

1 Revision 1

2 Identifying xenocrystic tourmaline in Himalayan leucogranites

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13 **ABSTRACT**

14 Tourmaline is a common autocrystic mineral in granitic and pegmatitic rocks that records
15 valuable information on the physicochemical evolution of magmas. However, xenocrystic
16 tourmaline that does not crystallize from host magmas are also common but seldom reported,
17 and notoriously difficult to identify. Here, autocrystic (Tur G) and xenocrystic (Tur P)
18 tourmalines are identified in two-mica granites and granitic pegmatites from the Cuonadong
19 leucogranites, eastern Himalaya. Electron backscatter diffraction (EBSD), coupled with electron-
20 probe micro-analysis (EPMA) and laser ablation ICP-MS analyses (LA-ICP-MS), is used to
21 discriminate xenocrystic from autocrystic tourmaline. Although both tourmalines have slightly
22 different chemical compositions, the differences are not sufficient for their unambiguous

23 discrimination. However, EBSD systematically shows complex intra-crystalline orientations and
24 deformation for xenocrystic grains, and undeformed crystal lattices are predominant in
25 autocrystic grains. EBSD could be a useful tool to identify the origin of tourmaline in granitic
26 rock, particularly useful when geochemical analyses and/or geochronological measurements are
27 impractical.

28 **KEY WORDS:**

29 Autocrystic and xenocrystic tourmaline, boron isotopes, Cuonadong leucogranites, electron
30 backscattered diffraction analyses, Himalayan granites

31 **INTRODUCTION**

32 Tourmaline occurs in granitic rocks and related pegmatites and mineral deposits (van
33 Hinsberg et al., 2011a, b) and is stable over wide ranges of pressures (P) and temperatures (T)
34 (Dutrow and Henry, 2011). It accommodates a diversity of elements and has extremely low rates
35 of intracrystalline diffusion (van Hinsberg et al., 2011a, b). This makes tourmaline a valuable
36 archive of the physicochemical conditions under which it grew (Marschall and Jiang, 2011;
37 Slack and Trumbull, 2011). As a result, tourmaline has been widely used to study magmatic-
38 hydrothermal evolution (e.g. Yang et al., 2015; Launay et al., 2018), ore-forming processes (e.g.
39 Slack and Trumbull, 2011; Su et al., 2019), fluid-rock interactions (e.g. Trumbull et al., 2009;
40 Berryman et al., 2017), and subduction-zone fluid compositions (van Hinsberg et al., 2017).
41 These studies combined macro-textural observations with geochemical data to distinguish
42 between tourmaline populations. In this study, compositional and isotopic information from the
43 techniques EPMA, LA-ICP-MS and multiple collector LA-ICP-MS (LA-MC-ICP-MS) analyses
44 is insufficient to discriminate between tourmaline populations that are suspected to have different
45 origins. However, micro-textural and crystallographic data from EBSD studies discriminates

46 between two populations, one of which is proposed to be xenocrystic, and the other, autocrystic.

47 **SAMPLE CONTEXT**

48 The collision between India and Asia occurred at ca. 60 Ma and the subsequent breakoff of
49 the subducted Neo-Tethyan slab occurred at ca. 45 Ma. However, intra-continental processes that
50 followed collision occurred at the Miocene (Wu et al., 2019; Han et al., 2020). The Cuonadong
51 leucogranites are located in the easternmost section of the Tethyan Himalaya, and are related to
52 the Indian plate rollback and breakoff during the intra-continental processes (DeCelles et al.,
53 2011), and are associated with Be-Sn-W mineralization (Cao et al., 2021). The leucogranites
54 consist mainly of two-mica granites, muscovite granites and granitic pegmatites, and were
55 produced by multistage anatexis during the Tertiary (45–16 Ma; Cao et al., 2021; Fan et al.,
56 2021). The two-mica granites and granitic pegmatites (Fig. 1A) are the main hosts of tourmaline,
57 lack apparent deformation, and yielded comparable monazite U-Th-Pb crystallization ages of
58 20.3 ± 0.2 and 20.5 ± 0.1 Ma (Han et al., 2020), respectively. The comparable ages, together with
59 their similar mineral assemblages consisting of plagioclase, k-feldspar, muscovite \pm tourmaline
60 and the occurrence of pegmatite veins in the two-mica granite, without clear boundaries between
61 them, as well as Zr/Hf in zircons, suggest that the Miocene two-mica granite evolved to the
62 Miocene granitic pegmatite by fractional crystallization (Han et al., 2020; Xie et al., 2020).
63 However, two xenocrystic monazite grains yielding older ages of 45.2 ± 1.6 and 43.9 ± 1.4 Ma
64 were also identified in the two-mica granites (Han et al., 2020). Tourmaline crystals from the
65 two-mica granite (Tur G; Fig. 1B) are small (1–3 mm), coexist with quartz, muscovite,
66 plagioclase, and K-feldspar, and occur as disseminated inter-granular euhedral needles and were
67 considered as autocrystic crystals crystallized from the Miocene two-mica granite. They also
68 commonly show core-rim zoning and are thus subdivided into Tur G-cores and Tur G-rims. By

69 contrast, tourmaline crystals from the pegmatites (Tur P; Fig. 1C) are large (3–8 cm) and are
70 systematically separated by quartz \pm feldspar-bearing fractures (Fig. 1C). Quartz \pm feldspar-
71 bearing fractures traversing tourmaline crystals may also be coeval with the evolution of the host
72 granitoids and such tourmaline crystals may also be autocrystic ones. Any dissolution or
73 overgrowth texture was not found on the Tur P. However, the Tur P previously yielded an
74 $^{40}\text{Ar}/^{39}\text{Ar}$ mini-plateau age of ca. 43 Ma, similar to that of the xenocrystic monazite, also
75 indicating a xenocrystic origin, 20 My. earlier than the Miocene pegmatite (Han et al., 2020).
76 Some other minerals such as quartz and/or feldspar may also be xenocrystic.

77 ANALYTICAL METHODS

78 The major element compositions of tourmalines were determined at the State Key
79 Laboratory of Geological Process and Mineral Resources, China University of Geoscience,
80 Wuhan, China (GPMR) using a JEOL JXA-8230 Electron Probe Micro Analyzer (EPMA) with
81 an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 5 μm . The
82 counting time for peaks and backgrounds were 10 s and 5 s, respectively, for all elements. The
83 following standards were used: hornblende for Si, Mg and Ca, rutile for Ti, cordierite for Al,
84 fayalite for Fe, rhodonite for Mn, jadeite for Na, sanidine for K and topaz for F. Data were
85 corrected on-line using a ZAF (atomic number, adsorption, fluorescence) correction procedure.
86 Tourmaline structural formulae were calculated by normalizing to 15 cations per formula unit
87 (pfu) in the tetrahedral and octahedral sites (T + Z + Y) (Henry and Dutrow, 1996), based on the
88 general formula $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$, where X = Na, Ca, K, vacancies; Y = Fe, Mg, Mn, Ti,
89 Al; Z = Al, Mg; T = Si, Al; B = B; V = OH^- and O^{2-} ; W = OH^- , F^- and O^{2-} . During the calculation,
90 we assume 3 B pfu, ignoring any tetrahedral B and assume there is no O at V site and calculating
91 Fe^{2+} vs Fe^{3+} by charge balance. Such calculation yields the minimum amount of Fe^{3+} in the

92 tourmaline. The maximum estimate of Fe^{3+} is calculated by treating all Fe as ferric and
93 calculating the ratio of O/OH at the VW sites. In such calculation, $V + W = \text{OH} + \text{O} + \text{F} = 4$
94 (Berryman et al., 2017). The method yielding the minimum amount of Fe^{3+} in the tourmaline is
95 more realistic because it results in the presence of both Fe^{2+} and Fe^{3+} in the normalized
96 tourmaline formula.

97 Trace element compositions were obtained on the same spots at the In situ Mineral
98 Geochemistry Lab, Ore Deposit and Exploration Centre (ODEC), Hefei University of
99 Technology, China, using an Agilent 7900 Quadrupole ICP-MS coupled to a Photon Machines
100 Analyte HE 193 nm ArF Excimer laser ablation system. The ablation protocol was performed
101 using a laser diameter of 44 μm with a repetition rate of 8 Hz and an energy of $\sim 4 \text{ J/cm}^2$.
102 Measurements were conducted during 40 s after 20 s of gas blank. Standard reference materials
103 BCR-2G and NIST SRM 610 and 612 glasses were analyzed after every eight spot analysis. The
104 raw data was processed using the procedure of Berryman et al. (2017), and using the Iolite data
105 processing software. The concentration of major elements (Na, Ca, K, Mg, Fe, Si) was also
106 measured and used to normalize the data to 15 cations at the Y, Z, and T sites, as was done with
107 the EMPA data. Such method of normalization avoids relying on a nonideal internal standard.

108 Boron isotopic compositions were measured on the same spots or nearby area at the Beijing
109 Createch Testing Technology Co., Ltd, Beijing, China, using a Neptune Plus MC-ICP-MS and
110 ESI NWR213 laser-ablation system. The ablation protocol was performed with a diameter of 60
111 μm at 10 Hz with energy of $\sim 4 \text{ J/cm}^2$ for 40 s after measuring the gas blank for 20 s. Carrier gas
112 consisting of mixed He, Ar, and N was used to carry the aerosols to the plasma. The ratios of
113 $^{11}\text{B}/^{10}\text{B}$ in tourmalines and standards were collected statically and simultaneously using two
114 Faraday cups. The standard sample-standard bracketing (SSB) method and the tourmaline

115 standard IAEA B4 ($\delta^{11}\text{B} = -8.71\%$, Tonarini et al., 2003) were adopted as external standards to
116 calibrate the instrument. Through repeated analysis of tourmaline reference material IMR RB1
117 ($\delta^{11}\text{B} = -12.96 \pm 0.97\%$, Hou et al., 2010), the SSB method was used to evaluate the analytical
118 quality and instrument mass fractionation (IMF). Instrumental mass fractionation (IMF) and
119 analytical quality were assessed by replicate analysis of tourmaline reference materials schorl
120 (HS #112566) from the Harvard Mineralogical Museum (Dyar et al., 2000). The similarity of
121 IMF values (Table S3) determined for the tourmaline standards demonstrates a lack of significant
122 chemical matrix effect with our analytical setup. The analytical precision was estimated to be
123 better than 0.5‰ based on replicate analyses of monitored tourmalines.

124 The crystallographic orientation of tourmaline was determined using an Oxford Instruments
125 HKL Nordlys II EBSD detector and AZtecHKL 5.0 software coupled to a ZEISS Sigma 300 VP
126 Field Emission scanning electron microscope (SEM), housed in the School of Earth Sciences,
127 China University of Geoscience, Wuhan, China. Working conditions were as follows: 20 kV
128 accelerating voltage, working distance of ~18 mm and 70° sample tilt under low vacuum
129 conditions (20 Pa of N gas) to avoid excessive electron charging. Orientation maps were
130 acquired in automatic mode with a step size of 41 μm for Tur-P and 5 μm for Tur-G. To assure
131 data quality, only those measurements with mean angular deviation values below 1.0° (between
132 detected and 199 simulated EBSD patterns) were accepted for analyses. The EBSD data clean up
133 and post-processing were analyzed using Oxford Instruments HKL Channel5 software. More
134 details can be found in Liu et al. (2021).

135 **RESULTS**

136 **Tourmaline Compositions**

137 Both the Tur G (including cores and rims) and Tur P tourmalines belong to the alkali group
138 of the X-site occupancy classification diagram (Henry et al., 2011a, b) (Fig. 2A), and plot in the
139 field of Li-poor granitoids and associated pegmatites and aplites in the diagrams using the molar
140 Al-Fe-Mg subsystem of Henry and Guidotti (1985) and Henry and Dutrow (2018) (Figs. 2B and
141 2C). All tourmalines plot in the schorl (Fe-rich) field (Fig. 2D), with Mg/(Mg+Fe) and
142 Na/(Na+Ca) ratios ranging from 0.19–0.24 and 0.93–0.98, respectively, for the Tur G-cores,
143 0.10–0.16 and 0.93–0.98, respectively, for the Tur G-rims and 0.19–0.30 and 0.82–0.96,
144 respectively, for the Tur P (Table S1). Relative to Tur G, the Tur P has higher Mg, Ti, and Mg#,
145 as well as more vacancies in the X-site (Table S1). The Fe vs. Mg diagram indicates the
146 important influence of $(X_{\square}Al)(NaMg)_{-1}$ substitution for the Tur P whereas the Tur G was
147 influenced by the $Fe^{2+}Mg_{-1}$ and $(X_{\square}Al)(NaMg)_{-1}$ substitution (Fig. 2E). Meanwhile, the Al_{tot} vs.
148 X_{\square} diagram indicates the influence of $(X_{\square}Al_2)(CaMg_2)_{-1}$ substitution (Fig. 2F).

149 Most trace elements in tourmalines have median concentrations ranging from 0.1 to tens of
150 ppm, in addition to slightly higher concentrations of Cr and Li (Fig. 3; Table S2). The Tur G has
151 lower concentrations of Be, Sc, V, Co, Cr, Ni, Sr, Ta and higher concentrations of Li, Sn than the
152 Tur P (Fig. 3). All tourmalines have very low REE concentrations, and enriched chondrite-
153 normalized light REE (LREE) compared to heavy REE (HREE) (Table S2).

154 The Tur G tourmalines have higher $\delta^{11}B$ values than the Tur P tourmalines (Fig. 4A). The
155 $\delta^{11}B$ values range from -8.1 to -7.3 ‰ (average -7.3 ‰, n=26) in Tur G, and from -10.6 to -9.2
156 ‰ (average -10.1 ‰, n=47; Table S4) in Tur P. Both families of tourmaline plot within the fields
157 of worldwide granites/pegmatites, continental crust, and mantle and mid-ocean ridge basalts
158 (MORB), although a part of the Tur P plot outside the field of mantle and MORB (Fig. 4B).

159 These ranges in $\delta^{11}\text{B}$ values are relatively narrow and overlap significantly, so the present
160 differences in $\delta^{11}\text{B}$ values are inconclusive in terms of B sources.

