferous unit is absent. The NE-trending Dachengshan anticline and the NNE-trending
135 Shenchong syncline are the major structures at Xinqiao, and have influenced the emplacement of
136 the magmatic rocks (Fig. 2a). The dominant igneous rock in the region is the Jitou stock, which
137 occurs in the core of the Shenchong syncline as a multiphase intrusion with quartz diorite at the

138 center and diorite porphyry along the margins. The quartz diorite has yielded Early Cretaceous
139 SHRIMP and LA-ICP-MS zircon U–Pb ages of 140.4 ± 2.2 Ma (Wang et al. 2004) and $139.6 \pm$
140 1.5 Ma (Zhang et al. 2017c), respectively.

141 There are two major mineralization types at Xinqiao, namely the economically significant
142 stratiform mineralization (No. I Orebody, accounting for 90% of the Cu, S and Fe reserves of
143 deposit) and the economically less important skarn mineralization (No. V Orebody). The
144 stratiform mineralization is confined to the unconformity between the Upper Devonian Wutong
145 Formation quartz sandstone and the Upper Carboniferous Huanglong Formation limestone,
146 whereas the skarn-type mineralization is hosted along the intrusive contact between the Jitou stock
147 and the Lower Permian Qixia Formation limestone (Fig. 2b).

148 The stratiform orebody is 2560 m long, 1810 m wide, averaging 21 m thick, striking NE and
149 dipping to the NW, parallel to the Upper Devonian Wutong and the Upper Carboniferous
150 Huanglong formations (Fig. 2b), with a quartz-pyrite stockwork in the Upper Devonian Wutong
151 Formation quartz sandstone acting as the footwall to the stratiform orebody. The stratiform ores
152 have replaced the limestones of the Middle and Upper Carboniferous Huanglong and Chuanshan
153 formations, with the Lower Permian Qixia Formation limestone and chert forming the hanging
154 wall (Fig. 2b). The ore minerals in the stratiform orebody include magnetite, chalcopyrite,
155 pyrrhotite, hematite, native gold and electrum (Dai and Liu 1984), whereas gangue minerals
156 include primarily garnet (two stages of garnet; Zhang et al. 2017b, 2018), diopside, epidote,
157 chlorite, quartz and calcite. The metallic mineral assemblages in the stratiform orebody show
158 proximal to distal zoning away from the Jitou stock: magnetite + pyrite → chalcopyrite + pyrite
159 → pyrite (Zhang et al. 2017c). The wall rock alteration includes garnet, sericite, quartz, chlorite

160 and kaolinite, with silicic alteration mainly developed in the footwall of the orebody. The
161 paragenetic sequences of mineralization and alteration within Xinqiao was documented by [Zhang](#)
162 [et al. \(2017a, c\)](#). It can be divided into five stages, the early skarn (Stage I, garnet – diopside), late
163 skarn (Stage II, epidote – magnetite), metallic oxide (Stage III, hematite), colloform pyrite (Stage
164 IV) and quartz-sulfide (Stage V, quartz – chalcopyrite – pyrite).

165 Both the endoskarn and exoskarn ore-bodies are calcic skarn, and consist predominately of
166 garnet, wollastonite and subordinate pyroxene ([Wang et al. 2011](#)). Major metallic minerals include
167 massive / vein / disseminated magnetite, pyrite, chalcopyrite, pyrrhotite, sphalerite and galena.

168

169 **SAMPLING AND ANALYTICAL METHODS**

170 **Sampling**

171 A total of ten magnetite-bearing samples (XQ11-3, XQ17-1, XQ17-3, XQ22-2, XQ22-7,
172 XQ33-11, XQ47-6, D006-5, D006-7 and D006-10) were collected from the Xinqiao stratiform
173 orebody. Samples XQ11-3, XQ17-1 and XQ17-3 were collected from the southwest part of the 60
174 m level in the Xinqiao open pit. Samples XQ22-2 and XQ22-7 were collected underground in the
175 E24 stope at depths of –270 m. Sample D006-5 were collected in the W16 stope underground at
176 depths of –270 m. Sample XQ47-6 was collected in the No. 6 Tunnel at a depth of –300 m, and
177 samples XQ33-11, D006-7 and D006-10 were collected in the W105 stope at a depth of –300 m.
178 Detailed sample locations are shown in [Figure 2](#).

179

180 **Analytical methods**

181 Prior to the EPMA and LA-ICP-MS in-situ major and trace elements analysis, BSE imaging

182 of the magnetite samples was carried out using a TESCAN MIRA3 field emission scanning
183 electron microprobe (FE-SEM) at the Testing Center, Tuoyan Analytical Technology Co. Ltd.
184 (Guangzhou, China). Working conditions of the BSE imaging include 20 kV accelerating voltage
185 and 15nA beam current.

186 In-situ major element analysis using EPMA was carried out in the School of Geosciences and
187 Info-Physics of the Central South University, using a 1720 EPMA (Shimadzu Corporation, Japan).
188 Analytical parameters include 15kv (acc. voltage), 2.0×10^{-8} A (probe current) and 1 μ m (spot size),
189 with a detection limit of 0.01%. By using a spot size of 1 μ m it as possible to effectively avoid the
190 influence of micro-inclusions trapped in magnetite. Elements analyzed include TiO₂, SiO₂, FeO,
191 MnO, NiO, CoO, Cr₂O₃, CaO, V₂O₃, Al₂O₃ and MgO. The analyses were calibrated using natural
192 and synthetic mineral standards as follows: spinel for Mg and Al, diopside for Si and Ca, ilmenite
193 for Ti, chromite for Cr and Fe, manganese oxide for Mn, niccolite (NiAs) for Ni, cobalt metal for
194 Co, and vanadium metal for V.

195 Magnetite LA-ICP-MS trace element analysis was carried out at the Key Laboratory of
196 Marine Resources and Coastal Engineering, Sun Yat-sen University. The detailed method for
197 in-situ trace-element analysis for magnetite is given in [Sun et al. \(2017\)](#). The analysis was
198 performed using a pulsed 193 nm ArF Excimer laser (GeoLasPro), and ion-signal intensities were
199 acquired using an Agilent 7700x ICP-MS. A 32 μ m spot was used with an energy density of 8
200 J/cm² and a repetition rate of 5 Hz. The trace element compositions of magnetite were calibrated
201 against the USGS synthetic basalt glass GSE-1G, using Fe determined by EPMA data as the
202 internal standard. Each analysis consisted of a 20 s background measurement (laser-off) followed
203 by 45 s of data acquisition. Data reduction was performed using the ICPMSDataCal software ([Liu](#)

204 [et al. 2010](#)). Twenty-three elements were analyzed (Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu,
205 Zn, Ga, Ge, As, Sn, W, Au, Pb, Bi, Th and U).

206

207

RESULTS

208 **Petrogenesis, internal texture and paragenesis of magnetite**

209 Based on mineral assemblages and textural relationships, six stages of magnetite were
210 identified in the Xinqiao stratiform orebody. Magnetite in the first four stages can be identified in
211 samples of XQ33-11, XQ47-6, D006-7, and D006-10. The fifth stage of magnetite (Mt5) is
212 corresponding to samples of XQ22-2, XQ22-7, and D006-5, whereas the sixth stage of magnetite
213 (Mt6) occurs in samples of XQ11-3, XQ17-1, and XQ17-3. These stages are described in greater
214 detail as follows:

215 The first stage of magnetite (Mt1) commonly occurs as anhedral grains ranging from 5 to 10
216 μm , and is dark gray under BSE ([Fig. 3a](#) and [b](#)). It is often replaced by porous anhedral second
217 stage magnetite (Mt2) which is light gray under BSE and 5 to 10 μm in size ([Fig. 3b](#)). The
218 boundary between Mt1 and Mt2 is irregular and sharp ([Fig. 3b](#)), consistent with replacement
219 textures.

220 The third stage of magnetite (Mt3) commonly coexists with epidote as disseminated or
221 massive forms and replaces the early garnet ([Fig. 3c](#)). It occurs as subhedral ([Fig. 3c](#)) or anhedral
222 ([Fig. 3d](#)) grains ranging from 200 to 400 μm , and is commonly replaced by quartz, apatite, and
223 pyrite ([Fig. 3d](#)). In BSE imaging, Mt3 are characterized by well-developed oscillatory zoning and
224 core-rim textures ([Fig. 3e–h](#)). Importantly, Mt1 and Mt2 are only found in the cores of Mt3 grains
225 ([Fig. 3e](#) and [f](#)). The cores (Mt3c; ca. 40–100 μm in size) of Mt3 are typically darker gray than the

226 rims (Mt3r; ca. 100–200 μm in size). Both Mt3c and Mt3r display chemical oscillatory zoning,
227 parallel to the contact interface between Mt3c and Mt3r (Fig. 3f and h), which is consistent with
228 growth zoning rather than replacement of multistage magnetite.

229 The local fourth stage of magnetite (Mt4) is porous and anhedral, and typically lighter gray
230 than Mt3r in BSE imaging (Fig. 3g and h). It dominantly occurs as irregular veins (ca. 2–5 μm in
231 width) or patches (ca. 1–5 μm in size) and truncates the oscillatory zoning of both Mt3c and Mt3r
232 (Fig. 3g and h), indicating it formed later than Mt3.

233 Mt5 occurs close to the Jitou stock with massive textures (Fig. 3i). It is commonly cut by
234 pyrite stockwork or replaced by disseminated pyrite (Fig. 3i). The magnetite primarily occurs as
235 anhedral grains between 50 and 300 μm and is characterized by a well-defined 120° triple junction
236 texture, an indication of textural equilibration and recrystallization of Mt1–Mt4 (Fig. 3j; Hu et al.
237 2015). The margins of the majority of magnetite grains are commonly oxidized into hematite (Fig.
238 3j). Mt5 shows homogeneous internal textures under BSE (Fig. 3k).

239 Mt6 commonly cuts the crystal (Fig. 3l) and colloform pyrite (Fig. 3m) as veins. The
240 colloform pyrite in the reaction front with this magnetite vein has commonly recrystallized to
241 crystal pyrite (Fig. 3m). Mt6 formed by replacement of hematite based on the metasomatic
242 pseudomorph textures, particularly the fine-grained foliaceous (Fig. 3m) or needle-like (Fig. 3n
243 and o) textures, generally 10–25 μm across but up to ca. 60 μm . Additionally, Mt6 is commonly
244 replaced by later pyrite that coexists with calcite (Fig. 3n). Siderite occurs as anhedral grains
245 among Mt6 grains in veins (Fig. 3m). Under BSE, Mt6 also shows homogeneous internal textures
246 (Fig. 3p). Importantly, Mt1 to Mt5 are commonly replaced by pyrite coexisting with quartz, which
247 is subsequently cut by Mt6 veins replaced by pyrite coexisting with calcite, indicating that Mt6 is

248 the final magnetite stage at Xinqiao.

249

250 **Major element geochemistry**

251 A total of 130 EPMA spot analyses were completed on the six magnetite samples, with 16, 15,
252 15, 17, 20, 37 and 10 spots on Mt1, Mt2, Mt3c, Mt3r, Mt4, Mt5 and Mt6, respectively. The major
253 element compositions of the six stages of magnetite at Xinqiao are listed in [Appendix 1](#) and shown
254 on [Figure 4a](#). The contents of FeO, CoO and Al₂O₃ were above detection limits in all samples. The
255 contents of TiO₂, SiO₂, Cr₂O₃, V₂O₃ and MgO in most analysis are above the detection limits,
256 whereas those of MnO, NiO and CaO were below detection limits. In general, Mt1 (86.25–90.02
257 wt. %; Avg. 88.37 wt. %) and Mt3c (87.80–89.28 wt. %; Avg. 88.49 wt. %) have lower FeO
258 contents than Mt2 (91.65–93.16 wt. %; Avg. 92.35 wt. %), Mt3r (90.17–91.85 wt. %; Avg. 90.91
259 wt. %), Mt4 (89.38–93.28 wt. %; Avg. 92.34 wt. %), Mt5 (90.12–93.20 wt. %; Avg. 91.97 wt. %)
260 and Mt6 (92.47–93.20 wt. %; Avg. 92.89 wt. %).

