

1 **Revision 2**

2 **Cathodoluminescence images and trace element compositions of fluorapatite**  
3 **from the Hongge layered intrusion in SW China: a record of prolonged**  
4 **crystallization and overprinted fluid metasomatism**

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6 **CHANG-MING XING<sup>1,2\*</sup>, CHRISTINA YAN WANG<sup>1,2</sup>**

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9 <sup>1</sup> Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of  
10 Geochemistry, Chinese Academy of Sciences, Guangzhou 510460, China

11 <sup>2</sup> Guangdong Provincial Key Laboratory of Mineral Physics and Materials,  
12 Guangzhou 510640, China

13

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15 \* Corresponding author: Dr. C.M. Xing ([cmxing@gig.ac.cn](mailto:cmxing@gig.ac.cn))

16 **ABSTRACT**

17 Cathodoluminescence (CL) and trace element analyses were performed for  
18 fluorapatite from the gabbro and Fe-Ti oxide ores in the upper zone of the Hongge  
19 Fe-Ti oxide-bearing, mafic-ultramafic layered intrusion in SW China. The fluorapatite  
20 is closely associated with Fe-Ti oxides and interstitial to plagioclase and  
21 clinopyroxene. The fluorapatite grains in one thin section vary from ~10 to 800  $\mu\text{m}$  in  
22 width and ~50 to 1,200  $\mu\text{m}$  in length. Coarse-grained fluorapatite crystals (>200 in  
23 width) in the same thin section show both simple and complex CL images. The  
24 coarse-grained fluorapatite crystals with simple CL images show discontinuous, thin  
25 dark rims along grain boundaries, whereas those with complex images show clearly  
26 bright veinlets across the grains. On the other hand, fine-grained fluorapatite crystals  
27 (<200  $\mu\text{m}$  in width) show complex CL images and can be divided into four types, i.e.,  
28 concentric, chaotic, banded and overall-dark. The concentric type shows distinctly  
29 bright core surrounded by dark mantle that is irregularly zoned, whereas the chaotic  
30 type shows disordered bright and dark sectors in the interior with a thin dark rim. The  
31 banded type shows unevenly distributed bright and dark bands. The overall-dark type  
32 shows a relatively dark and uneven image. Fluorapatite grains contain 1.84 to 2.74  
33 wt.% F, 0.07 to 0.19 wt.% Cl and 0.86 to 1.63 wt.% OH. Coarse-grained fluorapatite  
34 grains have total rare earth elements (REE) concentrations ranging from 2,278 to  
35 3,008 ppm and Sr/Y of 9 to 13. Fine-grained fluorapatite grains have relatively high  
36 REE (2,242 to 4,687 ppm) and low Sr/Y of 6 to 14 in the bright cores, sectors and  
37 bands and relatively low REE (1,881 to 2,728 ppm) and high Sr/Y of 9 to 15 in the

38 dark mantles, sectors, and rims under CL imaging. On the thin section scale, the  
39 bright sections under CL imaging for fine-grained fluorapatite have much higher REE  
40 contents overall than those for similar bright CL images for coarse-grained  
41 fluorapatite. The highly variable REE concentrations among fluorapatite grains and  
42 the sections within a single fluorapatite are attributed to a prolonged crystallization  
43 process and overprint by fluid metasomatism. The coarse-grained fluorapatite may  
44 have crystallized earlier than fine-grained fluorapatite. Then variable degrees of  
45 hydrothermal metasomatism released REE from the fine-grained fluorapatite so that  
46 diverse CL images developed in the crystals. This study reveals that magmatic apatite  
47 from a layered intrusion can be intensively modified by later-stage fluid-induced  
48 metasomatism in both trace element composition and CL image texture.  
49 Reconstruction of primary melt compositions using apatite from layered intrusions  
50 should therefore be treated with caution.

51 **Keywords:** Fluorapatite, cathodoluminescence image, trace element, fluid  
52 metasomatism, mafic-ultramafic layered intrusion

53

## 54 INTRODUCTION

55 Apatite mainly occurs in the upper zone of layered intrusions, such as the  
56 Skaergaard intrusion in Greenland and the Bushveld complex in South Africa, and is  
57 considered as a cumulus phase during late-stage magma differentiation (Cawthorn  
58 1994; Holness et al. 2007). Apatite can be substantially enriched in some layered  
59 intrusions and associated with Fe-Ti oxides, forming Fe-Ti-P-rich nelsonite with ~30

60 vol.% apatite (Reynolds 1985; Von Gruenewaldt 1993; Tollari et al. 2008). The origin  
61 of apatite-rich rocks/Fe-Ti oxide ores in layered intrusions has been a matter of debate  
62 between fractional crystallization and silicate liquid immiscibility models (Reynolds  
63 1985; Von Gruenewaldt 1993; Tegner et al. 2006; Tollari et al. 2008; Namur et al.  
64 2012; VanTongeren and Mathez 2012). Nevertheless, the growth process of apatite  
65 itself has been relatively neglected.

66 Magmatic apatite commonly has a hexagonal habit when crystallizing under  
67 near-equilibrium condition (Webster and Piccoli 2015). Cumulus apatite from layered  
68 intrusions has been widely used to reconstruct the trace element compositions of the  
69 melt in equilibrium with the apatite (Tollari et al. 2008; VanTongeren and Mathez  
70 2012; She et al. 2016). However, primary apatite may be intensively modified by  
71 post-crystallization processes, e.g., the trapped liquid shift effect and metasomatism  
72 by external fluids, which can cause extreme variations of the trace elements in the  
73 apatite (Harlov et al. 2002a; Harlov and Förster 2003; Harlov et al. 2005; Cawthorn  
74 2013). Therefore, tracing the cryptic compositional variations in apatite is significant  
75 for understanding the crystallization and overprinted post-crystallization processes in  
76 the magma chamber.

77 Cathodoluminescence (CL) can be activated by small amounts of trace elements  
78 in minerals, and has been used to identify episodes of mineral growth during  
79 magmatic processes (Murray and Oreskes 1997). The most common CL activators in  
80 apatite are REE and Mn, whereas Fe is a common quencher (Roeder et al. 1987;  
81 Barbarand and Pagel 2001). It has been shown that the luminescent intensity can be

82 influenced by tens of ppm to several weight percent variation of these elements in  
83 apatite (Filippelli and Delaney 1993; Kempe and Götze 2002).

84 In this paper, we present the CL images of fluorapatite from the gabbro, Fe-Ti  
85 oxide gabbro, and Fe-Ti oxide ore samples taken from the upper zone of the Hongge  
86 layered intrusion in SW China. The fluorapatite grains show diverse CL images.  
87 Combined with *in situ* LA-ICP-MS trace element analyses, we found that this  
88 diversity in the CL images is likely caused by variations in the REE concentrations in  
89 fluorapatite due to a prolonged crystallization process and late-stage hydrothermal  
90 metasomatism, which give further insights into the growth process of magmatic  
91 fluorapatite in a dynamic, slow-cooling magma chamber.

92

### 93 **FLUORAPATITE IN THE HONGGE INTRUSION**

94 The Hongge mafic-ultramafic layered intrusion is located in the Panxi region,  
95 SW China, and hosts a world-class Fe-Ti oxide deposit (Ma et al. 2003; Wang and  
96 Zhou 2013) (Fig. 1a). The intrusion is ~2.7 km thick and consists of olivine  
97 clinopyroxenite and minor wehrlite and dunite in the lower zone, clinopyroxenite and  
98 major Fe-Ti oxide ore layers in the middle zone and fluorapatite-bearing gabbro and  
99 Fe-Ti oxide ores in the upper zone (Wang and Zhou 2013). Magnetite in the lower  
100 zone and the lower part of the middle zone is Cr- and Ti-rich magnetite, which is  
101 disseminated and commonly enclosed in olivine and clinopyroxene, whereas  
102 magnetite in the upper part of the middle zone and the upper zone is Cr-poor, Ti-rich  
103 magnetite, which is interstitial to clinopyroxene and plagioclase. The Cr- and Ti-rich

104 magnetite in the lower and middle zones is interpreted as an early crystallized phase  
105 from less differentiated high-Ti basaltic magmas, whereas the Cr-poor, Ti-rich  
106 magnetite in the upper zone is thought to have formed from an immiscible  
107 Fe-Ti-(P)-rich melt developed from an evolved high-Ti basaltic magma (Wang and  
108 Zhou 2013).

109       The upper part of the upper zone is composed of gabbro, whereas the lower part  
110 is composed of Fe-Ti oxide gabbro and Fe-Ti oxide ore. Samples in this study were  
111 collected from the Luku open pit (Fig. 1b) and the sample locations are marked in the  
112 stratigraphic column of the intrusion (Fig. 1c). The boundaries between the gabbro,  
113 Fe-Ti oxide gabbro, and Fe-Ti oxide ore are sharp and characterized by an evident  
114 decrease in the proportion of Fe-Ti oxides between Fe-Ti oxide ore and Fe-Ti oxide  
115 gabbro and a sudden increase in the proportion of plagioclase between Fe-Ti oxide  
116 gabbro and gabbro. Gabbro in the upper part consists of 40-60 vol.% plagioclase,  
117 30-40% clinopyroxene, 10-15% Fe-Ti oxides, 5-7% fluorapatite, 2-3% amphibole,  
118 and <1% sulfide (Fig. 2a). On a localized scale, modal fluorapatite can be more than  
119 10% (Fig. 2d). The Fe-Ti oxide gabbro consists of 40-60% clinopyroxene, 20-30%  
120 plagioclase, 20-30% Fe-Ti oxides, 6-8% fluorapatite, 1-2% amphibole, and 1%  
121 sulfide (Fig. 2b). Fe-Ti oxide ore consists of 40-60% Fe-Ti oxides, 30%  
122 clinopyroxene, 10% plagioclase, 4-6% fluorapatite, 1-2% amphibole, and <1% sulfide  
123 (Fig. 2c). The rocks and ores show weak to intense alteration. Plagioclase commonly  
124 experienced saussuritization and albitization and the relicts of primary plagioclase can  
125 be observed in some altered grains (Supplemental Fig. 1a), whereas clinopyroxene

126 was partly altered to amphibole (Supplemental Fig. 1b).

127 Fluorapatite in gabbro, Fe-Ti oxide gabbro and Fe-Ti oxide ore is mostly  
128 euhedral to subhedral and shows a hexagonal or elongated shape, depending on the  
129 orientation of the grain in the thin section (Figs. 2d and e). Anhedral fluorapatite  
130 grains were also observed in the same thin section (Fig. 2d). Most fluorapatite grains  
131 are interstitial to clinopyroxene and plagioclase and closely associated with Fe-Ti  
132 oxides (Figs. 2d and e). The fluorapatite grains vary from ~10 to 800  $\mu\text{m}$  in width and  
133 ~50 to 1,200  $\mu\text{m}$  in length (Figs. 2d and e). They are denoted as coarse-grained (>200  
134  $\mu\text{m}$  in width) and fine-grained (<200  $\mu\text{m}$  in width) in this study. Fine-grained  
135 fluorapatite crystals (mostly <100  $\mu\text{m}$  in width) are also sporadically enclosed within  
136 clinopyroxene (Fig. 3a).

137 Rounded pyrrhotite is occasionally enclosed in both coarse-grained and  
138 fine-grained fluorapatite (Fig. 3b). Needle-like pyrrhotite inclusion are common and  
139 have an orientation parallel to the c-axis of fluorapatite (Fig. 3c and Supplemental Fig.  
140 2). Kink bands are developed in the cross sections parallel to the c-axis of fluorapatite  
141 (Fig. 3d). Dislocation planes are distinct between the kink bands with different  
142 extinction angles (Fig. 3d).

143

## 144 ANALYTICAL METHODS

### 145 Cathodoluminescence imaging

146 CL imaging of fluorapatite was performed on carbon coated thin sections, which  
147 were finely polished and ultrasonically cleaned in order to avoid possible pits and

148 stains on the fluorapatite grain surface that may influence the CL response. CL images  
149 of fluorapatite were acquired using a Gatan MonoCL4 system installed on a Carl  
150 Zeiss SUPRA 55 SAPPHIRE field emission electron microscope at the State Key  
151 Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG),  
152 Chinese Academy of Sciences (CAS). The CL images were all obtained using a 10 kV  
153 voltage and contrast-enhanced for better observation.

154

### 155 **Electron microprobe analysis**

156 Major elements in fluorapatite were analyzed using a JEOL JXA-8230 electron  
157 probe micro-analyzer (EPMA) at the Key Laboratory of Mineralogy and Metallogeny  
158 in GIGCAS. Operating conditions of 15 kV accelerating voltage, 20 nA probe current,  
159 and a 3  $\mu\text{m}$  beam were applied to the analyses for all elements. Peak and background  
160 counting times were 20 and 10s for Ca and P, 10 and 5s for F and Cl, 60 and 30  
161 seconds for Si and S.  $K\alpha$  line was chosen for all elements during analyses. Fluorine  
162 and Cl were first analyzed during the analysis routine to minimize their loss.  
163 Analytical results were reduced using the ZAF correction routines. The standards used  
164 were fluorapatite for Ca and P,  $\text{BaF}_2$  for F, tugtupite for Cl, diopside for Si and pyrite  
165 for S. Relative precisions are  $\pm 2\%$  for Ca, P and F and  $\pm 5\%$  for Si, Cl and S,  
166 respectively.

167

### 168 **Laser ablation inductively coupled-plasma mass spectrometry analysis**

169 *In situ* trace element analyses of fluorapatite were carried out using a laser

170 ablation inductively coupled-plasma mass spectrometry (LA-ICP-MS) at the Key  
171 Laboratory of Mineralogy and Metallogeny in GIGCAS. The Agilent 7500a ICP-MS  
172 instrument was coupled to a Resonetic 193 nm ArF excimer laser ablation system.  
173 Single spot ablation was adopted with a laser beam width of 31  $\mu\text{m}$ . Laser energy was  
174 80 mJ and ablation frequency was 6 Hz. Helium gas was used as a carrier gas. NIST  
175 SRM 610 glass was employed as an external standard and NIST SRM 612 was treated  
176 as an unknown sample. The CaO content of fluorapatite, as determined by EMPA,  
177 was used as an internal standard. Data reduction was performed using the  
178 ICPMSDataCal software (version 10.2) (Liu et al. 2008). The measured trace element  
179 concentrations of NIST SRM 610 and NIST SRM 612 and their recommended values  
180 are listed in Supplemental Table 1. The analytical uncertainty is better than 10%  
181 (relative) for most trace elements.

182

### 183 **CATHODOLUMINESCENCE IMAGE OF FLUORAPATITE**

184 Fluorapatite grains from the gabbro, Fe-Ti oxide gabbro and Fe-Ti oxide ore  
185 samples show similar but diverse CL images. Some coarse-grained fluorapatite grains  
186 show a simple CL image with a discontinuous, thin, dark rim along the grain  
187 boundary (Figs. 4a and b), whereas the other coarse grains display a complex, mosaic  
188 CL image with bright veinlets crosscutting the interior of the crystals (Fig. 4c).

189 Fine-grained fluorapatite shows four types of CL images, i.e., concentric, chaotic,  
190 banded, and overall-dark. The concentric type shows a bright, irregular to rounded  
191 core and a clearly dark mantle in the image (Fig. 5). The dark mantle in the image is

192 sometimes irregularly zoned (Fig. 5b). Such a concentric texture shown in the CL  
193 images (Fig. 5c), however, cannot be observed in the BSE images (Fig. 5d). The  
194 chaotic type is composed of disordered bright and dark sectors in the interior sharply  
195 bounded with a dark rim (Fig. 6). The rim is commonly  $<50\ \mu\text{m}$  in width, but is  
196 evidently coarsened in the corner of two crystal faces (Fig. 6). In local places, the rim  
197 is interconnected with dark veinlets that penetrate the bright and dark sectors (Fig. 6c).  
198 Rounded bright spots are occasionally preserved in both bright and dark sectors (Fig.  
199 6b), whereas tiny amphibole inclusions ( $20\text{-}50\ \mu\text{m}$  in diameter) are sporadically  
200 present in the dark sectors (Figs. 6b and c). The banded type shows bright and dark  
201 bands unevenly distributed in the image (Fig. 7). The dark bands vary in width from  
202  $\sim 10$  to  $100\ \mu\text{m}$ . The overall-dark type shows heterogeneous dark sectors in the CL  
203 images but without an obvious bright core or sector (the grain on the left in Figs. 5a  
204 and 5c).

205

## 206 **FLUORAPATITE COMPOSITIONS**

207 Fluorapatite grains from the gabbro, Fe-Ti oxide gabbro, and Fe-Ti oxide ore  
208 samples have similar F and  $\text{SO}_3$  contents and F/Cl, and there is no prominent variation  
209 between coarse-grained and fine-grained fluorapatite (Table 1). They contain 1.84 to  
210 2.73 wt.% F and 0.07 to 0.19 wt.% Cl with F/Cl varying from 11 to 31, and contain  
211 0.86 to 1.63 wt.% OH (Supplemental Table 2).

212 Coarse-grained and fine-grained fluorapatite have similar Sr, Fe, and Mn  
213 concentrations (Figs. 8a and b), however, they have remarkably different REE

214 concentrations (Table 1). Coarse-grained fluorapatite grains have total REE  
215 concentrations ranging from 2,278 to 3,008 ppm (Supplemental Table 3). They have  
216 830 to 1,115 ppm Ce and Sr/Y of 9 to 13, which shows a linear trend on the plot of Ce  
217 versus Sr/Y (Fig. 8c). Cerium within a single coarse-grained fluorapatite ranges from  
218 a maximum of 1,115 ppm in the core to a minimum of 938 ppm in the rim (see the  
219 insets in Figs. 9a, c and e).

220 Fine-grained fluorapatite has distinctly different REE concentrations in the bright  
221 and dark sections of the CL images. For example, the bright cores in the concentric  
222 type contain total REE ranging from 2,242 to 4,687 ppm with a maximum value that  
223 is nearly two times higher than those for coarse-grained fluorapatite in the same thin  
224 section. They contain 820 to 1,692 ppm Ce and have low Sr/Y (6 to 14) relative to  
225 that for coarse-grained fluorapatite (Fig. 8c). On the other hand, the dark mantles in  
226 the concentric type contain 1,981 to 2,408 ppm REE in total (Table 1). They contain  
227 742 to 872 ppm Ce, which is much lower than those for coarse-grained fluorapatite.  
228 However, they have Sr/Y (11 to 13), which is higher than those for coarse-grained  
229 fluorapatite (Fig. 8c). The dark sectors and bands in the chaotic and banded CL  
230 images have REE and Sr/Y similar to those for the dark mantles in the concentric type  
231 (Table 1 and Figs. 8c and 9). The overall-dark type has Ce concentrations comparable  
232 with those for the dark mantles in the concentric type (Supplemental Table 3). Note  
233 that in one thin section scale of a fine-grained fluorapatite, the bright sections have  
234 higher REE than those for the dark sections in the same grain (Fig. 9). Overall, the  
235 coarse-grained fluorapatite and the CL-bright sections from the concentric type,

236 fine-grained fluorapatite show parallel REE patterns without obvious Eu anomalies  
237 (Fig. 10).

238

## 239 **DISCUSSION**

### 240 **Diverse CL images of fluorapatite due to late-stage fluid metasomatism**

241 Fluorapatite grains from the Hongge intrusion overall have Mn concentrations  
242 lower than 250 ppm and there is no obvious difference in Mn and Mn/Fe between the  
243 bright and dark sections in the CL images (Fig. 8a). The diverse CL images of the  
244 fluorapatite are thus unlikely caused by the Mn activator and Fe quencher in the  
245 fluorapatite. Instead, it is likely that they are related to the large variation of REE in  
246 the fluorapatite (Fig. 9).

247 Large variations of REE within a single apatite could be caused by the mixing of  
248 compositionally different magmas during its growth (Lisowiec et al. 2013) or by  
249 post-crystallization modification such as the trapped liquid shift effect and fluid  
250 metasomatism (Cawthorn 2013; Harlov 2015). Large-scaled magma mixing in the  
251 magma chamber may develop regular and concentric zonation in the apatite (Lisowiec  
252 et al. 2013), and should also be recorded in other cumulus minerals such as  
253 plagioclase. The fluorapatite in the Hongge intrusion lacks regular zoning, and no  
254 obvious zonation was observed in plagioclase, which rules out the possibility of  
255 magma mixing during the formation of the fluorapatite. The progressive growth of  
256 primary apatite from an ambient melt may produce compositional zonation, and the  
257 trapped liquid shift effect may obscure the zonation by diffusion and increase REE in

258 the apatite (Barnes 1986; Cawthorn 2013). However this cannot explain the overall  
259 low REE in the dark rims and sectors of the CL image for the fine-grained fluorapatite  
260 in this study (Fig. 5).

261 It is known that hydrothermal fluids are capable of leaching REE from apatite,  
262 resulting in a substantial decrease of REE in apatite and the formation of new  
263 REE-phosphates, -silicates, -fluorides, and -carbonates in metasomatized domains  
264 (Harlov et al. 2002a; Harlov and Förster 2003; Harlov 2015; Li and Zhou 2015).  
265 Late-stage fluid metasomatism is common in iron-oxide apatite deposits, in which  
266 apatite can be partially or completely metasomatized by compositionally different  
267 fluids (Harlov et al. 2002b; Bonyadi et al. 2011; Li and Zhou 2015; Harlov et al.,  
268 2016).

269 Monomineralic inclusions of calcic amphibole are common in the fine-grained  
270 fluorapatite from the Hongge intrusion. The amphibole is sometimes associated with  
271 Fe-Ti oxides and sulfides in the inclusions (Fig. 11a). The enclosed amphibole in the  
272 fluorapatite has compositions similar to the amphibole rim on the clinopyroxene and  
273 plagioclase adjacent to Fe-Ti oxides (Fig. 11b; Supplemental Table 4), indicating that  
274 the amphibole may have been trapped in the fluorapatite during the late stage of  
275 magma fractionation. The presence of amphibole in fine-grained fluorapatite thus  
276 indicates that the interstitial liquid may have eventually become water-saturated and  
277 generated hydrothermal fluids during the late stage of magma fractionation.