161 **Crystallographic Features of Tourmalines**

162 Coexisting grains of Tur G show no clear relations in crystallographic orientations on the
163 orientation map using inverse pole figure color scheme (Fig. 5A) and the pole figure for
164 crystallographic orientations (Fig. 5B). The texture component map of grain #G1 shows very
165 limited intracrystalline misorientation of $0\text{--}3^\circ$ with respect to the reference orientation (yellow
166 cross; Fig. 5C). The total cumulative misorientation across the #G1 grain is $\leq 2^\circ$ along the
167 orthogonal a-a' and b-b' cross-sections (Fig. 5D).

168 Although the Tur P tourmaline also coexists with quartz and minor feldspars, it is shattered
169 into fragments of irregular shapes having grain sizes ranging from <1 mm to 1 cm (Fig. 1C).
170 Numerous tourmaline grains are strongly variegated in color and contain abundant
171 intracrystalline low angle (2° and 5°) boundaries in the crystallographic orientation EBSD map
172 (Fig. 6A). Several relationships exist in the crystallographic orientations amongst independent
173 tourmaline grains. For example, the #P1 and #P2 grains are parallel to the $\{10\bar{1}0\}$ plane, and the
174 #P3 and #P4 grains have very similar orientations, as shown in the equal area upper hemisphere
175 projection orientation (UHPO) pole map (Fig. 6B). The Tur P grains additionally display
176 intragranular misorientation of up to 10° with respect to the reference orientation (yellow cross;
177 Fig. 6C). The misorientation profiles along cross-sections x-x' (#P1) and y-y' (#P3) (Fig. 6D)
178 show maximum cumulative misorientations reaching up to $\sim 12^\circ$, with misorientations between
179 adjacent points reaching as much as $\sim 8^\circ$.

180 **DISCUSSION AND IMPLICATIONS**

181 **Comparison of Tur G and Tur P Tourmalines**

182 Before discussing the tourmaline geochemistry, it is important to restate two facts: 1) the
183 Miocene two-mica granite evolved to the Miocene granitic pegmatite by fractional
184 crystallization; 2) the Tur G are autocrystic crystals crystallized from the Miocene two-mica
185 granite whereas the Tur P yielding an $^{40}\text{Ar}/^{39}\text{Ar}$ mini-plateau age of ca. 43 Ma contained in the
186 Miocene pegmatite as xenocrystic crystals (Han et al., 2020). Given the small tourmaline-melt
187 partition coefficients for most elements at high temperatures, tourmaline may efficiently be used
188 to document the evolution of the magmas (Balen and Broska, 2011; Drivenes et al., 2015; Roda-
189 Robles et al., 2015). The Tur G coexist with quartz, muscovite, plagioclase, and K-feldspar, and
190 occur as disseminated inter-granular euhedral needles, indicating that they are autocrystic
191 crystals in the two-mica granite (Figs. 1B and 5A). However, the origin of the Tur P remains to
192 be uncertain as they were xenocrysts in the pegmatite and no more information were known
193 except for that they were separated by quartz \pm feldspar-bearing fractures. Here, both the Tur G
194 and the Tur P tourmalines plot within the field of Li-poor granitoids and associated pegmatites
195 and aplites using the molar Al-Fe-Mg subsystem of Henry and Guidotti (1985) and Henry and
196 Dutrow (2018) (Figs. 2B and 2C). This suggests that both families of tourmaline likely formed in
197 magmatic environments. The tourmalines in our study have compositions that are similar to the
198 magmatic tourmalines of the Gurla Mandhata tourmaline leucogranite, Northwest Himalaya and
199 the Nyalam leucogranite, South Tibetan Himalaya (Figs. 2A and 2B; Yang et al., 2015; Cheng et
200 al., 2021), further suggesting the magmatic origin of the Cuonadong tourmalines.

201 The $\delta^{11}\text{B}$ values of the Tur P and the Tur G both lie in the field of worldwide granites and
202 pegmatites (Fig. 4B). In combination with comparable monazite U-Th-Pb ages of ~ 20 Ma (Han
203 et al., 2020), a previous study of Zr/Hf in zircons concluded that the two-mica granite evolved to
204 the granitic pegmatite by fractional crystallization (Xie et al., 2020). Given that such fractional

205 crystallization is commonly accompanied by fluid exsolution and melt devolatilization (second
206 boiling), and since ^{11}B is preferentially partitioned in the fluid phase over the melt during
207 devolatilization (Jiang et al., 1998; Hervig et al., 2002; Maner and London, 2018), the lighter
208 $\delta^{11}\text{B}$ values in the pegmatite-hosted Tur P (avg. -10.1 ‰) than the two-mica granite-hosted Tur
209 G (avg. -7.3 ‰) (Fig. 4A) could *a priori* be explained by fractional crystallization and gradual
210 devolatilization, which is contrary to the fact that the Tur G are autocrystic crystals crystallized
211 from the Miocene two-mica granite whereas the Tur P as xenocrystic crystals crystallized from
212 an Eocene pegmatite.

213 In a closed system, major elements in tourmalines are usually controlled by intensive
214 thermodynamic parameters such as P and T whereas trace element abundances are normally
215 governed by partitioning amongst the different phases in presence (e.g., Van Hingsberg, 2011a,
216 b; Klemme et al., 2011). However, in certain circumstances, the major and trace element
217 concentrations in tourmaline were both controlled by intensive thermodynamic parameters
218 coupled with substitution mechanisms, as correlations occurred between trace and major
219 elements such as $\text{Fe}/(\text{Fe}+\text{Mg})$ or $\text{Ca}/(\text{Ca}+\text{Na})$ (Marks et al., 2013; Harlaux et al., 2020; Zhao et
220 al., 2021). Here, the Tur G are relatively enriched in Li and Sn, whereas the Tur P have higher
221 contents of Be, Sc, V, Co, Cr, Ni, Sr and Ta (Fig. 3), but no statistically valid correlations are
222 identified between $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Ca}/(\text{Ca}+\text{Na})$ on the one hand, and most trace elements on the
223 other hand (Figs. 7, 8). The absence of statically valid correlations between trace and major
224 elements preclude the influence of intensive thermodynamic parameters coupled with
225 substitution mechanisms on the trace elements concentrations in tourmalines. The higher
226 concentrations of Li and Sn in the Tur G and the higher contents of Be, Sc, V, Co, Cr, Ni, Sr and
227 Ta in the Tur P are thus taken to reflect the compositional differences of the melt from which

228 they grew, which is in agreement with the assertion that tourmaline chemistry mostly reflect the
229 compositional nature of its host melt (van Hinsberg, 2011a, b). As the Miocene two-mica granite
230 evolved to the Miocene granitic pegmatite by fractional crystallization, the autocrystic
231 tourmalines in the Miocene granitic pegmatite should have higher Li and lower Sc, V, Cr, Ni, Sr
232 contents than Tur G in the Miocene two-mica granite. Then the lower Li and higher Sc, V, Cr,
233 Ni, Sr contents of Tur P further support that they were not autocrystic tourmalines in the
234 Miocene granitic pegmatite.

235 **Discrimination of Autocrystic and Xenocrystic Tourmalines**

236 Although age discrepancies between host magmatic rocks and xenocrystic mineral grains
237 may directly discriminate autocrystic and xenocrystic mineral grains, many minerals are
238 notoriously difficult, and possibly impossible to date, and the age difference obtained for
239 minerals that are possible to date may fall within the range of analytical uncertainty. Furthermore,
240 differences in compositions between different generations of individual minerals are usually
241 inconclusive in terms of age, and may be ambiguous. Although the compositions of the Tur P and
242 Tur G grains are somewhat similar, the crystallographic features of the tourmalines established
243 using EBSD allow discriminating the xenocrystic Tur P from the autocrystic Tur G tourmaline
244 grains.

245 In undeformed granitoids that are not affected by any mechanical disturbances, any
246 autocrystic crystals crystallized from the melt will have very weak intracrystalline deformation
247 and should be randomly distributed, without any obvious mineral orientation. Although the #G1,
248 #G2 and #G3 tourmaline crystals from the two-mica granite occur together in the crystallographic
249 orientation map (Fig. 5A), they appear disseminated throughout the sample in the UHPO pole
250 map (Fig. 5B). Very few low-angle boundaries are observed in these grains (Fig. 5A), and other

251 tourmaline crystals from this sample share similar microstructural characteristics. These euhedral
252 tourmaline crystals with randomly distributed orientations and deficient of low-angle boundaries
253 have very weak intracrystalline deformation (Figs. 5C and 3D) and are typical of autocrystic
254 crystals in undeformed granitoids.

255 By contrast, in the pegmatite, the #P1, #P2, #P3, and #P4 grains clearly display a restricted
256 amount of distinct orientations (Figs. 6A and 4B). According to the UHPO pole map, the #P3 and
257 #P4 grains have a very similar orientation (Fig. 6B), whereas the #P1 and #P2 grains are parallel
258 to one (1010) plane (Fig. 6B). Abundant, discrete low-angle boundaries are observed in the Tur P
259 (Figs. 6A and 6C), which also display cumulative intragranular misorientations reaching up to
260 10° across the grain, and misorientations between adjacent points as large as $\sim 8^\circ$ (Figs. 6C and
261 6D). This is taken to indicate that the xenocrystic “Tur P” were affected by deformation.
262 Combined with textural petrographic information, the relations of orientation between these
263 tourmaline grains indicate that they were likely xenocrysts as a single tourmaline crystal which
264 was subsequently torn apart into multiple fragments during deformation. The EBSD data thus
265 provide quantitative evidence of crystal-plastic and brittle deformation of the Tur P. As the
266 comagmatic Miocene (ca. 20 Ma) two-mica granites and pegmatites were not influenced by later
267 deformation (Fig. 1A), which is here supported by the lack of deformation of the Tur G, the
268 deformation of Tur P highlighted here must have occurred during or before the Miocene
269 magmatism, thus evidencing their xenocrystic origin.

270 **Implications**

271 Isotope geochronology and mineral chemistry may in some cases be incapable of
272 discriminating xenocrystic from autocrystic crystals. Electron backscatter diffraction (EBSD)
273 analyses focusing on intracrystalline deformation and crystallographic relations may nevertheless

274 prove useful and provide critical information discriminating grains of different generations. The
275 EBSD method is applied here for the first time on tourmaline and can be used in conjunction
276 with- and in support of *in situ* geochronology, and may also be used to discriminate xenocrystic
277 from autocrystic grains when geochronology data is not available, or when the age differences
278 are smaller than the related analytical uncertainties.

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284 REFERENCES CITED

- 285 Balen, D., and Broska, I. (2011) Tourmaline nodules: Products of devolatilization within the
286 final evolutionary stage of granitic melt? Geological Society, London, Special Publications,
287 350, 53–68.
- 288 Berryman, E.J., Kutzschbach, M., Trumbull, R.B., Meixner, A., van Hinsberg, V., Kasemann,
289 S.A., and Franz, G. (2017) Tourmaline as a petrogenetic indicator in the Pfitsch Formation,
290 Western Tauern Window, Eastern Alps. *Lithos*, 284-285 (Special issue), 138–155.
- 291 Cao, H.W., Li, G.M., Zhang, R.Q., Zhang, Y.H., Zhang, L.K., Dai, Z.W., Zhang, Z., Liang, W.,
292 Dong, S.L., and Xia, X.B. (2021) Genesis of the Cuonadong tin polymetallic deposit in the
293 Tethyan Himalaya: Evidence from geology, geochronology, fluid inclusions and multiple
294 isotopes. *Gondwana Research*, 92, 72–101.
- 295 Cheng, L., Zhang, C., Liu, X., Yang, X., Zhou, Y., Horn, I., Weyer, S., and Holtz, F. (2021)
296 Significant boron isotopic fractionation in the magmatic evolution of Himalayan
297 leucogranite recorded in multiple generations of tourmaline. *Chemical Geology*, 571,
298 120194, DOI: [10.1016/j.chemgeo.2021.120194](https://doi.org/10.1016/j.chemgeo.2021.120194).
- 299 Codeço, M.S., Weis, P., Trumbull, R.B., Pinto, F., Lecumberri-Sanchez, P., and Wilke, F.D.
300 (2017) Chemical and boron isotopic composition of hydrothermal tourmaline from the
301 Panasqueira W-Sn-Cu deposit, Portugal. *Chemical Geology*, 468, 1–16.
- 302 Dyar, M.D., Wiedenbeck, M., Robertson, D., Cross, L.R., Delaney, J.S., Ferguson, K., Francis,
303 C.A., Grew, E.S., Guidotti, C.V., Hervig, R.L., Hughes, J.M., Husler, J., Leeman, W.,
304 McGuire, A.V., Rhede, D., Rothe, H., Paul, R.L., Richards, I., and Yates, M. (2001)
305 Reference minerals for the microanalysis of light elements. *Geostandards Newsletter*, 25,
306 441–463.