261

262 **Trace element geochemistry**

263 Mt1, Mt2 and Mt4 were too small for LA-ICP-MS analysis. Therefore, LA-ICP-MS spot
264 analysis were conducted on six magnetite samples, with 18, 29, 38 and 13 spots on Mt3c, Mt3r,
265 Mt5 and Mt6, respectively. All data was examined using time-resolved LA-ICP-MS signals, and
266 only flat and stable signals of trace elements were selected to calculate their contents. Trace
267 elements contents for the Xinqiao magnetite are listed in [Appendix 2](#) and shown on [Fig. 4b](#), with
268 the corresponding detection limits listed in [Appendix 3](#). Most of the data (> 60%) for Cu, As, Au
269 and Bi are below detection limits. In general, Mt3, Mt5 and Mt6 have higher Mg, Al, Si, Ca and

270 Mn contents (generally higher than 100 ppm; [Fig. 4](#)) than the other stages of magnetite. Mt3 has
271 higher Al (Avg. 8131 ppm), Si (Avg. 8266 ppm), Ti (Avg. 484 ppm) contents than Mt5 (Al: Avg.
272 482 ppm, Si: Avg. 2658 ppm, Ti: Avg. 18.827 ppm) and Mt6 (Al: Avg. 1447 ppm, Si: Avg. 2398
273 ppm, Ti: Avg. 19.381 ppm), and Mt6 has the lowest contents of Al, Ti and Sn (Avg. 2.940 ppm),
274 and the highest contents of Sc (Avg. 8.780 ppm), Ni (Avg. 1.565 ppm), Ge (Avg. 10.632 ppm), As
275 (Avg. 51.331 ppm), W (Avg. 61.554 ppm), Pb (Avg. 4.781 ppm) and U (Avg. 1.790 ppm). Mt3c
276 have higher Mg, Al, Si, Ca, Sc, Ti, Cu and Ga, and lower Cr, Mn, Co, Ni, Zn, As, Pb and Th
277 contents than Mt3r. More importantly, Mt2 and Mt4 have lower trace-element concentrations (esp.,
278 Ti, Si, Ca and Mg; [Fig. 4](#)) than Mt1 and Mt3.

279

280

DISCUSSION

281 **Origin of the Xinqiao magnetite**

282 The trace-element geochemistry of magnetite can be used to investigate both the origin and
283 paragenesis of the mineralized system ([Dupuis and Beaudoin 2011](#); [Nadoll et al. 2012, 2014,](#)
284 [2015](#)). Therefore, it is essential to document the origin of the six-stages of the Xinqiao magnetite
285 prior to discussing the ore-forming processes and the origin of the mineralization.

286 The FeO contents of Mt1, Mt3c, Mt2 and Mt4 are similar, but TiO₂, SiO₂, MnO, Cr₂O₃, CaO,
287 Al₂O₃ and MgO vary between Mt1 and Mt3c, and SiO₂, MnO and CaO between Mt2 and Mt4 ([Fig.](#)
288 [4a](#)) reveal that Mt1 is not the residue of Mt3c after being replaced by Mt4, and that porous Mt2 is
289 not equal to porous Mt4, supporting four distinct stages for the magnetite consistent with the
290 internal textural differences between Mt3c with chemical oscillatory zoning and homogenous Mt1.
291 [Dare et al. \(2014\)](#) proposed a Ti versus Ni/Cr discriminant diagram to distinguish magnetite from

292 igneous and hydrothermal origins based on the different behavior of Ni and Cr in magmatic and
293 hydrothermal systems, but it is not very useful for hydrothermal magnetite formed in aqueous
294 fluids at high temperature (T) or magmatic magnetite in absence of coprecipitating Fe sulfides
295 ([Knipping et al. 2015](#); [Huang et al. 2019a](#)). Some other diagrams, including Ti versus V ([Nadoll et](#)
296 [al. 2015](#)) and V/Ti versus Fe ([Wen et al. 2017](#)), have also been proposed to discriminate between
297 igneous and hydrothermal magnetite. At Xinqiao, most of the magnetite plots in the hydrothermal
298 magnetite zone in both Ti versus V ([Fig. 5a](#)) and V/Ti versus Fe ([Fig. 5b](#)) diagrams. Furthermore,
299 the Xinqiao magnetite contains low Ti (0.268–802 ppm) and V (0.483–625 ppm) ([Appendices 1](#)
300 [and 2](#)), distinct from igneous magnetite which is ubiquitously enriched in these lithophile elements
301 when compared to hydrothermal magnetite ([Dare et al. 2014](#); [Nadoll et al. 2015](#)).

302 Mt1 and Mt3 have been extensively replaced by light grey Mt2 ([Fig. 3b](#)) and Mt4 ([Fig. 3g](#)
303 [and h](#)), respectively, preferentially along microfractures within or along grain margins. The
304 well-developed microporosity in Mt2 and Mt4, their sharp contacts with Mt1 and Mt3, and the
305 lower trace element contents (esp., Si, Ca, Mg, and Ti) from Mt1 to Mt2, and Mt3 to Mt4
306 ([Appendix 1](#); [Fig. 4a](#)) suggest that they formed by coupled dissolution and reprecipitation (DRP)
307 of the precursor Mt1 and Mt3 grains ([Putnis 2009](#); [Putnis and John 2010](#); [Dare et al. 2015](#); [Hu et](#)
308 [al. 2015](#); [Heidarian et al. 2016](#)). The DRP is facilitated by a fluid-assisted process with dissolution
309 of early magnetite and precipitation of a secondary variety near the reaction front, with Si, Ca, Mg,
310 and Ti being removed from the early magnetite, and volume loss resulted in pervasive
311 micro-porosities, that were conducive for fluid infiltration that contributed to further dissolution of
312 magnetite ([Hu et al. 2014, 2015](#)).

313 Mt5 is characterized by 120° triple junction textures, which can form from either

314 high-temperature annealing in a closed system or fluid-assisted replacement in an open system
315 ([Nakamura and Watson 2001](#); [Ciobanu and Cook 2004](#); [Hu et al. 2015](#)). Mt5 is characterised by
316 distinct trace-element compositions compared to the other magnetite stages (esp., Mg, Al, Ca, V,
317 Co, Ni and Cu; [Fig. 4b](#)), suggesting that Mt5 is most likely the result of fluid-assisted
318 recrystallization processes rather than high-T annealing, and consistent with a hydrothermal
319 origin.

320 Mt6 veins cut the euhedral and colloform pyrite which formed from magmatic hydrothermal
321 fluids ([Zhang et al. 2017a](#); [Li et al. 2018a](#)), and the colloform pyrite in the reaction front with Mt6
322 has recrystallized to euhedral pyrite ([Fig. 3m](#)). This suggest a hydrothermal origin for Mt6 and
323 early hematite. The fact that hydrothermal magnetite and hematite formed later than the main
324 sulfide mineralization stage is not common in either skarn-type or SEDEX deposits, and may
325 reflect a distinct geological process. At Xinqiao, mineralization would have resulted in the
326 conversion of carbonate to skarn that would release abundant CO₂, and gradually increase the
327 pressure within the mineralization system ([Meinert et al. 2005](#)). When the fluid pressure exceeds
328 the lithostatic load, increasing shear stress creates extensive hydraulic fractures ([Sibson et al.](#)
329 [1988](#)), consistent with the magmatic hydrothermal origin of the broadly coeval quartz-pyrite
330 stockwork mineralization in the Wutong Formation quartz sandstone (Rb–Sr isotope isochron age
331 of quartz fluid inclusions from stockwork mineralization: 138.0 ± 2.3 Ma; zircon U–Pb dating of
332 Jitou stock: 139.6 ± 1.5 Ma; [Zhang et al. 2017c](#)) and initial ⁸⁷Sr/⁸⁶Sr values (quartz fluid inclusions
333 from stockwork mineralization: 0.71138 ± 0.00014 , [Zhang et al. 2017c](#); Jitou stock: 0.7065, [Yu et](#)
334 [al. 1998](#)) between stockwork mineralization and the Jitou stock. This fracturing caused a sudden
335 drop in fluid pressure, which would result in a short-lived FeS₂ supersaturation event, and promote

336 rapid growth of pyrite (Wu et al. 2018) probably causing the formation of colloform pyrite. It
337 could also have resulted in phase separation and partitioning of reduced H₂S into the vapor phase
338 to subsequently elevate the oxygen fugacity (*f*O₂) of the fluids (Ohmoto 1972; Drummond and
339 Ohmoto 1985). This is consistent with the negative δ³⁴S_{CDT} values in the Xinqiao colloform pyrite
340 (Zhang et al. 2017a) as fluid oxidation has been proposed to generate negative δ³⁴S values in
341 sulfides (Drummond and Ohmoto 1985; Hodkiewicz et al. 2009; LaFlamme et al. 2018). The
342 short-lived FeS₂ supersaturation and elevated *f*O₂ caused by the fracturing would create suitable
343 conditions for hematite formation. The fine-grained, foliaceous and needle-like textures of Mt6
344 suggest the early hematite replaced by Mt6 formed rapidly in unstable conditions, consistent with
345 the fracturing. Sealing of the fractures would allow fluid pressures to rebuild and the ore-forming
346 system to revert back to lower oxygen fugacities, which, coupled with continuous release of CO₂,
347 may explain the replacement of precursor hematite by Mt6 and the formation of siderite in the Mt6
348 veins. Therefore, Mt6 may have been genetically associated with fracturing.

349

350 **Controlling factors for magnetite precipitation**

351 Given that the trace-element composition of hydrothermal magnetite is determined by a
352 number of factors, including the physicochemical conditions (esp., T and *f*O₂), fluid composition
353 (intensity of fluid-rock interactions), and co-crystallizing minerals (e.g., Dare et al. 2012, 2014;
354 Nadoll et al. 2014; Li et al. 2018b; Huang et al. 2019b), the trace element geochemistry can be
355 used to constrain the precipitation conditions of the Xinqiao magnetite.

356 Temperature is thought to significantly influence the incorporation of trace elements into
357 magnetite (McIntire 1963; Nadoll et al. 2014; Knipping et al. 2015; Deditius et al. 2018). A

358 positive correlation between the formation temperature and Ti contents in magnetite has been
359 widely proven ([Lindsley 1991](#); [Rapp et al. 2010](#); [Dare et al. 2012](#); [Nadoll et al. 2012](#)). At Xinqiao,
360 the decreasing TiO₂ from Mt3c (Avg. 0.11 wt.%) through Mt3r (Avg. 0.05 wt.%), Mt4 (Avg. 0.03
361 wt.%) and Mt5 (Avg. 0.01 wt.%) to Mt6 (below detection limit) ([Appendix 1](#); [Fig. 4a](#)) is
362 consistent with gradual cooling from Mt3c to Mt6. However, the increasing Ti concentrations
363 from Mt1 (Avg. 0.05 wt.%) and Mt2 (Avg. 0.04 wt.%) to Mt3c suggest the temperature increased
364 during their formation. Plots of Al + Mn vs. Ti + V can also reflect the formation temperature of
365 magnetite ([Nadoll et al. 2014](#); [Deditius et al. 2018](#)). The Xinqiao magnetite plots in Al + Mn vs. Ti
366 + V diagram ([Fig. 5c](#)) consistent with the gradually decreasing temperatures from Mt3c to Mt6.
367 Although the dataset for Mt1 is small, there is evidence for increasing temperatures from Mt1 to
368 Mt3 ([Fig. 5c](#)).

369 Vanadium concentrations in hydrothermal magnetite can record the fO_2 evolution of
370 hydrothermal fluids as vanadium is incompatible at high oxygen fugacities ([Toplis and Corgne](#)
371 [2002](#); [Dupuis and Beaudoin 2011](#); [Nadoll et al. 2014](#); [Knipping et al. 2015](#); [Papike et al. 2005](#)).
372 EPMA V₂O₃ data in different types of magnetite are consistent within error ([Fig. 4a](#)), but
373 LA-ICP-MS V data of Mt3, Mt5, and Mt6 decrease from Mt3c (Avg. 72.392 ppm) and Mt3r (Avg.
374 76.842 ppm) to Mt5 (Avg. 21.263 ppm), and increase from Mt5 to Mt6 (Avg. 72.000 ppm), which
375 suggests that fO_2 during the formation of Mt5 was higher than during the formation of Mt3 and
376 Mt6. This is consistent with variations in the Sn content that increase from Mt3c (Avg. 33.417
377 ppm) and Mt3r (Avg. 36.648 ppm) to Mt5 (Avg. 75.100 ppm), and then decrease from Mt5 to Mt6
378 (Avg. 2.940 ppm) because Sn is redox sensitive in magnetite ([Carew 2004](#); [Huang et al. 2019b](#)).
379 The similar contents of V and Sn in Mt3c and Mt3r suggest that fO_2 conditions were stable during

380 their formation.

381 Extensive fluid-rock interactions commonly result in hydrothermal magnetite being enriched
382 in Mn, Mg, Al, and Si (Einaudi et al. 1981; Carew 2004; Meinert et al. 2005; Nadoll et al. 2014;
383 Deditius et al. 2018), but temperature can also influence the Mn content in magnetite (Nadoll et al.
384 2014; Deditius et al. 2018), so Liu et al. (2019) used Mg + Al + Si contents to investigate the
385 intensity of fluid-rock interactions. For the Xinqiao magnetite, Mt1 and Mt3c have the highest Mg
386 + Al + Si contents (Fig. 5d), suggesting that they have undergone the strongest fluid-rock
387 interactions during their formation. The lower Mg + Al + Si contents of Mt3c to Mt3r (Fig. 5d)
388 suggests a gradual decrease in the intensity of fluid-rock interactions. Both Mt5 and Mt6 have
389 lower Mg + Al + Si contents than Mt3c, suggesting they were affected by less intense fluid-rock
390 interactions, consistent with Mt5 having formed from fluid-assisted recrystallization processes and
391 Mt6 having grown rapidly under unstable conditions associated with fracturing. Moreover, Mt2
392 and Mt4 have the lowest Mg + Al + Si contents (Fig. 5d), consistent with them having formed by
393 DRP of pre-existing Mt1 and Mt3, respectively.