278 The veinlets across the coarse-grained fluorapatite (Fig. 4c) are direct evidences  
279 for the mobility of hydrothermal fluids in the Hongge intrusion. Given the common

280 presence of kink bands in fluorapatite, the micro-fractures crosscutting the grains may  
281 have developed due to intensive deformation and progressive compaction of  
282 overloaded crystal mush. They in turn functioned as channels to transport REE-rich  
283 fluids resulting in bright veinlets in the CL images (Fig. 4c). The orientated  
284 needle-like pyrrhotite inclusions in the fluorapatite (Fig. 3c) may be also attributed to  
285 late-stage hydrothermal activity. The pyrrhotite inclusions were likely formed by the  
286 fluid-mediated reaction, e.g.,  $\text{H}_2\text{S} + \text{Fe}^{2+} = \text{FeS} + 2\text{H}^+$  (Broska et al. 2014). In such a  
287 scenario, the fluids leached Fe and S either from the Fe-Ti oxides and sulfides or more  
288 likely from the fluorapatite and preferentially grew the pyrrhotite inclusions parallel  
289 to the c-axis of the host fluorapatite in a topotaxial manner (cf., Pan et al. 1993;  
290 Broska et al. 2014) similar to what is seen for monazite and xenotime inclusions in  
291 apatite (cf. Harlov, 2015).

292 Large variations in Sr/Y in a single fluorapatite or in fluorapatite grains in one  
293 thin section (Fig. 8c) are likely resulted from fluid metasomatically released Y from  
294 fluorapatite. Note that the CL-dark section for fine-grained fluorapatite has Sr/Y  
295 lower than that for the CL-bright section (Fig. 8c). This is because they have  
296 comparable Sr against highly variable Y (Supplemental Table 3).

297 Late-stage fluid metasomatism could explain the diverse CL images for  
298 fine-grained fluorapatite in the Hongge intrusion. The fluids would have reacted with  
299 grain boundaries and decreased the REE, causing the low REE content in the dark  
300 mantle in the concentric-type CL images and in the dark rim and sector in the  
301 chaotic-type images relative to the bright CL cores and sectors (Figs. 9b, c and d). The

302 fluids would have passed through the interior of the grain and leached REE along  
303 their path ways, leaving behind REE-contrasted sections in the grain (cf., Harlov et al.  
304 2005). The fluids would have then percolated along micro-fractures in the grain,  
305 forming the chaotic CL image (Fig. 6). If the fluids penetrated through the grain,  
306 bright and dark bands would have developed and unevenly distributed forming  
307 banded CL images (Fig. 7). When the fine-grained fluorapatite was strongly modified  
308 by the fluids, an overall-dark CL image would have formed (Fig. 5c) and the  
309 fluorapatite would have low REE concentrations relative to bright CL sections in  
310 other grains. Therefore, the diverse CL images seen for fine-grained fluorapatite  
311 reveal the different degrees of the reaction between the fluorapatite and late-stage  
312 hydrothermal fluids.

313

#### 314 **Prolonged crystallization of fluorapatite in igneous cumulates**

315 Coarse-grained and fine-grained fluorapatite display a good linear trend on the  
316 plot of U/Zr versus Th/Zr (Fig. 8d), which is interpreted as the melts from which the  
317 coarse-grained and fine-grained fluorapatite crystallized are co-genetic. Because U  
318 and Th have similar partition coefficients in fluorapatite and Zr is highly incompatible  
319 in fluorapatite, U/Zr and Th/Zr in the fluorapatite reflect the composition of  
320 equilibrated melt and should not change significantly during crystallization of the  
321 fluorapatite (cf., VanTongeren and Mathez 2012). The parallel REE patterns of the  
322 coarse-grained and fine-grained fluorapatite (Fig. 10) also support the idea that they  
323 crystallized from co-genetic melts.

324 Note that many coarse-grained fluorapatite grains have simple CL images (Figs.  
325 3a and b), and have only slightly low REE in their rims (see the inset of Figs. 8a, c  
326 and e). We therefore assume that majority of the coarse-grained fluorapatite cores may  
327 have preserved primary trace element compositions, and that the rims experienced  
328 variable degrees of fluid metasomatism. In contrast, the bright cores in some  
329 concentric-type CL images for fine-grained fluorapatite have REE up to two times  
330 higher than those for coarse-grained fluorapatite (Fig. 10), indicating that the  
331 fine-grained fluorapatite may have crystallized from an interstitial liquid with a  
332 relatively high REE. The prominent REE variations in apatite from layered intrusions  
333 may be related to liquid immiscibility (VanTongeren and Mathez 2012) or intensive  
334 differentiation of an interstitial liquid (Meurer and Meurer 2006). In the top 600 m  
335 section of the Upper Zone of the Bushveld complex, the apatite from the upper ~300  
336 m contains REE three times higher than those for the apatite from the lower ~300 m  
337 (VanTongeren and Mathez 2012). The large REE interval between the apatite from the  
338 upper and lower sections is attributed to the idea that the upper and lower sections  
339 formed from immiscible Si-rich and Fe-rich melts, respectively (VanTongeren and  
340 Mathez 2012), even though such a model is debatable (Cawthorn 2013). However, the  
341 coarse-grained and fine-grained fluorapatite with distinctively different REE contents  
342 in the Hongge intrusion are actually present in the same thin section. Therefore, it is  
343 unlikely they were derived from a pair of conjugate immiscible melts.

344 In a basaltic magma system, REE are compatible in apatite with  $D_{\text{REE}}^{\text{Ap/melt}}$  ranging  
345 from ~1 to 8 (Prowatke and Klemme 2006). However, they are moderately to highly

346 incompatible in plagioclase, clinopyroxene and Fe-Ti oxides (Nielsen et al. 1992; Hart  
347 and Dunn 1993; Bindeman et al. 1998). Given that the major rock types in the upper  
348 zone of the Hongge intrusion are all composed of plagioclase, clinopyroxene, Fe-Ti  
349 oxides, and fluorapatite with mode of 4 to 8 vol.%, the bulk partition coefficient for  
350 REE ( $D_{\text{REE}}^{\text{bulk}}$ ) was calculated to be <1. The evolved interstitial liquid would therefore  
351 have REE concentration higher than the less differentiated melt. Fluorapatite,  
352 crystallized from the interstitial liquid, would then have higher REE than fluorapatite  
353 crystallized earlier from less differentiated melt. One example of this is the Stillwater  
354 complex in the United States, where the intercumulus fluorapatite in the olivine  
355 gabbro is interstitial to the silicate minerals, and the smallest fluorapatite grains have  
356 the highest REE content (Meurer and Meurer 2006). We therefore propose that the  
357 fluorapatite in the upper zone of the Hongge intrusion may have crystallized during a  
358 prolonged process. Coarse-grained fluorapatite crystallized from a less differentiated  
359 melt in cumulus stage, whereas the fine-grained fluorapatite crystallized from an  
360 evolved interstitial liquid during the last stages of crystallization. This explains why  
361 the bright areas in the CL images of the fine-grained fluorapatite have an overall  
362 higher REE content than the coarse-grained fluorapatite.

363 The crystallization temperature of the amphibole enclosed in fine-grained  
364 fluorapatite is estimated to range from 660 to 995 °C using the amphibole Ti content  
365 (Otten 1984) and from 712 to 926 °C using the empirical equation of Ridolfi and  
366 Renzulli (2012). This broad variation in temperature should be considered as the  
367 upper limit for the crystallization temperature of the fine-grained fluorapatite, and are

368 supportive of the prolonged crystallization of fluorapatite even on the thin section  
369 scale. In addition, the interstitial amphibole have similar ranges of crystallization  
370 temperatures (Supplemental Table 4). The intergrowth of magnetite and amphibole  
371 (Fig. 11c) indicates that the evolved interstitial liquid should be Fe-rich and H<sub>2</sub>O-rich,  
372 from which fine-grained fluorapatite crystallized.

373

#### 374 **A schematic model for prolonged growth of fluorapatite in the Hongge intrusion**

375 We propose that fluorapatite in the upper zone of the Hongge intrusion  
376 experienced a prolonged crystallization process and was metasomatized by late-stage  
377 hydrothermal fluids. The coarse-grained fluorapatite represents an early-crystallized  
378 cumulus phase from a less differentiated melt (Fig. 12a). With progressive  
379 crystallization of cumulus clinopyroxene, plagioclase, fluorapatite and Fe-Ti oxides,  
380 the interstitial liquid in the crystal mush became enriched in incompatible REE and  
381 volatiles. Fine-grained fluorapatite eventually crystallized from the interstitial liquid  
382 and was enriched in REE (Fig. 12b). At the same time, amphibole inclusions were  
383 entrapped in some fine-grained apatite grains and amphibole rims developed in  
384 limited interstices and commonly between silicate minerals and Fe-Ti oxides (Fig.  
385 12b). Late-stage fluid metasomatism substantially remobilized REE in the fluorapatite  
386 in different ways and left behind diverse CL patterns in the fluorapatite (Fig. 12c).

387

388

### **IMPLICATIONS**

389 Cumulus fluorapatite in the upper zone of the mafic-ultramafic layered intrusions

390 has been used to trace late-stage differentiation of the parent magma. This study,  
391 however, demonstrates that the fluorapatite grains in igneous cumulates crystallized in  
392 multiple stages during a prolonged crystallization process. Later stage fluid  
393 metasomatism substantially modified both REE concentrations of primary fluorapatite  
394 and altered the CL texture of the fluorapatite. This study also demonstrates that a  
395 combination of CL imaging and *in situ* LA-ICP-MS trace element analysis is a  
396 powerful tool for unraveling the growth process of fluorapatite during crystallization  
397 of a magma chamber.

398

399

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406 this manuscript.

407

408

#### REFERENCES CITED

- 409 Barbarand, J., and Pagel, M. (2001) Cathodoluminescence study of apatite crystals.  
410 American Mineralogist, 86(4), 473–484.
- 411 Barnes, S.J. (1986) The effect of trapped liquid crystallization on cumulus mineral

- 412 compositions in layered intrusions. *Contributions to Mineralogy and Petrology*  
413 93(4), 524–531.
- 414 Bindeman, I.N., Davis, A.M., and Drake, M.J. (1998) Ion microprobe study of  
415 plagioclase-basalt partition experiments at natural concentration levels of trace  
416 elements. *Geochimica et Cosmochimica Acta*, 62(7), 1175–1193.
- 417 Broska, I., Ravna, E.J.K., Vojtko, P., Janák, M., Konečný, P., Pentrák, M., Bačík, P.,  
418 Luptáková, J., and Kullerud, K. (2014) Oriented inclusions in apatite in a  
419 post-UHP fluid-mediated regime (Tromsø Nappe, Norway). *European Journal of*  
420 *Mineralogy*, 26(5), 623–634.
- 421 Bonyadi, Z., Davidson, G.J., Mehrabi, B., Meffre, S., and Ghazban, F. (2011)  
422 Significance of apatite REE depletion and monazite inclusions in the brecciated  
423 Se-Chahun iron oxide-apatite deposit, Bafq district, Iran: insights from  
424 paragenesis and geochemistry. *Chemical Geology*, 281, 253–269.
- 425 Cawthorn, R.G. (2013) Rare earth element abundances in apatite in the Bushveld  
426 Complex-A consequence of the trapped liquid shift effect. *Geology*, 41(5),  
427 603–606.
- 428 Cawthorn, R.G. (1994) Formation of chlor- and fluor-apatite in layered intrusions.  
429 *Mineralogical Magazine*, 58, 299–306.
- 430 Filippelli, G.M., and Delaney, M.L. (1993) The effects of manganese (II) and iron (II)  
431 on the cathodoluminescence signal in synthetic apatite. *Journal of Sedimentary*  
432 *Research*, 63(1), 167–173.
- 433 Harlov, D.E., Meighan, C.J., Kerr, I.D., and Samson, I.M. (2016) *Mineralogy*,

- 434 chemistry, and fluid-aided evolution of the Pea Ridge Fe oxide-(Y+ REE)  
435 deposit, southeast Missouri, USA. *Economic Geology*, 111(8), 1963–1984.
- 436 Harlov, D.E. (2015) Apatite: a fingerprint for metasomatic processes. *Elements*, 11(3),  
437 171–176.
- 438 Harlov, D.E., Wirth, R., and Förster, H.-J. (2005) An experimental study of  
439 dissolution-precipitation in fluorapatite: fluid infiltration and the formation of  
440 monazite. *Contributions to Mineralogy and Petrology*, 150(3), 268–286.
- 441 Harlov, D.E., and Förster, H.-J. (2003) Fluid-induced nucleation of  
442 (Y+REE)-phosphate minerals within apatite: Nature and experiment. Part II.  
443 Fluorapatite. *American Mineralogist*, 88(8-9), 1209–1229.
- 444 Harlov, D.E., Förster, H.-J., and Nijland, T.G. (2002a) Fluid-induced nucleation of  
445 (Y+REE)-phosphate minerals within apatite: Nature and experiment. Part I.  
446 Chlorapatite. *American Mineralogist*, 87(2-3), 245–261.
- 447 Harlov, D.E., Andersson, U.B., Förster, H.-J., Nyström, J.O., Dulski, P., and Broman,  
448 C. (2002b) Apatite-monazite relations in the Kiirunavaara magnetite-apatite ore,  
449 northern Sweden. *Chemical Geology*, 191(1), 47–72.
- 450 Hart, S.R., and Dunn, T. (1993) Experimental cpx/melt partitioning of 24 trace  
451 elements. *Contributions to Mineralogy and Petrology*, 113(1), 1–8.
- 452 Holness, M.B., Tegner, C., Nielsen, T.F., Stripp, G., and Morse, S.A. (2007) A textural  
453 record of solidification and cooling in the Skaergaard intrusion, East Greenland.  
454 *Journal of Petrology*, 48(12), 2359–2377.
- 455 Kempe, U., and Götze, J. (2002) Cathodoluminescence (CL) behaviour and crystal

- 456 chemistry of apatite from rare-metal deposits. *Mineralogical Magazine*, 66(1),  
457 151–172.
- 458 Li, X., and Zhou, M.-F. (2015) Multiple stages of hydrothermal REE remobilization  
459 recorded in fluorapatite in the Paleoproterozoic Yinachang Fe-Cu-(REE) deposit,  
460 Southwest China. *Geochimica et Cosmochimica Acta*, 166, 53–73.
- 461 Lisowiec, K., Słaby, E., and Götze, J. (2013) Cathodoluminescence (CL) of apatite as  
462 an insight into magma mixing in the granitoid pluton of Karkonosze, Poland.  
463 Conference on Raman and Luminescence Spectroscopy in the Earth Sciences,  
464 67–68. University of Vienna, Austria.
- 465 Liu, Y., Hu, Z., Gao, S., Günther, D., Xu, J., Gao, C., and Chen, H. (2008) In situ  
466 analysis of major and trace elements of anhydrous minerals by LA-ICP-MS  
467 without applying an internal standard. *Chemical Geology*, 257(1), 34–43.
- 468 Ma, Y., Ji, X.T., Li, J.C., Huang, M., and Kan, Z.Z. (2003) Mineral Resources of the  
469 Panzhihua Region. Sichuan Science and Technology Press, Chengdu. 275 pp. (in  
470 Chinese).
- 471 McDonough, W.F., and Sun, S.-S. (1995) The composition of the Earth. *Chemical*  
472 *geology*, 120(3), 223–253.
- 473 Meurer, W., and Meurer, M. (2006) Using apatite to dispel the “trapped liquid”  
474 concept and to understand the loss of interstitial liquid by compaction in mafic  
475 cumulates: an example from the Stillwater Complex, Montana. *Contributions to*  
476 *Mineralogy and Petrology*, 151(2), 187–201.
- 477 Murray, J.R., and Oreskes, N. (1997) Uses and limitations of cathodoluminescence in

- 478 the study of apatite paragenesis. *Economic Geology*, 92(3), 368–376.
- 479 Namur, O., Charlier, B., and Holness, M.B. (2012) Dual origin of Fe-Ti-P gabbros by  
480 immiscibility and fractional crystallization of evolved tholeiitic basalts in the  
481 Sept Iles layered intrusion. *Lithos*, 154, 100–114.
- 482 Nielsen, R.L., Gallahan, W.E., and Newberger, F. (1992) Experimentally determined  
483 mineral-melt partition coefficients for Sc, Y and REE for olivine, orthopyroxene,  
484 pigeonite, magnetite and ilmenite. *Contributions to Mineralogy and Petrology*,  
485 110(4), 488–499.
- 486 Otten, M.T. (1984) The origin of brown hornblende in the Artfjället gabbro and  
487 dolerites. *Contributions to Mineralogy and Petrology*, 86(2), 189–199.
- 488 Pan, Y., Fleet, M.E., and Macrae, N.D. (1993) Oriented monazite inclusions in apatite  
489 porphyroblasts from the Hemlo gold deposit, Ontario, Canada. *Mineralogical*  
490 *Magazine*, 57, 697–707.
- 491 Prowatke, S., and Klemme, S. (2006) Trace element partitioning between apatite and  
492 silicate melts. *Geochimica et Cosmochimica Acta*, 70(17), 4513–4527.
- 493 Reynolds, I.M. (1985) The nature and origin of titaniferous magnetite-rich layers in  
494 the upper zone of the Bushveld Complex; a review and synthesis. *Economic*  
495 *Geology*, 80(4), 1089–1108.
- 496 Ridolfi, F., and Renzulli, A. (2012) Calcic amphiboles in calc-alkaline and alkaline  
497 magmas: thermobarometric and chemometric empirical equations valid up to  
498 1,130 °C and 2.2 GPa. *Contributions to Mineralogy and Petrology*, 163(5),  
499 877–895.

- 500 Roeder, P.L., MacArthur, D., Ma, X.-P., Palmer, G.R., and Mariano, A.N. (1987)  
501 Cathodoluminescence and microprobe study of rare-earth elements in apatite.  
502 American mineralogist, 72(7-8), 801–811.
- 503 She, Y.-W., Song, X.-Y., Yu, S.-Y., Chen, L.-M., and Zheng, W.-Q. (2016) Apatite  
504 geochemistry of the Taihe layered intrusion, SW China: Implications for the  
505 magmatic differentiation and the origin of apatite-rich Fe-Ti oxide ores. Ore  
506 Geology Reviews, 78, 151–165.
- 507 Tegner, C., Cawthorn, R.G., and Kruger, F.J. (2006) Cyclicality in the Main and Upper  
508 Zones of the Bushveld Complex, South Africa: crystallization from a zoned  
509 magma sheet. Journal of Petrology, 47(11), 2257–2279.
- 510 Tollari, N., Barnes, S.-J., Cox, R., and Nabil, H. (2008) Trace element concentrations  
511 in apatites from the Sept-Îles Intrusive Suite, Canada-implications for the genesis  
512 of nelsonites. Chemical Geology, 252(3), 180–190.
- 513 VanTongeren, J., and Mathez, E. (2012) Large-scale liquid immiscibility at the top of  
514 the Bushveld Complex, South Africa. Geology, 40(6), 491–494.
- 515 Von Gruenewaldt, G. (1993) Ilmenite-Apatite Enrichments in the Upper Zone of the  
516 Bushveld Complex: A Major Titanium-Rock Phosphate Resource. International  
517 Geology Review, 35(11), 987–1000.
- 518 Wang, C.Y., and Zhou, M.-F. (2013) New textural and mineralogical constraints on  
519 the origin of the Hongge Fe-Ti-V oxide deposit, SW China. Mineralium Deposita,  
520 1–12.
- 521 Webster, J.D., and Piccoli, P.M. (2015) Magmatic apatite: a powerful, yet deceptive,

522 mineral. Elements, 11(3), 177–182.

523

524

525 **Figure captions**

526 **FIGURE 1.** Geological maps showing the distribution of the Emeishan large igneous  
527 province **(a)** and the distribution of major rock types in the Hongge intrusion (after  
528 Wang and Zhou 2013) **(b)**, and a stratigraphic column of the Hongge intrusion  
529 showing the sample locations **(c)**.

530

531 **FIGURE 2.** Plain polarized, transmitted light photomicrographs of the gabbro  
532 (sample HG1532) **(a)**, Fe-Ti oxide gabbro (sample HG1539) **(b)** and Fe-Ti oxide ore  
533 (sample HG1540) **(c)** in the upper zone of the Hongge intrusion. **(d)** Close-up of **(a)**  
534 showing abundant fluorapatite (Ap) grains associated with Fe-Ti oxides and  
535 interstitial to clinopyroxene (Cpx) and plagioclase (Pl). Note that plagioclase is  
536 altered in local places. **(e)** Close-up of **(c)** showing disseminated fluorapatite grains  
537 associated with Fe-Ti oxides and interstitial to clinopyroxene.

538

539 **FIGURE 3.** Occurrence of fluorapatite in the rocks of the Hongge intrusion. **(a)** BSE  
540 image of fluorapatite (Ap) is associated with magnetite (Mag), ilmenite (Ilm) and  
541 pyrrhotite (Po). Note that fluorapatite has variable grain sizes in the same thin section  
542 (sample HG1540). **(b)** BSE image of rounded pyrrhotite inclusion enclosed within  
543 fluorapatite and a sulfide veinlet extending along fracture in the fluorapatite (sample

544 HG1539). (c) Plain polarized, transmitted light image of fluorapatite with abundant,  
545 elongated pyrrhotite inclusions elongated parallel to the fluorapatite c-axis in a  
546 topotaxial relationship. Dislocation planes are nearly perpendicular to the c-axis  
547 (sample HG1540). (d) Cross polarized, transmitted light image of an elongated  
548 fluorapatite, which has kink bands with different extinction angles on two sides of the  
549 dislocation planes (sample HG1532).