- 307 DeCelles, P.G., Kapp, P., Quade, J., and Gehrels, G.E. (2011) Oligocene–Miocene Kailas basin,
308 southwestern Tibet: Record of postcollisional upper-plate extension in the Indus-Yarlung
309 suture zone. *Geological Society of America Bulletin*, 123 (7-8), 1337–1362.
- 310 Drivenes, K., Larsen, R.B., Müller, A., Sørensen, B.E., Wiedenbeck, M., and Raanes, M.P.
311 (2015) Late-magmatic immiscibility during batholith formation: assessment of B isotopes
312 and trace elements in tourmaline from the Land’s End granite, SW England. *Contributions*
313 *to Mineralogy and Petrology*, 169, 1–27.
- 314 Dutrow, B.L., and Henry, D.J. (2011) *Tourmaline: A Geologic DVD*. *Elements*, 7, 301–306.
- 315 Fan, J.J., Wang, Q., Li, J., Wei, G.J., Ma, J.L., Ma, L., Li, Q.W., Jiang, Z.Q., Zhang, L., Wang,
316 Z.L., and Zhang, L. (2021) Boron and molybdenum isotopic fractionation during crustal
317 anatexis: Constraints from the Conadong leucogranites in the Himalayan Block, South
318 Tibet. *Geochimica et Cosmochimica Acta*, 297, 120–142.
- 319 Han, J.S., Hollings, P., Jourdan, F., Zeng, Y.C., and Chen, H.Y. (2020) Xenocrystic Eocene
320 magmatic tourmaline captured by the Miocene Himalayan leucogranites. *American*
321 *Mineralogist*, 105, 1436–1440.
- 322 Harlaux, M., Kouzmanov, K., Gialli, S., Laurent, O., Rielli, A., Dini, A., Chauvet, A., Menzies,
323 A., Kalinaj, M., and Fontboté, L. (2020) Tourmaline as a Tracer of Late-Magmatic to
324 Hydrothermal Fluid Evolution: The World-Class San Rafael Tin (-Copper) Deposit, Peru.
325 *Economic Geology*, 115, 1665–1697.
- 326 Henry, D.J., and Guidotti, C.V. (1985) Tourmaline as a petrogenetic indicator mineral—An
327 example from the staurolite-grade metapelites of NW Maine. *American Mineralogist*, 70, 1–
328 15.
- 329 Henry, D.J., and Dutrow, B.L. (1996) Metamorphic tourmaline and its petrologic applications.
330 *Reviews in Mineralogy and Geochemistry*, 33, 503–557.
- 331 Henry, D.J., Novak, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P., and Pezzotta, F.
332 (2011) Nomenclature of the tourmaline-supergrroup minerals. *American Mineralogist*, 96,
333 895–913.
- 334 Henry, D.J., and Dutrow, B.L. (2018) Tourmaline studies through time: Contributions to
335 scientific advancements. *Journal of Geosciences (Czech Republic)*, 63, 77–98.
- 336 Hergig, R.L., Moore, G.M., Williams, L.B., Peacock, S.M., Holloway, J.R., and Roggensack, K.
337 (2002) Isotopic and elemental partitioning of boron between hydrous fluid and silicate melt.
338 *American Mineralogist*, 87, 769–774.
- 339 Hou, K.J., Li, Y.H., Xiao, Y.K., Liu, F., and Tian, Y.R. (2010) In situ boron isotope
340 measurements of natural geological materials by LA-MC-ICP-MS. *Chinese Science*
341 *Bulletin*, 55, 3305–3311.
- 342 Jiang, S.Y., and Palmer (1998) Boron isotope systematics of tourmaline from granites and
343 pegmatites: A synthesis. *European Journal of Mineralogy*, 10, 1253–1265.
- 344 Klemme, S., Marschall, H.R., Jacob, D.E., Prowatke, S., and Ludwig, T. (2011) Trace-element
345 partitioning and boron isotope fractionation between white mica and tourmaline. *The*
346 *Canadian Mineralogist*, 49, 165–176.
- 347 Liu, W.L., Xu, H.J., and Shi, F. (2021) Decorated dislocations in naturally deformed olivine with
348 C-type fabric: A case study in the Lüliangshan garnet peridotite from the North Qaidam
349 ultrahigh-pressure belt, NW China. *Tectonophysics*, 814, 228971, DOI:
350 10.1016/j.tecto.2021.228971.
- 351 Launay, G., Sizaret, S., Guillou-Frotier, L., Gloaguen, E., and Pinto, F. (2018) Deciphering fluid
352 flow at the magmatic-hydrothermal transition: A case study from the world-class

- 353 Panasqueira W–Sn–(Cu) ore deposit (Portugal). *Earth and Planetary Science Letters*, 499,
354 1–12.
- 355 Maner, J.L., and London, D. (2018) Fractionation of the isotopes of boron between granitic melt
356 and aqueous solution at 700 °C and 800 °C (200 MPa). *Chemical Geology*, 489, 16–27.
- 357 Marks, M.A., Marschall, H.R., Schühle, P., Guth, A., Wenzel, T., Jacob, D.E., Barth, M., and
358 Markl, G. (2013) Trace element systematics of tourmaline in pegmatitic and hydrothermal
359 systems from the Variscan Schwarzwald (Germany): The importance of major element
360 composition, sector zoning, and fluid or melt composition. *Chemical Geology*, 344, 73–90.
- 361 Marschall, H.R., and Jiang, S.Y. (2011) Tourmaline Isotopes: No Element Left Behind.
362 *Elements*, 7, 313–319.
- 363 Pal, D.C., Trumbull, R.B., and Wiedenbeck, M. (2010) Chemical and boron isotope
364 compositions of tourmaline from the Jaduguda U (–Cu–Fe) deposit, Singhbhum shear zone,
365 India: Implications for the sources and evolution of mineralizing fluids. *Chemical Geology*,
366 277, 245–260.
- 367 Roda-Robles, E., Simmons, W., Pesquera, A., Gil-Crespo, P.P., Nizamoff, J., and Torres-Ruiz, J.
368 (2015) Tourmaline as a petrogenetic monitor of the origin and evolution of the Berry-Havey
369 pegmatite (Maine, U.S.A.). *American Mineralogist*, 100, 95–109.
- 370 Slack, J.F., and Trumbull, R.B. (2011) Tourmaline as a Recorder of Ore-Forming Processes.
371 *Elements*, 7, 321–326.
- 372 Su, Z.K., Zhao, X.F., Zeng, L.P., Zhao, K.D., and Hofstra, A.H. (2019) Tourmaline boron and
373 strontium isotope systematics reveal magmatic fluid pulses and external fluid influx in a
374 giant iron oxide-apatite (IOA) deposit. *Geochimica et Cosmochimica Acta*, 259, 233–252.
- 375 Tonarini, S., Forte, C., Petrini, R., and Ferrara, G. (2003) Melt/biotite ¹¹B/¹⁰B isotopic
376 fractionation and the boron local environment in the structure of volcanic glasses.
377 *Geochimica et Cosmochimica Acta*, 67, 1863–1873.
- 378 Trumbull, R.B., Krienitz, M.-S., Grundmann, G., and Wiedenbeck, M. (2009) Tourmaline
379 geochemistry and δ¹¹B variations as a guide to fluid–rock interaction in the Habachtal
380 emerald deposit, Tauern Window, Austria. *Contributions to Mineralogy and Petrology*, 157,
381 411–427.
- 382 van Hinsberg, V. J., Franz, G., and Wood, B.J. (2017) Determining subduction-zone fluid
383 composition using a tourmaline mineral probe. *Geochemical Perspectives Letters*, 160–169.
- 384 van Hinsberg, V. J., Henry, D.J., and Dutrow, B.L. (2011a) Tourmaline as a Petrologic Forensic
385 Mineral: A Unique Recorder of Its Geologic Past. *Elements*, 7, 327–332.
- 386 van Hinsberg, V. J., Henry, D.J., and Marschall, H.R. (2011b) Tourmaline: an ideal indicator of
387 its host environment. *The Canadian Mineralogist*, 49, 1–16.
- 388 Wu, F.-Y., Liu, X.-C., Liu, Z.-C., Wang, R.-C., Xie, L., Wang, J.-M., Ji, W.-Q., Yang, L., Liu,
389 C., Khanal, G.P., and He, S.-X., 2020, Highly fractionated Himalayan leucogranites and
390 associated rare-metal mineralization: *Lithos*, 352-353, p. 105319, doi:
391 10.1016/j.lithos.2019.105319.
- 392 Xie, L., Tao, X., Wang, R., Wu, F., Liu, C., Liu, X., Li, X., and Zhang, R. (2020) Highly
393 fractionated leucogranites in the eastern Himalayan Cuonadong dome and related magmatic
394 Be–Nb–Ta and hydrothermal Be–W–Sn mineralization. *Lithos*, 354-355, 105286, DOI:
395 10.1016/j.lithos.2019.105286.
- 396 Yang, S.Y., Jiang, S.Y., and Palmer, M.R. (2015) Chemical and boron isotopic compositions of
397 tourmaline from the Nyalam leucogranites, South Tibetan Himalaya: Implication for their
398 formation from B-rich melt to hydrothermal fluids. *Chemical Geology*, 419, 102–113.

399 Zhao, H.D., Zhao, K.D., Palmer, M.R., Jiang, S.Y., and Chen, W. (2021) Magmatic-
400 Hydrothermal Mineralization Processes at the Yidong Tin Deposit, South China: Insights
401 from In Situ Chemical and Boron Isotope Changes of Tourmaline. *Economic Geology*, 116,
402 1625–1647.
403

404 **FIGURE CAPTIONS**

405 **Figure 1.** Photographs and photomicrographs showing field relations and typical mineral
406 paragenesis and microstructures of the Cuonadong leucogranites, eastern Himalaya. (A) Field
407 occurrence of tourmaline from the Cuonadong two-mica granite and pegmatite; (B) cross-
408 polarized light photomicrograph showing the mineralogy and textural relations in the two-mica
409 granite. Note the autocrystic tourmaline (Tur G) circled in red; (C) plane-polarized light
410 photomicrograph highlighting the coarse-grained and fragmented texture of xenocrystic
411 tourmaline (Tur P) from the pegmatite.

412

413 **Figure 2.** (A) Tourmaline X-site occupancy classification diagram (Henry et al., 2011) showing
414 alkali-group tourmalines from the Cuonadong leucogranites; (B) upper half of the ternary Al-Fe-
415 Mg diagram showing the fields of: (1) Li-rich granitoids and associated pegmatites and aplites;
416 (2) Li-poor granitoids and associated pegmatites and aplites; (3) Fe³⁺-rich quartz–tourmaline-
417 bearing hydrothermally altered granites; (4) metapelites and metapsammites coexisting with an
418 Al-saturated phase; (5) metapelites and metapsammites not coexisting with an Al-saturated
419 phase; (6) Fe³⁺-rich quartz–tourmaline-bearing rocks, calc silicate rocks, and metapelites; (7)
420 low-Ca meta-ultramafics and Cr-V-rich metasediments; and (8) marbles and metapyroxenites
421 (Henry and Guidotti, 1985). All autocrystic Tur G and xenocrystic Tur P tourmalines from the
422 Cuonadong leucogranites plot in the field of Li-poor granitoids and associated pegmatites and
423 aplites; (C) Diagram correlating tourmaline compositions with source-rock type using the molar

424 Al-Fe-Mg subsystem (Henry and Dutrow, 2018); (D) Atomic Mg/(Mg+Fe) vs. Na/(Na+Ca)
425 diagram showing the fields of schorl and dravite; (E) Mg vs. Fe diagram expressed in atoms per
426 formula unit (a.p.f.u.) showing the fields of schorl, dravite, foitite and Mg-foitite. Both the
427 Mg/(Mg+Fe) vs. Na/(Na+Ca) and the Mg vs. Fe diagrams are from Pal et al. (2010); (F) Plot of
428 Al vs. X-site vacancy.

429

430 **Figure 3.** Box-whisker plots showing the trace element composition of tourmalines from the
431 Cuonadong leucogranites, eastern Himalaya, China.

432

433 **Figure 4.** (A) Boron isotopic composition of the Tur P and Tur G tourmalines from the
434 Cuonadong leucogranites, eastern Himalaya; (B) comparison of the B isotopic composition of
435 different B reservoirs (Marschall and Jiang, 2011).

436

437 **Figure 5.** Electron backscattered diffraction (EBSD) analyses of autocrystic Tur G tourmaline
438 from the Cuonadong two-mica granite. (A) Orientation map using inverse pole figure color
439 scheme (IPF-X, where X is vertical on the map). Low-angle boundaries are color-coded as a
440 function of misorientations according to the legend in the panel; (B) pole figure for the
441 orientation of {0001}, {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} crystallographic orientations in the upper hemisphere
442 equal area projections of the orientations (UHPO); (C) texture component map of the #G1
443 tourmaline grain, color-coded for misorientation angles from the yellow “+”; (D) misorientation
444 profiles of #G1 tourmaline grain along the a-a’ and b-b’ cross-sections shown in (C).

445

446 **Figure 6.** EBSD analysis of xenocrystic Tur P tourmaline from the Cuonadong pegmatite. (A)
447 Orientation map using inverse pole figure color scheme (IPF-X, where X is vertical on the map).
448 Low-angle boundaries are color-coded as a function of misorientations according to the legend in
449 the panel; (B) pole figure for the orientation of {0001}, {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} crystallographic in
450 the upper hemisphere equal area projections of the orientations (UHPO); (C) texture component
451 maps of #P1 and #P3 tourmaline grains from (A), color-coded for disorientation angle from the
452 yellow “+”; (D) misorientation profiles along the x-x’ (in #P1) and y-y’ (in #P3) cross-sections
453 shown in (C).

454

455 **Figure 7.** Binary plots showing the concentration of selected trace elements as a function of
456 Mg/(Mg+Fe) in tourmalines from the Cuonadong leucogranites.

457

458 **Figure 8.** Binary plots showing the concentration of selected trace elements as a function of
459 Ca/(Ca+Na) in tourmalines from the Cuonadong leucogranites.