394 Dissolution and reprecipitation processes can be driven by variations in the properties of the
395 fluids, such as fluid compositions, T, pressure and fO_2 (Hemley and Hunt 1992; Putnis 2002;
396 Putnis and Putnis 2007). Mixing of saline fluids with Fe-rich magmatic-hydrothermal solutions, an
397 increase in T, and decreasing pressure and fO_2 are considered the most important causes for DRP
398 of primary magnetite (Hu et al. 2015) because these would enhance the solubility and
399 consequently the undersaturation of iron in the fluids (Hemley and Hunt 1992; Hu et al. 2014).
400 The lack of obvious increase in V_2O_3 and TiO_2 contents from Mt1 to Mt2 (V_2O_3 : Avg. 0.14 wt.%
401 vs. 0.18 wt.%; TiO_2 : Avg. 0.05 wt.% vs. 0.04 wt.%), and Mt3r to Mt4 (V_2O_3 : Avg. 0.02 wt.% vs.

402 0.03 wt.%; TiO₂: Avg. 0.05 wt.% vs. 0.03 wt.%), and the gradually increasing pressure before the
403 formation of the colloform pyrite associated with hydraulic fractures suggests variations in T, fO₂
404 and pressure may not be the cause of DRP at Xinqiao. Previous multi-isotopic data (Re–Os, S and
405 Pb) of pyrite has shown that the Xinqiao stratiform mineralization was predominantly formed by
406 intensive water-rock interaction between the magmatic-hydrothermal fluids associated with the
407 Jitou stock and the Late Permian metalliferous black shales (Li et al. 2017, 2018a), which is
408 consistent with high Cl⁻ concentrations in fluid inclusions (up to 3.346 μg/g; Zhang 2015) at
409 Xinqiao. The saline fluids resulted from this water-rock interaction may be responsible for DRP of
410 the Xinqiao magnetite.

411

412 **Metallogenic implications**

413 Several diagrams, such as Ca + Al + Mn vs. Ti + V, Ni/(Cr + Mn) vs. Ti + V (Dupuis and
414 Beaudoin 2011) and Mn + Al vs. Ti + V (Nadoll et al. 2014) have been proposed to discriminate
415 various deposit types. Given that Ca and Ni concentrations in some EPMA analyses are below the
416 detection limits, the Mn + Al vs. Ti + V diagram (Fig. 6) was applied in this study, and Mt3, Mt4,
417 Mt5 and Mt6 dominantly plot in the skarn zones, suggesting that these stages of magnetite are
418 genetically associated with magmatic hydrothermal fluids, consistent with the hypothesis that the
419 Xinqiao stratiform mineralization is genetically associated with the Early Cretaceous
420 magmatic-hydrothermal fluids as a skarn deposit (e.g., Pan and Done 1999; Mao et al. 2009, 2011;
421 Zhang et al. 2017b, c, 2018; Li et al. 2017, 2018a, 2019). A large variation in Ti + V and relatively
422 stable Mn + Al in Figure 6 may be ascribed to the intensive fluid-rock interactions in the skarn
423 system. Mt1 plots in the BIF and IOCG zones close to skarn zone (Fig. 6), but a BIF source can be

424 excluded by the absence of Precambrian banded iron formations in the Tongling district, and the
425 IOCG mineralization is not supported by the low Ni contents of Mt1 and the absence of Na-Ca
426 alteration at Xinqiao (Huang et al. 2019a). The dark Mt1 under BSE has relatively high contents
427 of Si, Al, Ca, and Mg, which might be related to a major contribution of magmatic-derived fluids
428 due to a large fluid-rock ratio (Nadoll et al. 2012, 2014; Dare et al. 2014). Therefore, the
429 formation of Mt1 was influenced by both sedimentary and skarn-type processes, namely intensive
430 fluid-rock interactions, coinciding with the high Mg + Al + Ca of Mt1 (Fig. 5d), and the Xinqiao
431 magnetite may have been genetically associated with skarn mineralization derived from magmatic
432 hydrothermal fluids.

433 If the Xinqiao deposit formed from a single hydrothermal event, the ore-forming temperature
434 would gradually decrease over time. Although the temperatures decrease from Mt3 to Mt6, the
435 increase from Mt2 to Mt3c implies that the Xinqiao stratiform mineralization may reflect at least
436 two hydrothermal events. The combination of close spatial and temporal relationship between the
437 Jitou stock (zircon U–Pb age of 139.6 ± 1.5 Ma; Zhang et al. 2017c) and the stratiform orebody
438 (quartz fluid inclusions Rb–Sr isotope isochron age of 138.0 ± 2.3 Ma (Zhang et al. 2017c) and
439 Re–Os isotope isochron ages of 136.7 ± 4.6 Ma, 143 ± 16 Ma, and 135.5 ± 4.0 Ma for colloform
440 pyrite, pyrite from garnet-bearing skarn ore, and euhedral pyrite cemented by calcite, respectively
441 (Li et al. 2018a)), the iron ($\delta^{57}\text{Fe}$: -1.22% to 0.15% ; Wang et al. 2011, 2013), S isotope
442 compositions ($\delta^{34}\text{S}_{\text{CDT}}$ of -0.6 to 2.7% , 1.8 to 2.5% , and 1.9 to 4.4% for colloform pyrite,
443 fine-grained pyrite formed from recrystallization of colloform pyrite, and coarse-grained pyrite
444 coexisting with quartz and calcite, respectively; Zhang et al. 2017a) and Co/Ni ratios (0.67 – 2.94 ,
445 1.05 – 3.24 , and 1.03 – 4.67 for colloform pyrite, fine-grained pyrite, and coarse-grained pyrite;

446 [Zhang et al. 2017a](#)) of pyrite in the stratiform orebody, and the H–O isotope data ($\delta D_{SMOW} =$
447 $-48.02-61.82\%$, $\delta^{18}O_{SMOW} = 12.56-22.74\%$; [Liu, 2002](#)) of ore-bearing quartz in the stratiform
448 orebody suggests that the magmatic hydrothermal fluids associated with the Jitou stock are
449 dominantly responsible for the stratiform mineralization. One diorite porphyry dyke has been
450 found in the Xinqiao mining area, but it yielded a zircon U–Pb age of 130.6 ± 1.1 Ma ([Li et al.](#)
451 [2017](#)) and obviously cut through the stratiform orebody ([Zhang 2015](#)). Additionally, there is no
452 evidence to support other concealed intrusions in the region. Therefore, we conclude that the
453 increasing fluid temperatures from Mt2 to Mt3 likely resulted from episodic release of
454 hydrothermal fluids derived from magma associated with the Early Cretaceous Jitou stock, given
455 that the injection of multiple pulses of fluid is typical of magmatic-hydrothermal systems
456 ([Hedenquist and Lowenstern 1994](#)). Moreover, multiple influxes of fluid are also consistent with
457 the formation of multigenerational garnet at Xinqiao ([Zhang et al. 2017b](#)).

458 Here we propose a textural and trace-element geochemical evolution ([Fig. 7](#)) for the Xinqiao
459 magnetite. The first Si + Fe-rich magmatic-derived hydrothermal fluids released from the deep
460 magma chamber associated with the Jitou stock, entered the low-pressure unconformity between
461 the Upper Devonian Wutong Formation quartz sandstone and the Upper Carboniferous Huanglong
462 Formation limestone and interacted with limestone to form Mt1 enriched in Si, Al, Ca, and Mg.
463 Meanwhile, some fluids evolved into high-salinity fluids after intensive interaction with the Late
464 Permian metalliferous black shales, and mixed with the magmatic hydrothermal fluids to enhance
465 the solubility of iron in the fluids resulting in the formation of porous Mt2 by DRP which is
466 depleted in Ti, Si, Ca, V and Mg, that replaced Mt1. Subsequently, a second pulse of abundant Si
467 + Fe-rich magmatic hydrothermal fluid was released. Fluctuating fluid compositions and

468 physicochemical conditions resulted in the formation of core-rim magnetite (Mt3) with oscillatory
469 zoning. Similarly, high-salinity fluids derived from interaction between magmatic hydrothermal
470 fluids and the metalliferous black shales induced the dissolution of Mt3 and precipitation of Mt4.
471 During this process, Ti, Si, Ca, Al, and Mg were removed from Mt3, and the FeO content
472 increased. During mineralization early magnetite (Mt1–Mt4) recrystallized to Mt5 under
473 conditions of decreasing temperature and fluid-rock interactions intensity and increasing fO_2 .
474 Lastly, the gradual increase in ore-forming pressure due to the release of abundant CO_2 during the
475 conversion of carbonate to skarn would have exceeded the lithostatic load to create extensive
476 hydraulic fractures in the Wutong Formation quartz sandstone. This fracturing would have resulted
477 in elevated fO_2 fluids that formed hematite with fine-grained foliaceous and needle-like textures.
478 After sealing of the fractures, fluid pressures would increase and the ore-forming system revert
479 back to low oxygen fugacity, with Mt6 replacing the precursor hematite.

480

481

IMPLICATIONS

482 Primary magnetite easily undergoes dissolution and reprecipitation, oxy-exsolution, and/or
483 recrystallization to reach chemical and textural reequilibration, and consequently texture
484 examination is necessary before conducting trace-element analyses. At Xinqiao, the microporosity
485 of Mt2 and Mt4 magnetite, and their sharp contacts with Mt1 and Mt3, suggest that they formed
486 via coupled dissolution and reprecipitation of the precursor Mt1 and Mt3 magnetite, respectively.
487 Based on the metasomatic pseudomorph textures, Mt6 formed by replacement of hematite as a
488 result of fracturing. Moreover, this study also demonstrates that in-situ trace elements analysis
489 based on detailed texture examination under robust geological and petrographic frameworks can

490 effectively constrain the mineralization processes and ore genesis. Increasing Ti content from Mt2
491 to Mt3 suggests the elevated temperature during their formation, which is ascribed into multiple
492 pulses of magmatic-hydrothermal fluids, and reveals that the Xinqiao stratiform mineralization
493 was genetically associated with multiple influxes of magmatic hydrothermal fluids derived from
494 the Early Cretaceous Jitou stock.

495

496

ACKNOWLEDGEMENTS

497 Our especial thank goes to Dr. Minghong Zheng and Dr. Zhongfa Liu for their field
498 assistance, and to Dr. Huajie Tan for assisting with the EPMA analysis. In particular, thanks are
499 extended to Prof. Julie Roberge and two anonymous reviewers for constructive and insightful
500 suggestions that greatly improved this manuscript.

501

502

FUNDING

503 This research was financially supported by the National Natural Science Foundation of
504 China (41972081), the Open Fund for the Important Instruments of Central South University
505 (CSUZC201902) and the Research Start-up Fund of Central South University (202045009).

506

507

REFERENCES CITED

508 Beaudoin, G., Dupuis, C., Gosselin, P., Jébrak, M. (2007) Mineral chemistry of iron oxides: application to mineral
509 exploration. Ninth Biennial SGA Meeting SGA, Dublin. pp. 497–500.

510 Cao, Y., Zheng, Z.J., Du, Y.L., Gao, F.P., Qin, X.L., Yang, H.M., Lu, Y.H., Du, Y.S. (2017) Ore geology and fluid

- 511 inclusions of the Hucunnan deposit, Tongling, Eastern China: Implications for the separation of copper and
512 molybdenum in skarn deposits. *Ore Geology Reviews*, 81, 925–939.
- 513 Carew, M.J. (2004) Controls on Cu-Au mineralisation and Fe oxide metasomatism in the Eastern Fold Belt, NW
514 Queensland, Australia. Ph.D. thesis, James Cook University, Queensland, pp 213–277.
- 515 Chang, Y.F., Liu, X.P., Wu, Y.Z. (1991) Metallogenic belt of the Middle-Lower Yangtze River. Beijing:
516 Geological Publishing House, 1–379 (in Chinese).
- 517 Ciobanu, C.L., Cook, N.J. (2004) Skarn textures and a case study: the Ocna de Fier-Dognecea orefield, Banat,
518 Romania. *Ore Geology Reviews*, 24, 315–370.
- 519 Dare, S.A.S., Barnes, S.J., Beaudoin, G. (2012) Variation in trace element content of magnetite crystallized from a
520 fractionating sulfide liquid, Sudbury, Canada: implications for provenance discrimination. *Geochimica et*
521 *Cosmochimica Acta*, 88, 27–50.
- 522 Dare, S.A.S., Barnes, S.J., Beaudoin, G., Méric, J., Boutroy, E., Potvin-Doucet, C. (2014) Trace elements in
523 magnetite as petrogenetic indicators. *Mineralium Deposita*, 49, 785–796.
- 524 Dare, S.A.S., Barnes, S.J., Beaudoin, G. (2015) Did the massive magnetite “lava flows” of El Laco (Chile) form by
525 magmatic or hydrothermal processes? New constraints from magnetite composition by LAICP-MS.
526 *Mineralium Deposita*, 50, 607–617.
- 527 Deditius, A.P., Reich, M., Simon, A.C., Suvorova, A., Knipping, J., Roberts, M.P., Rubanov, S., Dodd, A.,
528 Saunders, M. (2018) Nanogeochemistry of hydrothermal magnetite. *Contributions to Mineralogy and*
529 *Petrology*, 173, 46.
- 530 Drummond, S.E., Ohmoto, H. (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems.
531 *Economic Geology*, 80, 126–147.
- 532 Du, Y.L., Deng, J., Cao, Y., Li, D.D. (2015) Petrology and geochemistry of Silurian–Triassic sedimentary rocks in