550

551 **FIGURE 4.** CL images for coarse-grained fluorapatite from the Hongge intrusion. (a)  
552 Simple image with clear dislocation planes (sample HG1539). (b) Simple image with  
553 clear dislocation planes and localized, discontinuous dark rims along the grain  
554 boundary (sample HG1539). (c) Complex image with mosaic-like sectors crosscut by  
555 bright veinlets (sample HG1540).

556

557 **FIGURE 5.** Concentric-type CL images of fine-grained fluorapatite from the Hongge  
558 intrusion showing that euhedral to subhedral fluorapatite grains have a bright, rounded  
559 to irregular core and dark mantle (samples HG1539 and HG1529) (a, b). The dark  
560 mantle is irregularly zoned in contrast to the overall-dark type CL image (sample  
561 HG1540) (c). The concentric texture in the CL image is not seen in the BSE image of  
562 the same grain (d).

563

564 **FIGURE 6.** Chaotic-type CL images of fine-grained fluorapatite from the Hongge  
565 intrusion showing that bright and dark sectors are irregularly (sample HG1539) (a, b,

566 **c)** and that the dark rim penetrates the fluorapatite as veinlets (**c, d**). Note that tiny  
567 amphibole inclusions are enclosed in the veinlets (**c**). (**d**) is taken from sample  
568 HG1532.

569

570 **FIGURE 7.** Banded-type CL images of fine-grained fluorapatite from the Hongge  
571 intrusion showing dark and bright bands distributed unevenly in the fluorapatite. (**a**) is  
572 taken from sample HG1539 and (**b**) is taken from sample HG1532.

573

574 **FIGURE 8.** Binary plots of Mn/Fe versus Mn (**a**), Ce versus Sr (**b**), Ce versus Sr/Y  
575 (**c**), and Th/Zr versus U/Zr (**d**) for the fluorapatite in the Hongge intrusion. Note that  
576 the fluorapatite in this study has restricted Th/Zr and U/Zr, similar to those for the  
577 fluorapatite from the Bushveld Complex (VanTongeren and Mathez 2012).

578

579 **FIGURE 9.** Variation of REE within a single fluorapatite grain from the gabbro (**a, b**),  
580 the Fe-Ti oxide-bearing gabbro (**c, d**), and the Fe-Ti oxide ore (**e, f**). Note that the  
581 coarse-grained fluorapatite shows a restricted variation in REE, whereas the  
582 fine-grained fluorapatite shows a large REE variation. Normalization values are from  
583 McDonough and Sun (1995).

584

585 **FIGURE 10.** Chondrite-normalized REE patterns for fine-grained fluorapatite from  
586 the Fe-Ti oxide ore with concentric-type zoning under CL imaging and a  
587 coarse-grained fluorapatite with no obvious zoning. REE concentrations in the melt in

588 equilibrium with the fluorapatite were calculated using the partition coefficients as  
589 Muerer and Meurer (2006). Normalization values are from McDonough and Sun  
590 (1995).

591

592 **FIGURE 11. (a)** Plain polarized, transmitted light image of brown amphibole (Amp)  
593 inclusion enclosed within a fine-grained fluorapatite from the Fe-Ti oxide gabbro.  
594 Note that magnetite (Mag) is enclosed within the amphibole inclusion. Sample  
595 HG1539. **(b)** Plain polarized, transmitted light image of brown amphibole rimming  
596 along the Fe-Ti oxide, clinopyroxene, and plagioclase grains in the gabbro. **(c)** Plain  
597 polarized, transmitted light image showing the irregular amphibole grained in Fe-Ti  
598 oxides. **(d)** BSE image of the close-up of (c) showing the intergrowth of magnetite  
599 and amphibole.

600

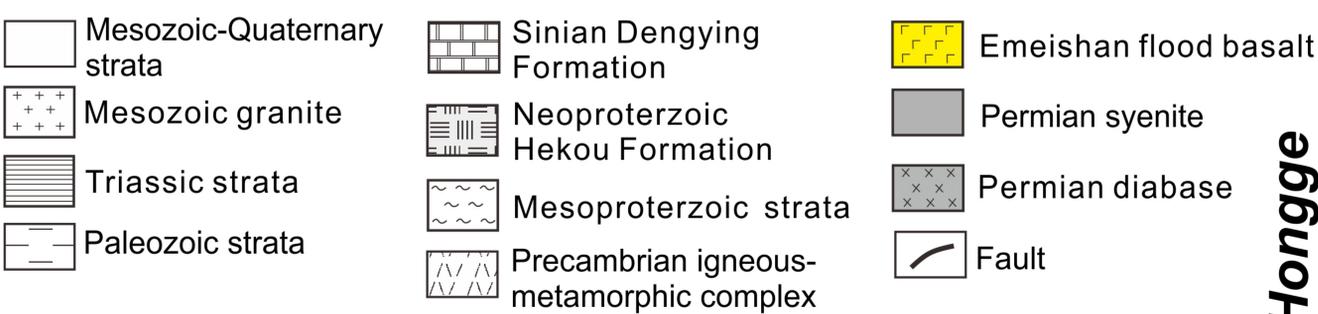
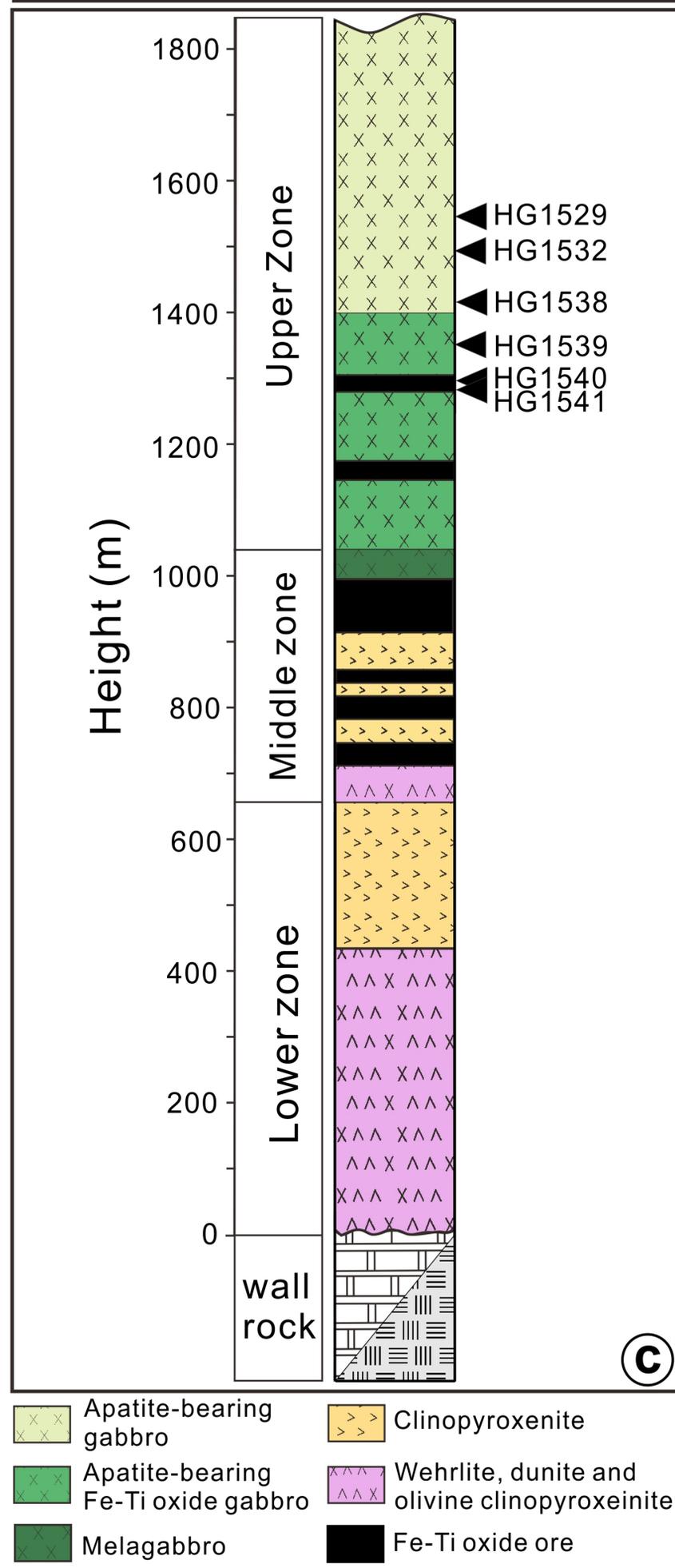
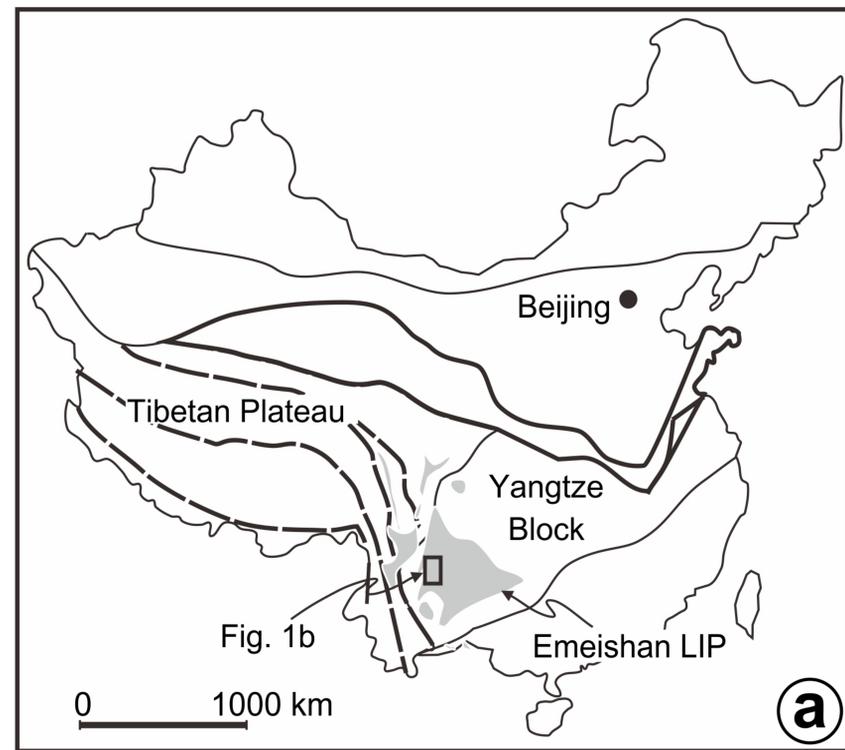
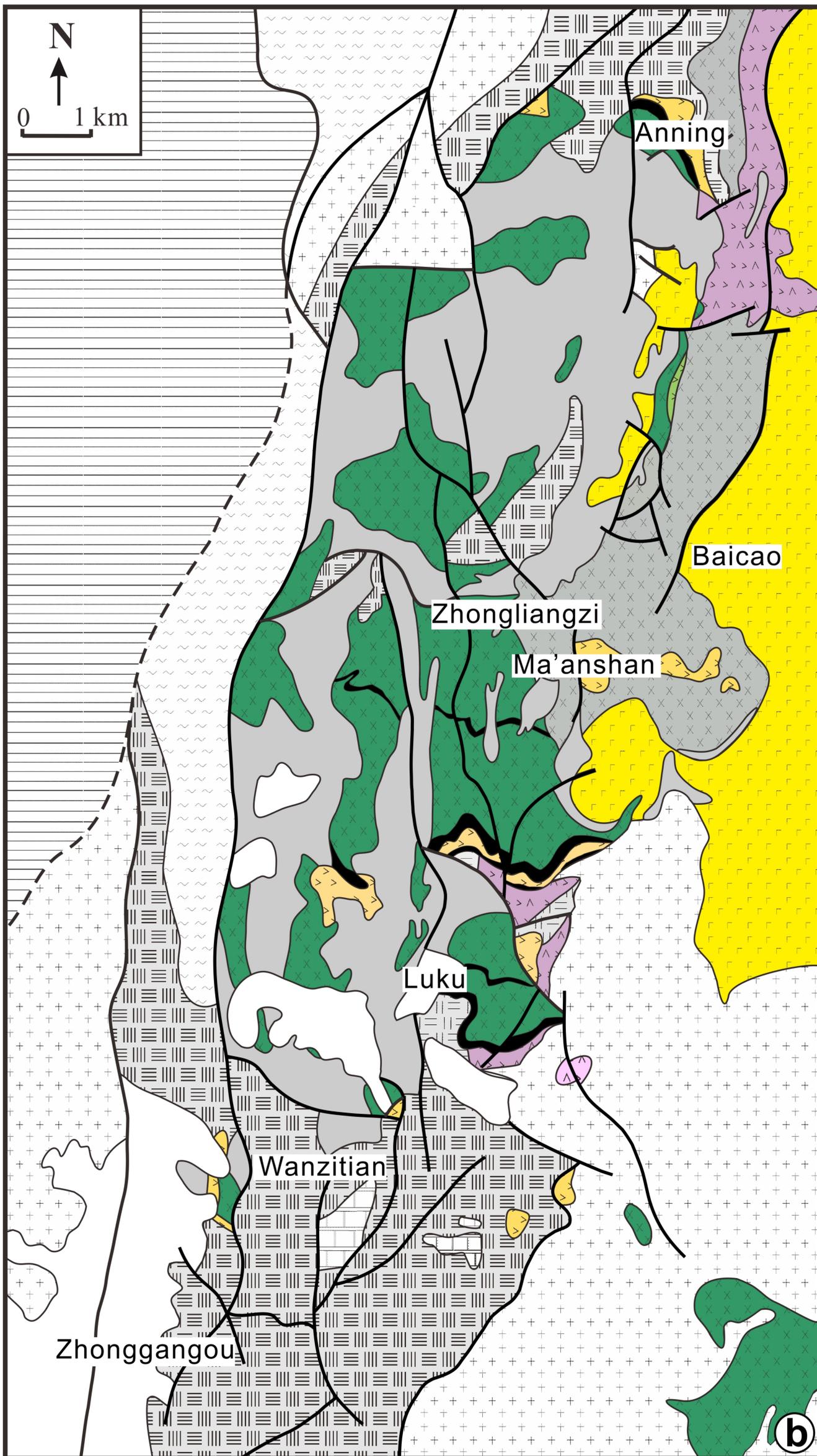
601 **FIGURE 12.** Cartoon showing a prolonged crystallization process of fluorapatite and  
602 overprinting later fluid metasomatism responsible for the complex textures in  
603 fluorapatite seen under CL imaging.

Table 1 Representative data of major and trace element compositions of apatite from the Hongge layered intrusion, SW China

Sample No.	HG1532			HG1539			HG1540		
Rock type	Gabbro			Fe-Ti oxide gabbro			Fe-Ti oxide ore		
Analysis No.	1-5	2-1	3-1	4-3	2-3	2-2	2-2	1-1	1-2
Apatite	Coarse-grained	Fine-grained	Fine-grained	Coarse-grained	Fine-grained	Fine-grained	Coarse-grained	Fine-grained	Fine-grained
Analysis position	Core	CL-bright	CL-dark	Core	CL-bright	CL-dark	Core	CL-bright	CL-dark
Major oxides (wt.%) by EPMA									
CaO	54.81	55.37	54.53	55.29	55.06	55.17	55.08	55.32	55.47
P <sub>2</sub> O <sub>5</sub>	41.61	41.73	41.78	42.23	42.51	41.77	42.36	43.02	42.48
SiO <sub>2</sub>	0.02	0.06	0.03	0.05	0.11	0.22	0.09	0.05	0.06
SO <sub>3</sub>	0.11	0.08	0.19	0.09	0.22	0.10	0.14	0.13	0.14
F	2.07	2.32	1.97	1.95	2.62	2.49	2.09	2.39	2.58
Cl	0.13	0.14	0.09	0.15	0.17	0.15	0.12	0.10	0.09
OH	1.41	1.21	1.51	1.54	0.93	1.04	1.43	1.20	1.03
Total	100.16	100.90	100.10	101.30	101.63	100.94	101.30	102.21	101.84
F/Cl	16.41	16.90	22.18	13.38	15.32	16.50	18.04	24.43	29.28
Trace elements (ppm) by LA-ICP-MS									
Si	1333	1779	4114	1883	2226	1932	1511	2030	1479
Mn	257	118	130	256	163	141	202	143	90.8
Fe	520	1005	1475	2587	930	2723	527	557	250
Sr	2714	2705	2580	2543	2467	2484	2689	2601	2594
Y	223	254	177	286	331	197	239	465	208
La	342	376	293	454	516	311	352	686	307
Ce	862	944	731	1115	1262	768	892	1692	772
Pr	125	137	106	157	176	107	129	247	112
Nd	646	710	550	802	894	549	669	1283	576
Sm	130	146	106	160	182	113	139	262	118
Eu	34.5	39.3	28.9	43.6	48.8	30.4	37.0	70.6	31.9
Gd	113	128	95.3	138	160	96.2	120	227	105
Tb	12.2	13.7	10.2	15.2	17.5	10.6	12.6	25.1	11.4
Dy	57.0	63.2	46.4	71.9	82.7	49.0	59.7	114	51.7
Ho	8.74	10.3	7.41	11.8	13.3	7.75	9.54	18.5	8.47
Er	18.2	20.8	14.3	23.7	28.1	15.7	19.8	36.4	16.7
Tm	1.74	1.92	1.39	2.56	2.81	1.66	1.98	3.70	1.66
Yb	8.30	10.3	7.14	13.1	14.8	8.61	9.07	18.7	8.81
Lu	0.98	1.22	0.80	1.64	1.84	1.06	1.12	2.32	1.00
Zr	4.64	36.5	3.23	13.8	15.3	8.74	7.49	16.5	7.90
Th	6.80	7.12	4.64	7.79	9.14	5.73	6.68	28.5	8.05
U	1.21	1.30	0.89	1.69	1.96	1.34	1.44	5.17	1.70
total REE	2360	2602	1997	3008	3400	2070	2451	4687	2122
Mn/Fe	0.49	0.12	0.09	0.10	0.18	0.05	0.38	0.26	0.36
Sr/Y	12.2	10.7	14.6	8.9	7.5	12.6	11.3	5.6	12.5

Note: OH was calculated assuming  $F + Cl + OH = 1$  per formula unit. The complete dataset is listed in Supplemental Tables 2 and 3.