460

Figure 1

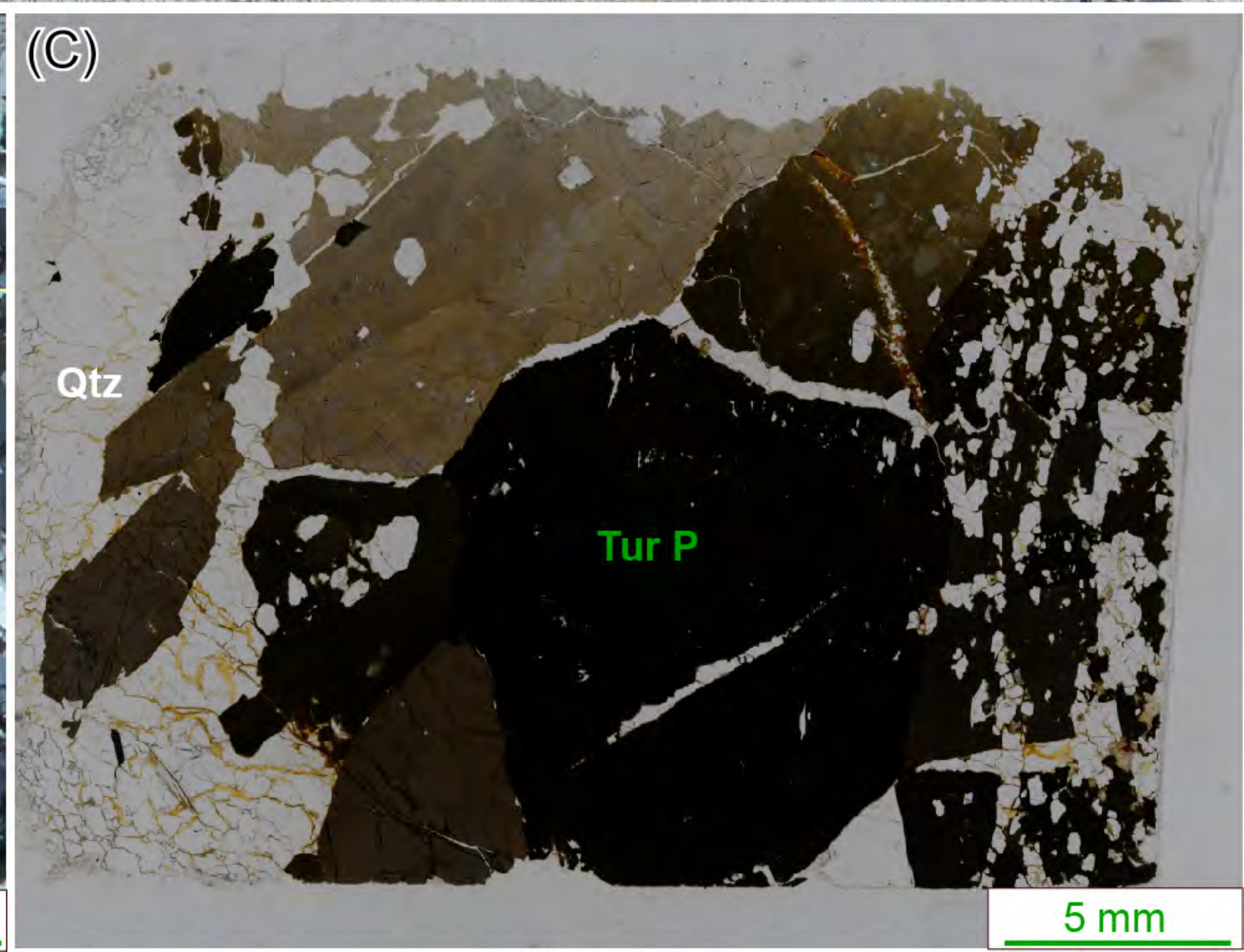
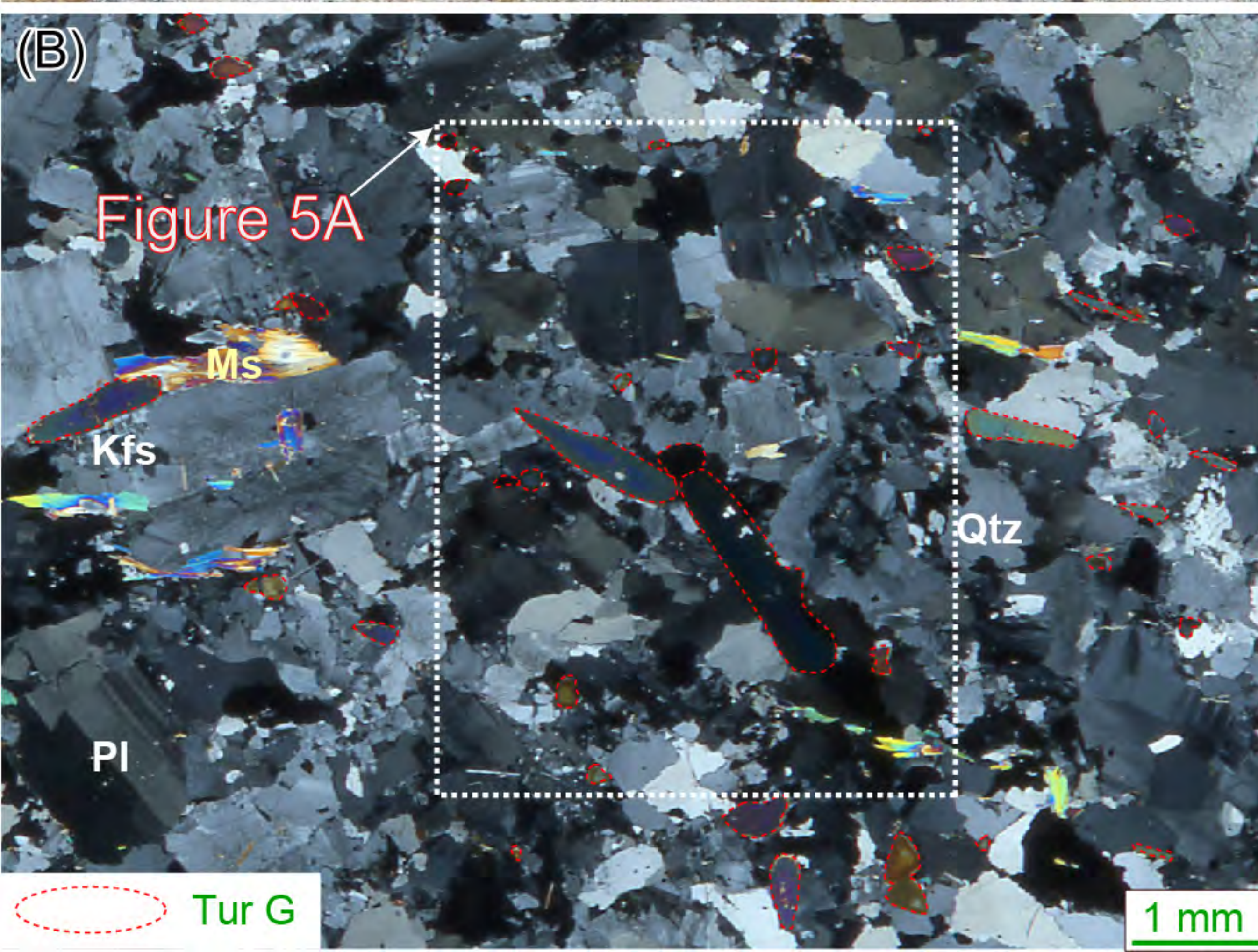
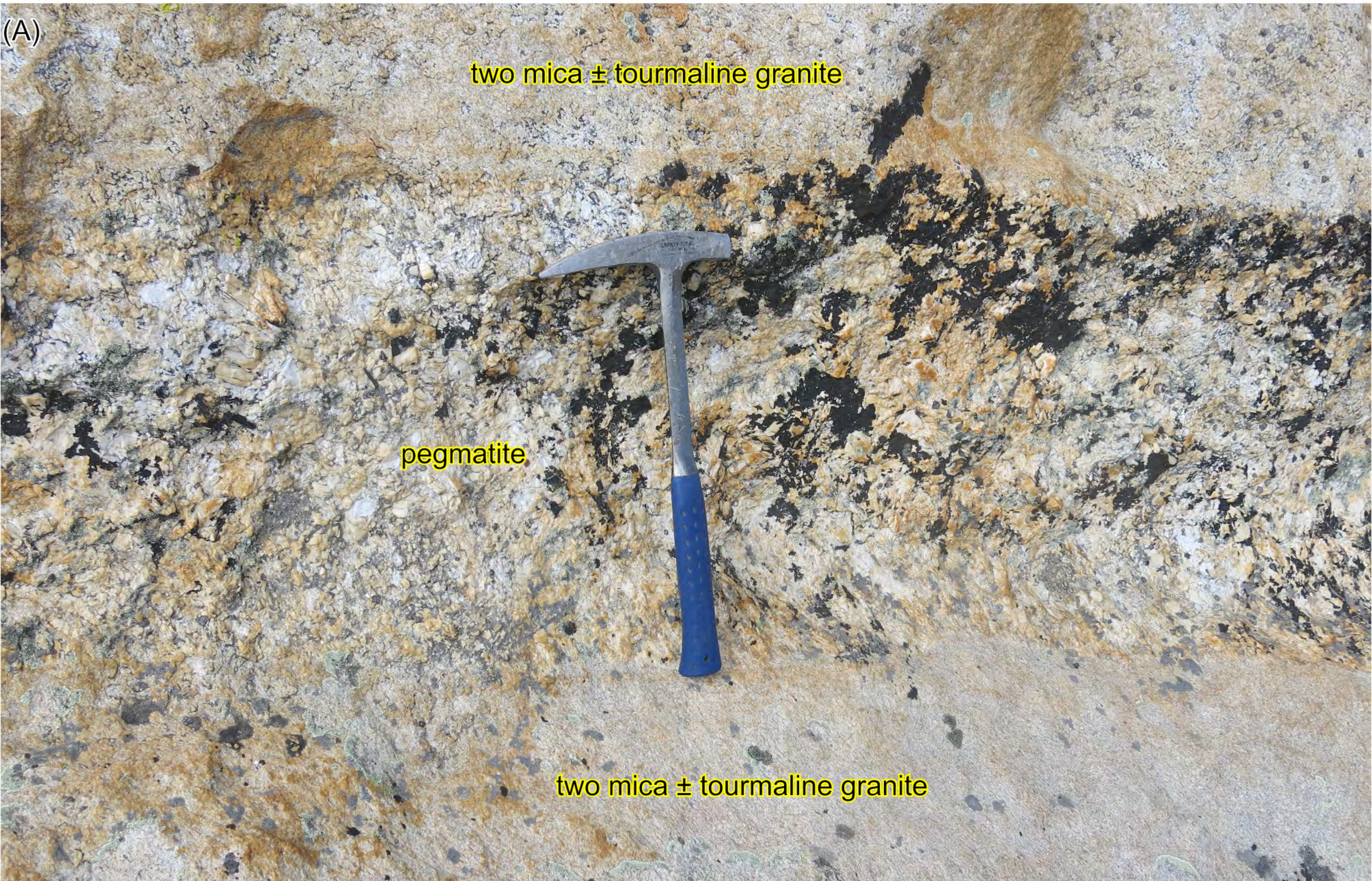
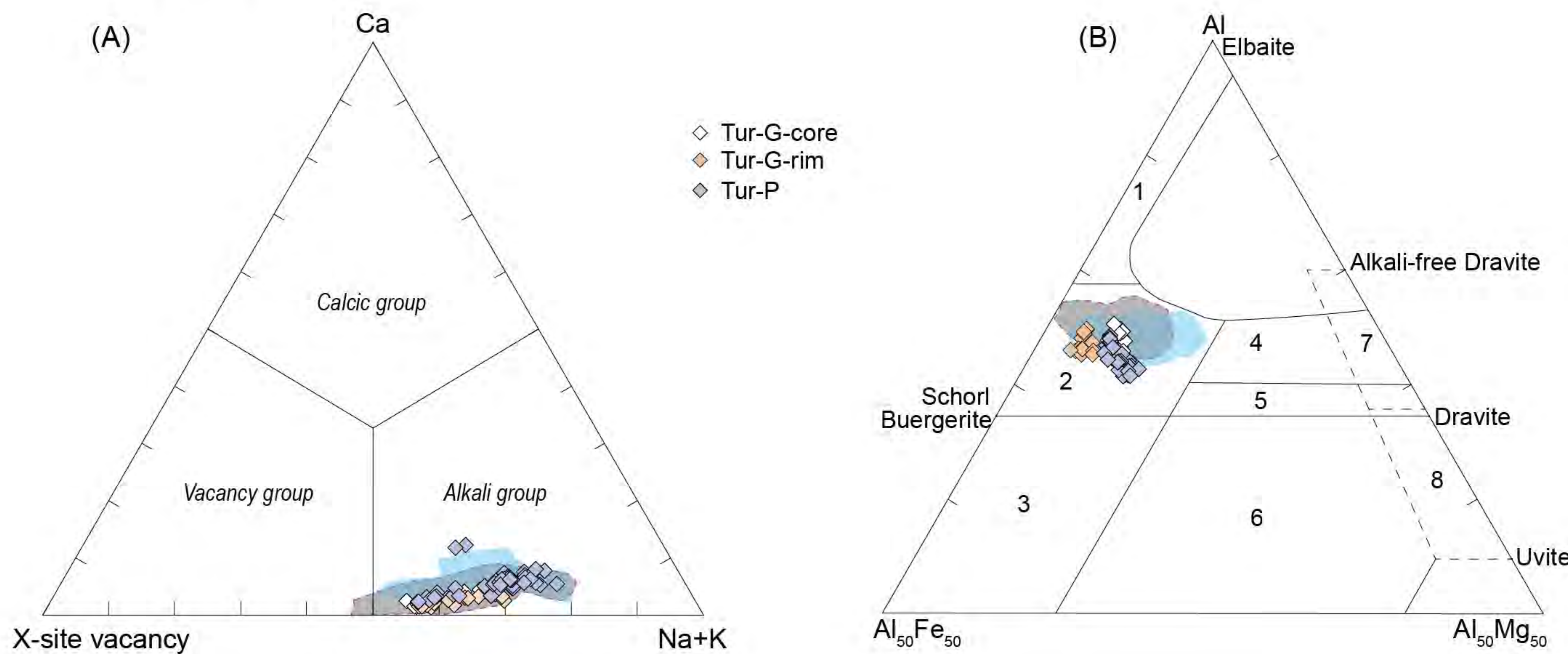


Figure 2



■ Magmatic tourmaline from the Gurla Mandhata tourmaline leucogranites, Northwest Himalaya (Cheng et al., 2021)
■ Magmatic tourmaline from the Nyalam leucogranites, South Tibetan Himalaya (Yang et al., 2015)

