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1 Chemical and boron isotope composition of tourmaline from the Kiaka
2 orogenic gold deposit (Burkina Faso, West African Craton) as a proxy
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4

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23

24 **Abstract**

25 The Kiaka orogenic gold deposit (Burkina Faso), located in the Paleoproterozoic domain of the
26 West African Craton, is characterized by a two-stage gold mineralization hosted in volcano-
27 sedimentary metamorphic rocks that was formed during the Eoeburnean (2.20-2.13 Ga) and
28 Eburnean (2.13-2.05 Ga) orogenic cycles. These two stages include an early disseminated low-
29 grade gold mineralization and a late vein-hosted high-grade gold mineralization. A paragenetic
30 study indicates that the first gold stage was coeval with the deposition of hydrothermal
31 tourmaline. The aim of this paper is twofold: (i) to determine the processes responsible for the
32 economic disseminated gold mineralization, and (ii) to identify the source of the mineralizing
33 fluids. To this end, we combine *in situ* analyses obtained from electron probe microanalysis and
34 secondary ion mass spectrometry measurements. A dravite composition characterizes the
35 hydrothermal tourmaline hosted in metamafic volcanic rocks and metagreywackes, and $\delta^{11}\text{B}$
36 values range within the two intervals [-25.1‰; -22.0‰] and [-19.6‰; -15.1‰]. Our results
37 suggest that tourmaline formed from a high-temperature (ca. 400°C), reduced, and low-salinity
38 hydrothermal fluid that interacted with the local host rocks. From the modeling of tourmaline-
39 fluid boron isotope fractionation, we infer a metamorphic fluid origin derived from
40 devolatilization of deeply-buried muscovite schists during the regional prograde to peak
41 metamorphism prior ca. 2.13 Ga. This metamorphic fluid-rock interaction model may possibly
42 extend to other orogenic gold deposits in the West African Craton.

43 **Keywords**

44 Tourmaline, Boron isotopes, Orogenic gold deposit, West African Craton, Burkina Faso.

45 INTRODUCTION

46

47 Tourmaline is the most important borosilicate mineral on Earth and represents a reliable
48 monitor of the physico-chemical conditions of the environment in which it crystallized due to
49 three main properties: (i) it is a stable mineral over a large range of pressure and temperature
50 conditions, (ii) it has a complex crystal chemistry incorporating a large range of chemical
51 elements, and (iii) it shows negligible intracrystalline diffusion, making it an excellent
52 petrogenetic indicator for determining fluid sources and processes (Dutrow and Henry 2011;
53 Slack and Trumbull 2011; van Hinsberg et al. 2011). Tourmaline is a common mineral in
54 orogenic gold deposits worldwide, often found disseminated in gold-bearing quartz veins or as
55 metasomatic replacements along the host rock vein selvages. Deposition of tourmaline and gold
56 is generally interpreted to be synchronous (King and Kerrich 1989; Mueller et al. 1991; Kotzer
57 et al. 1993; Anglin et al. 1996; Frei and Pettke 1996; Slack 1996; Rowins et al. 1997; Jiang
58 1998; Béziat et al. 1999), suggesting that tourmaline can be used as a proxy for tracing the ore-
59 forming processes.

60 Fluid and metal sources in orogenic golds deposits, including Au and B, are still debated,
61 therefore a large diversity of genetic models have been proposed. This diversity may either
62 reflect an intrinsic variability of orogenic gold deposits or may show divergence between
63 interpretations. The current paradigm for the formation of orogenic gold deposits involves a
64 metamorphic fluid derived from devolatilization of thick metasedimentary sequences during
65 prograde to retrograde metamorphic evolution of greenstone belts (e.g. Wyman and Kerrich
66 1988; Goldfarb et al. 2005; Phillips and Powell 2010; Goldfarb and Groves 2015; Fusswinkel
67 et al. 2017; Groves et al. 2019). Alternatively, a magmatic origin for fluids and metals related
68 to reduced intrusions has been proposed (Burrows and Spooner 1987; Wang et al. 1993;
69 Tomkins 2013; Xue et al. 2013), as well as mixed magmatic-metamorphic fluid origins (Rogers

70 et al. 2013; Molnár et al. 2016). The source of boron in orogenic gold environments may be
71 derived from (i) metamorphic fluids produced during devolatilization reactions of
72 metasedimentary sequences that occur above 650°C (Spear et al. 1999; van Hinsberg et al.
73 2011), and/or (ii) magmatic fluids released from boron-rich reduced magmas (Trumbull and
74 Slack 2018). In previous studies, tourmaline has been used as a proxy for (i) to identify trace
75 elements that discriminate tourmaline from gold-bearing veins from orogenic gold deposits
76 (Sciuba et al. 2020), (ii) tracing the origin of hydrothermal fluids and metals (distal vs.
77 proximal; metamorphic vs. magmatic) and for (iii) determining the ore-forming processes
78 yielding to deposition of gold, such as in the Yilgarn craton (Jiang et al. 2002), the Archean
79 Abitibi belt (King and Kerrich 1989; Beaudoin et al. 2013), the Archean Barberton greenstone
80 belt (Byerly and Palmer 1991), the Archean Hattu schist belt (Molnár et al. 2016), the Hutti-
81 Maski Greenstone Belt (Hazarika et al. 2015), and the Paleoproterozoic West African Craton
82 (Lambert-Smith et al. 2016; this study).