Fig. 1

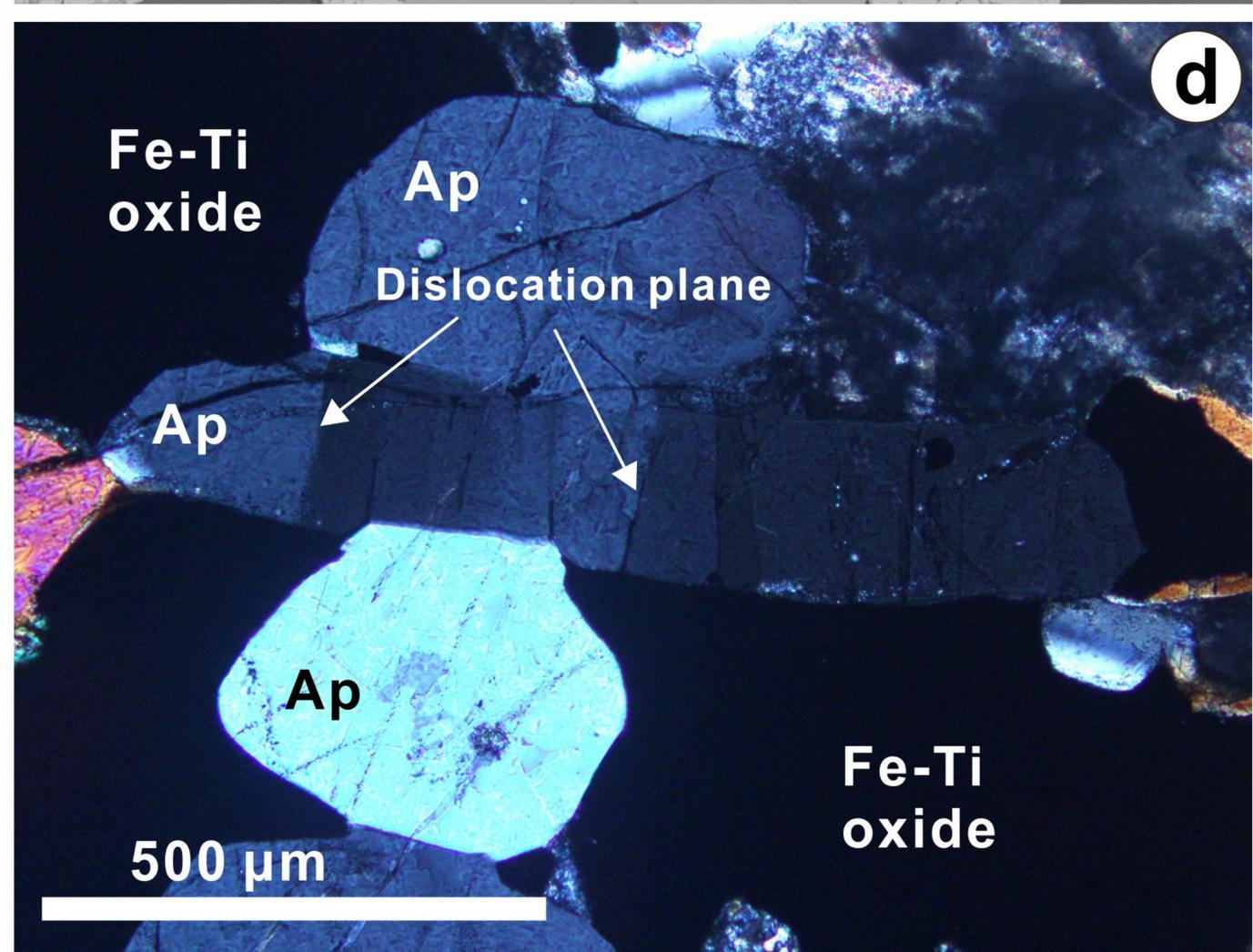
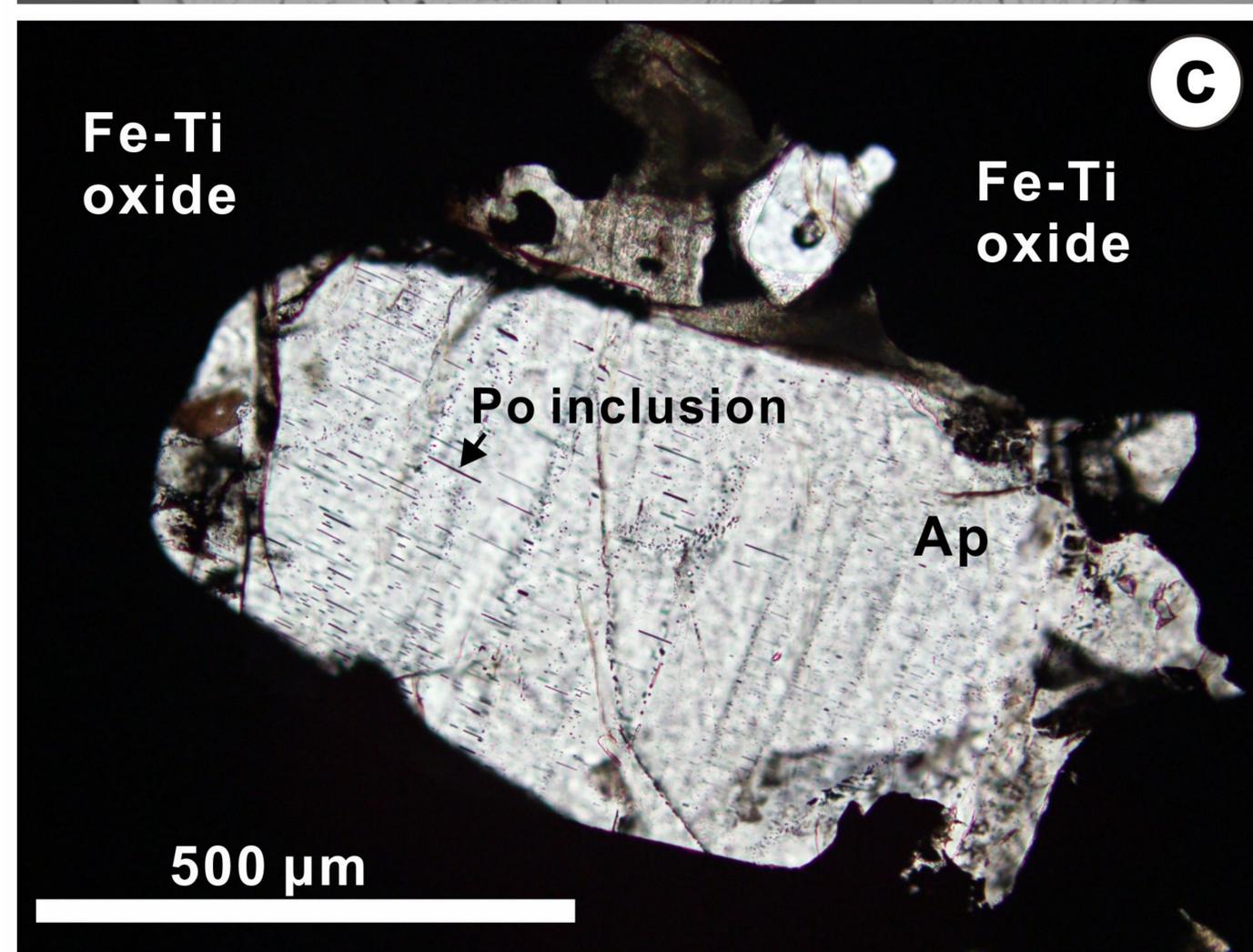
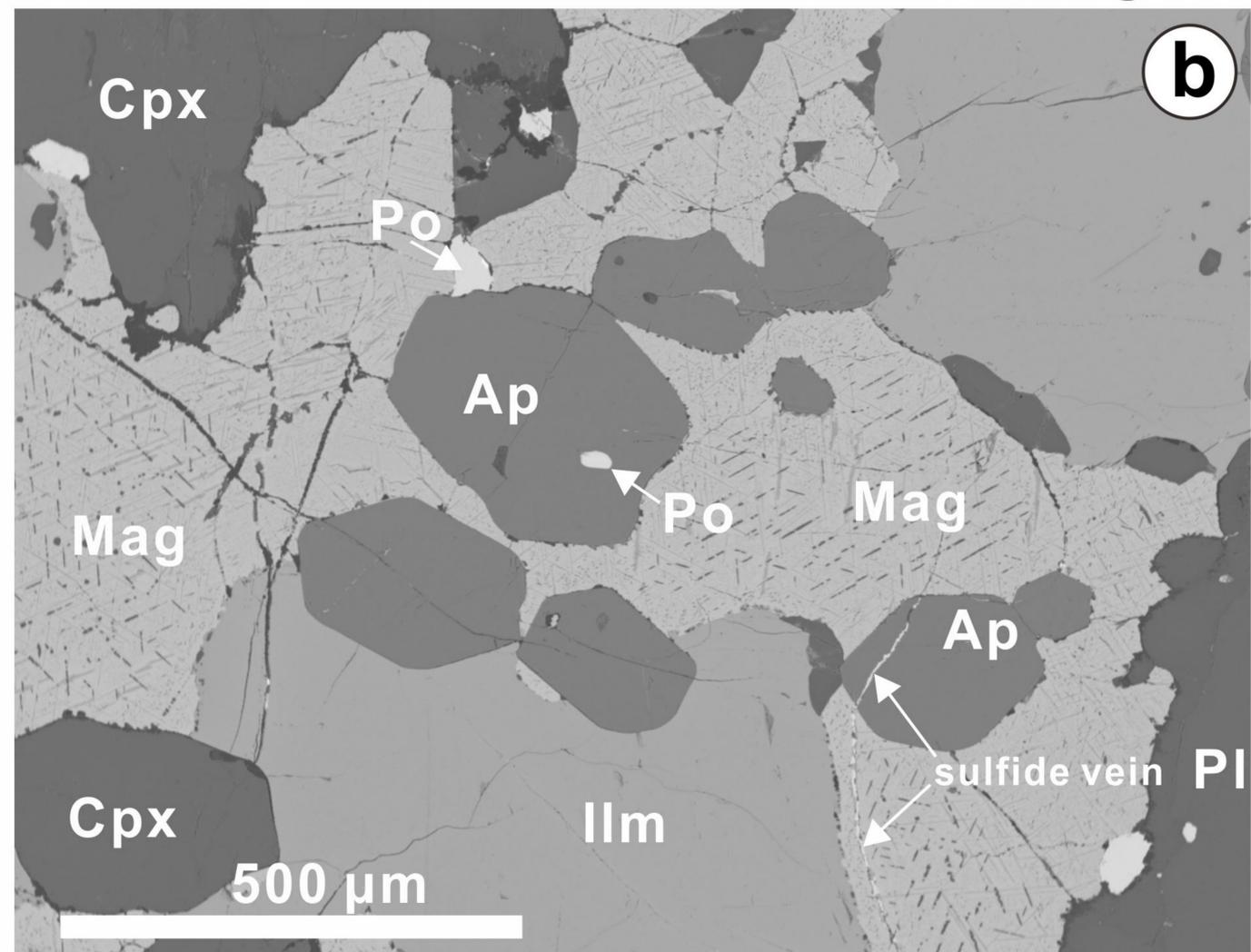
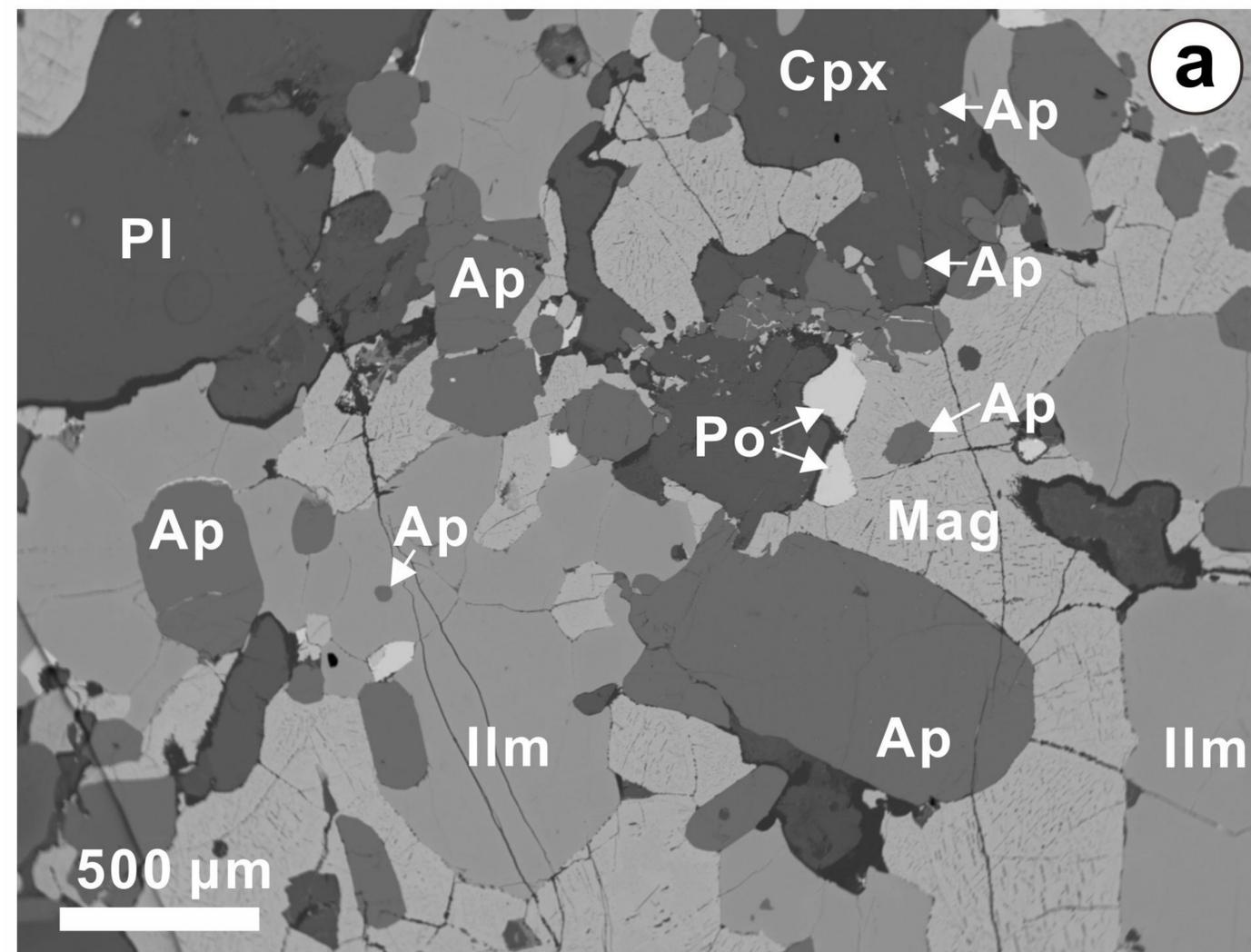


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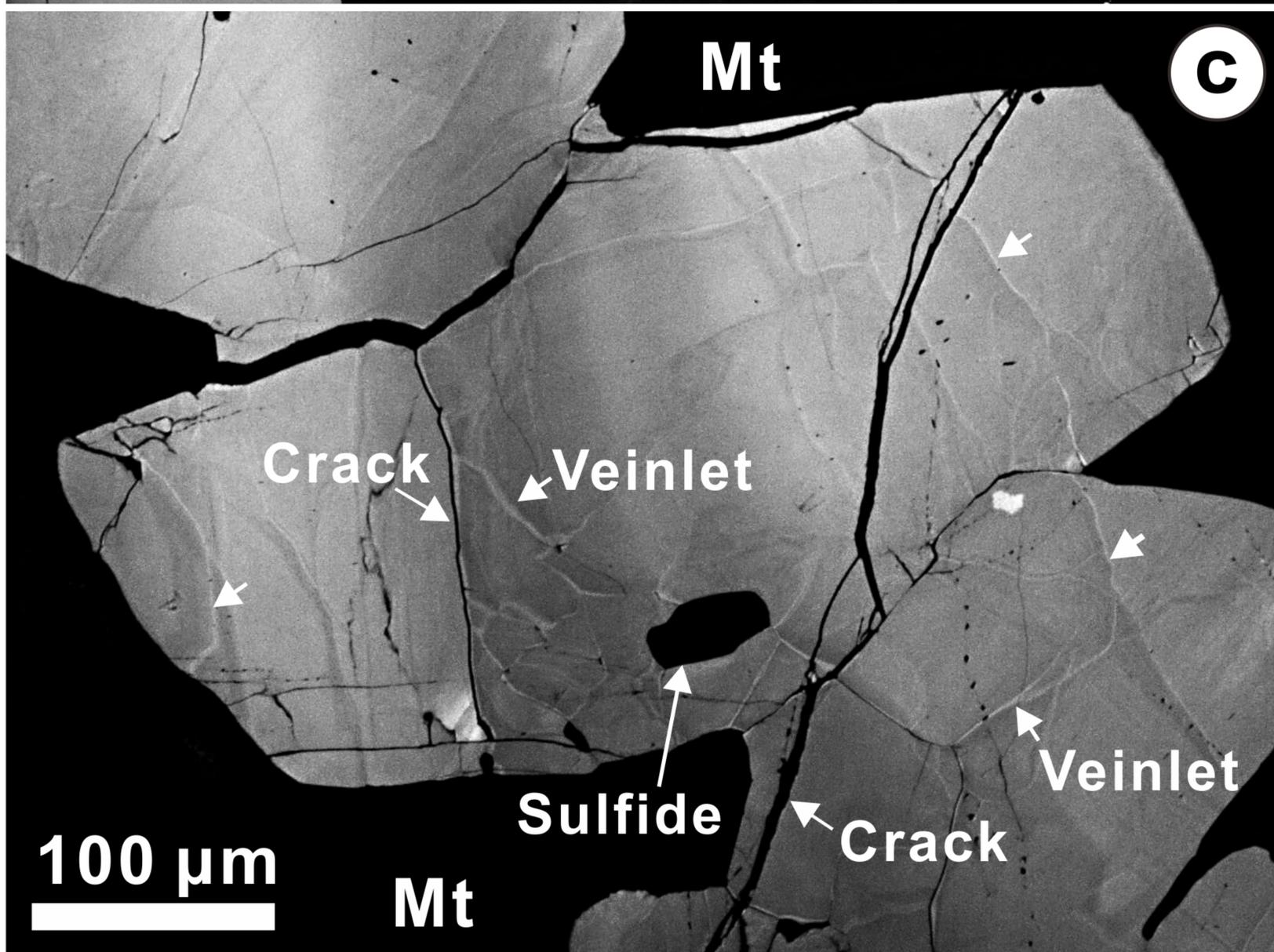
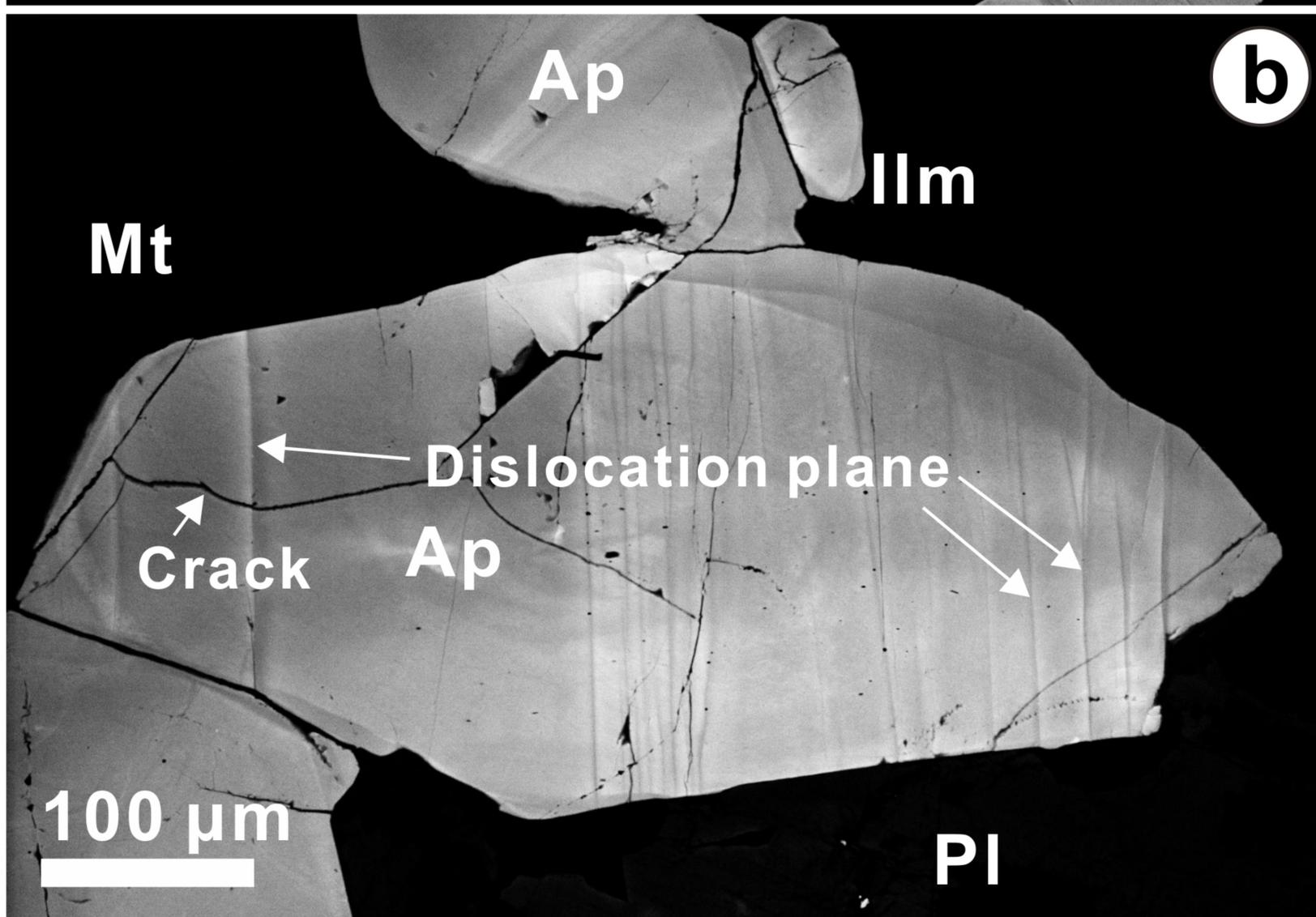
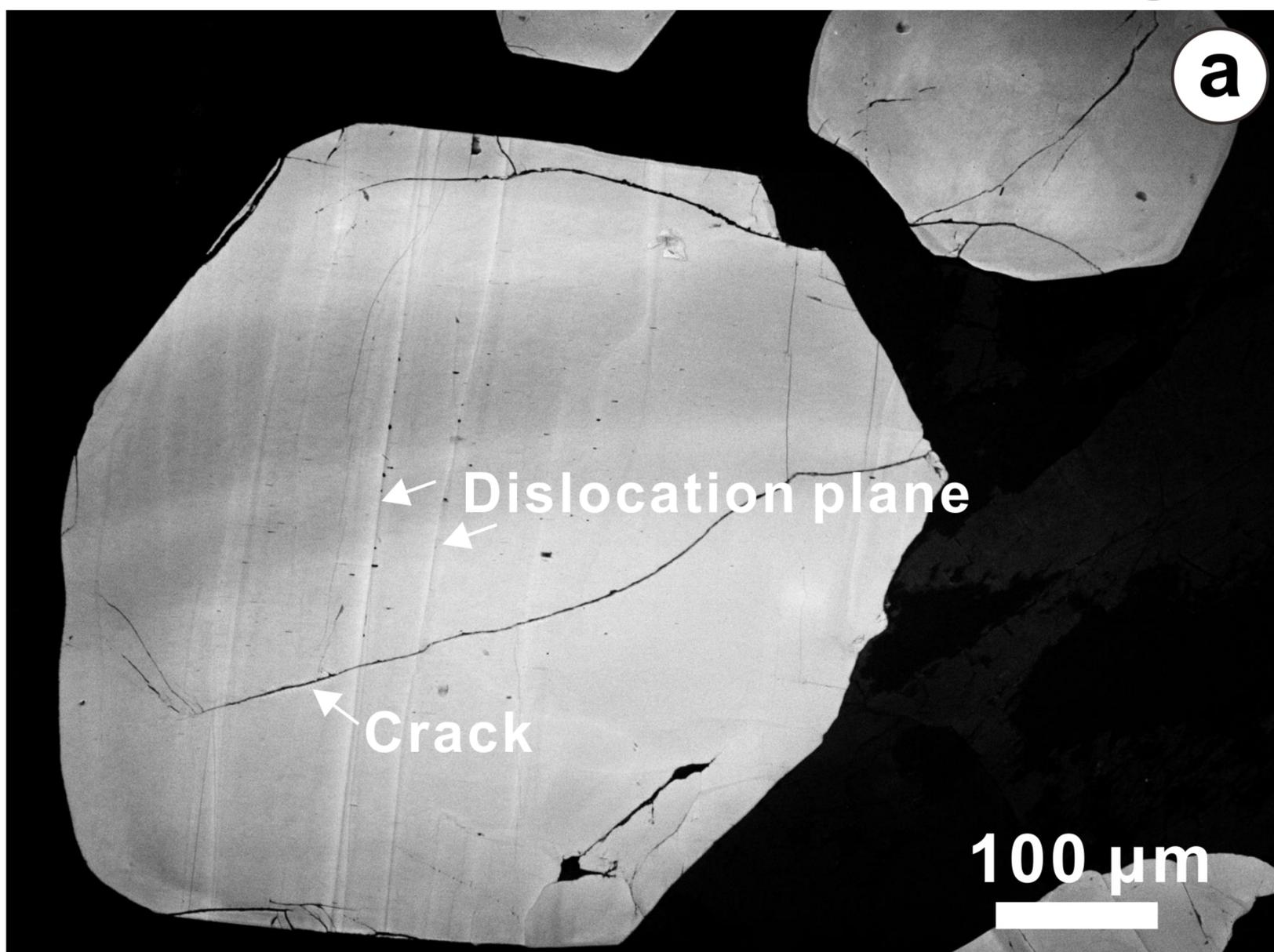