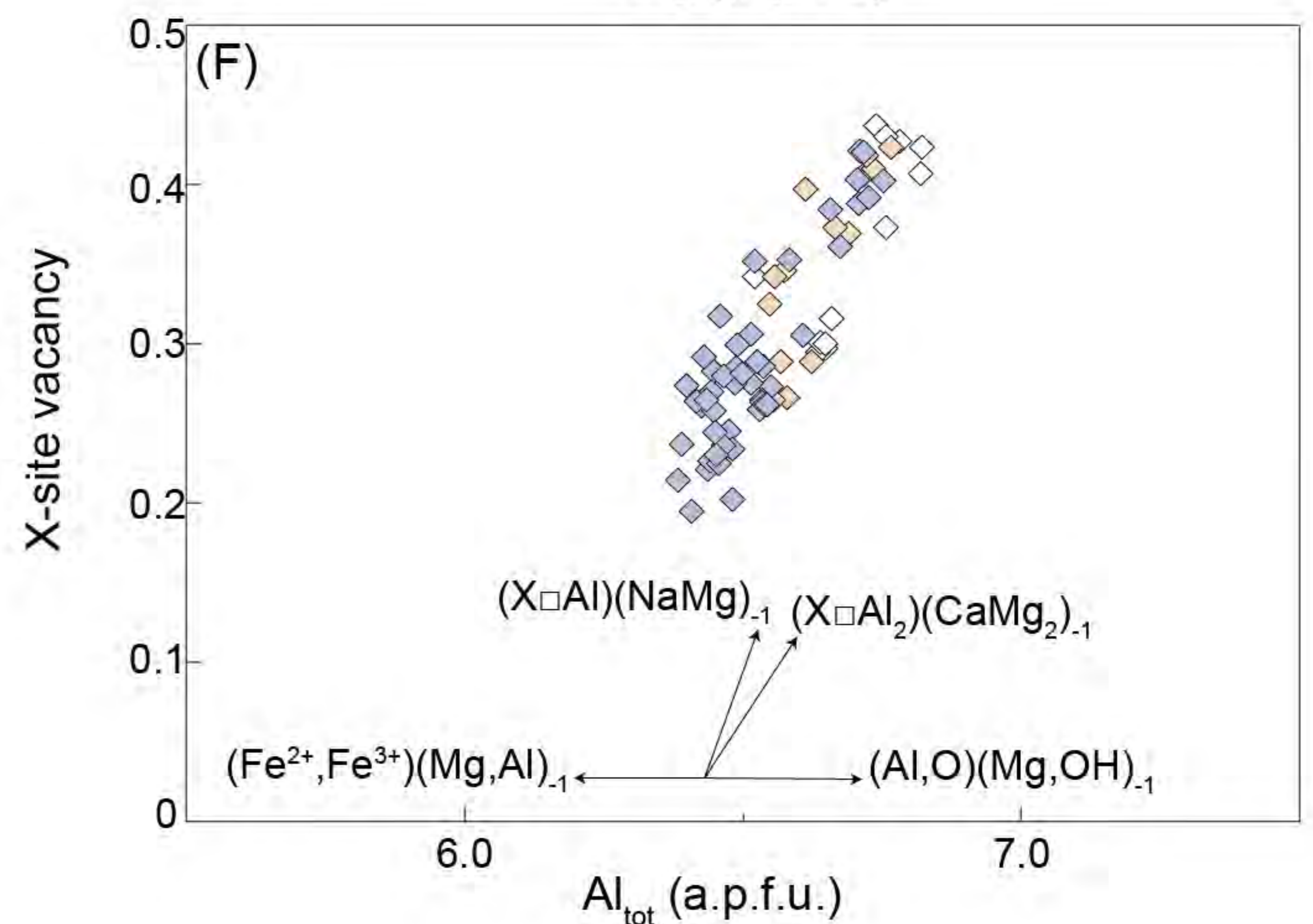
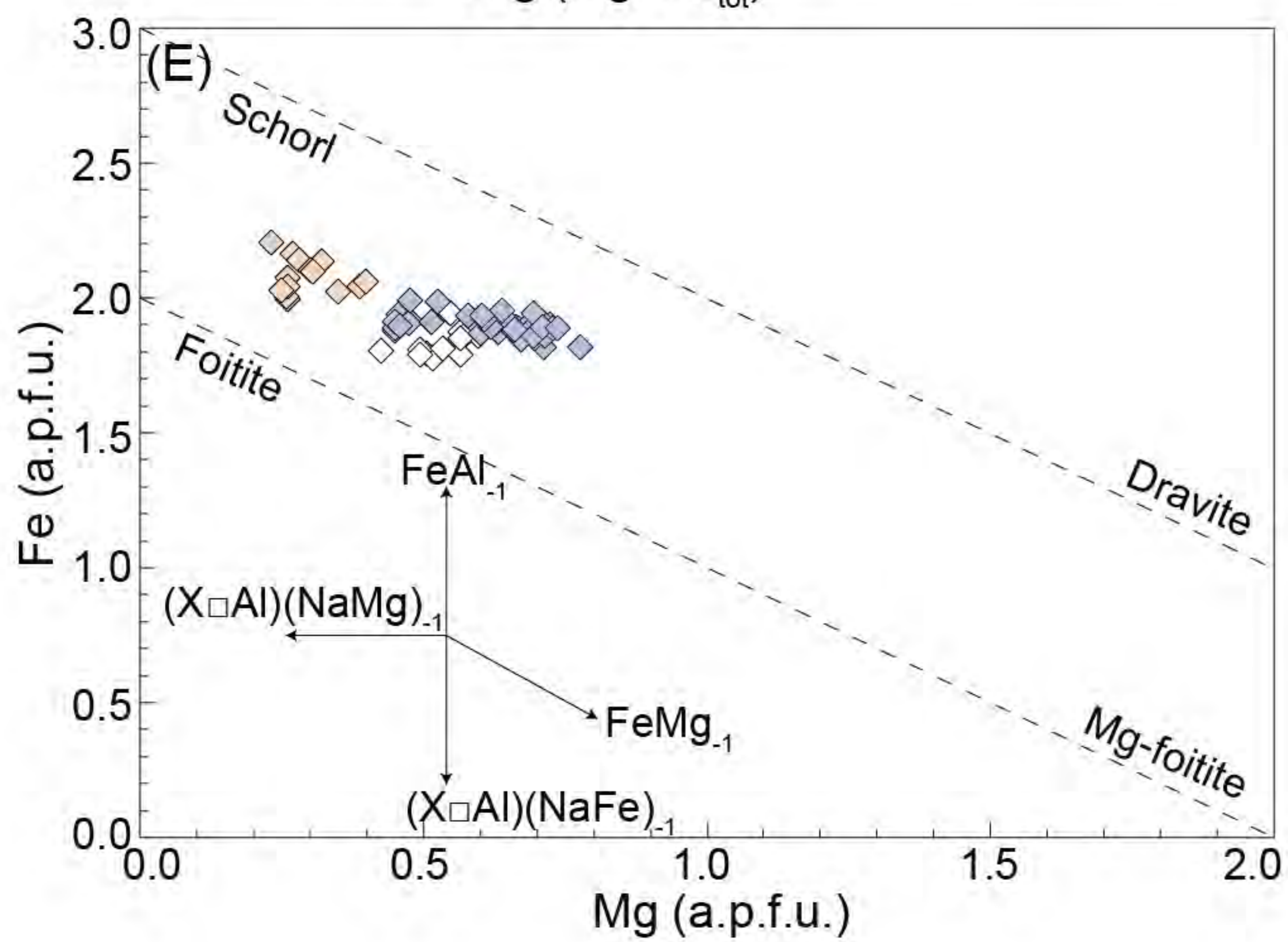
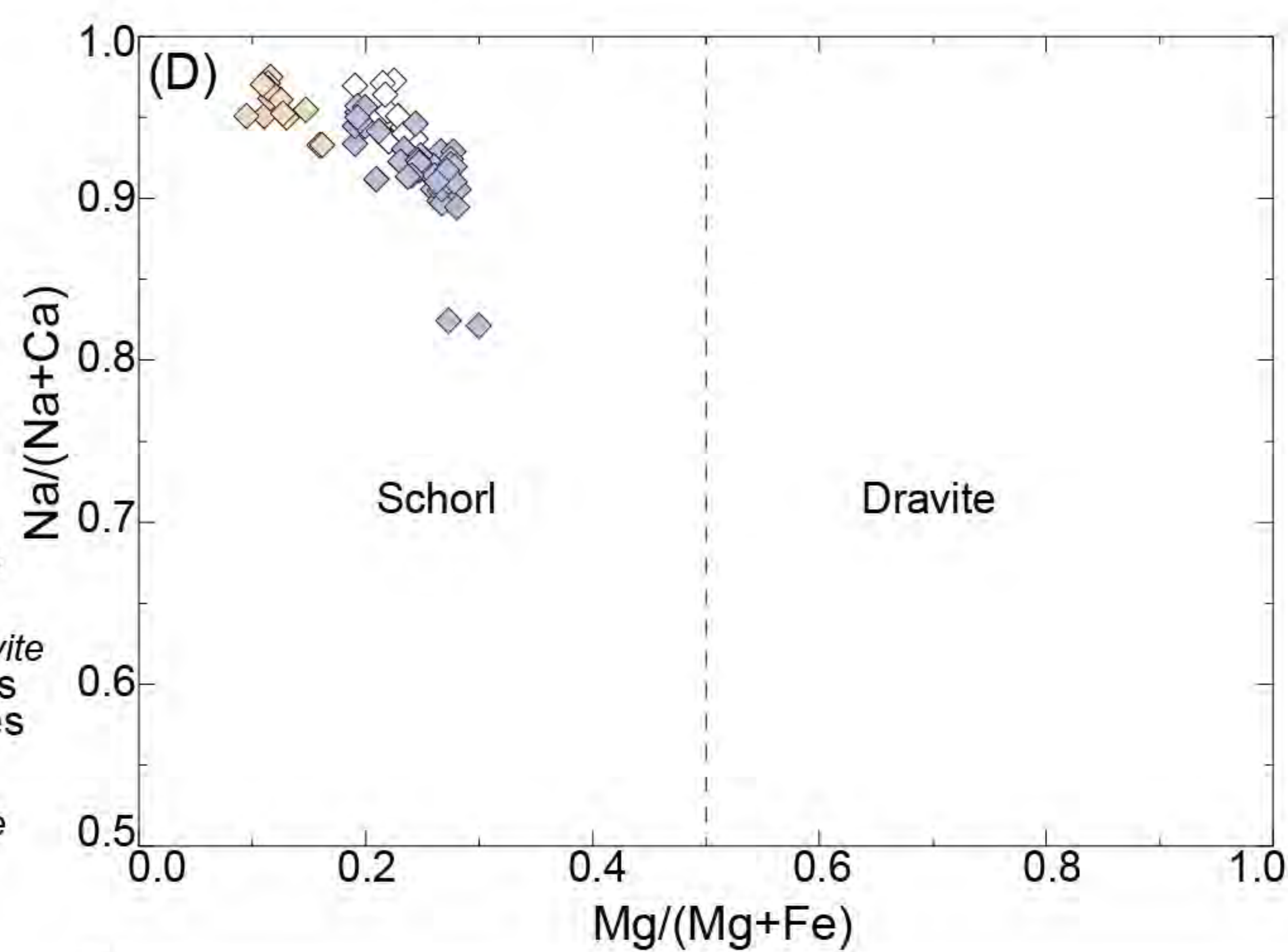
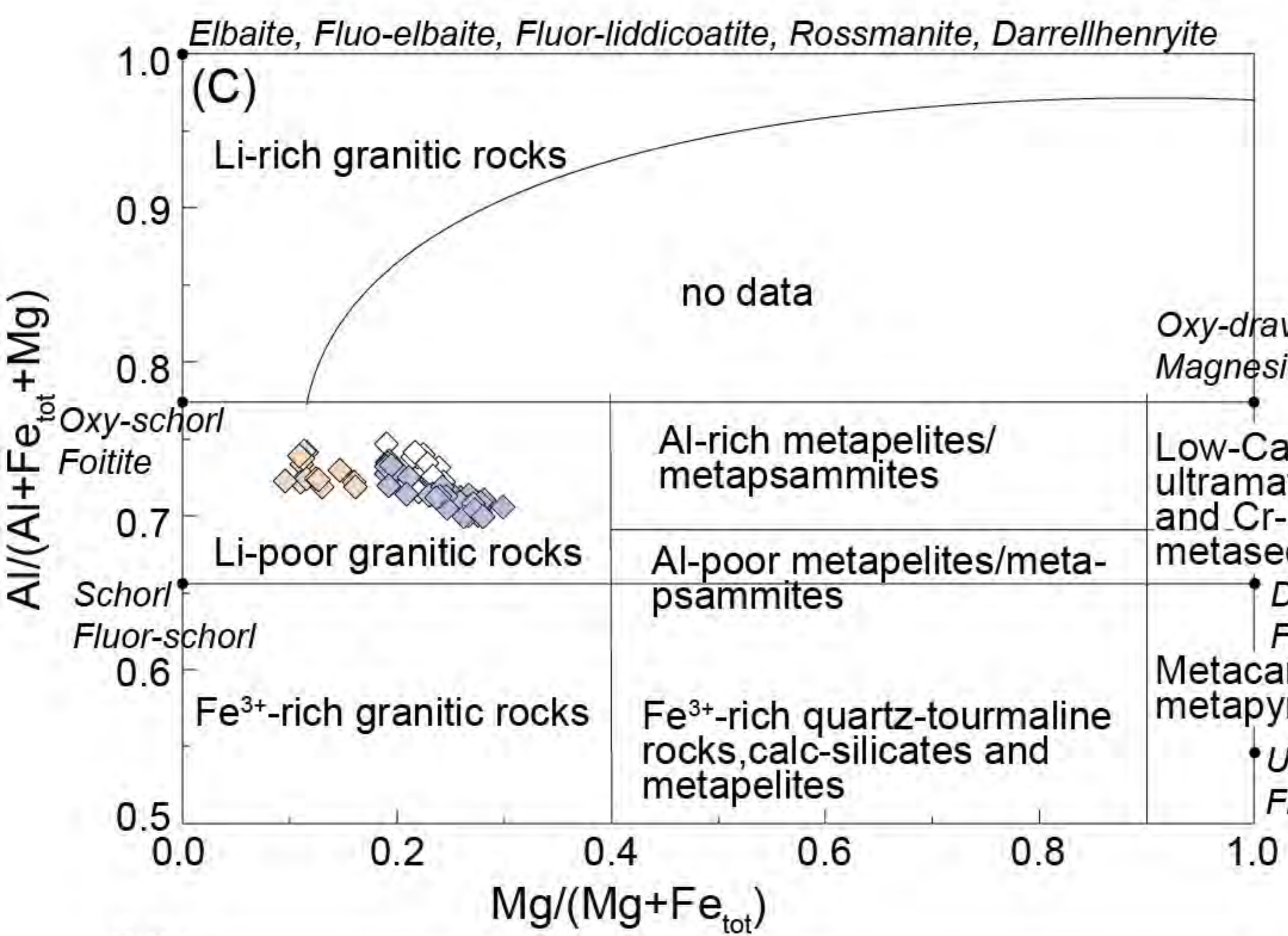