- 533 the Tongling region of Eastern China: Their roles in the genesis of large stratabound skarn ore deposits. *Ore*
534 *Geology Reviews*, 67, 255–263.
- 535 Dupuis, C., Beaudoin, G. (2011) Discriminant diagrams for iron oxide trace element fingerprinting of mineral
536 deposit types. *Mineralium Deposita*, 46, 1–17.
- 537 Einaudi, M.T., Meinert, L.D., Newberry, R.J. (1981) Skarn deposits. *Economic Geology*. 75th Anniversary
538 Volume, 317–391.
- 539 Gu, L.X., Hu, W.X., He, J.X. (2000) Regional variations in ore composition and fluid features of massive sulfide
540 deposits in South China: Implications for genetic modeling. *Episodes*, 23(2), 110–118.
- 541 Guo, W.M., Lu, J.J., Jiang, S.Y., Zhang, R.Q., Qi, L. (2011) Re-Os isotope dating of pyrite from the footwall
542 mineralization zone of the Xinqiao deposit, Tongling, Anhui Province: Geochronological evidence for
543 submarine exhalative sedimentation. *Chinese Science Bulletin*, 56(36), 3860–3865 (in Chinese with
544 English abstract).
- 545 Hemley, J.J., Hunt, J.P. (1992) Hydrothermal ore-forming processes in the light of studies in rock-buffered
546 systems; II, some general geologic applications. *Economic Geology*, 87, 23–43.
- 547 Hedenquist, J.W., Lowenstern, J.B. (1994) The role of magmas in the formation of hydrothermal ore deposits.
548 *Nature*, 370, 519–527.
- 549 Hodkiewicz, P.F., Groves, D.I., Davidson, G.J., Weinberg, R.F., Hagemann, S.G. (2009) Influence of structural
550 setting on sulphur isotopes in Archean orogenic gold deposits, Eastern Goldfields Province, Yilgarn,
551 Western Australia. *Mineralium Deposita*, 44, 129–150.
- 552 Hu, H., Li, J.W., Lentz, D., Ren, Z., Zhao, X.F., Deng, X.D. Hall, D. (2014) Dissolution–reprecipitation process of
553 magnetite from the Chengchao iron deposit: Insights into ore genesis and implication for in-situ chemical
554 analysis of magnetite. *Ore Geology Reviews*, 57, 393–405.

- 555 Hu, H., Lentz, D., Li, J.W., McCarron, T., Zhao, X.F., Hall, D. (2015) Reequilibration process in magnetite from
556 iron skarn deposits. *Economic Geology*, 110, 1–8.
- 557 Hu, X., Chen, H.Y., Beaudoin G., Zhang, Y. (2020) Textural and compositional evolution of iron oxides at Mina
558 Justa (Peru): Implications for mushketovite and formation of IOCG deposits. *American Mineralogist*, 105,
559 397–408.
- 560 Huang, X.W., Sappin, A.A., Boutroy, E., Beaudoin, G., Makvandi, S. (2019a) Trace element composition of
561 igneous and hydrothermal magnetite from porphyry deposits: Relationship to deposit subtypes and
562 magmatic affinity. *Economic Geology*, 114, 917–952.
- 563 Huang, X.W., Boutroy, E., Makvandi, S., Beaudoin, G., Corriveau, L., De Toni, A.F. (2019b) Trace element
564 composition of iron oxides from IOCG and IOA deposits: relationship to hydrothermal alteration and
565 deposit subtypes. *Mineralium Deposita*, 54, 525–552.
- 566 Knipping, J.L., Bilenker, L.D., Simon, A.C., Reich, M., Barra, F., Deditius, A.P., Walle, M., Heinrich, C.A., Holtz,
567 F., Munizaga, R. (2015) Trace elements in magnetite from massive iron oxide-apatite deposits indicate a
568 combined formation by igneous and magmatic-hydrothermal processes. *Geochimica et Cosmochimica*
569 *Acta*, 171, 15–38.
- 570 Lai, J.Q., Chi, G.X. (2007) CO₂-rich fluid inclusions with chalcopyrite daughter mineral from the Fenghuangshan
571 Cu–Fe–Au deposit, China: implications for metal transport in vapor. *Mineralium Deposita*, 42, 293–299.
- 572 LaFlamme, C., Sugiono, D., Thébaud, N., Caruso, S., Fiorentini, M., Selvaraja, V., Jeon, H., Vouste, F., Martin, L.
573 (2018) Multiple sulfur isotopes monitor fluid evolution in an orogenic gold deposit. *Geochimica et*
574 *Cosmochimica Acta*, 222, 436–446.

- 575 Li, S., Yang, X.Y., Huang, Y., Sun, W.D. (2014) Petrogenesis and mineralization of the Fenghuangshan skarn
576 Cu–Au deposit, Tongling ore cluster field, Lower Yangtze metallogenic belt. *Ore Geology Reviews*, 58,
577 148–162.
- 578 Li, W., Xie, G., Mao, J.W., Zhu, Q.Q., Zheng, J.H. (2019) Mineralogy, fluid Inclusion, and stable isotope studies
579 of the Chengchao deposit, Hubei Province, Eastern China: Implications for the formation of high-Grade Fe
580 skarn deposits. *Economic Geology*, 114, 325–352.
- 581 Li, Y., Li, J.W., Li, X.H., Selby, D., Huang, G.H., Chen, G.H., Chen, L.J., Zheng, K. (2017) An Early Cretaceous
582 carbonate replacement origin for the Xinqiao stratabound massive sulfide deposit, Middle-Lower Yangtze
583 Metallogenic Belt, China. *Ore Geology Review*, 80, 985–1003.
- 584 Li, Y., Selby, D., Li, X.H., Ottley, C.J. (2018a) Multisourced metals enriched by magmatic-hydrothermal fluids in
585 stratabound deposits of the Middle–Lower Yangtze River metallogenic belt, China. *Geology*, 46, 391–394.
- 586 Li, D.F., Chen, H.Y., Hollings, P., Zhang, L., Sun, X.M., Zheng, Y., Xia, X.P., Xiao, B., Wang, C.M., Fang, J.
587 (2018b) Trace element geochemistry of magnetite: Implications for ore genesis of the Talate skarn Pb-Zn (-Fe)
588 deposit, Altay, NW China. *Ore Geology Reviews*, 100, 471–257.
- 589 Li, Y., Li, Q.L., Yang, J.H. (2019) Tracing water-rock interaction in carbonate replacement deposits: A SIMS
590 pyrite S-Pb isotope perspective from the Chinese Xinqiao system. *Ore Geology Review*, 107, 248–257.
- 591 Lindsley, D.H. (1991) Experimental studies of oxide minerals. *Reviews in Mineralogy and Geochemistry*, 25,
592 69–106.
- 593 Ling, M.X., Wang, F.Y., Ding, X., Hu, Y.H., Zhou, J.B., Zartman, R.E., Yang, X.Y. (2009) Cretaceous rifge
594 subduction along the Lower Yangtze River Belt, Eastern China. *Economic Geology*, 104, 303–321.
- 595 Liu, X.B. (2002) Geological characteristics and ore-controlling factor analysis of Xinqiao S–Fe deposit. *Express
596 Information of Mining Industry*, 22, 13–15 (in Chinese).

- 597 Liu, Y., Fan, Y., Zhou, T., Xiao, X., White, N.C., Thompson, J., Hong, H., Zhang, L. (2019) Geochemical
598 characteristics of magnetite in Longqiao skarn iron deposit in the Middle-Lower Yangtze Metallogenic
599 Belt, Eastern China. *Mineralium Deposita*, 10.1007/s00126-019-00871-x.
- 600 Mao, J.W., Shao, Y.J., Xie, G.Q., Zhang, J.D., Chen, Y.C. (2009) Mineral deposit model for porphyry-skarn
601 polymetallic copper deposits in Tongling ore dense district of Middle-Lower Yangtze Valley metallogenic
602 belt. *Mineral Deposits*, 28(2), 109–119 (in Chinese with English abstract).
- 603 Mao, J.W., Xie, G.Q., Duan, C., Franco, P., Dazio, I., Chen, Y.C. (2011) A tectono-genetic model for
604 porphyry-skarn-stratabound Cu-Au-Fe and magnetite-apatite deposit along the Middle-Lower Yangtze
605 River Valley, Eastern China. *Ore Geology Review*, 43(1), 294–314.
- 606 McIntire, W.L. (1963) Trace element partition coefficients—a review of theory and applications to geology.
607 *Geochimica et Cosmochimica Acta*, 27, 1209–1264.
- 608 Meinert, L.D., Dipple, G.M., Nicolescu S. (2005) World skarn deposits. In *Economic Geology 100th Anniversary*
609 *Volume 1905–2005*; Elsevier: Amsterdam, The Netherlands, pp. 299–336.
- 610 Nadoll, P., Mauk, J.L., Hayes, T.S., Koenig, A.E., Box, S.E. (2012) Geochemistry of magnetite from hydrothermal
611 ore deposits and host rocks of the Mesoproterozoic Belt Supergroup, United States. *Economic Geology*,
612 107, 1275–1292.
- 613 Nadoll, P., Angerer, T., Mauk, J.L., French, D., Walshe, J. (2014) The chemistry of hydrothermal magnetite: a
614 review. *Ore Geology Review*, 61, 1–32.
- 615 Nadoll, P., Mauk, J.L., Leveille, R.A., Koenig, A.E. (2015) Geochemistry of magnetite from porphyry Cu and
616 skarn deposits in the southwestern United States. *Mineralium Deposita*, 50, 493–515.
- 617 Ohmoto, H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Economic Geology* 67,
618 551–578.

- 619 Pan, Y., Done, P. (1999) The lower Changjiang (Yangtzi/Yangtze River) metallogenic belt, east-center China:
620 intrusion and wall rock hosted Cu-Fe-Au, Mo, Zn, Pb, Ag deposits. *Ore Geology Review*, 15(4), 177–242.
- 621 Papike, J.J., Purger, P.V., Bell, A.S., Shearer, C.K., Le L., Jones, J. (2015) Normal to inverse transition in martian
622 spinel: understanding the interplay between chromium, vanadium, and iron valence state partitioning
623 through a crystal-chemical lens. *American Mineralogist*, 100, 2018–2025.
- 624 Putnis, A. (2002) Mineral replacement reactions: from macroscopic observations to microscopic mechanisms.
625 *Mineralogical Magazine*, 66, 689–708.
- 626 Putnis, A., Putnis, C.V. (2007) The mechanism of reequilibration of solids in the presence of a fluid phase. *Journal*
627 *of Solid State Chemistry*, 180, 1783–1786.
- 628 Rapp, J.F., Klemme, S., Butler, I.B., Harley, S.L. (2010) Extremely high solubility of rutile in chloride and
629 fluoride-bearing metamorphic fluids: An experimental investigation. *Geology*, 38, 323–326.
- 630 Salazar, E., Barra, F., Reich, M., Simon, A., Leisen, M., Palma, G., Romero, R., Rojo, M. (2019) Trace element
631 geochemistry of magnetite from the Cerro Negro Norte iron oxide–apatite deposit, northern Chile.
632 *Mineralium Deposita*, 10.1007/s00126-019-00879-3.
- 633 Sibson, R.H., Robert, F., Poulsen, K.H. (1988) High-angle reverse faults, fluid-pressure cycling, and mesothermal
634 gold-quartz deposits. *Geology*, 16, 551–555.
- 635 Stowell, H., Zuluaga, C., Boyle, A., Bulman, G. (2011) Garnet sector and oscillatory zoning linked with changes
636 in crystal morphology during rapid growth, North Cascades, Washington. *American Mineralogist*, 96,
637 1354–1362.
- 638 Sun, W., Yuan, F., Jowitt, S.M., Zhou, T.F., Liu, G., Li, X., Wang, F., Troll, V.R. (2019) In situ LA–ICP–MS
639 trace element analyses of magnetite: genetic implications for the Zhonggu orefield, Ningwu volcanic basin,
640 Anhui Province, China. *Mineralium Deposita*, 10.1007/s00126-019-00872-w.