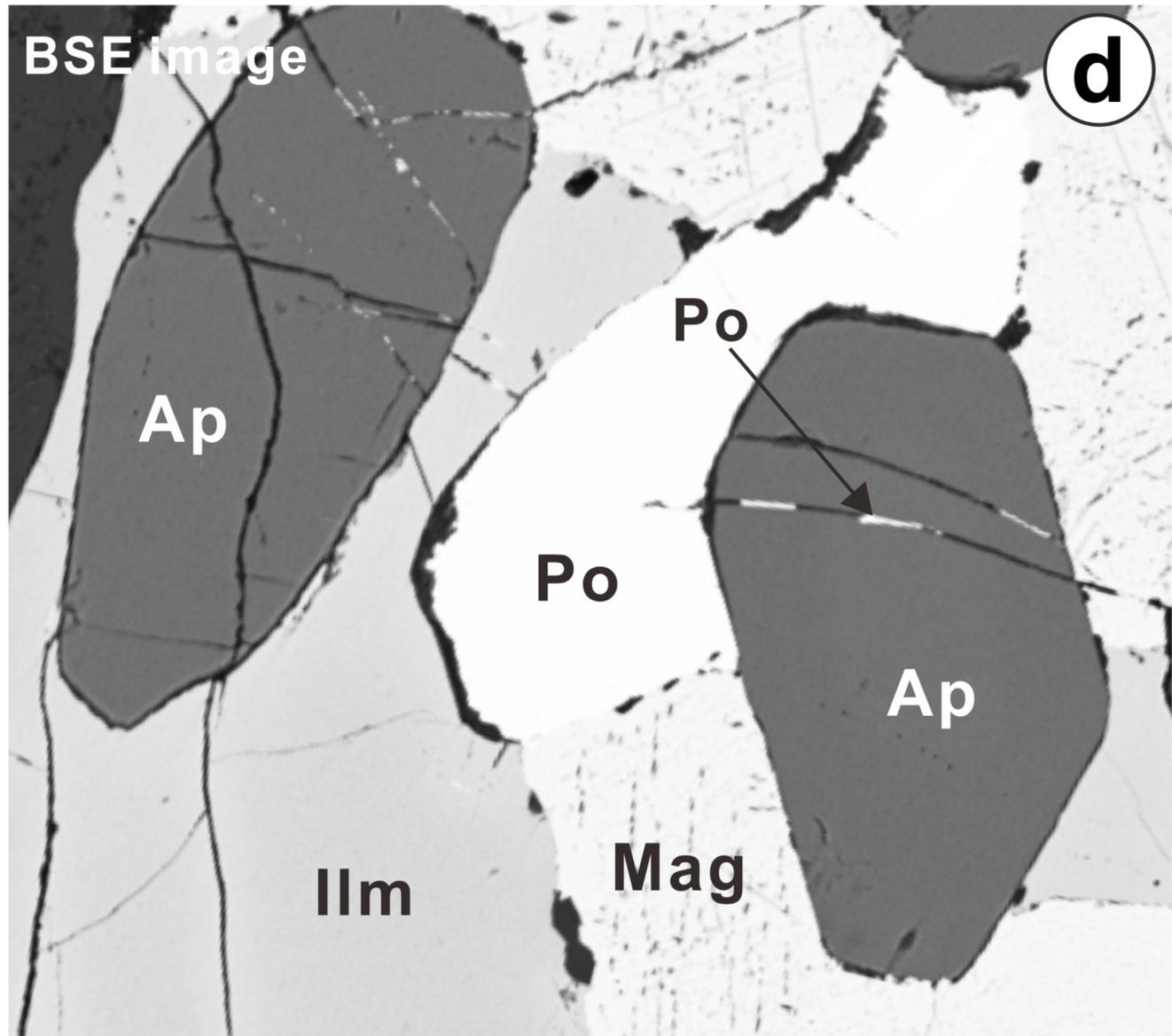
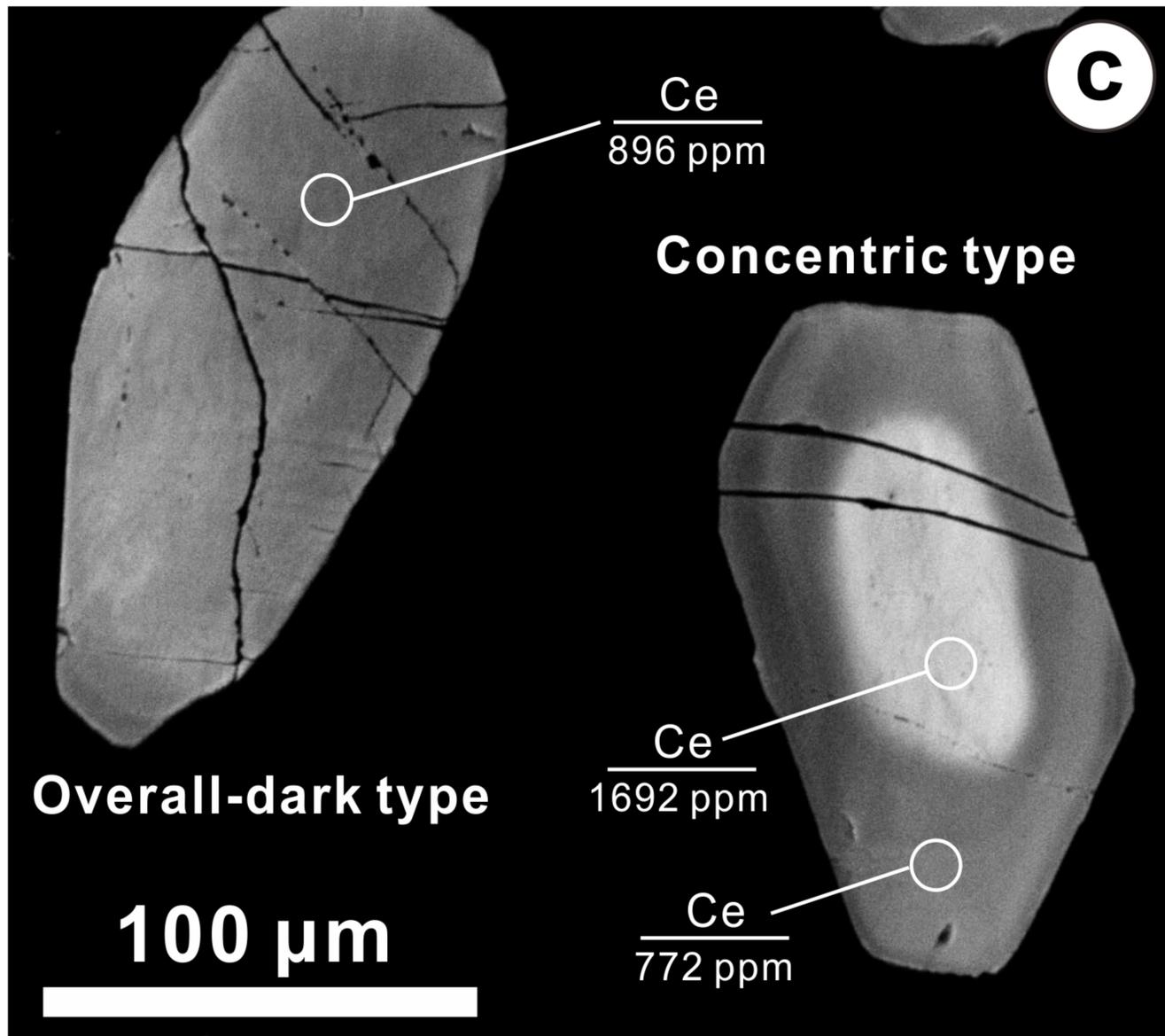
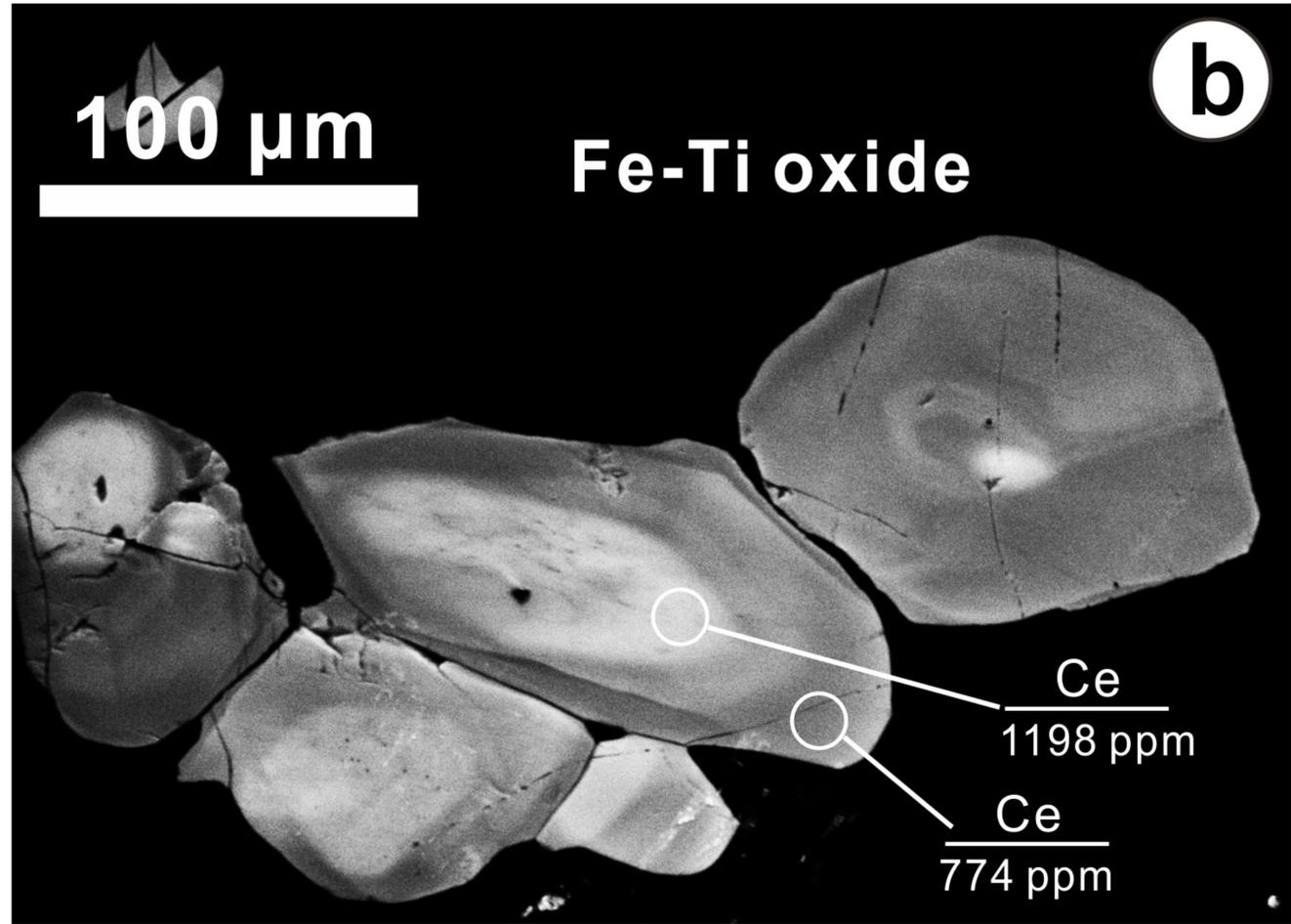
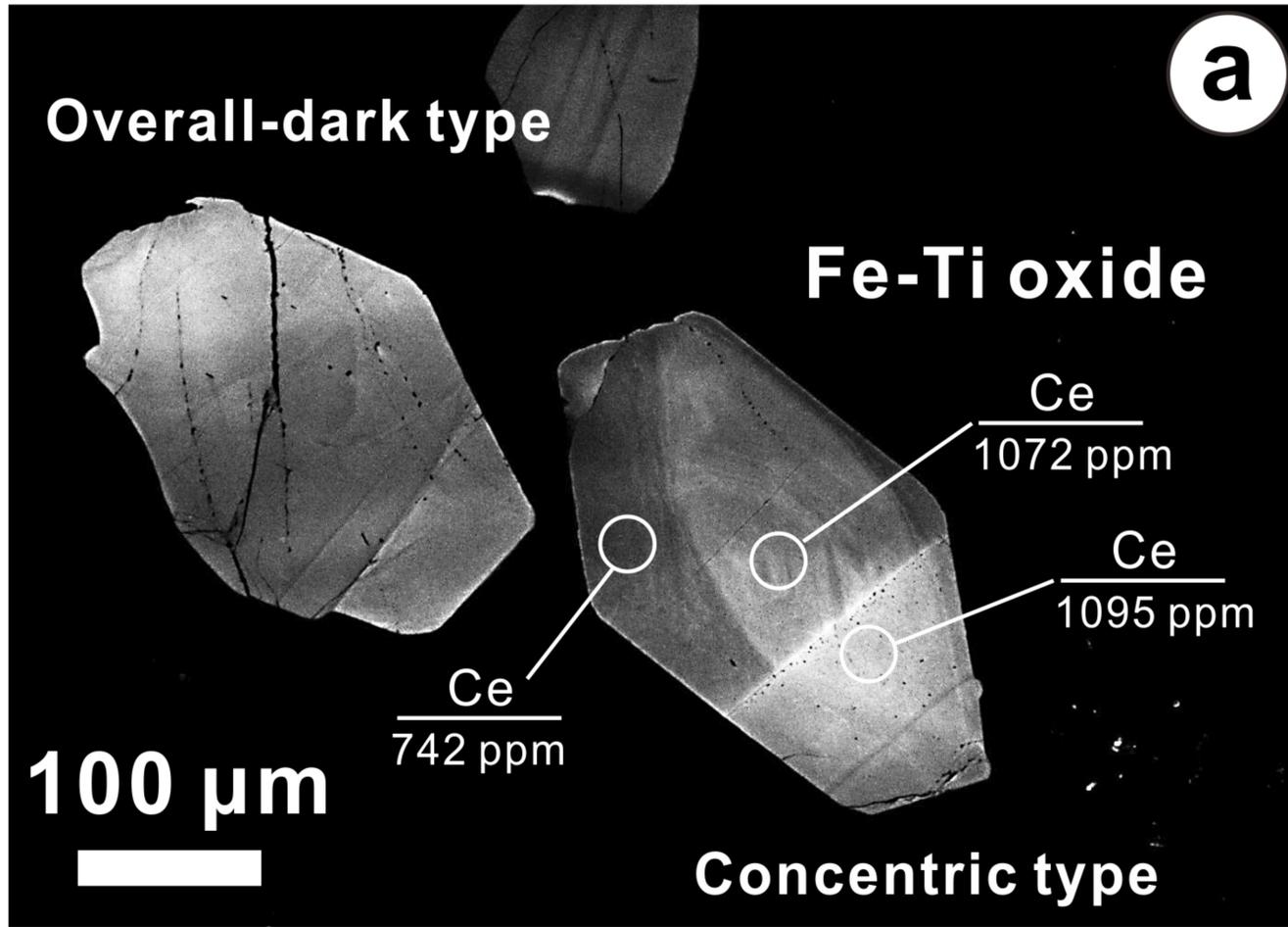
**Fig. 3**