Figure 3

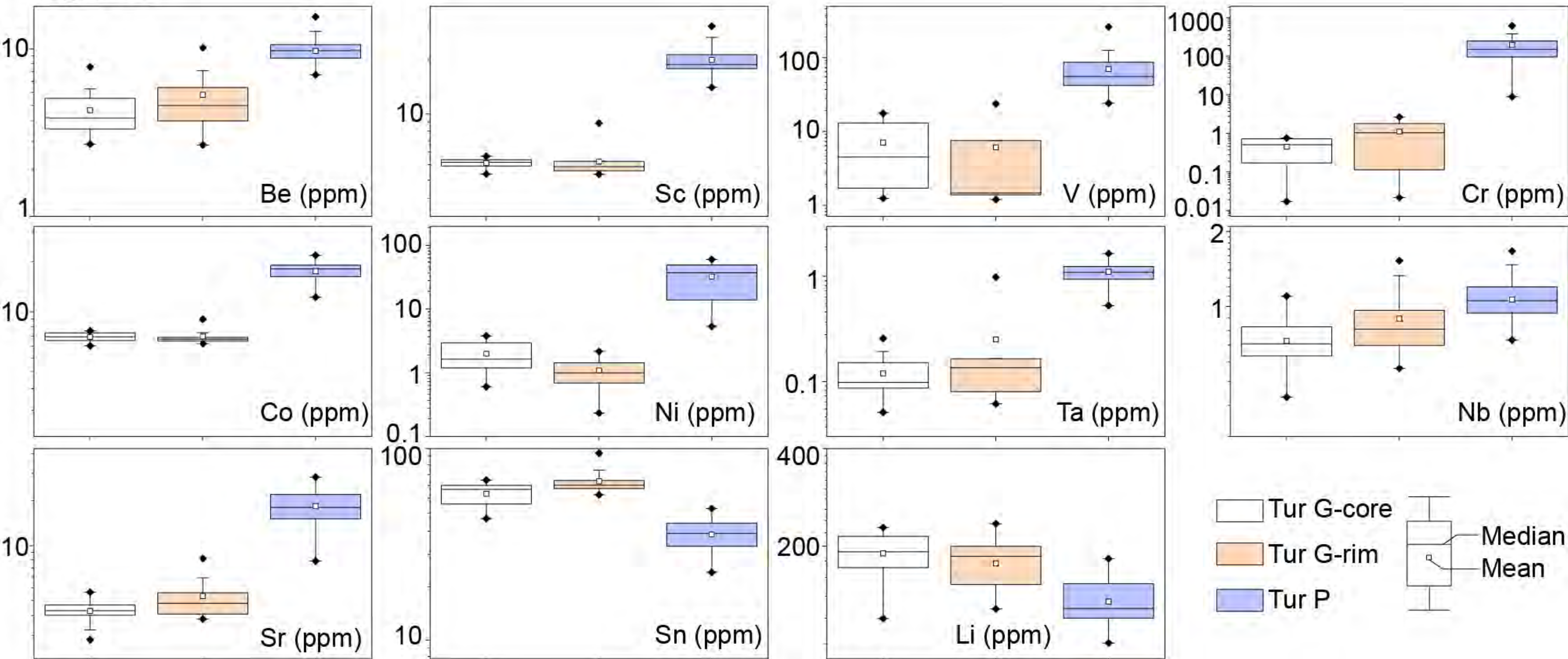


Figure 4

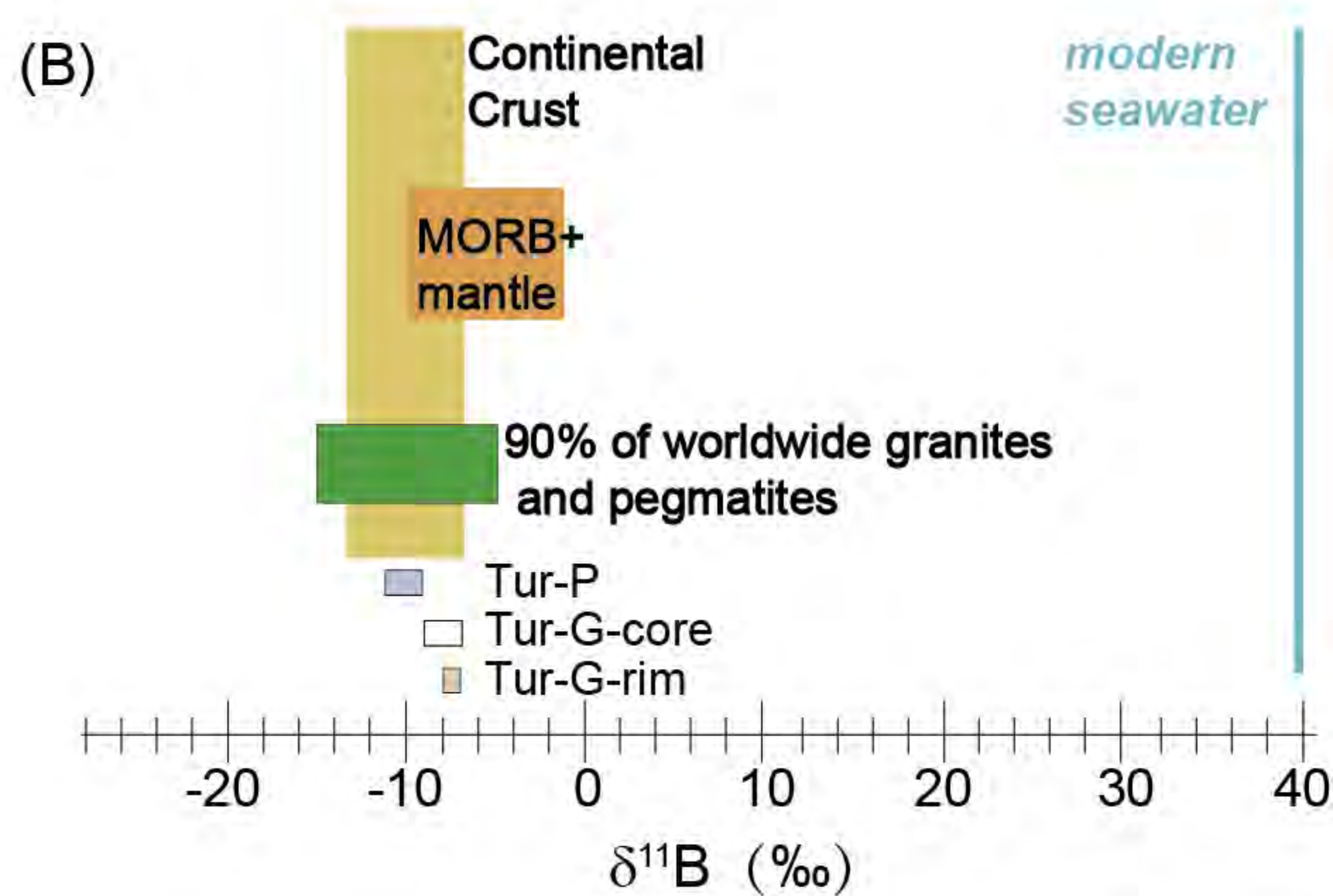
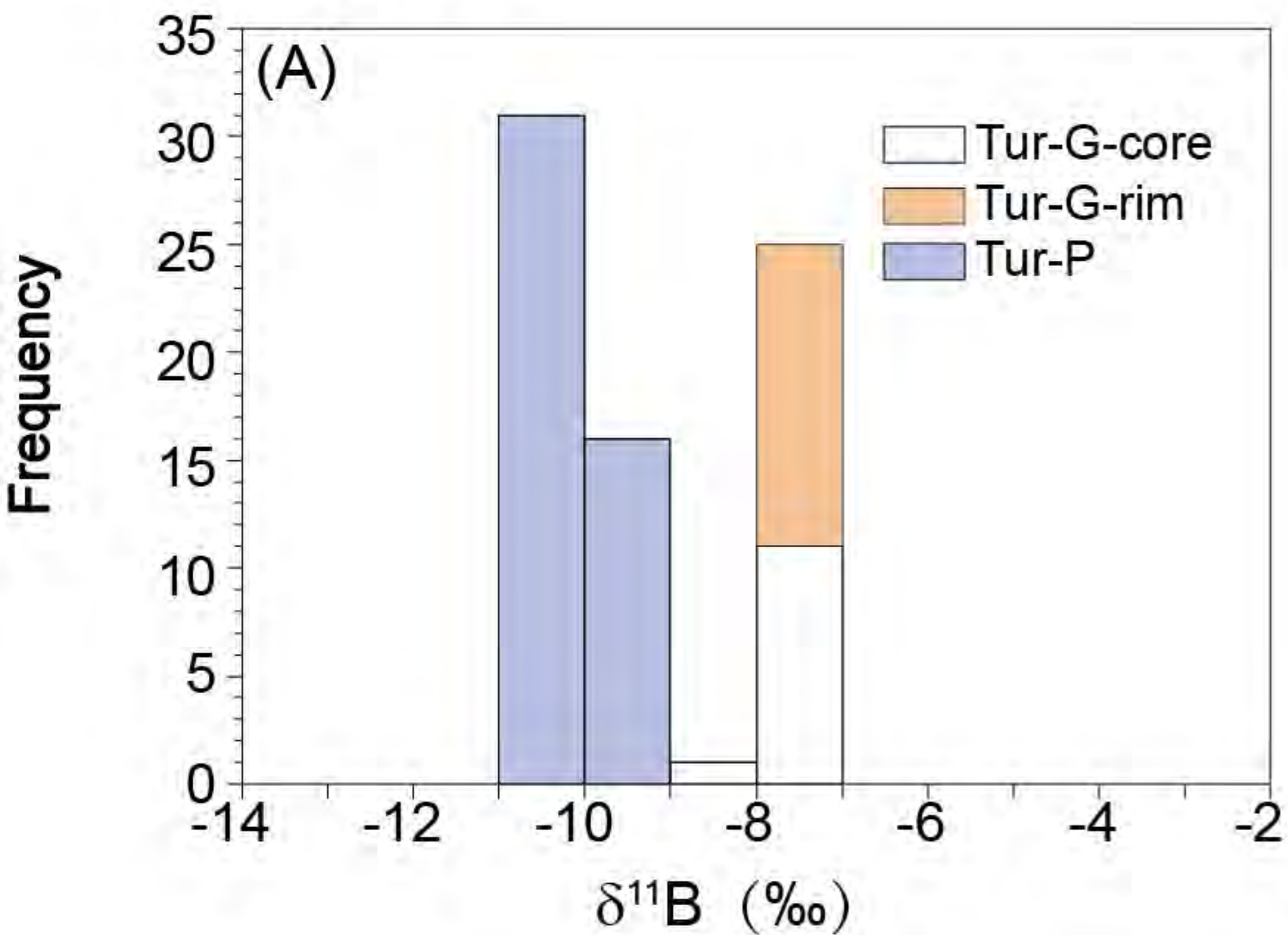