- 641 Sun, T., Chen, F., Zhong, L.X., Liu, W.M., Wang, Y. (2019) GIS-based mineral prospectivity mapping using
642 machine learning methods: A case study from Tongling ore district, eastern China. *Ore Geology Reviews*,
643 109, 26–49.
- 644 Sun, X., Lin, H., Fu, Y., Li, D., Hollings, P., Yang, T, Liu, Z. (2017) Trace element geochemistry of magnetite
645 from the giant Beiya gold-polymetallic deposit in Yunnan Province, Southwest China and its implications
646 for the ore forming processes. *Ore Geology Reviews*, 91, 477–490.
- 647 Tang, Y.C., Wu, Y.Z., Cu, G.Z., Xing, F.M., Wang, Y.M., Cao, F.Y., Chang, Y.F. (1998) Copper gold
648 polymetallic ore deposit geology in the region along Yangtze River in Anhui Province. Beijing: Geological
649 Publishing House, 1–351 (in Chinese).
- 650 Toplis, M.J., Corgne, A. (2002) An experimental study of element partitioning between magnetite, clinopyroxene
651 and iron-bearing silicate liquids with particular emphasis on vanadium. *Contributions to Mineralogy and
652 Petrology*, 144, 22–37.
- 653 Wang, S.W., Zhou, T.F., Yuan, F., Fan, Y., Zhang, L.J., Song, Y.L. (2015) Petrogenesis of Dongguashan
654 skarn-porphyry Cu-Au deposit related intrusion in the Tongling district, eastern China: Geochronological,
655 mineralogical, geochemical and Hf isotopic evidence. *Ore Geology Reviews*, 64, 53–70.
- 656 Wang, Y., Zhu, X.L., Mao, J.W, Li, Z.H., Cheng, Y.B. (2011) Iron isotope fractionation during skarn-type
657 metallogeny: A case study of Xiao Cu–S–Fe–Au deposit in the Middle-Lower Yangtze Valley. *Ore Geology
658 Review*, 43, 194–202.
- 659 Wang, Y., Zhu, X.K., Cheng, Y.B. (2013) Ore microscopy & Fe isotope of the Xinqiao deposit and their
660 constraints on the ore genesis. *Journal of Jilin University: Earth Science Edition*, 43(6), 1787–1798 (in
661 Chinese with English abstract).

- 662 Wen, G., Li, J.W., Hofstra, A., Koenig, A.E., Lowers, H.A., Adams D. (2017) Hydrothermal reequilibration of
663 igneous magnetite in altered granitic plutons and its implications for magnetite classification schemes:
664 insights from the Handan-Xingtai iron district, North China Craton. *Geochimica et Cosmochimica Acta*,
665 213, 255–270.
- 666 Wu, C.L., Dong, S.W., Robinson, P.T., Frost, B.R., Gao, Y.H., Lei, M., Chen, Q.L., Qin, H.P. (2014) Petrogenesis
667 of high-K, calc-alkaline and shoshonitic intrusive rocks in the Tongling area, Anhui Province (eastern China),
668 and their tectonic implications. *Geological Society of America Bulletin*, 126, 78–102.
- 669 Wu, Y.F., Li, J.W., Evans, K., Koenig, A.E., Li, Z.K., O'Brien, H., Lahaye, Y., Rempel, K., Hu, S.Y., Zhang, Z.P.,
670 Yu, J.P. (2018) Ore-forming processes of the Daqiao epizonal orogenic gold deposit, West Qinling Orogen,
671 China: constraints from textures, trace elements, and sulfur isotopes of pyrite and marcasite, and Raman
672 spectroscopy of carbonaceous material. *Economic Geology*, 113, 1093–1132.
- 673 Xiao, X., Zhou, T.F., Fan, Y., Xie, J., Zhang, L.J. (2016) LA-ICP-MS in situ trace elements and FE-SEM analysis
674 of pyrite from the Xinqiao Cu-Au-S deposit in Tongling, Anhui and its constraints on the ore genesis. *Acta*
675 *Petrologica Sinica*, 32(2), 369–376 (in Chinese with English abstract).
- 676 Xu, G., Zhou, J. (2001) The Xinqiao Cu-S-Fe-Au deposit in the Tongling mineral district, China: Synorogenic
677 remobilization of a stratiform sulfide deposit. *Ore Geology Review*, 18, 77–94.
- 678 Yu, C.W., Cen, K., Bao, Z.Y. (1998) Dynamics of mineralization. Geological Publishing House, Beijing, pp.
679 1–224 (in Chinese)
- 680 Zang, W.S., Wu, G.G., Zhang, D., Liu, A.H. (2004) Geological and geochemical characteristics and genetic
681 analyses of Xinqiao Iron Orefield, Tongling. *Geotectonica et Metallogenia*, 28(2), 187–193 (in Chinese
682 with English abstract).

- 683 Zhai, Y.S., Yao, S.Z., Lin, X.D., Jin, F.Q., Zhou, X.R., Wan, T.F., Zhou, Z.G. (1992) Metallogenic regularity of
684 iron and copper deposits in the Middle-Lower valley of the Yangtze River. *Mineral Deposits*, 11(1), 1–235
685 (in Chinese with English abstract).
- 686 Zhang, Y. (2015) Genesis of Xinqiao Cu-S-Fe deposit, Tongling, Anhui Province, China. Ph. D. Dissertation.
687 Central South University (in Chinese with English abstract).
- 688 Zhang, Y., Shao, Y.J., Chen, H.Y., Liu, Z.F., Li, D.F. (2017a) A hydrothermal origin for the large Xinqiao Cu–S–Fe
689 deposit, Eastern China: Evidence from sulfide geochemistry and sulfur isotopes. *Ore Geology Reviews*, 88,
690 534–549.
- 691 Zhang, Y., Shao, Y.J., Wu, C.D., Chen, H.Y., (2017b) LA-ICP-MS trace element geochemistry of garnets:
692 Constraints on hydrothermal fluid evolution and genesis of the Xinqiao Cu–S–Fe–Au deposit, eastern China.
693 *Ore Geology Reviews*, 86, 426–439.
- 694 Zhang, Y., Shao, Y.J., Li, H.B., Liu, Z.F. (2017c) Genesis of the Xinqiao Cu–S–Fe–Au deposit in the
695 Middle-Lower Yangtze River Valley metallogenic belt, Eastern China: Constraints from U–Pb–Hf, Rb–Sr, S,
696 and Pb isotopes. *Ore Geology Reviews*, 86, 100–116.
- 697 Zhang, Y., Shao, Y.J., Zhang, R.Q., Li, D.F., Liu, Z.F., Chen, H.Y. (2018) Dating ore deposit using garnet U–Pb
698 geochronology: Example from the Xinqiao Cu–S–Fe–Au deposit, Eastern China. *Minerals*, 8, 31.
- 699 Zhang, Y., Cheng, J.M., Tian, J., Pan, J., Sun, S.Q., Zhang, L.J., Zhang, S.T., Chu, G.B., Zhao, Y.J., Lai, C. (2019)
700 Texture and trace element geochemistry of quartz in skarn system: Perspective from Jiguanzui Cu–Au skarn
701 deposit, Eastern China. *Ore Geology Reviews*, 109, 534–544.
- 702 Zhou, T.F., Zhang, L.J., Yuan, F., Fang, Y., Cooke, D.R. (2010) LA-ICP-MS in situ trace element analysis of
703 pyrite from the Xinqiao Cu–Au–S Deposit in Tongling, Anhui, and its constrains on the ore genesis.
704 *Geoscience Frontiers*, 17(2), 306–319 (in Chinese with English abstract).

705

706

FIGURE CAPTIONS

707 **FIGURE 1.** (a) Location of the Tongling ore district in the Middle-Lower Yangtze River Valley
708 metallogenic belt (after [Mao et al. 2011](#)). TLF: Tancheng–Lujiang fault; XGF: Xiangfan–Guangji
709 fault; YCF: Yangxing–Changzhou fault. (b) Geological map of the Tongling district (modified
710 from [Chang et al. 1991](#)).

711

712 **FIGURE 2.** (a) Geological map and (b) representative cross section of the Xinqiao Cu–Fe–Au
713 deposit (after [Tang et al. 1998](#) and [Zang et al. 2004](#), respectively).

714

715 **FIGURE 3.** Photographs showing representative mineral assemblages and textural features of
716 magnetite in the Xinqiao stratiform orebody. (a) Anhedral Mt1 grain replaced by porous Mt2
717 (BSE); (b) Irregular and abrupt contact boundary between Mt1 and Mt2, indicating replacement
718 texture (BSE); (c) Subhedral Mt3 grain coexisting with epidote occurs among garnet grains (PPL);
719 (d) Anhedral Mt3 grain coexisting with and replaced by quartz, apatite, and pyrite; (e) Mt1 and
720 Mt2 only trapped in the core of Mt3 (BSE); (f) The same chemical oscillatory zoning occurrence
721 of Mt3c and Mt3r, parallel to the contact interface between Mt3c and Mt3r (BSE); (g) Mt4 veins
722 and patches replacing Mt3c and truncating the chemical oscillatory zoning of Mt3c (BSE); (h)
723 Mt4 veins truncating the chemical oscillatory zoning of Mt3r (BSE); (i) Mt5 replaced by
724 stockwork and disseminated pyrite; (j) Mt5 grains with 120° triple junction texture and locally
725 replaced by hematite; (k) Homogeneous Mt5 replaced by pyrite and quartz (BSE); (l) Mt6 vein
726 cutting through crystal pyrite; (m) Mt6 coexisting siderite cuts through colloform pyrite as vein; (n)

727 Mt6 replaced hematite in the form of metasomatic pseudomorph textures; (o) Needle-like Mt6 is
728 replaced by pyrite coexisting with calcite; (p) Homogeneous internal texture of Mt6.

729 **Abbreviations:** Ep = epidote, Cal = calcite, Grt = garnet, Qtz = quartz, Ap = apatite, Hem =
730 hematite, Py = crystal pyrite, Py_c = colloform pyrite.

731

732 **FIGURE 4.** Box diagram of major (a) and trace (b) elements concentrations for the Xinqiao
733 magnetite.

734

735 **FIGURE 5.** Ti versus V (a), V/Ti versus Fe (b), (Al + Mn) vs. (Ti + V) (c; modified after [Nadoll](#)
736 [et al. \(2014\)](#) and [Deditius et al. \(2018\)](#)) and (Mg + Al + Si) vs. Ti (d) diagrams for the Xinqiao
737 magnetite.

738

739 **FIGURE 6.** Discrimination plot of Mn + Al vs. Ti + V for the Xinqiao magnetite mineralization
740 types ([Nadoll et al. 2014](#)).

741

742 **FIGURE 7.** Schematic diagram showing the textural and trace-element geochemical evolution for
743 the Xinqiao magnetite. See text for details.

744

745 **APPENDIX CAPTIONS**

746 **APPENDIX 1.** EPMA geochemical data (wt.%) of the Xinqiao magnetite. “b.d.l” means below
747 detection limit.

748

749 **APPENDIX 2.** LA-ICP-MS trace element data (ppm) of the Xinqiao magnetite. “b.d.l” means

750 below detection limit.

751

752 **APPENDIX 3.** LA-ICP-MS trace element detection limits (ppm) of the Xinqiao magnetite.