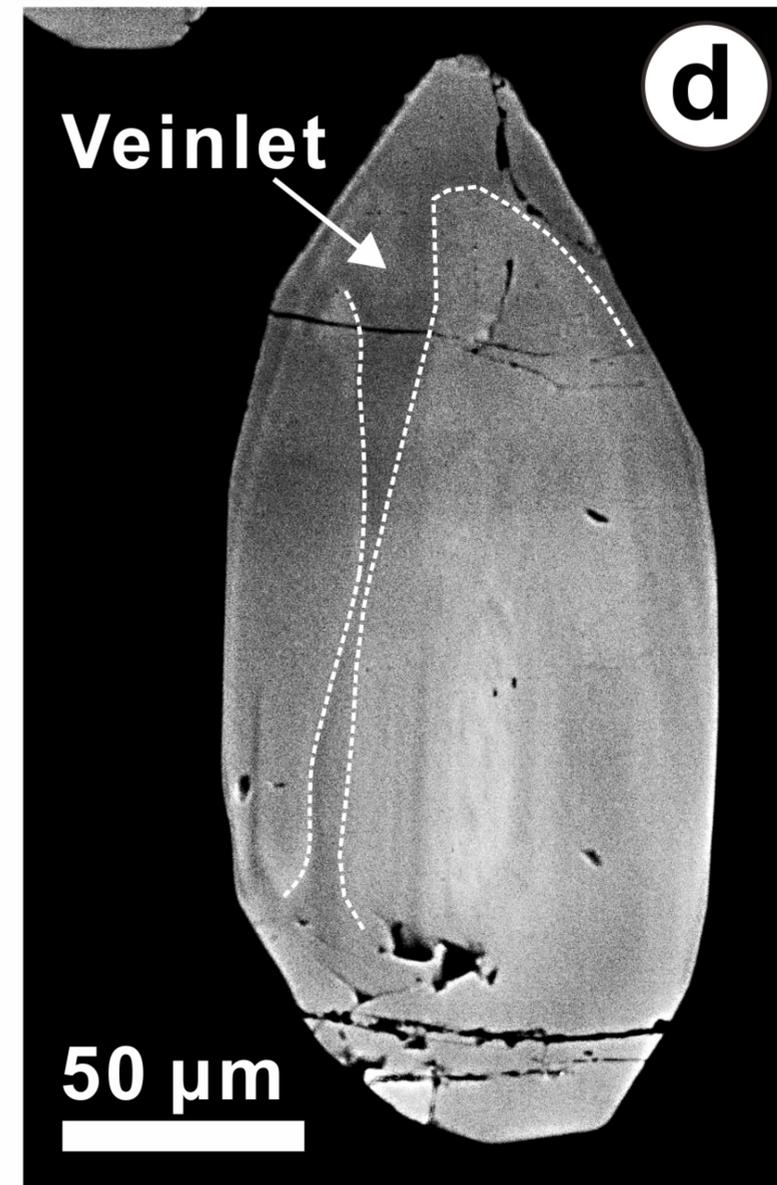
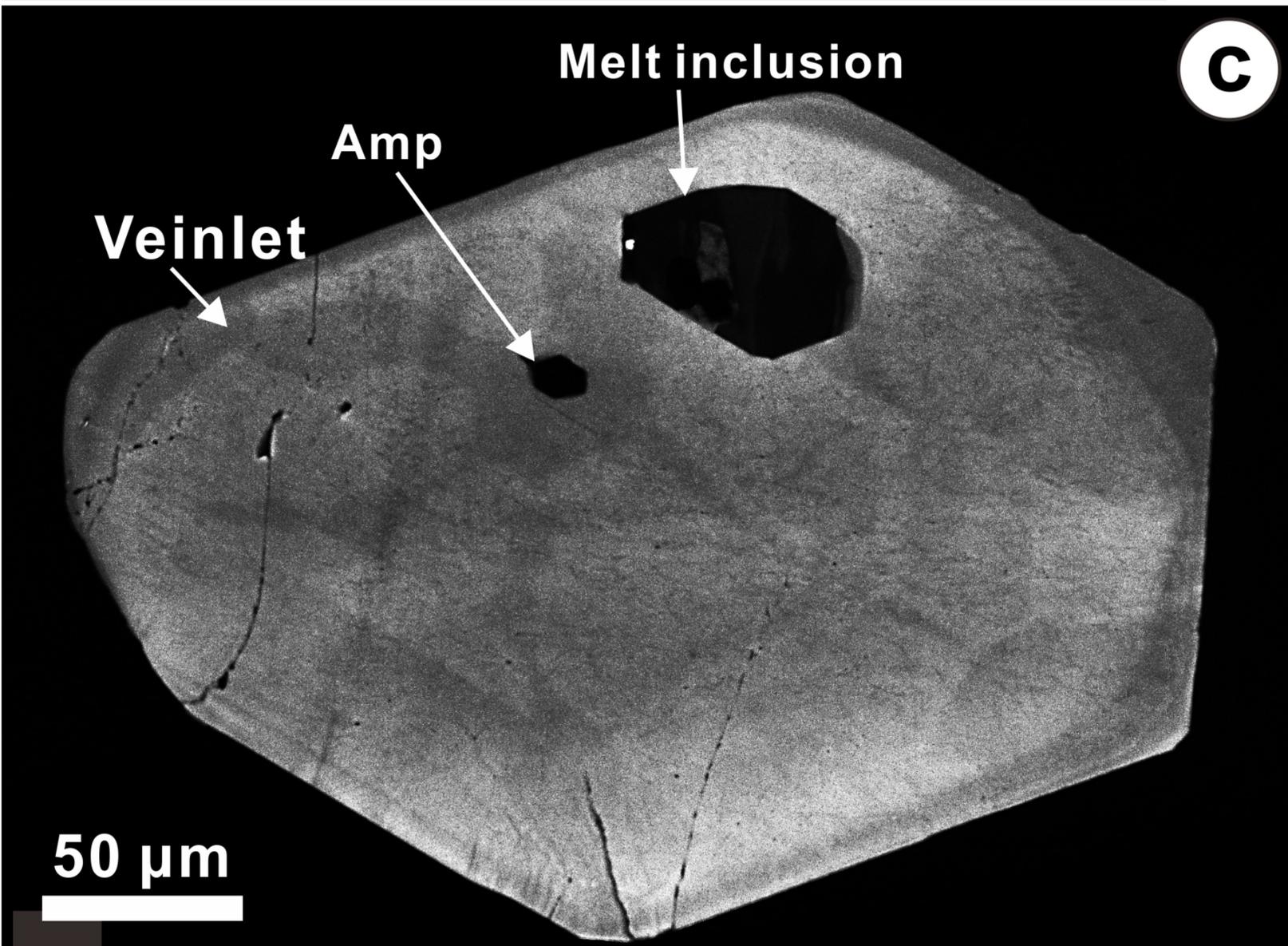
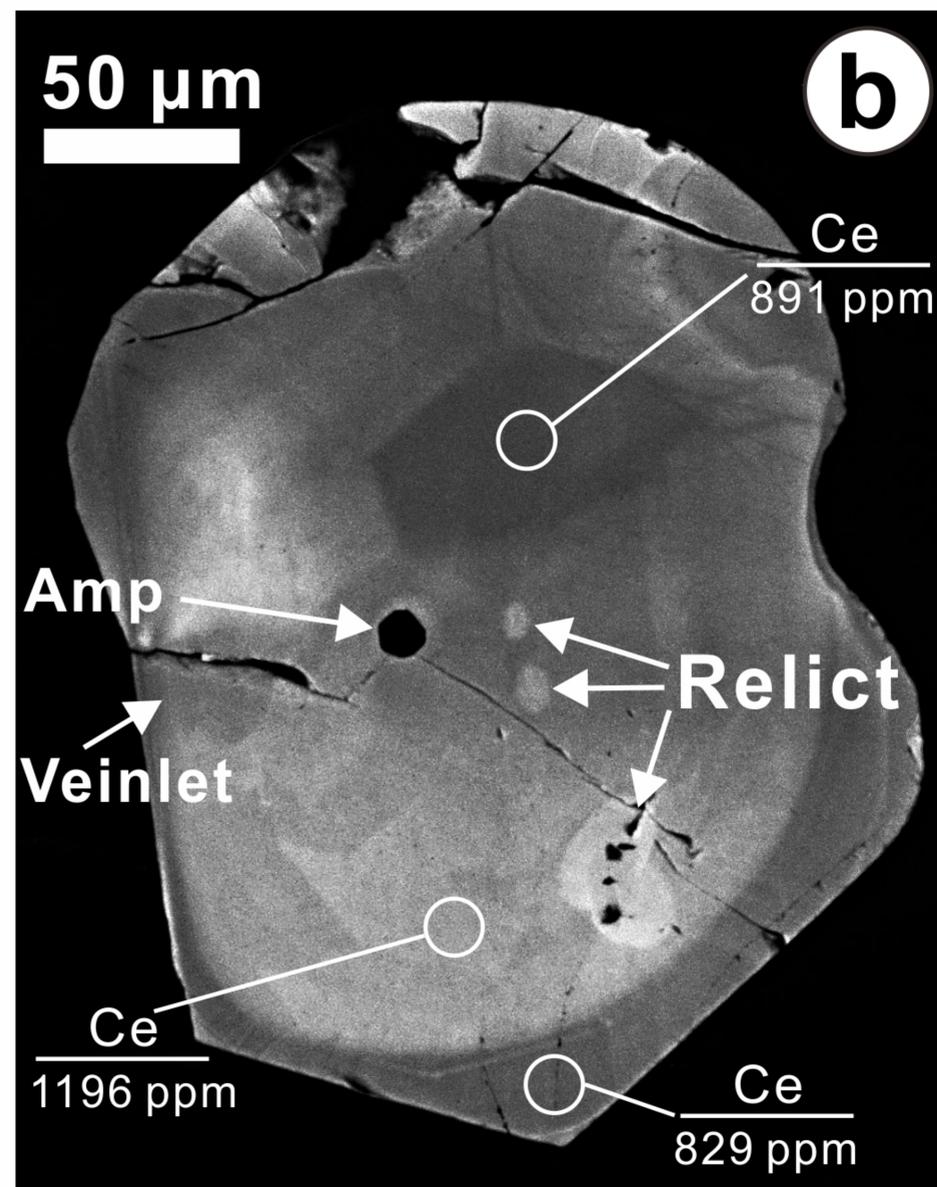
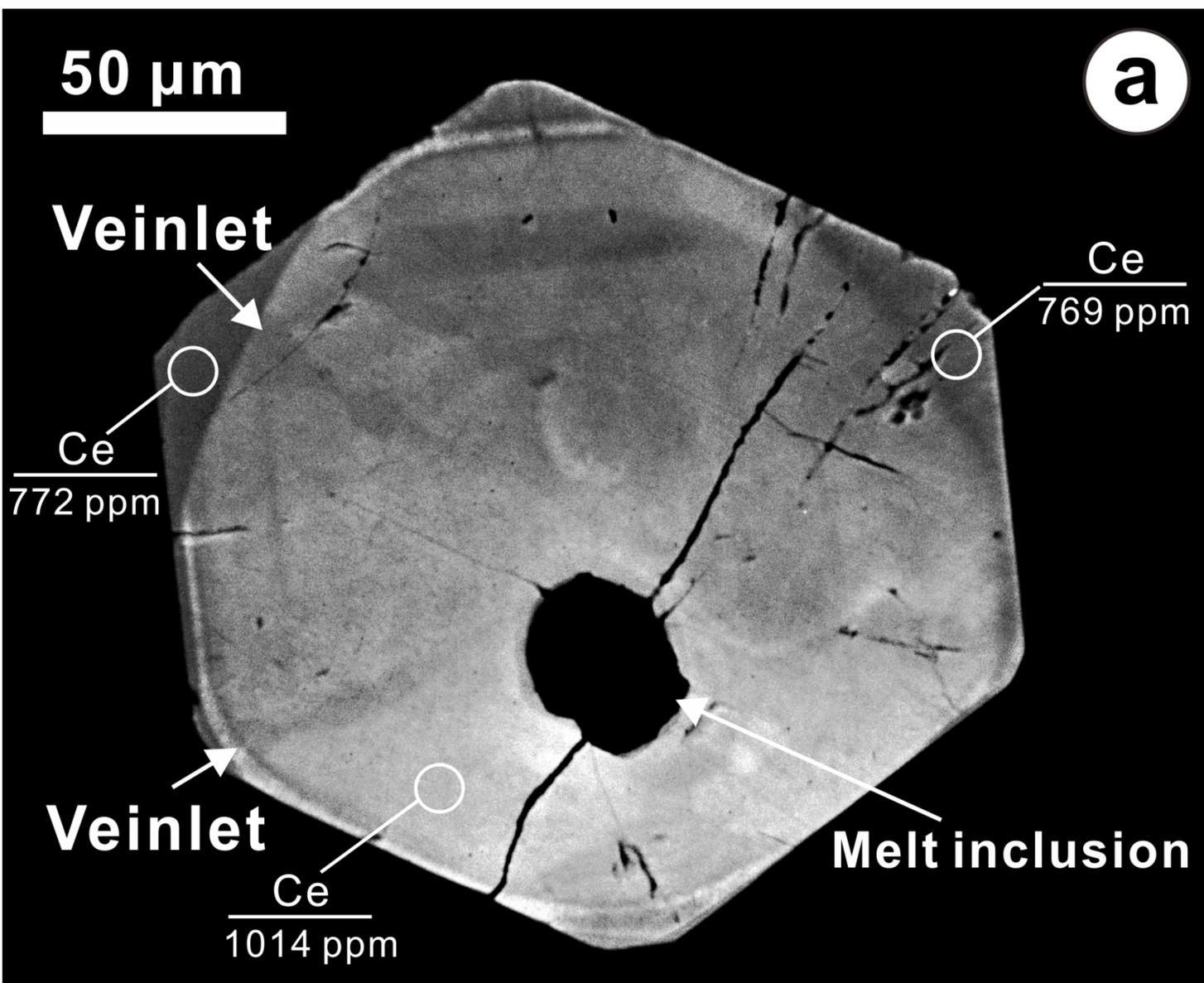
**Fig. 4**



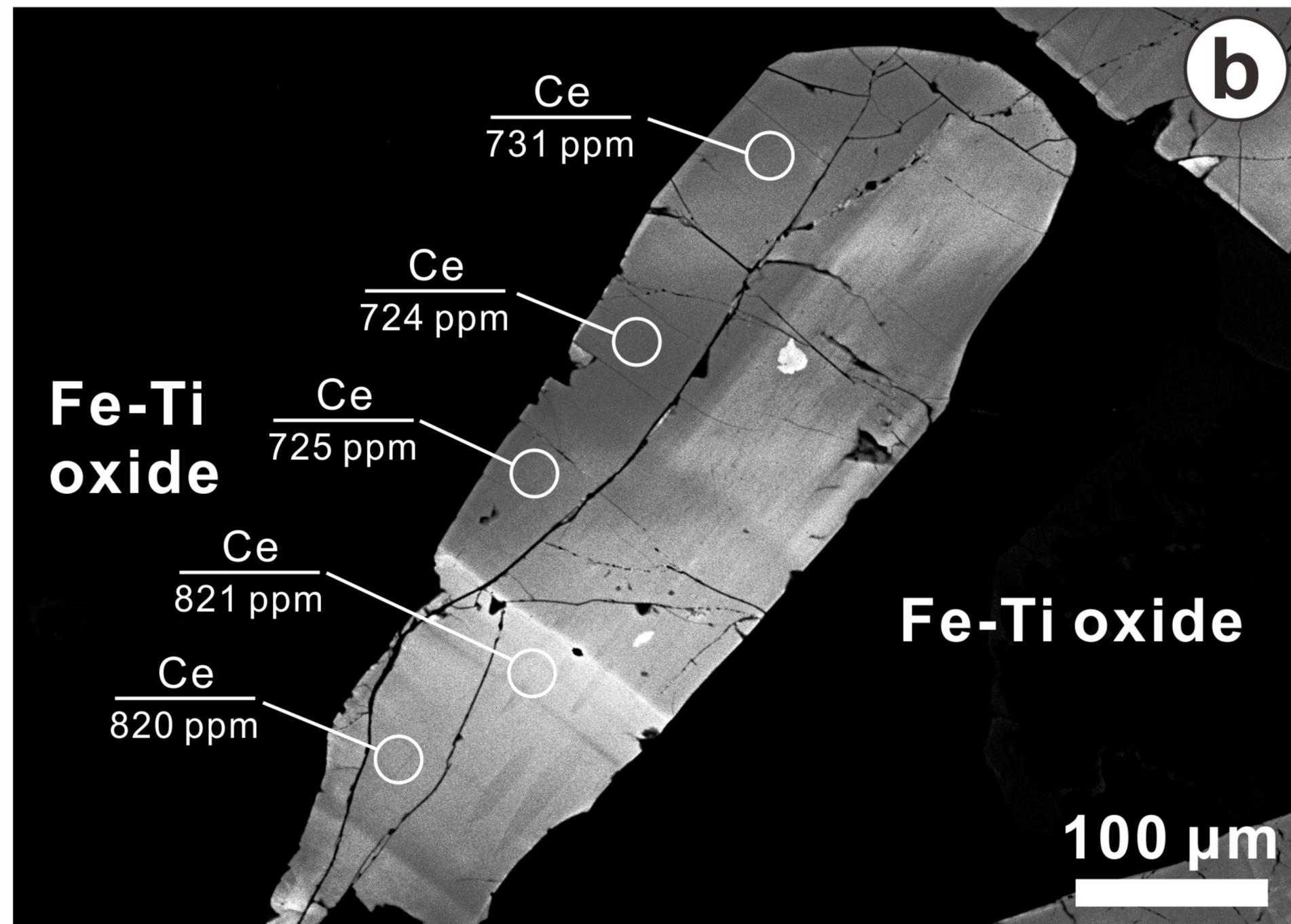
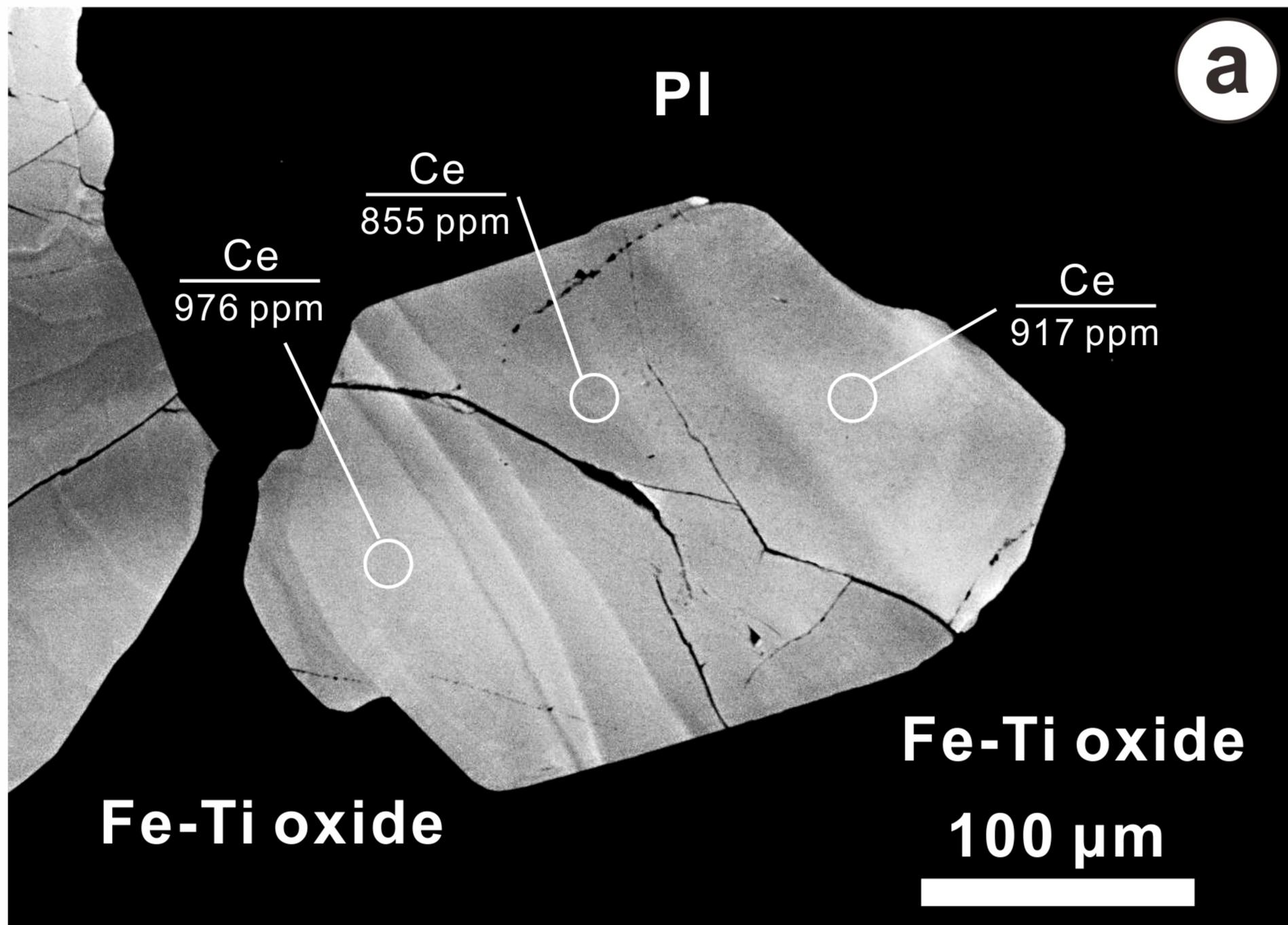
**Fig. 5**