Figure 5

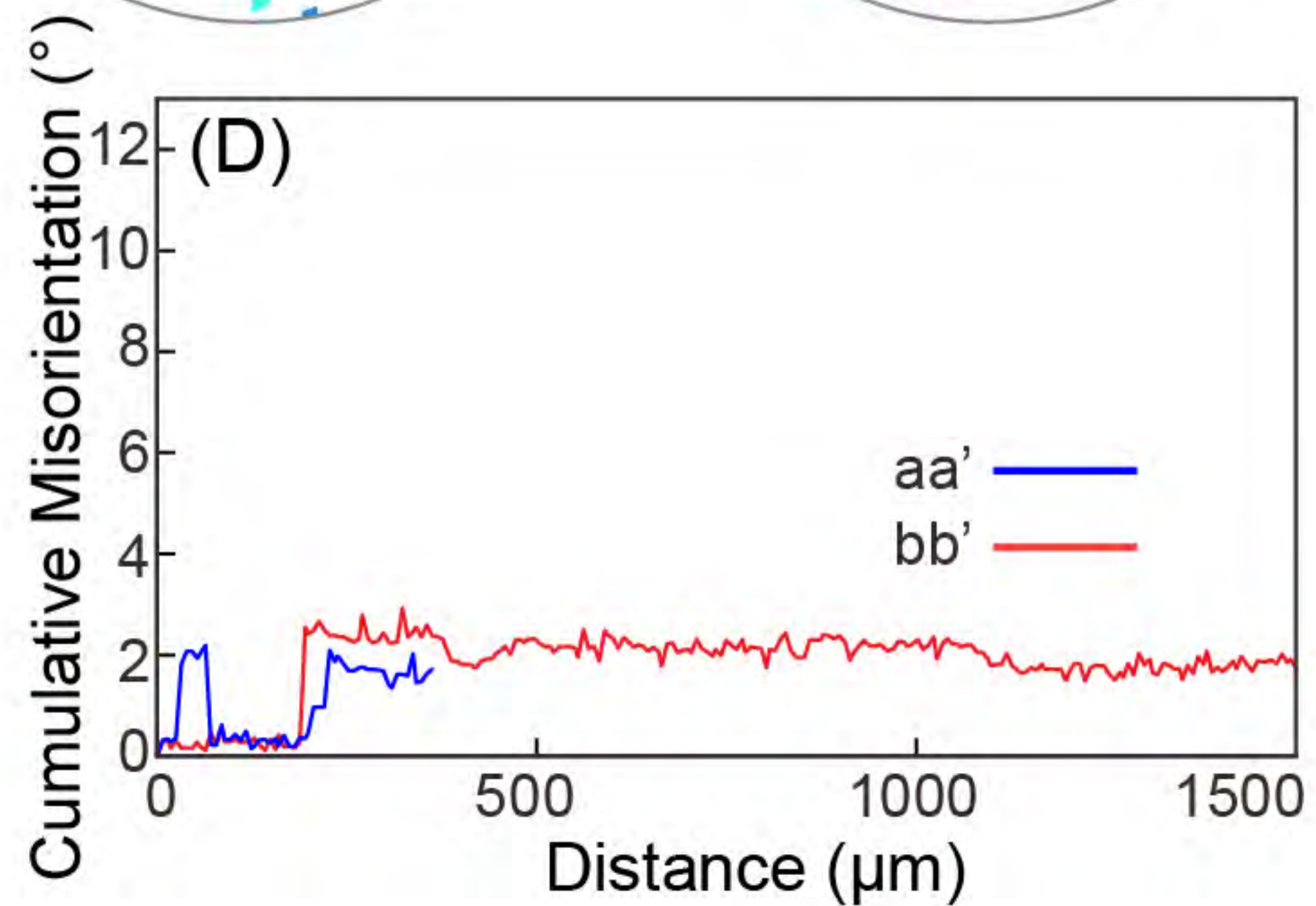
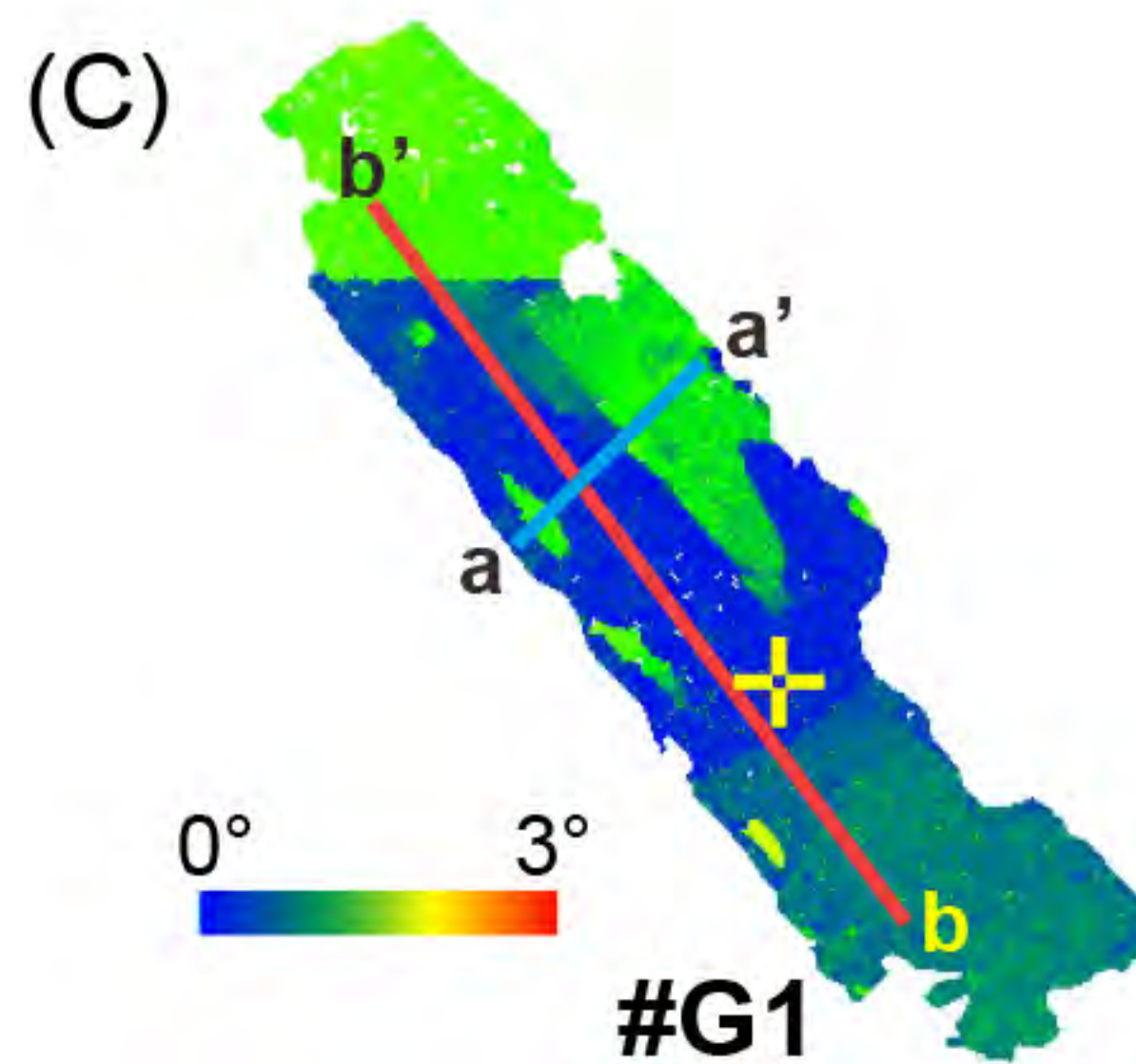
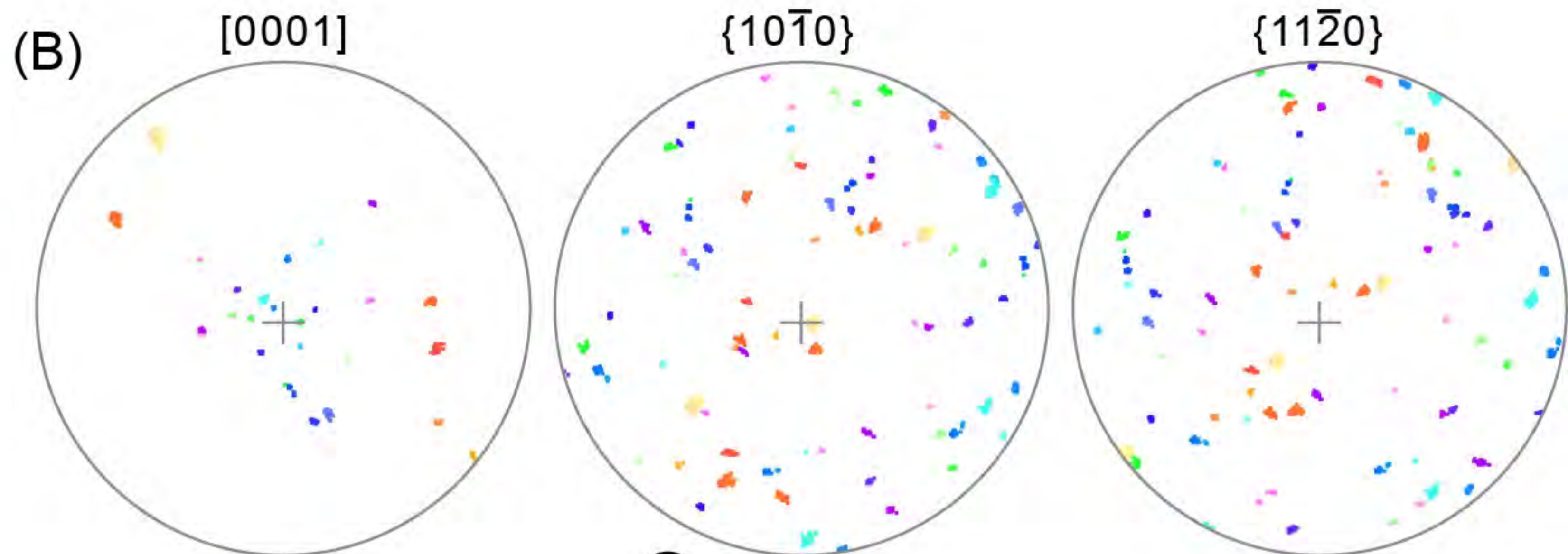
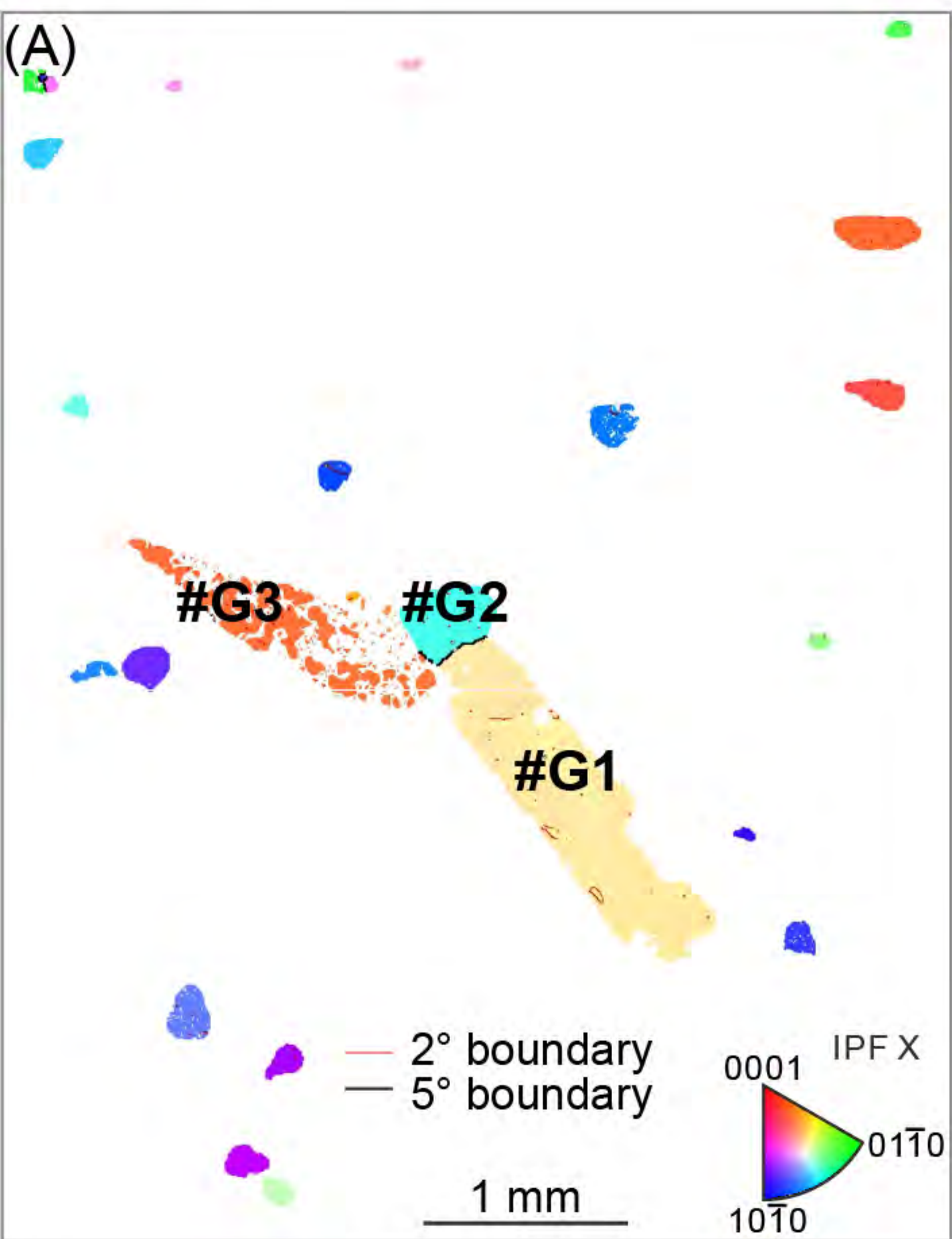