Fig. 1

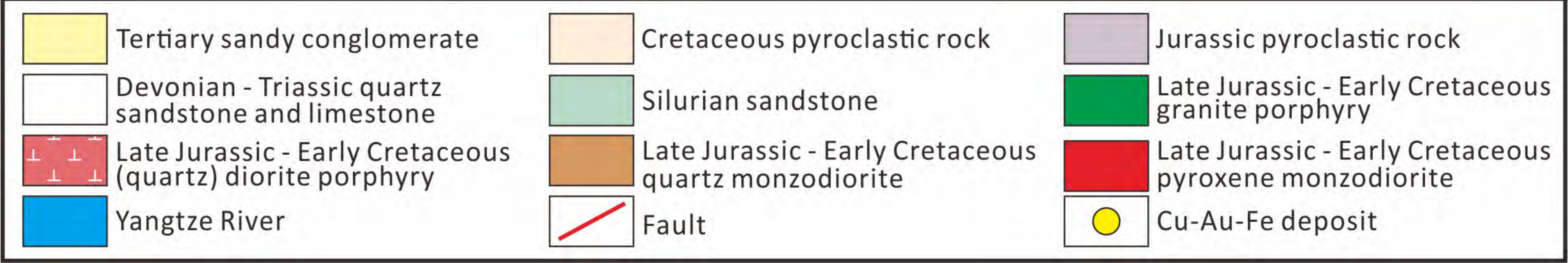
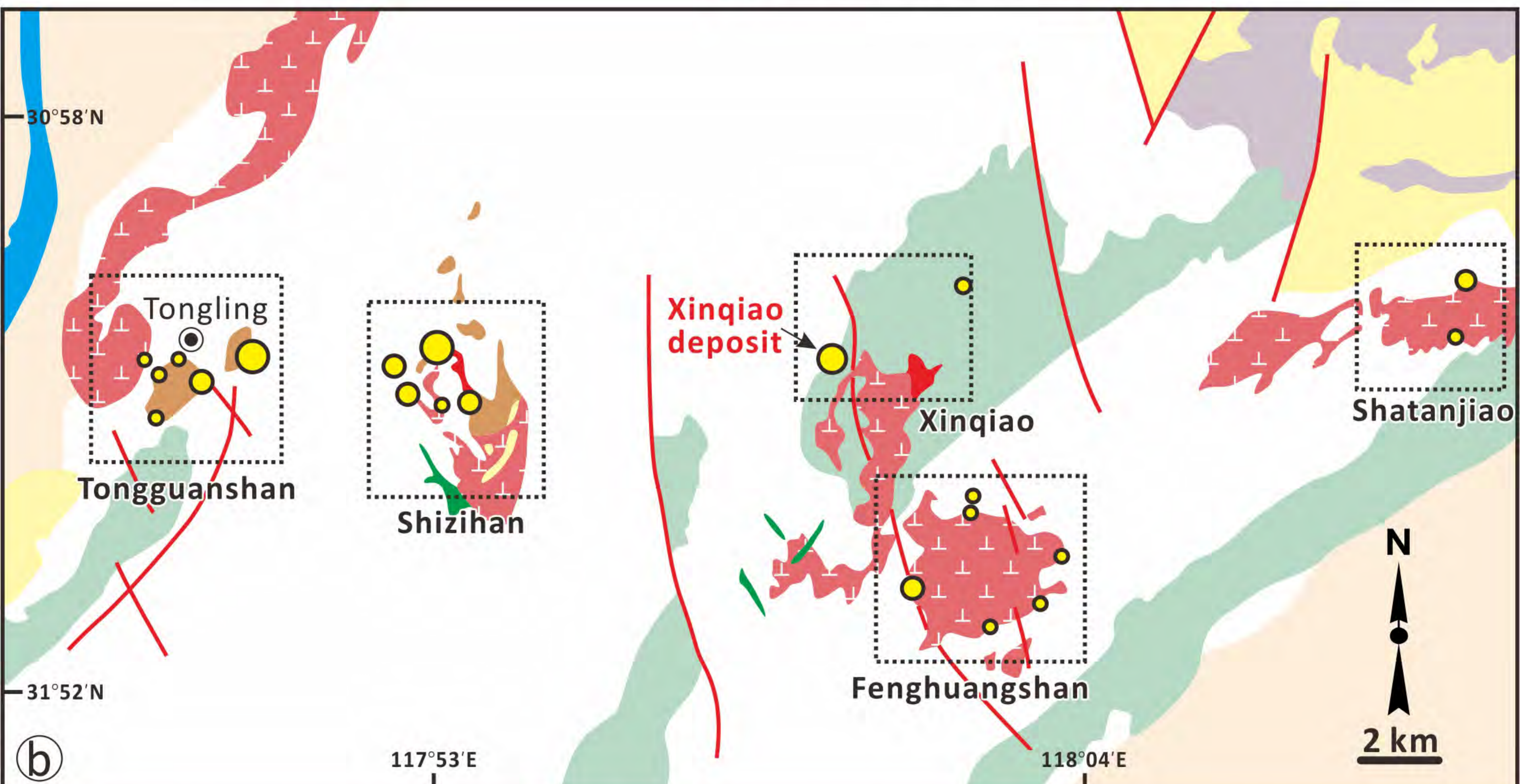
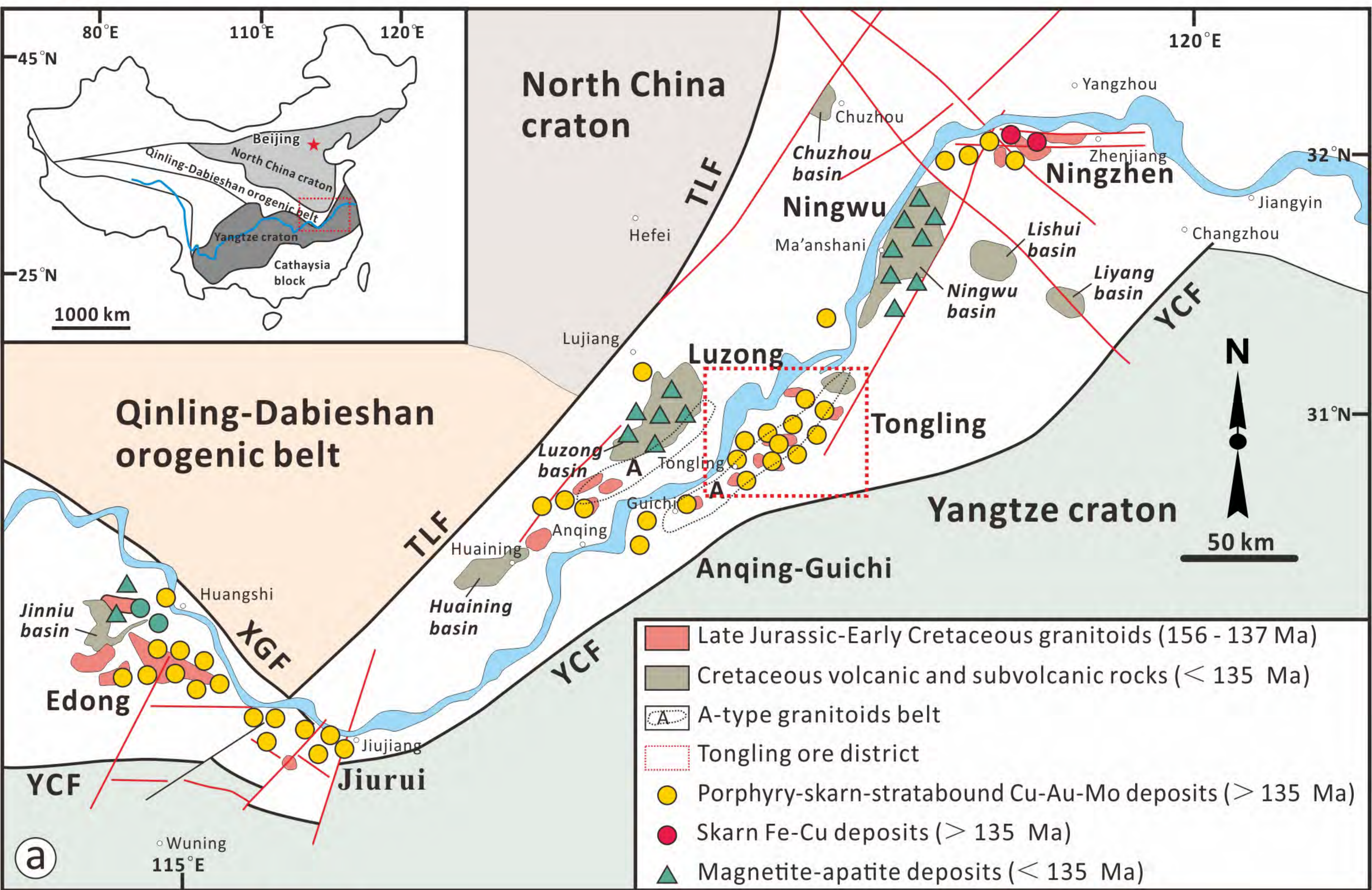