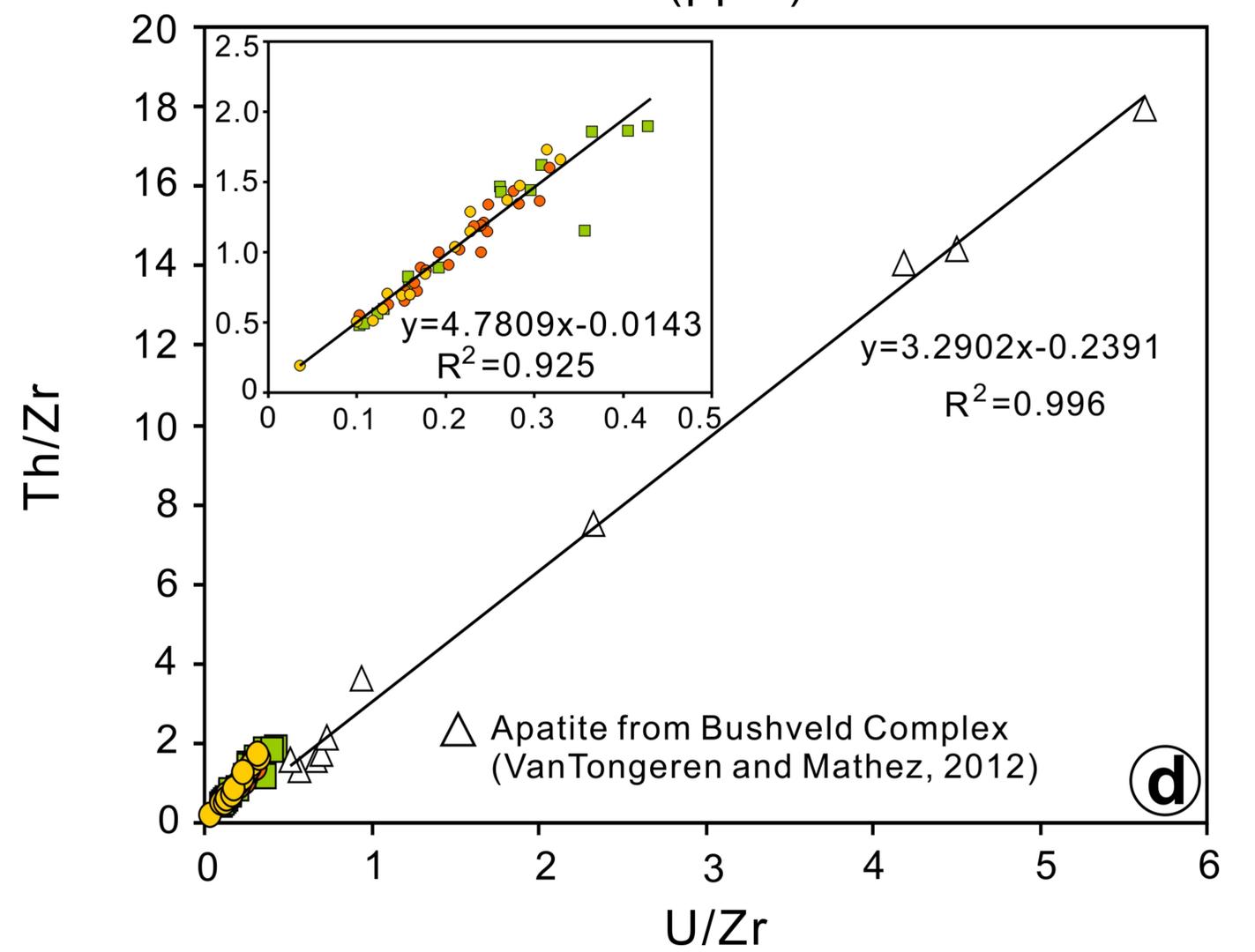
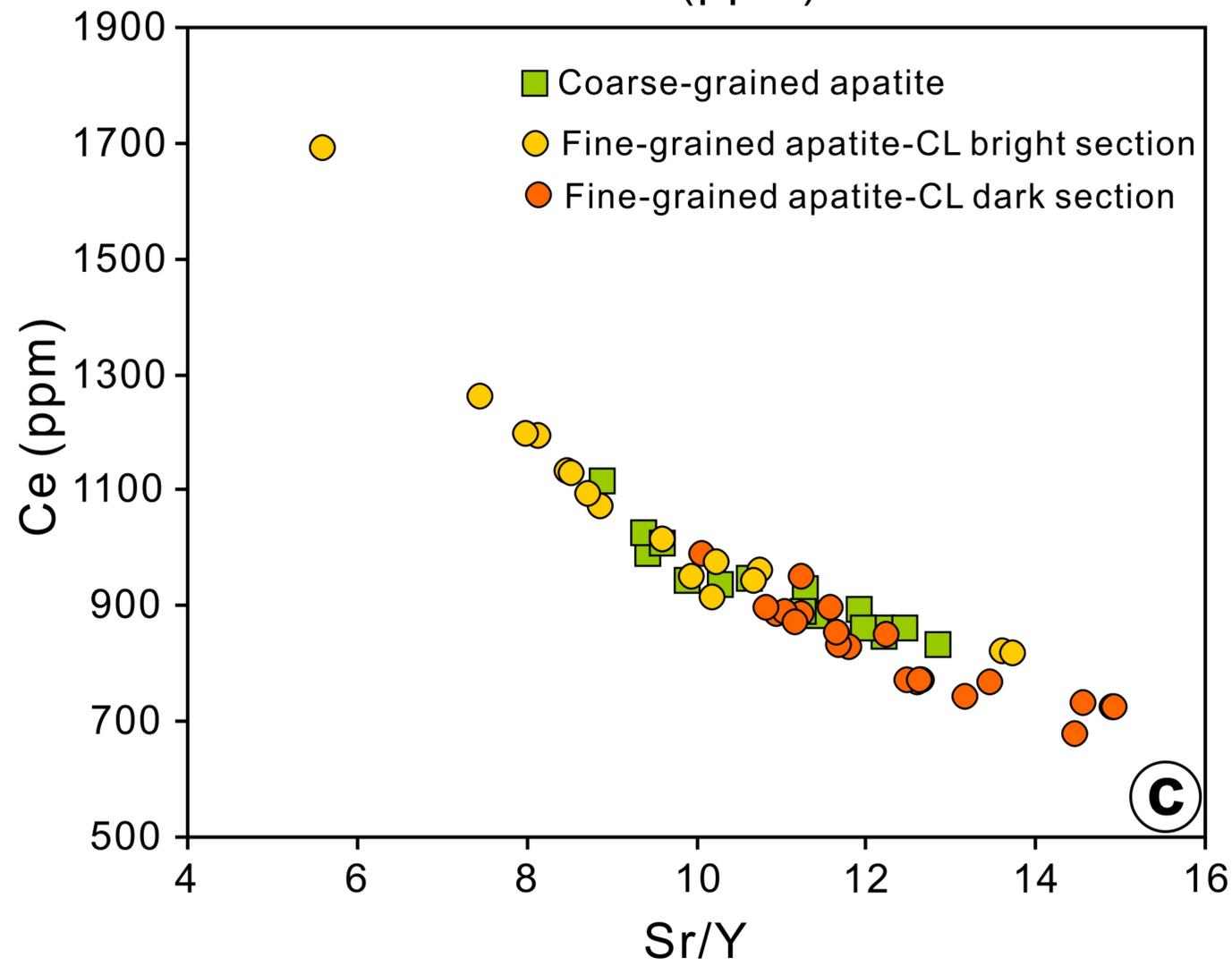
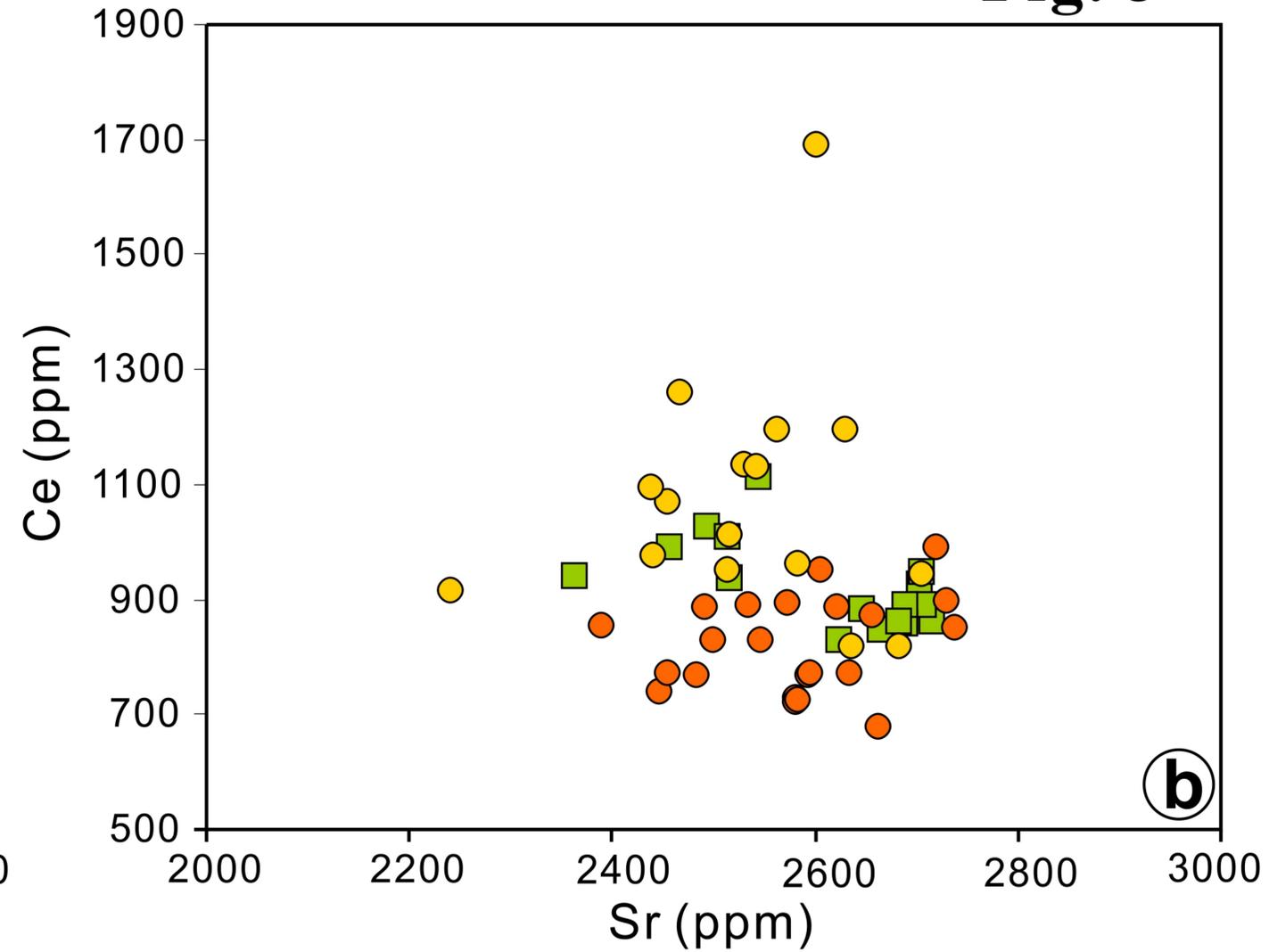
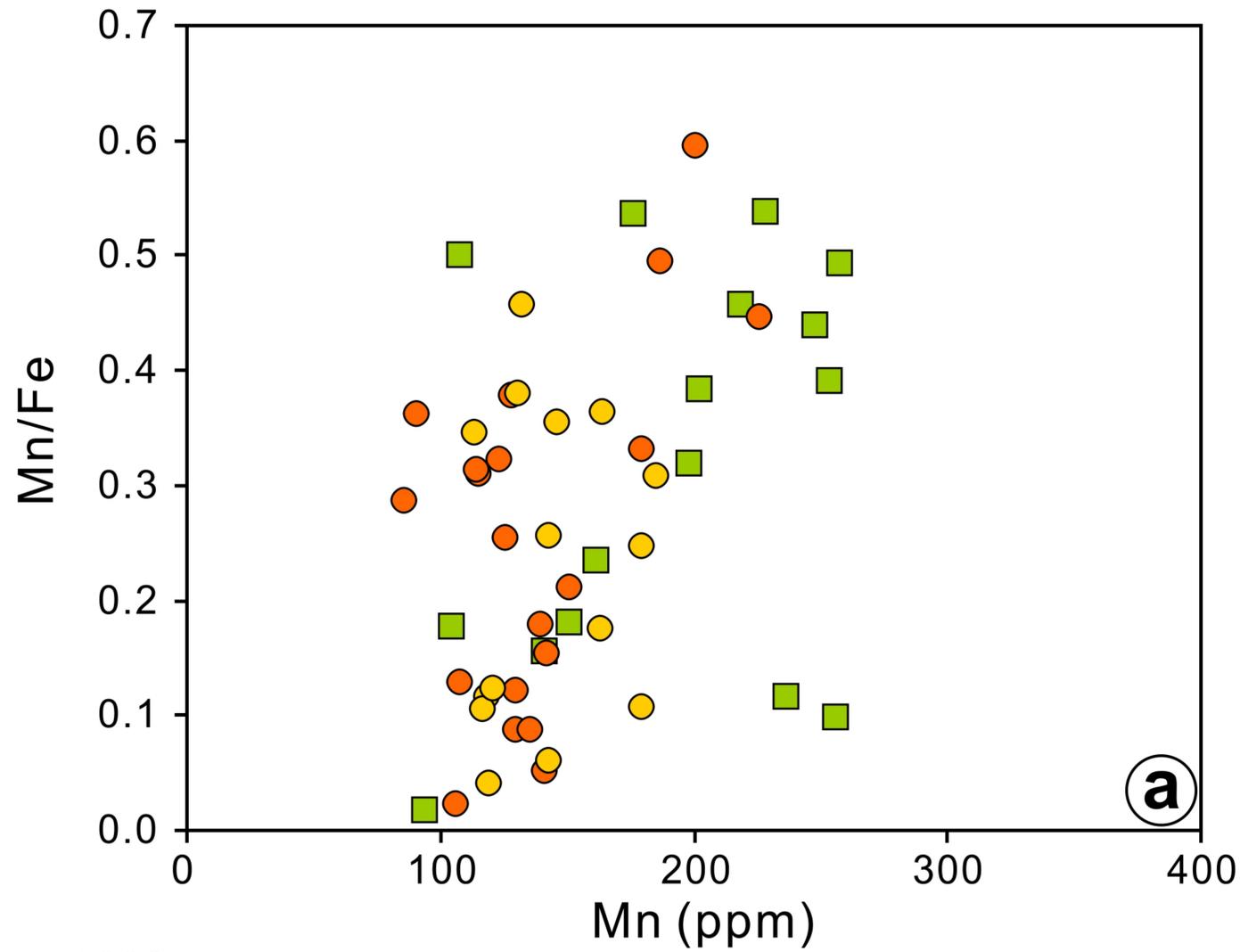