Figure 6

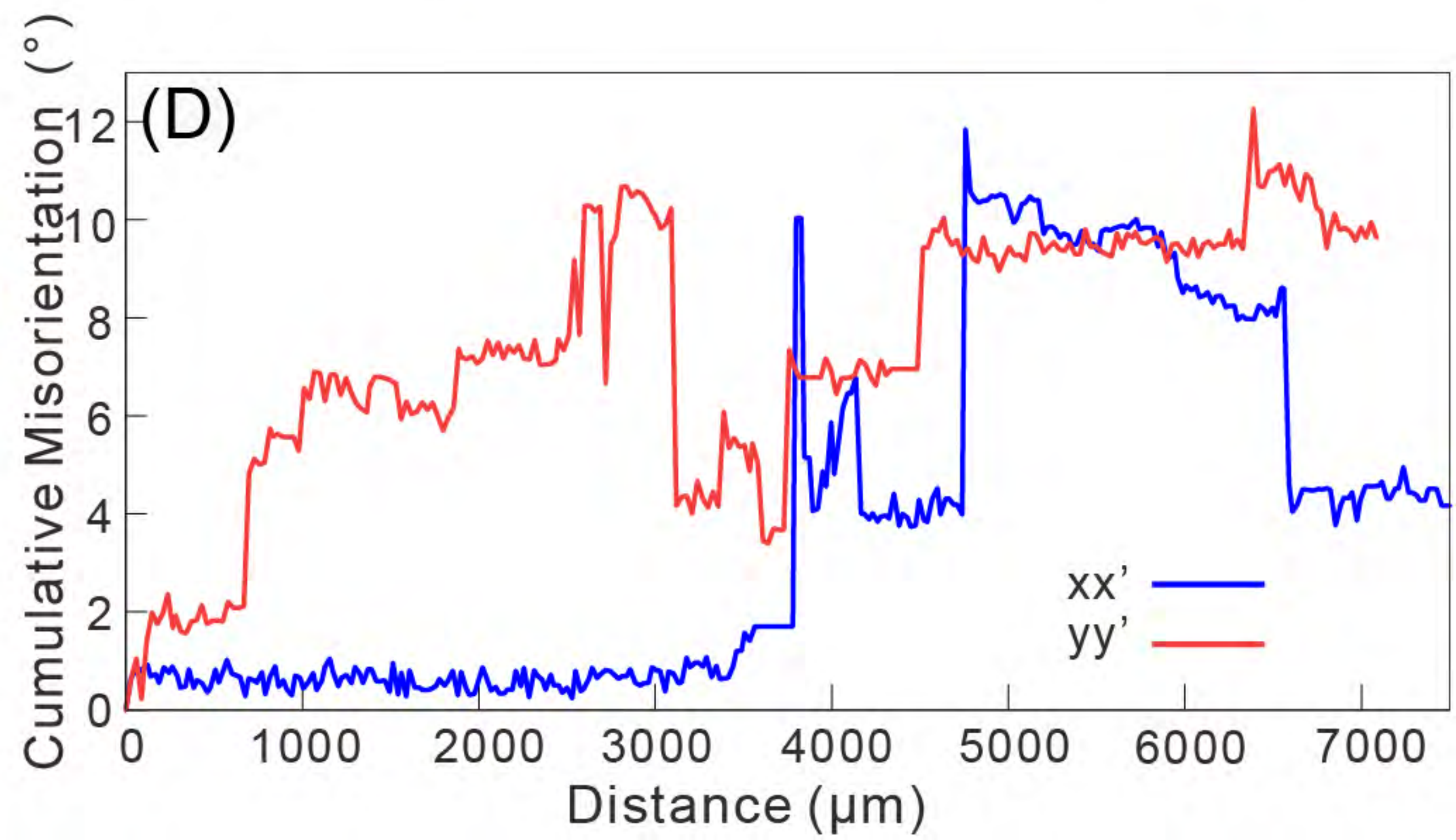
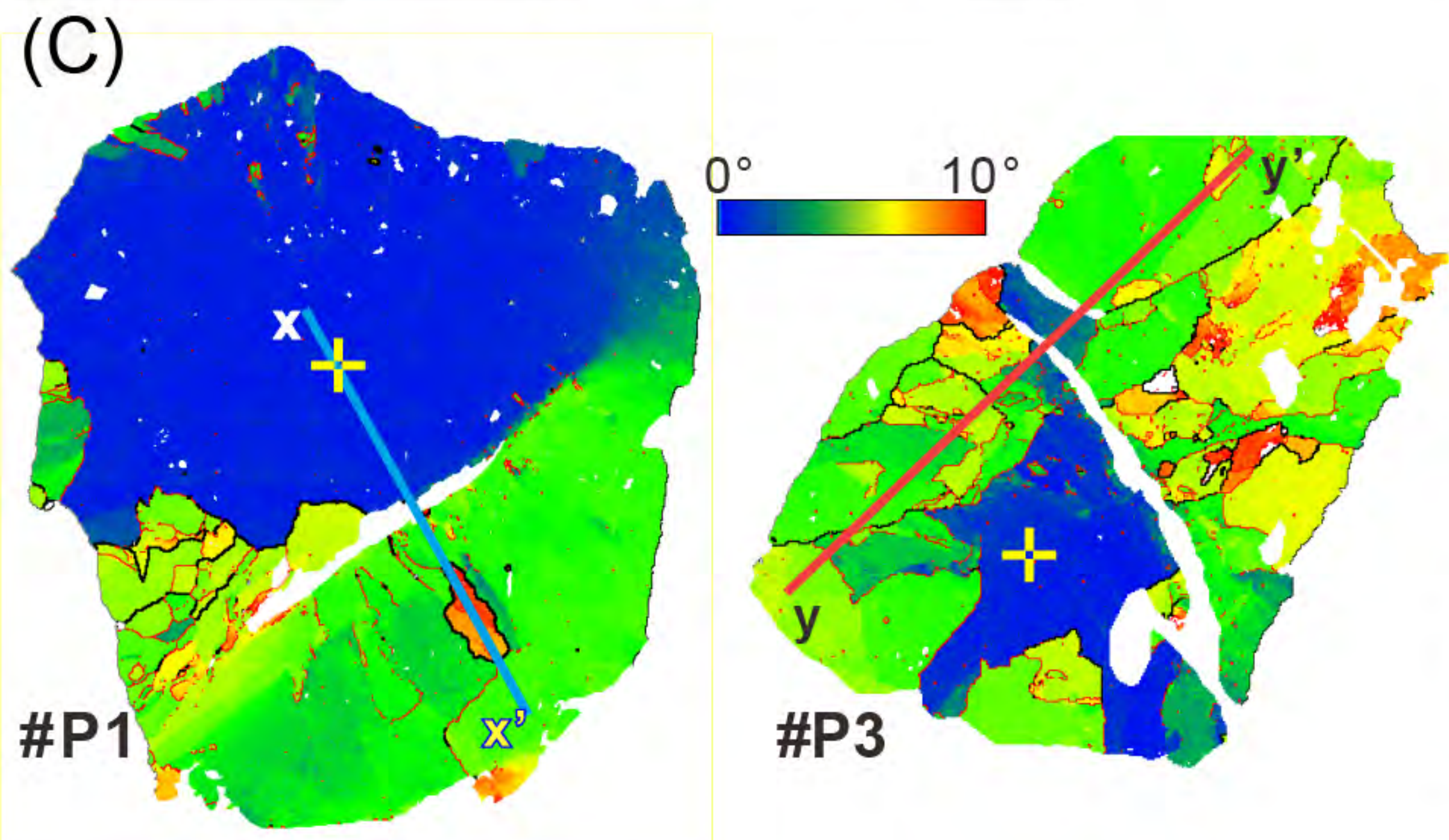
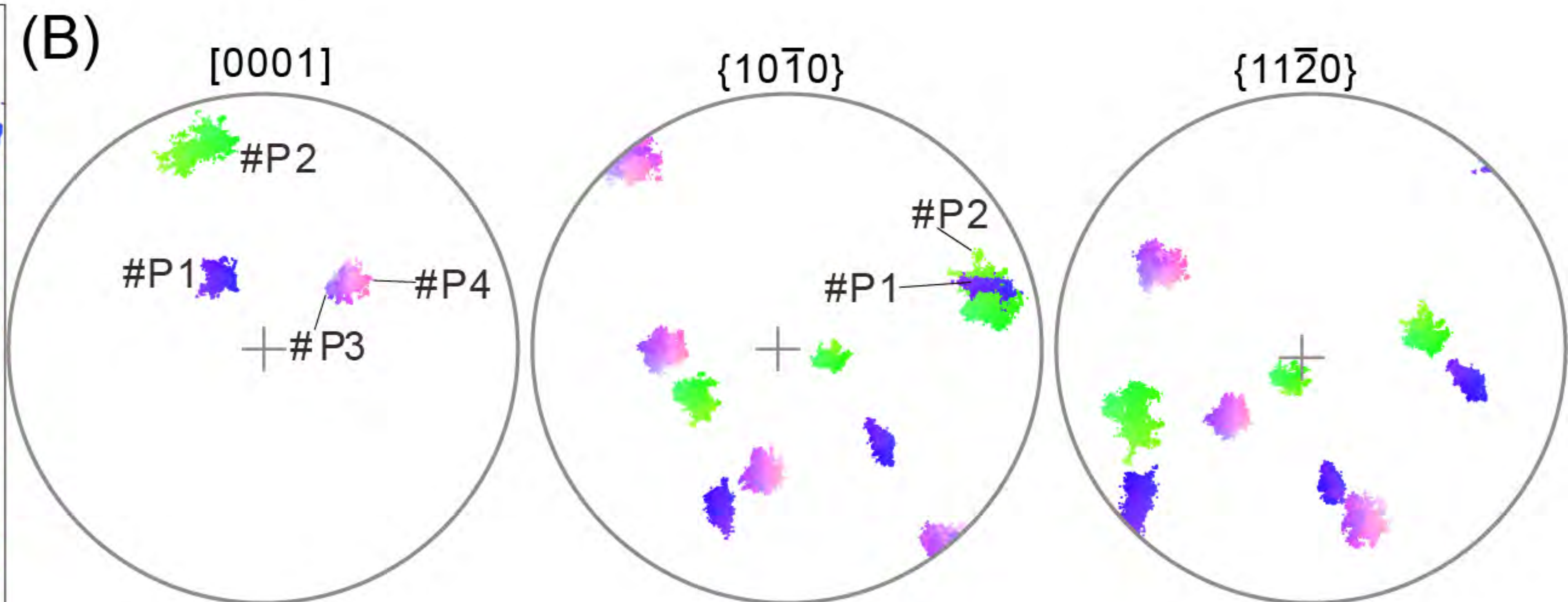
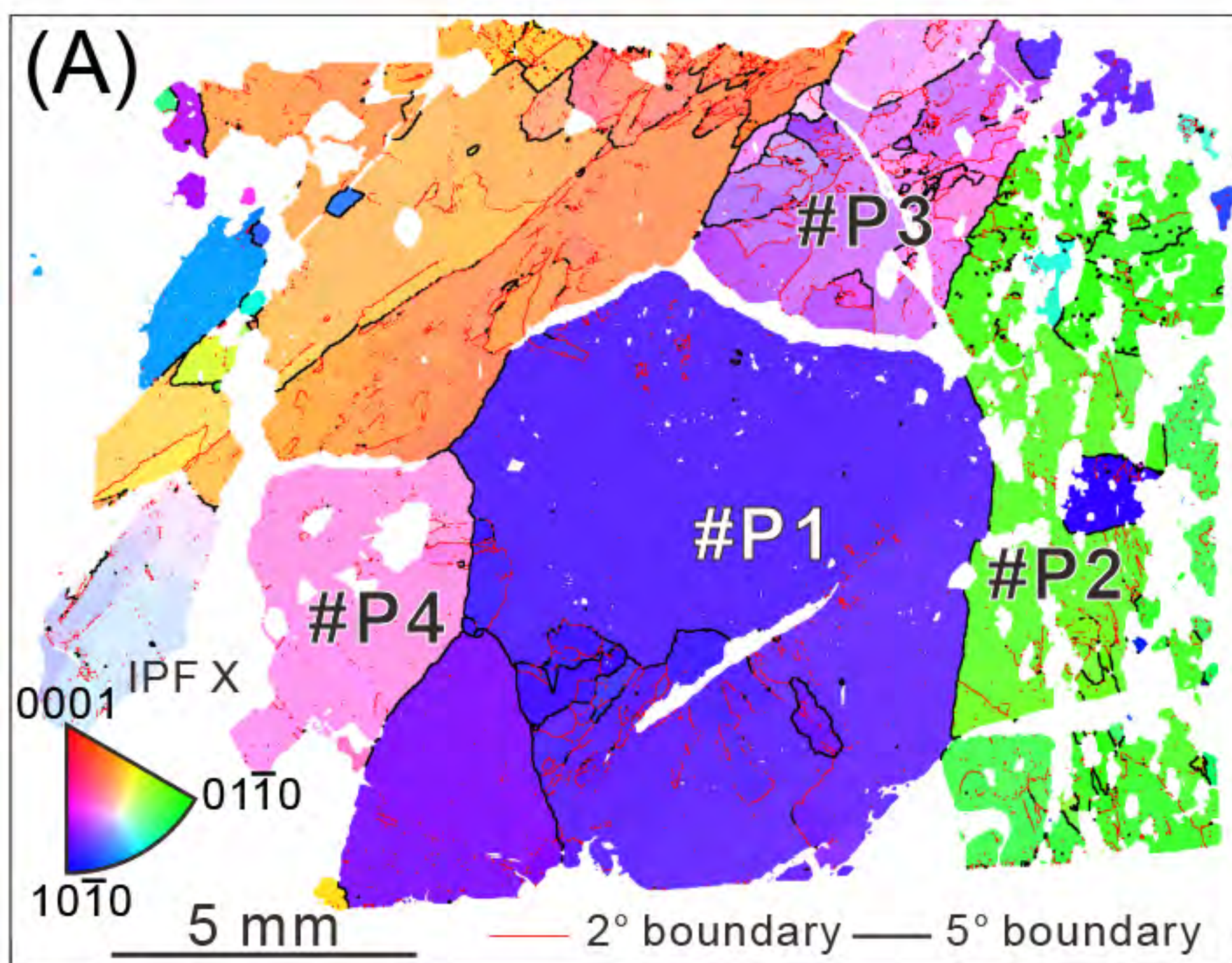


Figure 7

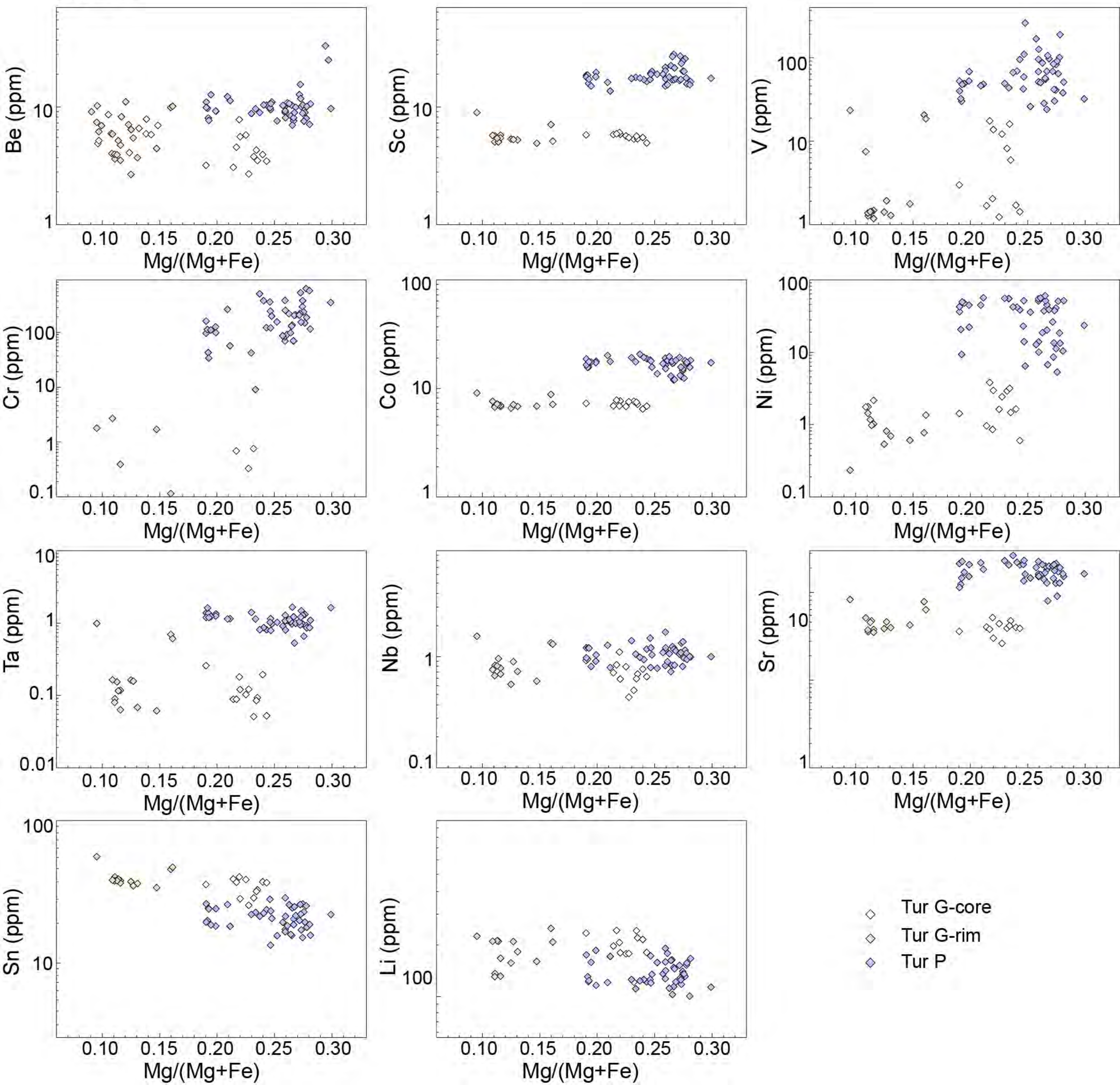


Figure 8