Fig. 2

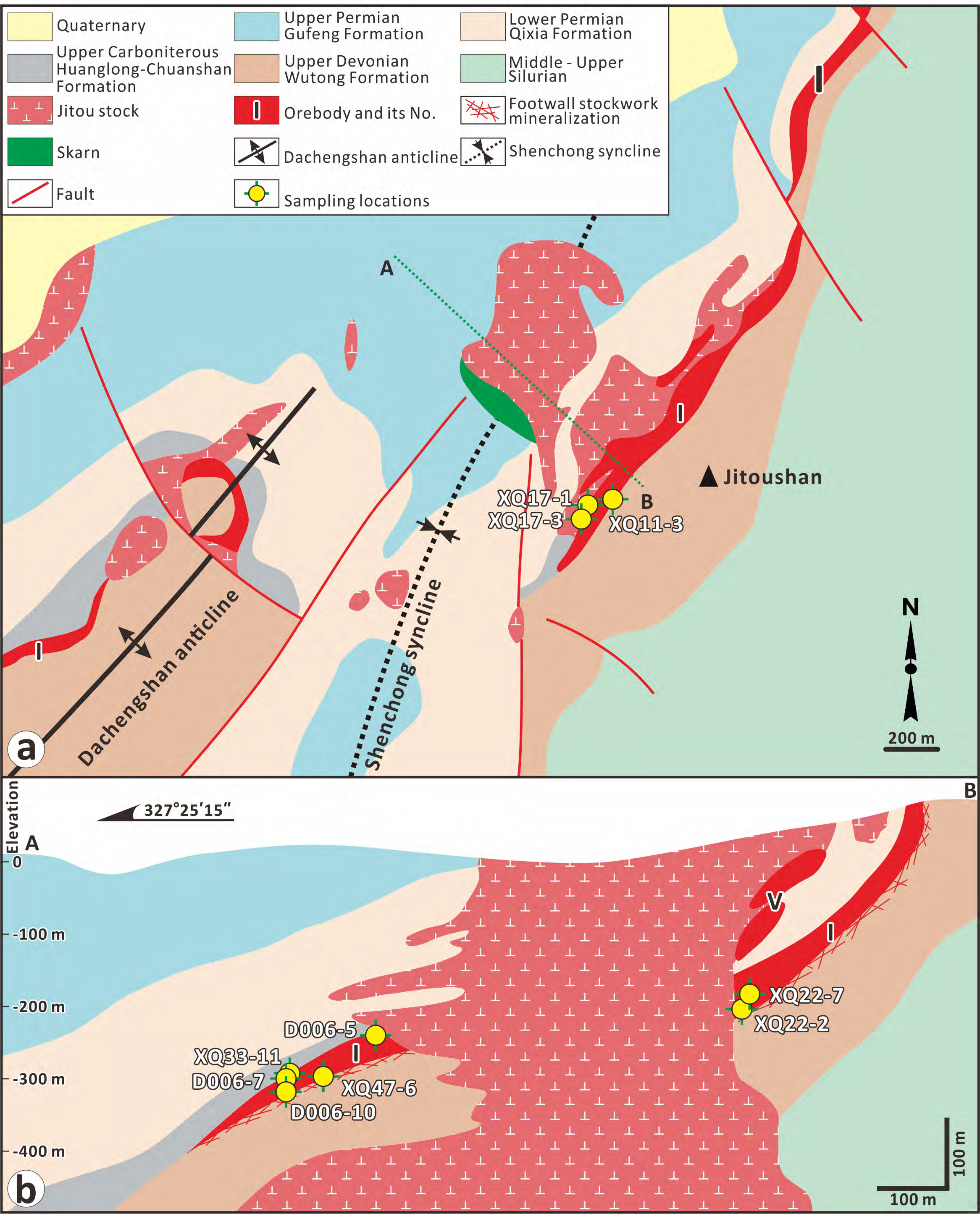


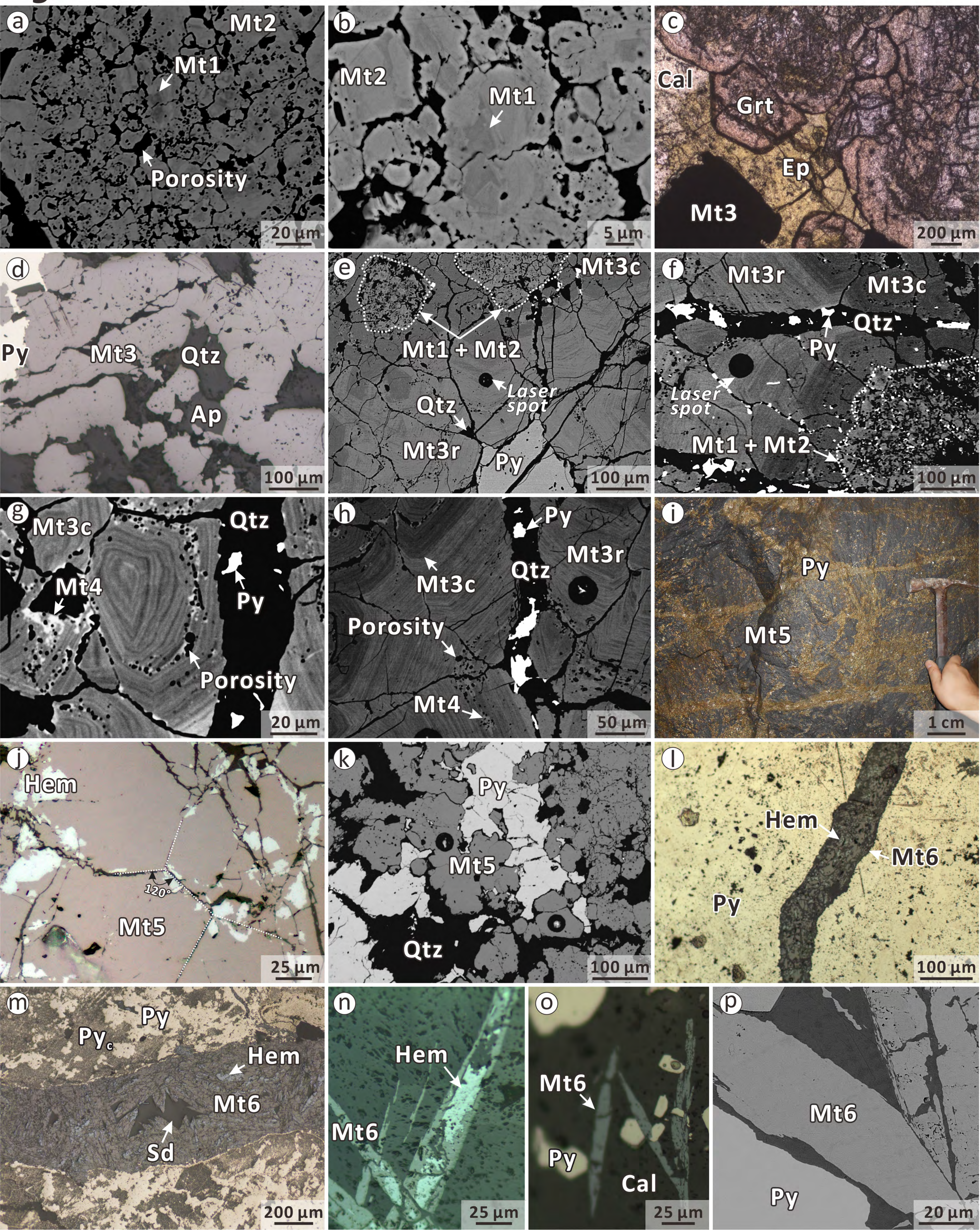
Fig. 3

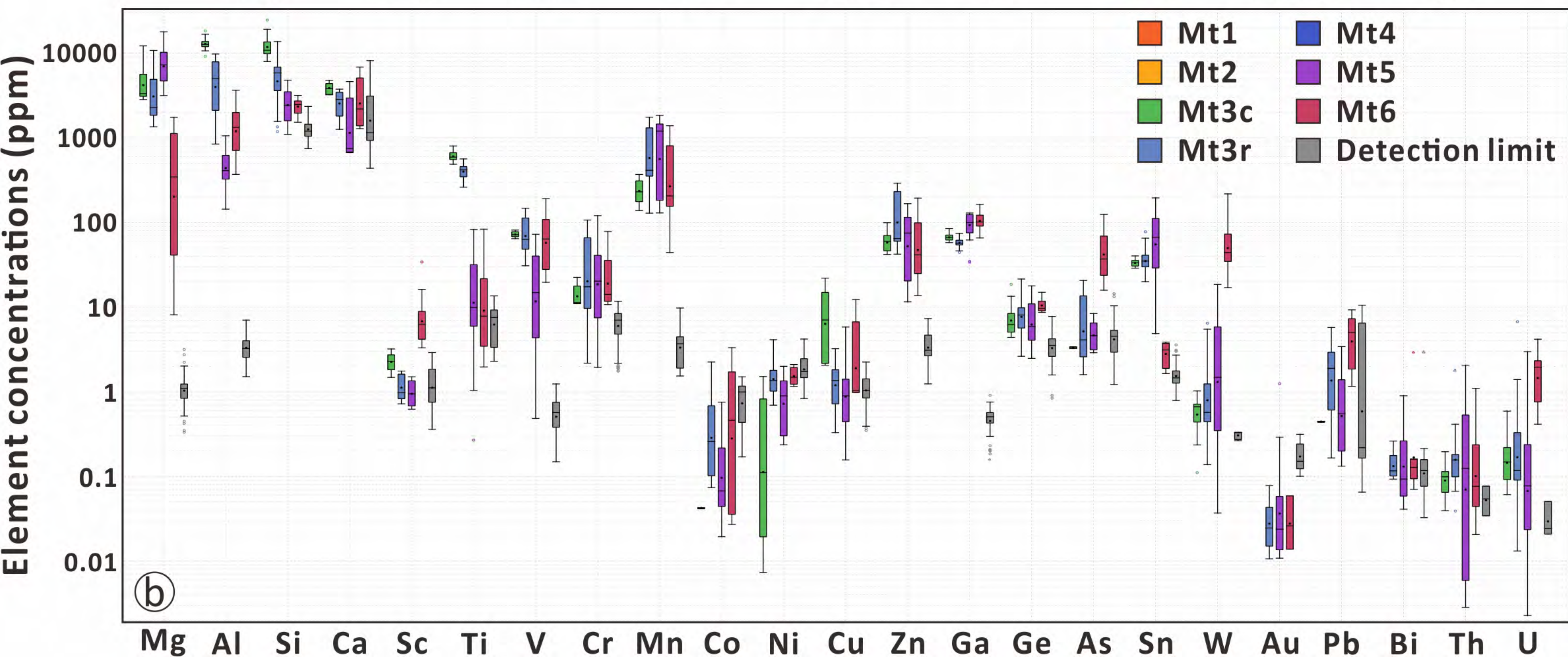
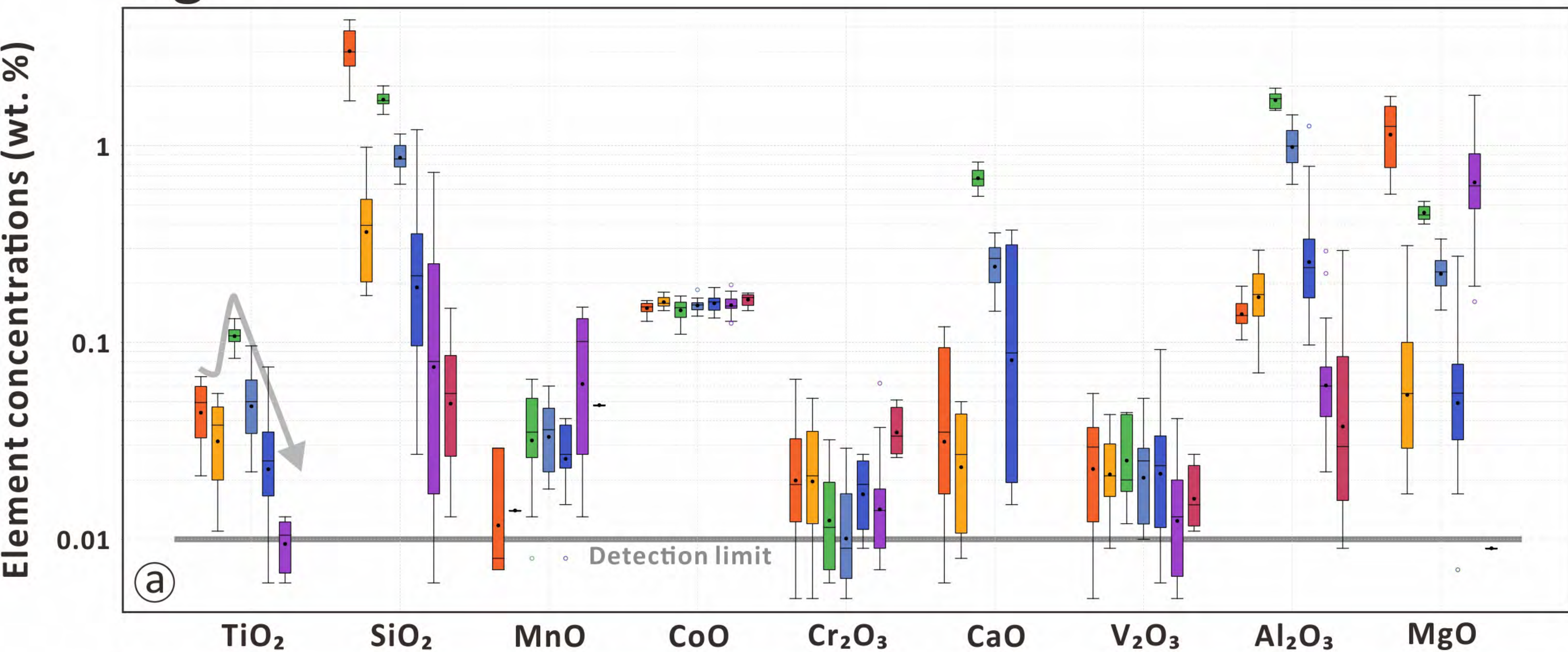
Fig. 4