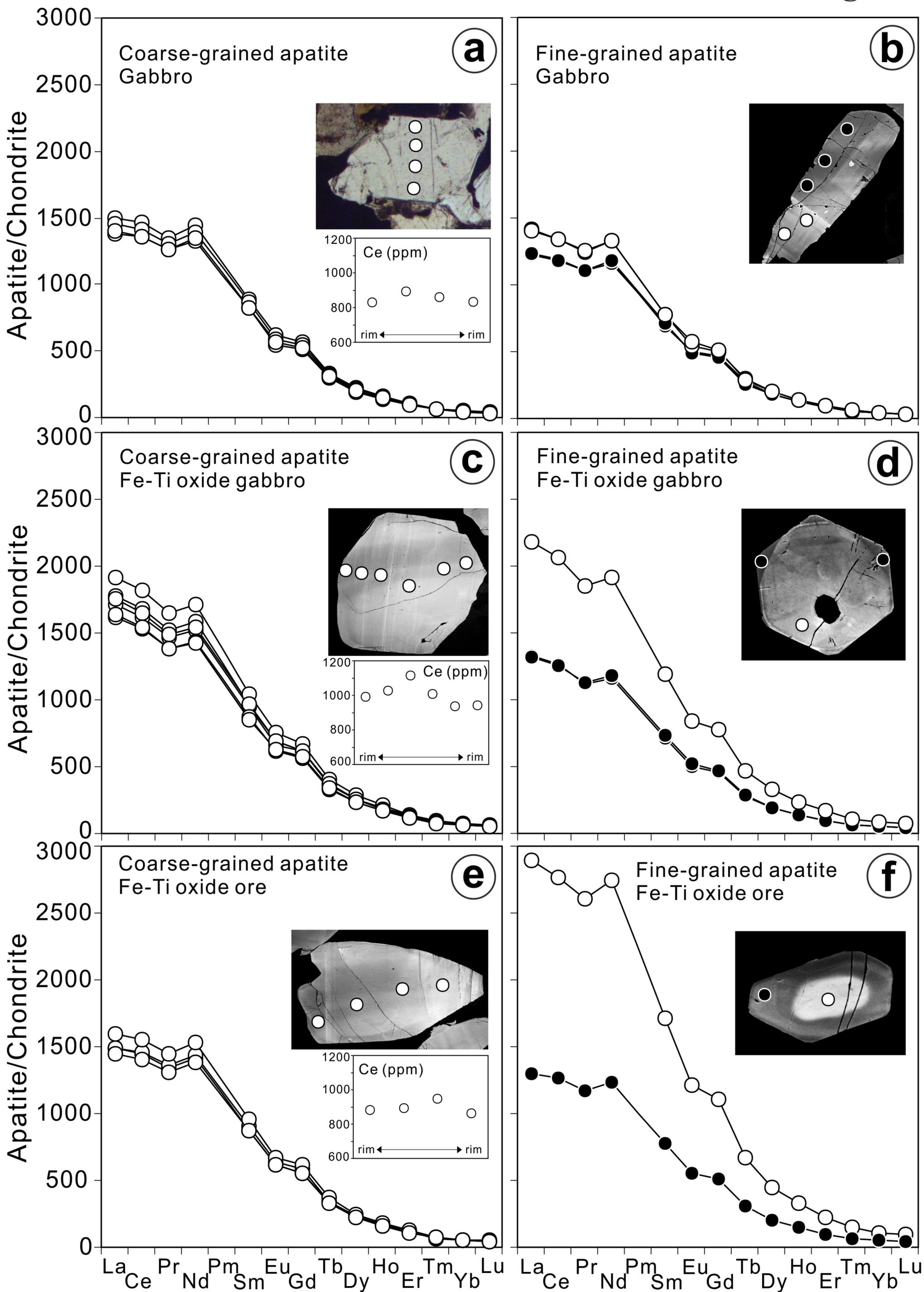
**Fig. 6**



**Fig. 7**



**Fig. 8**

**Fig. 9**

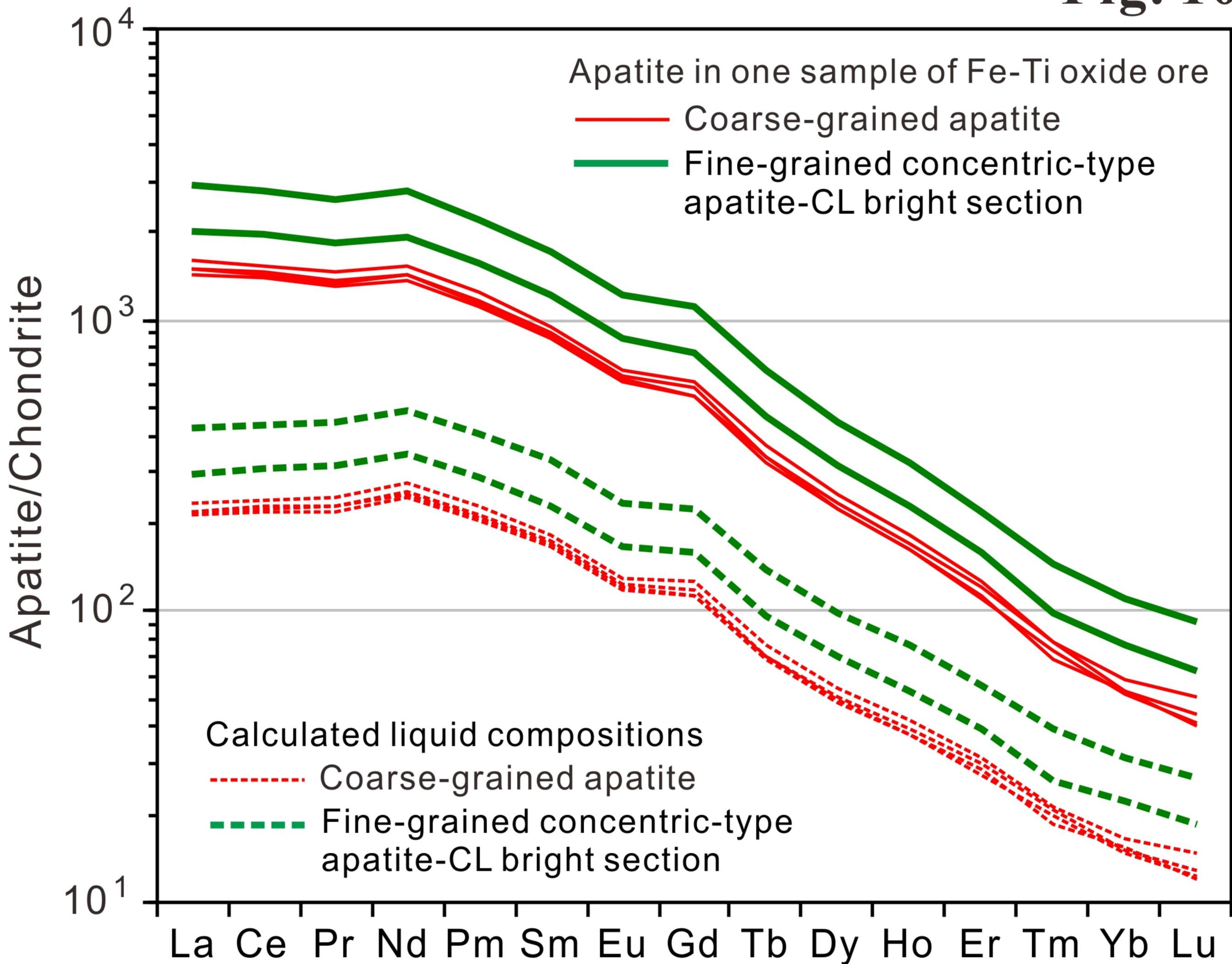
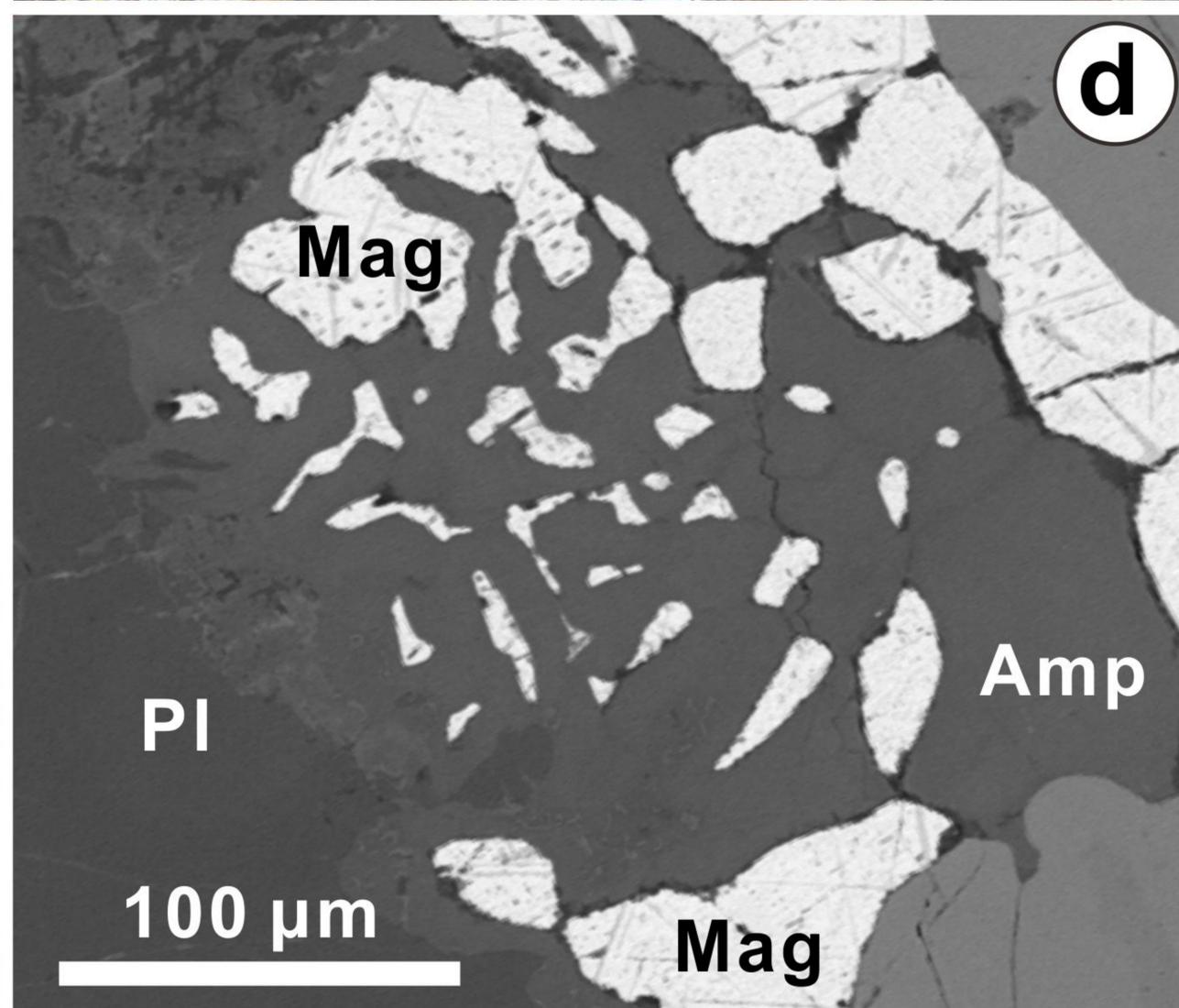
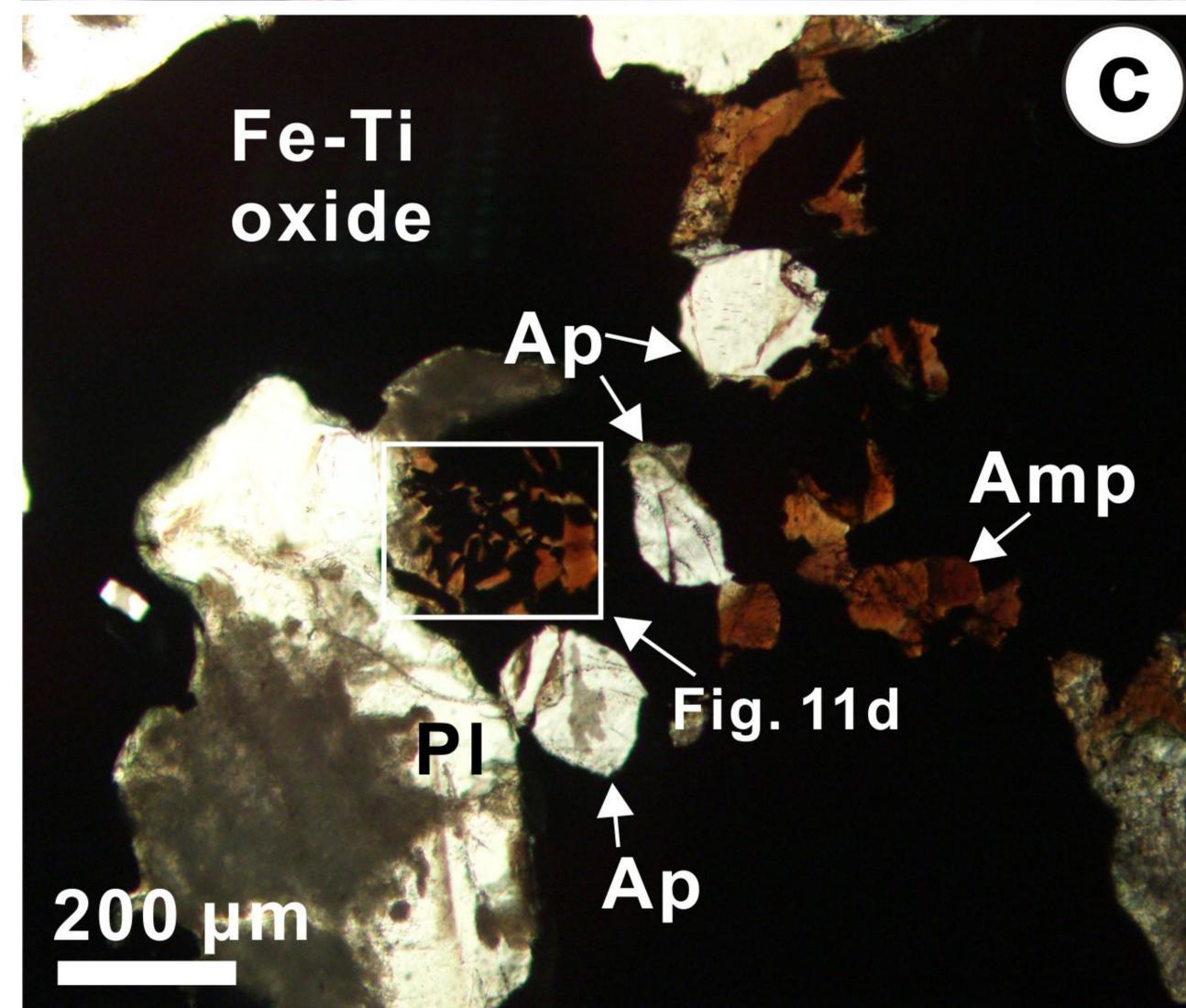
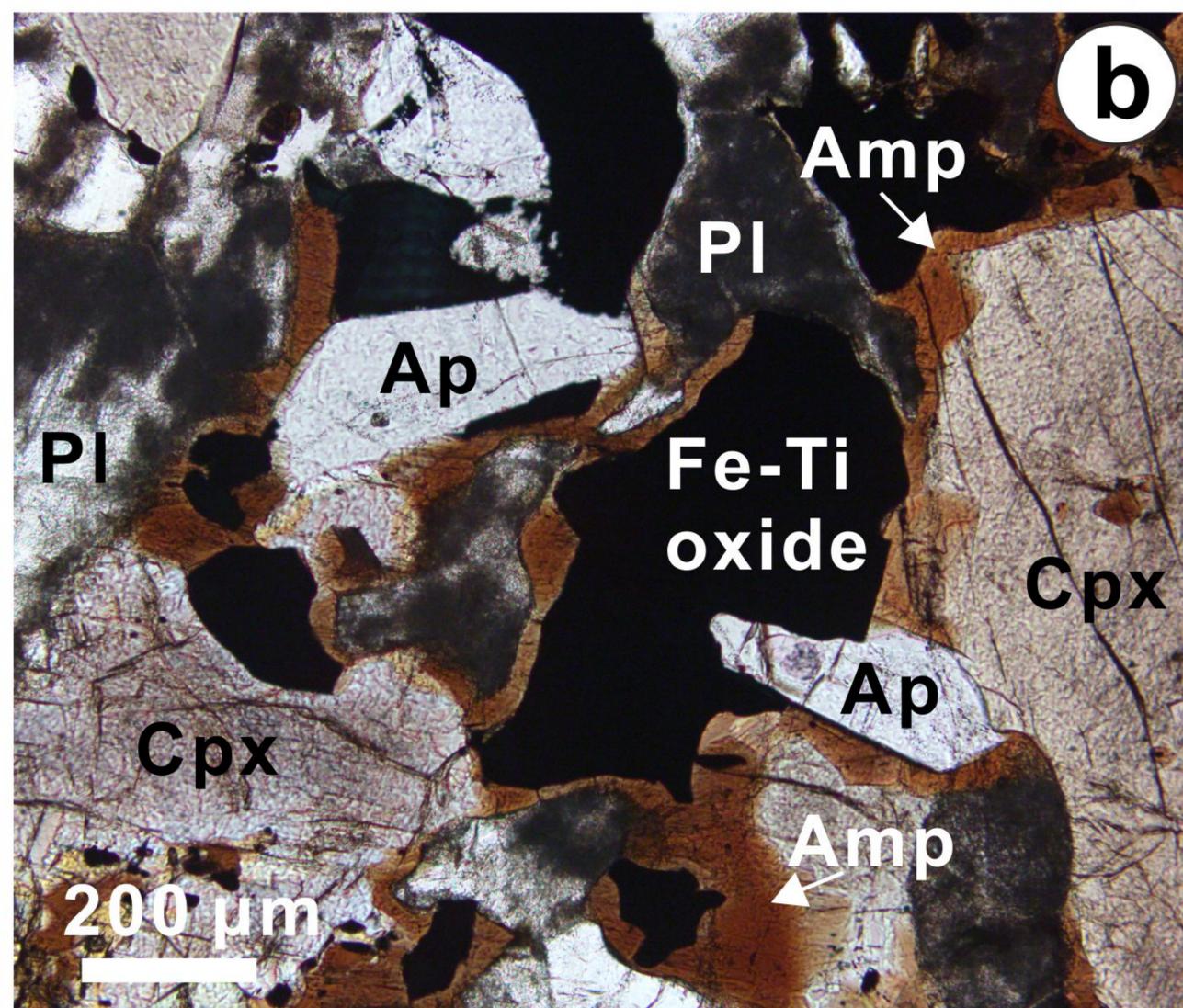
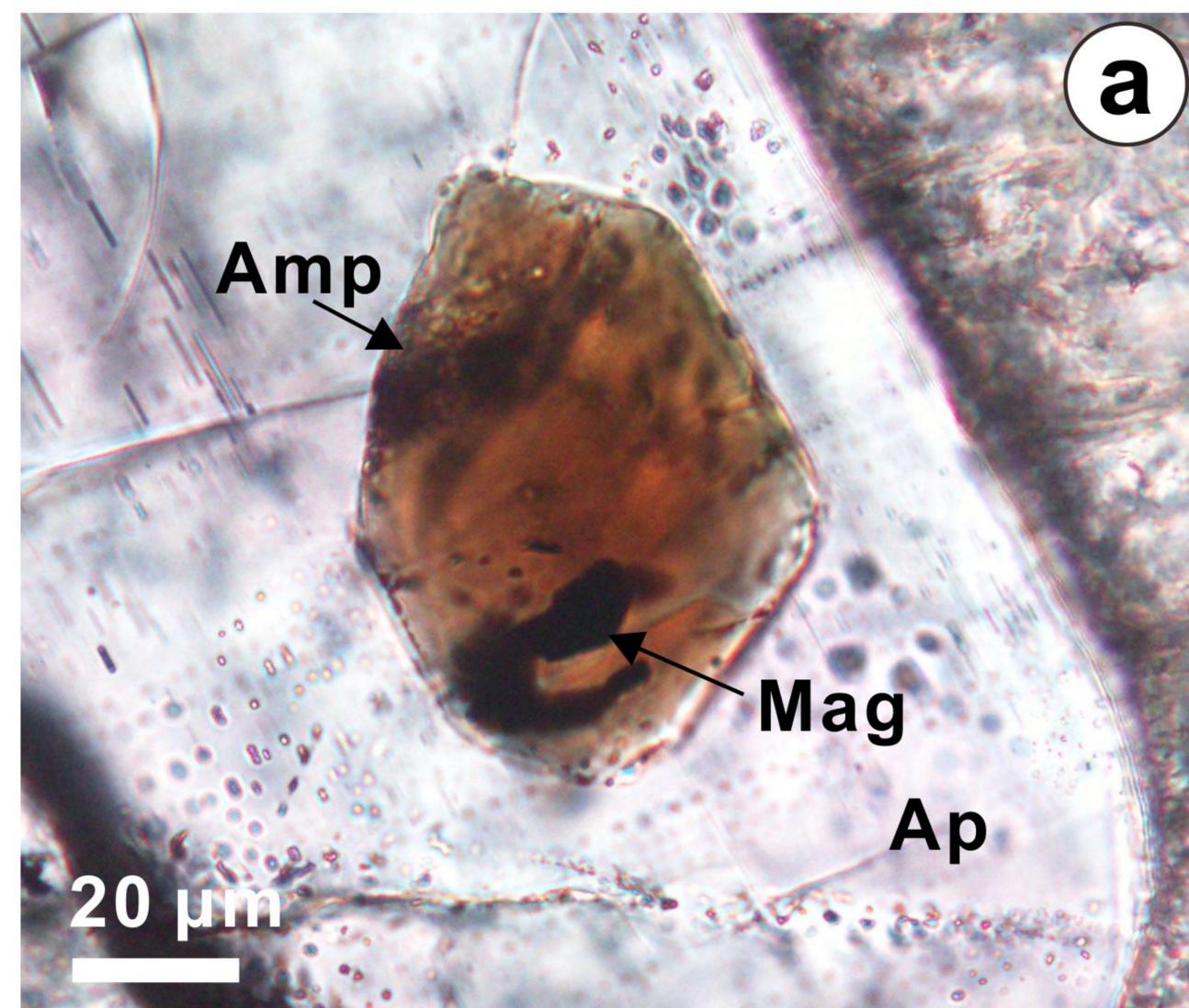
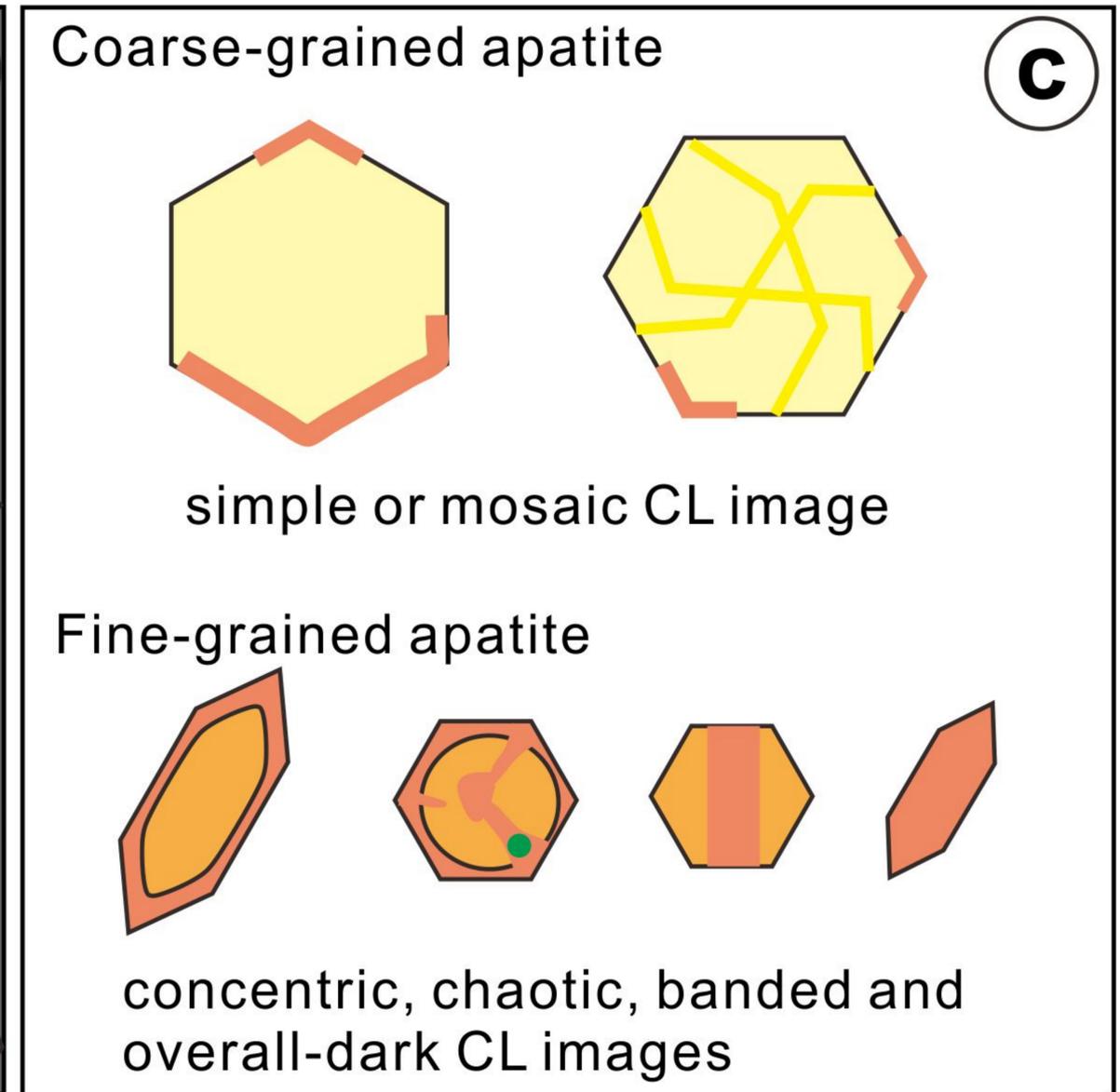
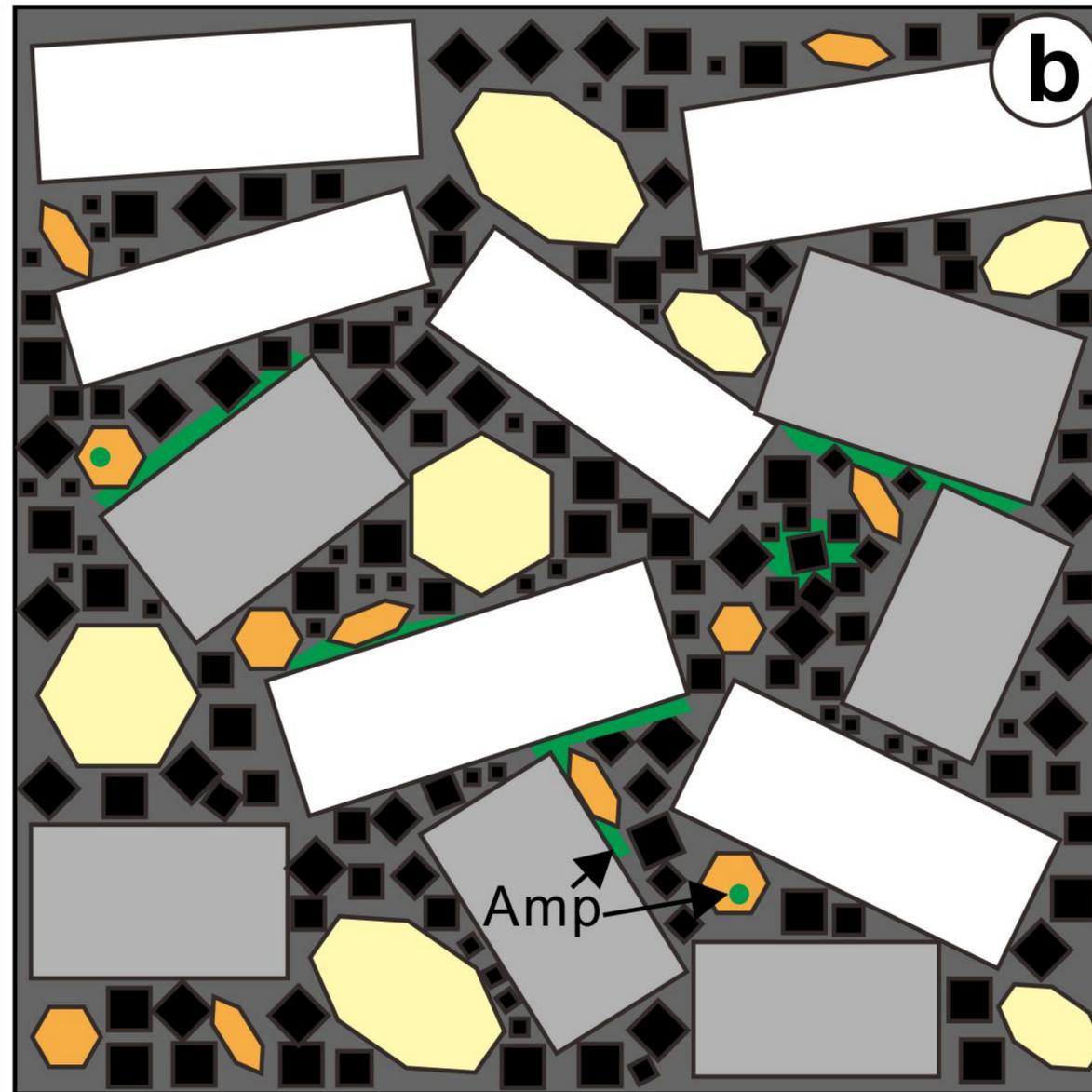
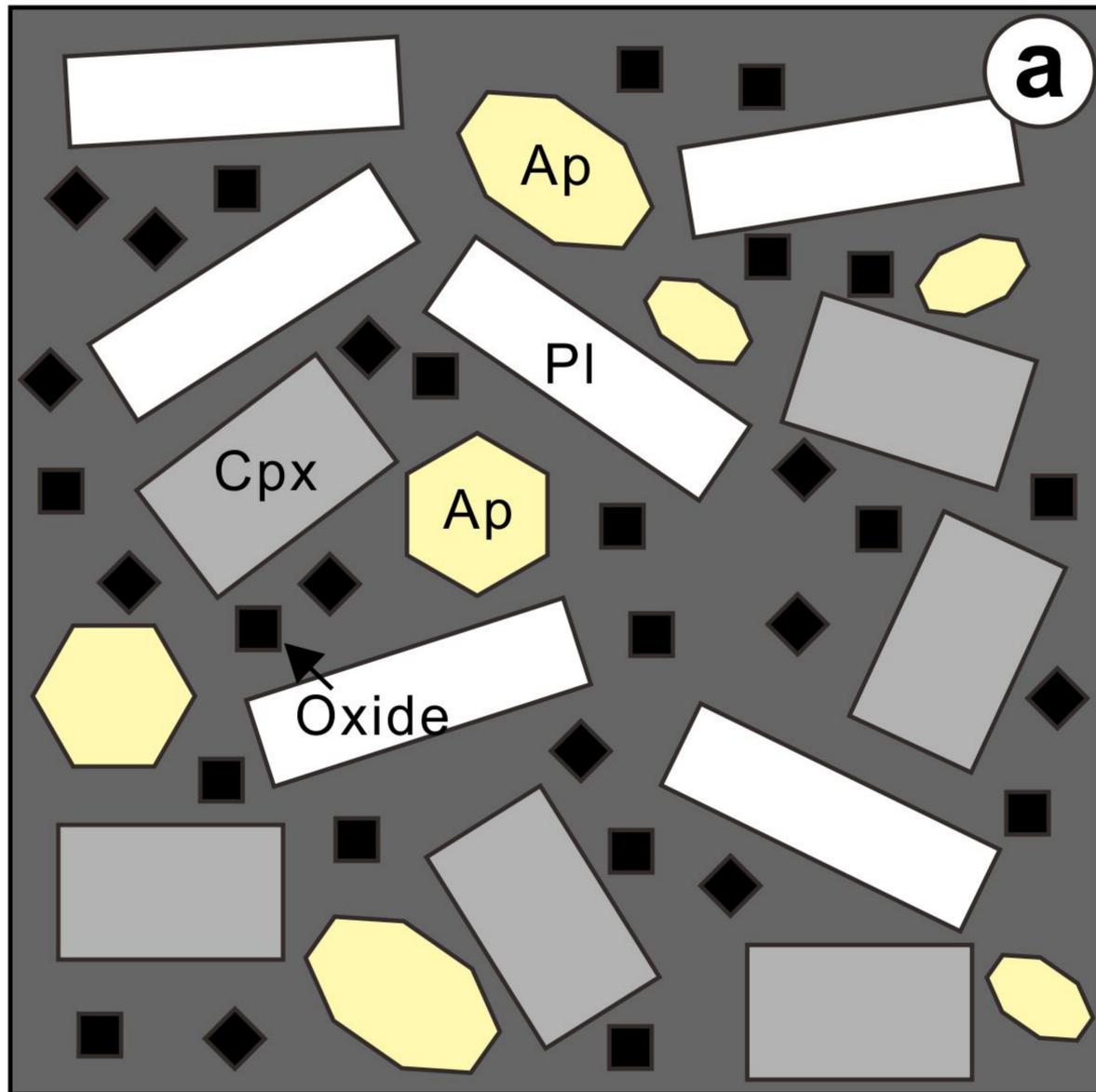
**Fig. 10**

Fig. 11





Early crystallization of apatite  
 (i) intermediate REE  
 (ii) intermediate Sr/Y

Apatite crystallized from interstitial liquid  
 (i) high REE  
 (ii) low Sr/Y  
 (iii) contain amphibole inclusion

Apatite after fluid metasomatism  
 (i) low REE  
 (ii) high Sr/Y  
 (iii) diverse CL images