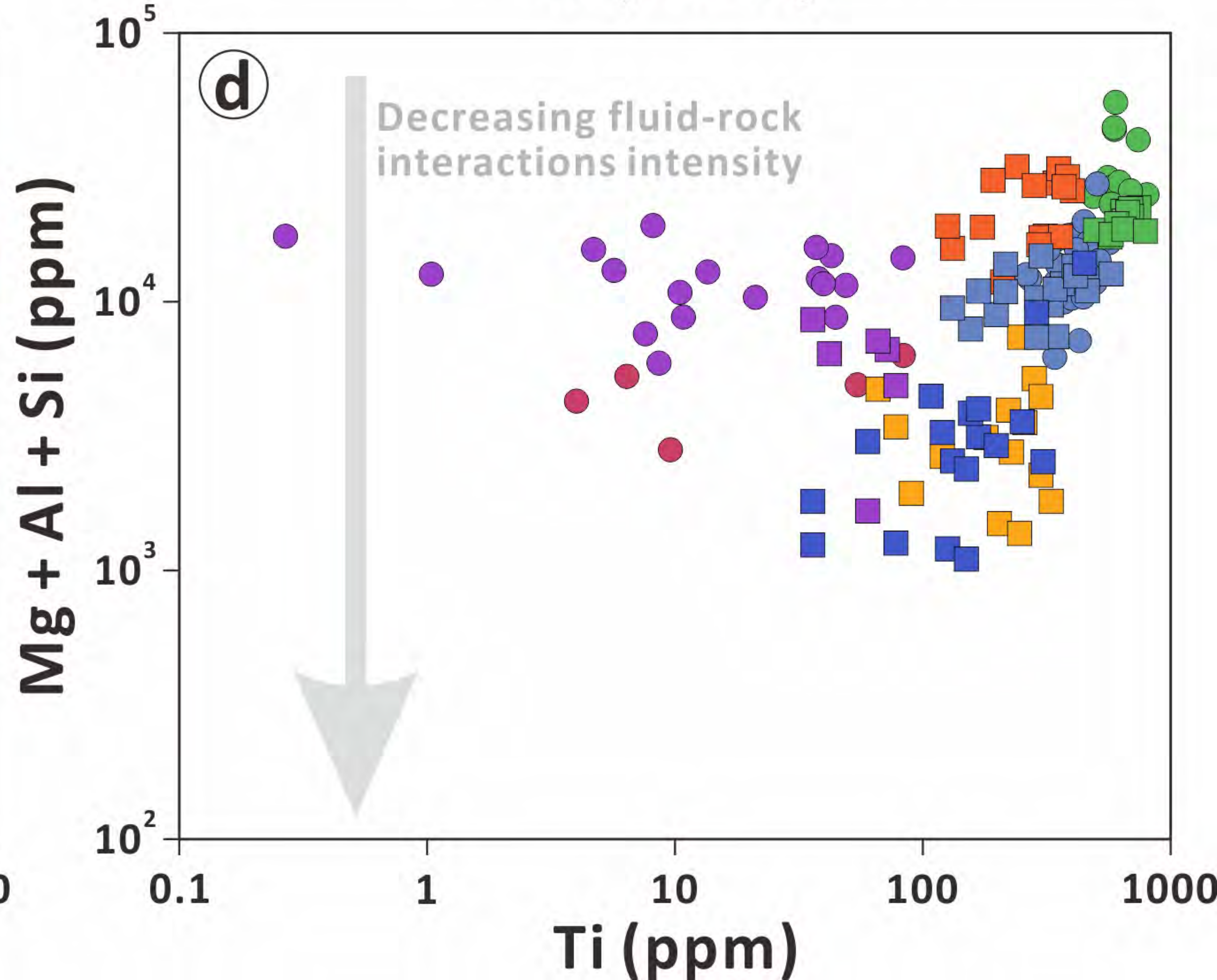
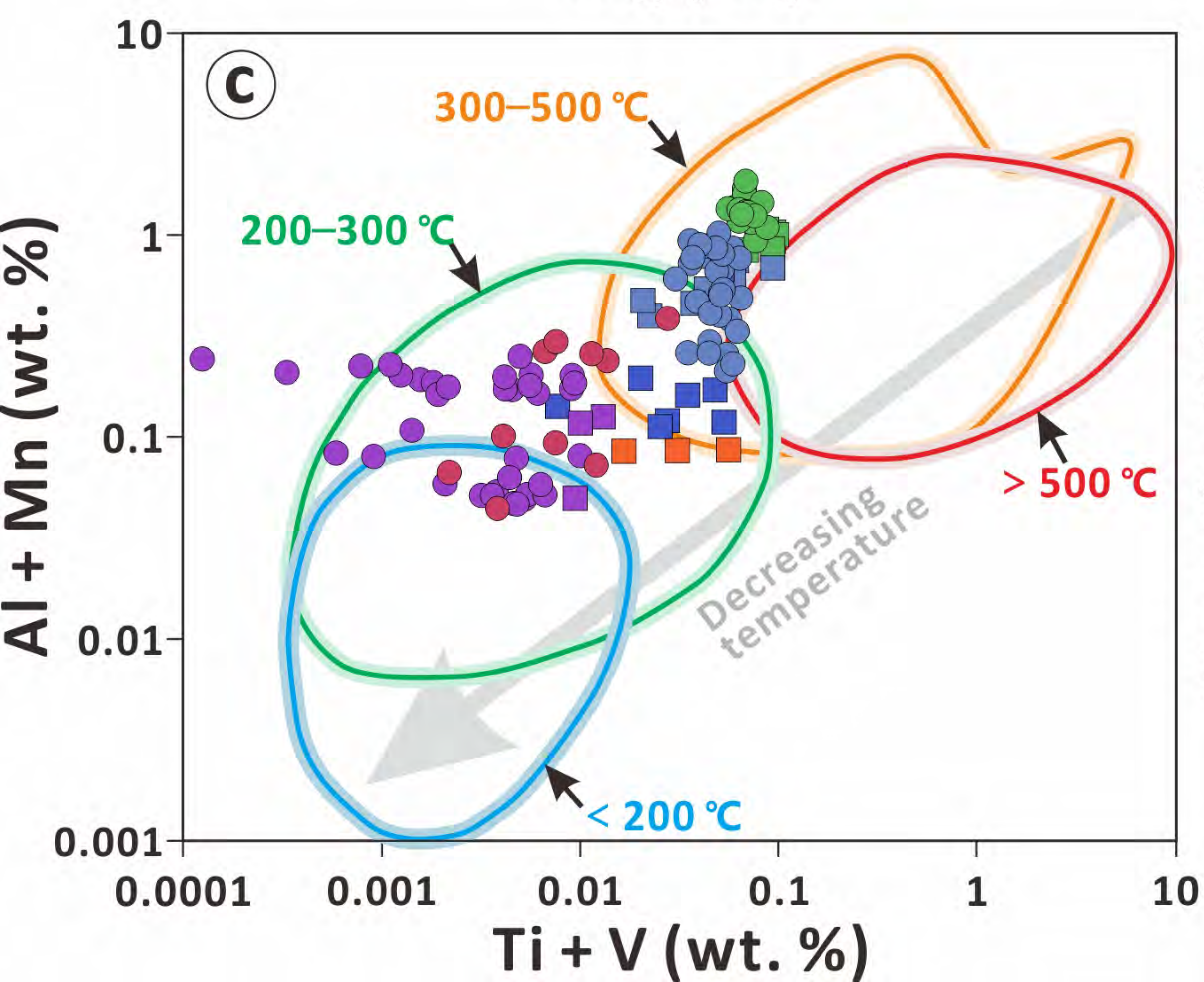
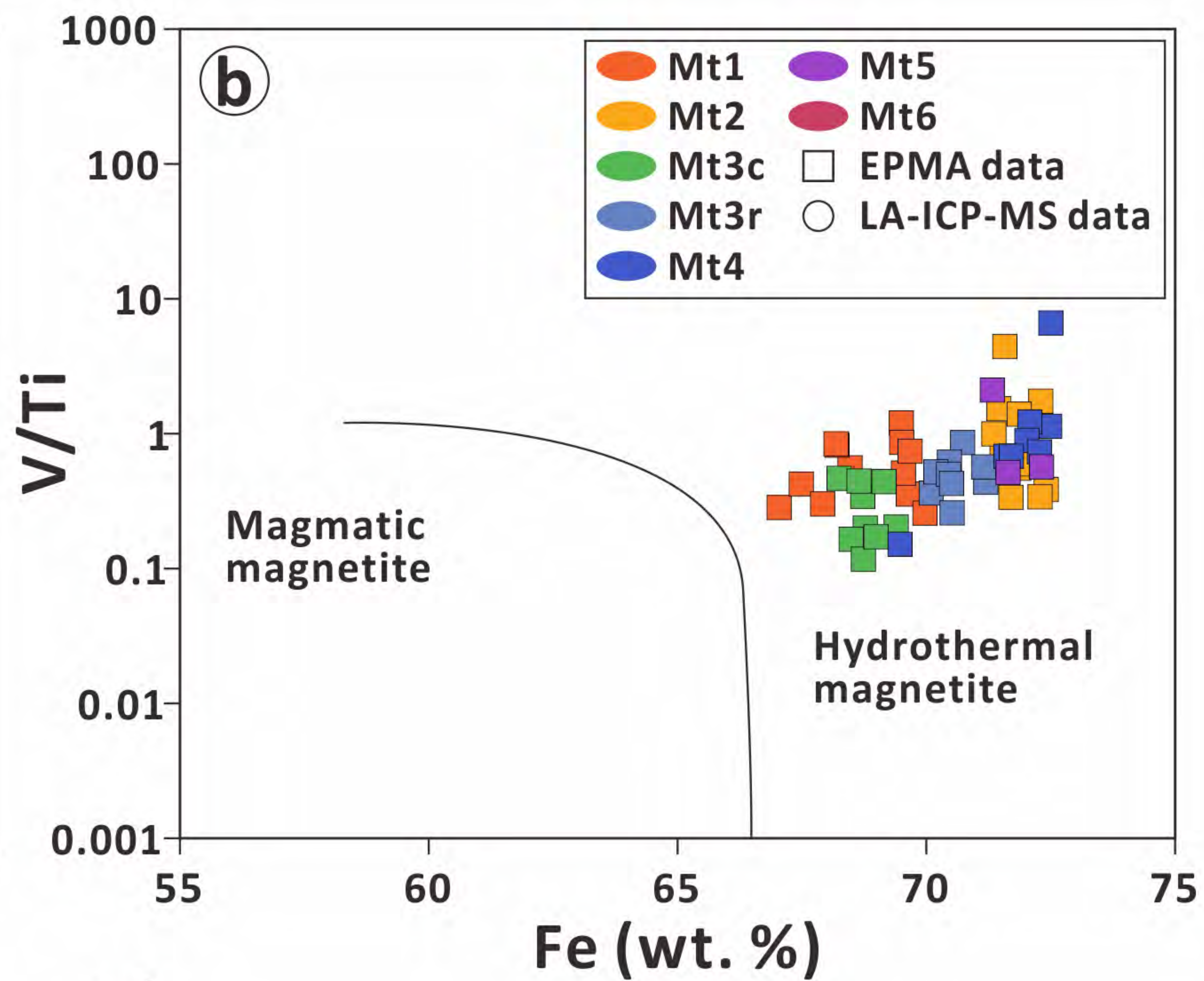
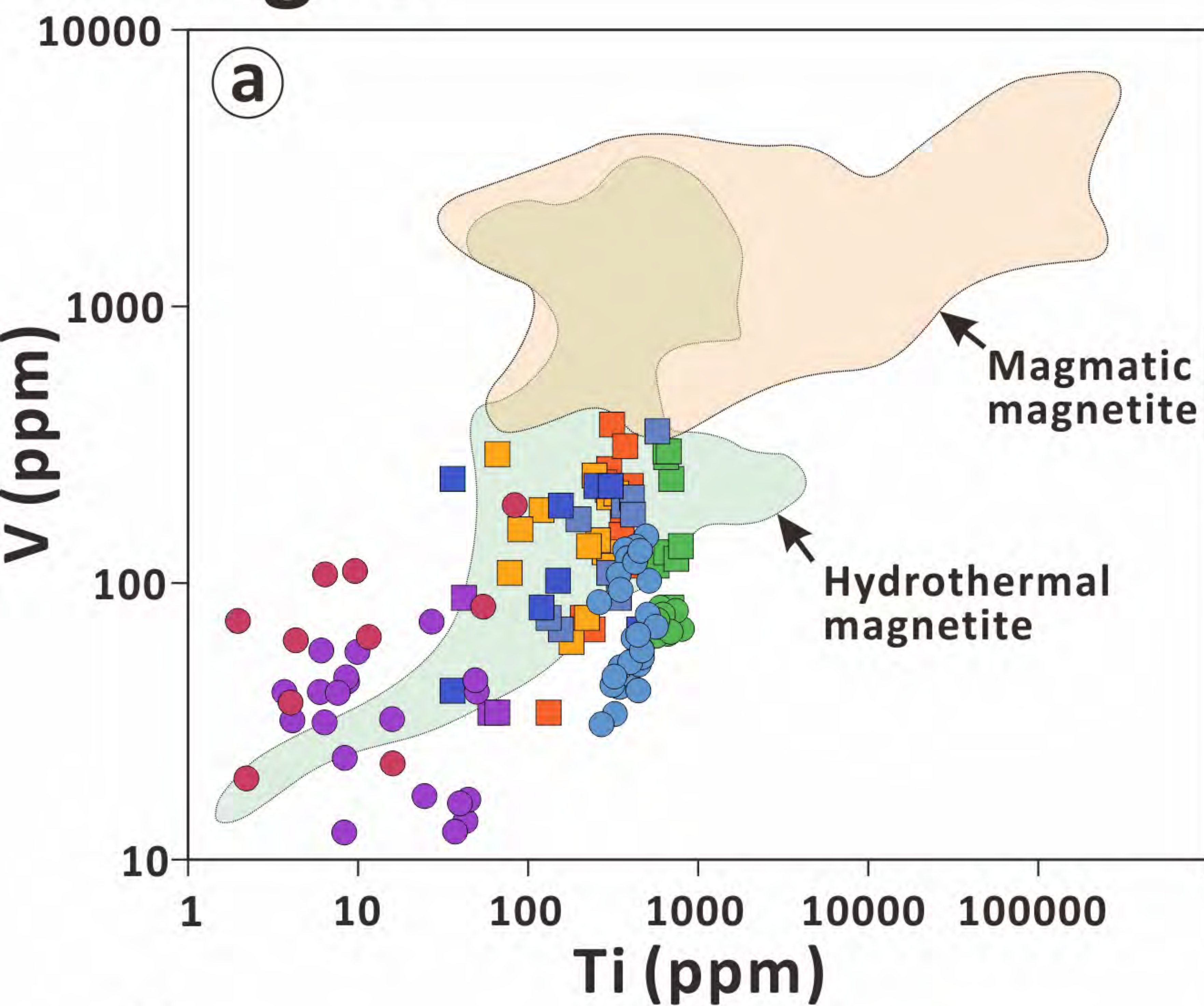
Fig. 5

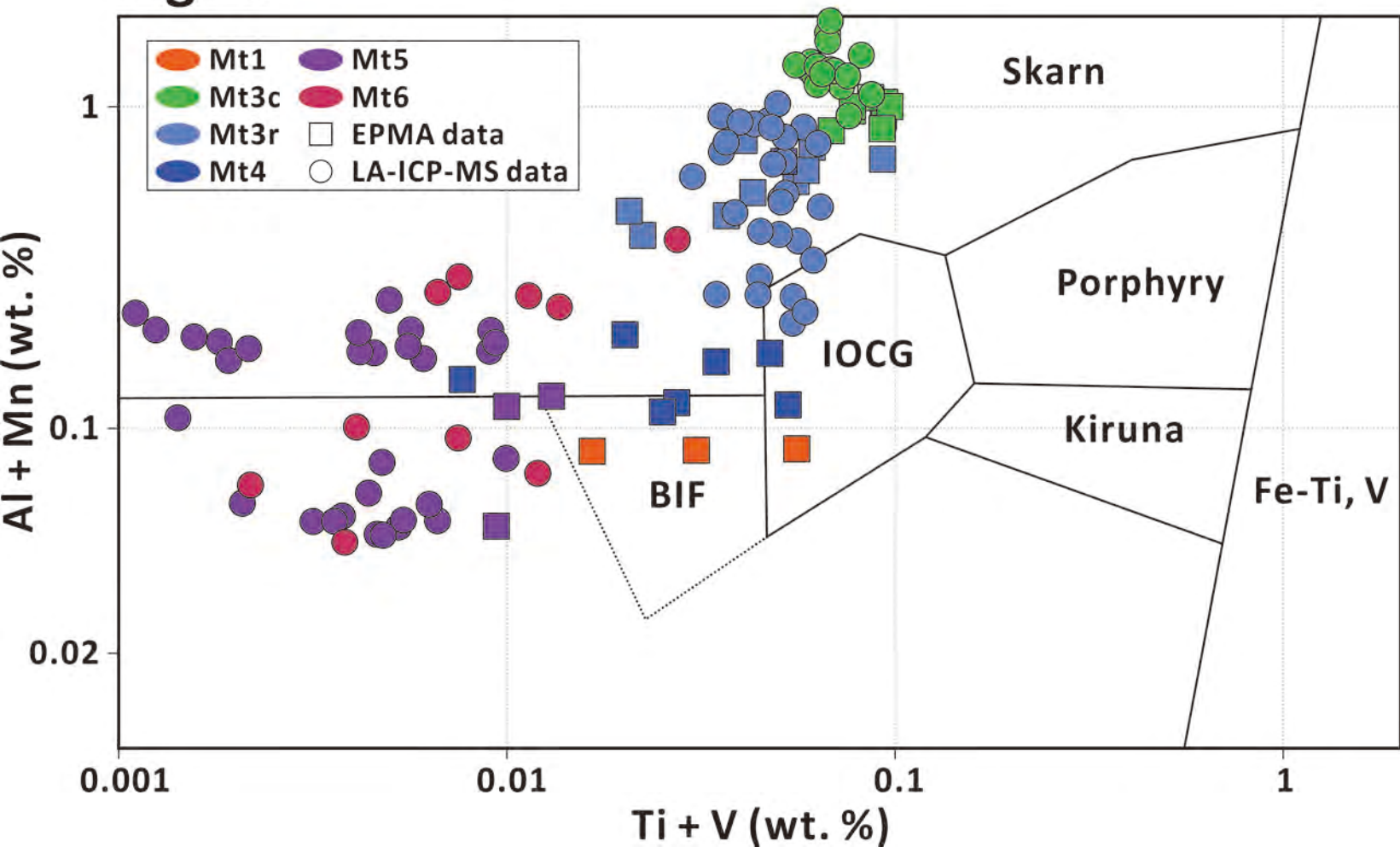
Fig. 6

Fig. 7