83 The Kiaka orogenic gold deposit (Burkina Faso) is hosted in the Manga Fada N’Gourma
84 Paleoproterozoic greenstone belt, located on the southeast domain of the West African Craton.
85 The regional host rocks consist of metavolcanic and metasedimentary units composed of
86 metapelites, greywackes, and schists. A dioritic pluton dated at 2140 ± 7 Ma (Fontaine et al.
87 2017) intruded the schists contemporaneously with a regional shearing event. The Kiaka deposit
88 contains a polyphase gold mineralization formed between ca. 2150 Ma and 2080 Ma that is
89 interpreted to be coeval with the deposition of hydrothermal tourmaline (Fontaine et al. 2017;
90 Le Mignot et al. 2017). This paper provides new data on the chemical and boron isotopic
91 composition of hydrothermal tourmaline, as well as whole-rock boron isotope composition of
92 the host rocks. The objective is to trace the ore-forming processes and the origin of mineralizing
93 fluids in the Kiaka gold deposit, focusing specifically on hydrothermal tourmaline associated
94 to the ca. 2150 Ma disseminated gold mineralization. The origin of the mineralizing fluids is

95 discussed relative to the two potential sources: the dioritic intrusion (magmatic origin) and the
96 metasedimentary rocks (metamorphic origin).

97

98 **GEOLOGICAL CONTEXT**

99

100 **The Paleoproterozoic Baoulé-Mossi domain**

101 The Paleoproterozoic southern part of the West African Craton (WAC) is composed of low-
102 grade volcanic and volcano-sedimentary Birimian rocks (ca. 2.20-2.14 Ga) and siliciclastic
103 sediments (ca. 2.13-2.09 Ga) that were intruded by voluminous granites (Grenholm et al. 2019).

104 The oldest Birimian sequence consists of tholeiitic basalt, gabbro, pyroxenite, and minor calc-
105 alkaline ultramafic-mafic to differentiated suites (Baratoux et al. 2011). The geodynamic
106 context of formation of the Birimian rocks remains unclear and several interpretations have
107 been proposed, including a plume-related oceanic plateau (Abouchami et al. 1990; Boher et al.
108 1992; Augustin and Gaboury 2017) and an oceanic context evolving from a MORB-like domain
109 to an increasingly mature volcanic arc domain (Pouclet et al. 2006; Baratoux et al. 2011; Labou
110 et al. 2020). This period characterizes the Eoeburnean cycle, defined by an early magmatic
111 accretion stage followed by an arc construction stage in a convergent setting (Baratoux et al.
112 2011; McFarlane et al. 2019). The Eburnean orogenic cycle started with the filling of major
113 sedimentary basins by flysch sequences derived from the erosion of the Birimian crust and their
114 inversion between ca. 2.13 Ga and 2.10 Ga (Davis et al. 2015; Grenholm et al. 2019). Different
115 depositional settings have been proposed such as syn-orogenic foreland basin sedimentation
116 (Feybesse et al. 2006; Block et al. 2016) or back-arc and fore-arc basin sedimentation controlled
117 by extensional detachments (Perrouy et al. 2012; Grenholm et al. 2019). The paroxysm of the
118 Eburnean cycle is characterized by tectonic accretion and crustal reworking between ca. 2.09
119 and 2.05 Ga (e.g. Masurel et al. submitted). Large transpressional shear zones cross-cut the

120 Baoulé-Mossi domain contemporaneously with the emplacement of high-K calc-alkaline to
121 shoshonitic granitic plutons (Feybesse and Milési 1994; Egal et al. 2002; Parra-Avila et al.
122 2019) in syn- to post-collisional settings (Eglinger et al. 2017; Masurel et al. 2017; Thébaud et
123 al. 2020).

124

125 **Paleoproterozoic gold metallogeny of the Baoulé-Mossi domain**

126 West Africa is currently the largest Paleoproterozoic gold-producing region in the world with
127 an annual gold production of ca. 250 t (Béziat et al. 2008; Markwitz et al. 2016; Robertson and
128 Peters 2016; Goldfarb et al. 2017). The majority of gold deposits are closely located to major
129 first-order tectonic structures such as the Markoye shear zone (MSZ, Fig. 1A) in Burkina Faso
130 (Tshibubudze and Hein 2013), the Ashanti shear zone (AS, Fig. 1A) in Ghana (Perrouty et al.
131 2012) and the Senegal-Mali shear zone (Ledru et al. 1991, Lawrence et al. 2013) that affected
132 greenstone belts. Gold deposits in the southern WAC formed during the long-lived period of a
133 magmatic accretion stage, defined as the Eoeburnean cycle, and broadly during the reworking
134 and tectonic accretion stages of the Eburnean orogenic cycle (Masurel et al. submitted). Few
135 absolute, and some relative ages constrain gold mineralization between ca. 2.18 and 2.06 Ga,
136 and a few are linked to polyphase mineralization processes (such as the Obuasi Au deposit;
137 Fougrouse et al. 2017; Le Mignot et al. 2017; Augustin et al. 2017). The oldest orogenic gold
138 deposits are mostly known in the eastern part of the Baoulé-Mossi domain, formed during the
139 Eoeburnean deformation between ca. 2.14 and 2.13 Ga (Lawrence et al. 2017; Le Mignot et al.
140 2017). They include the ~5.8 Moz Kiaka gold deposit, hosted by volcano-sedimentary rocks
141 which were deformed and metamorphosed under amphibolite facies conditions (Fontaine et al.
142 2017). Early Eburnean gold deposits (ca. 2.11-2.09 Ga) correspond to different types of gold
143 deposits including orogenic (Obuasi deposit; Fougrouse et al. 2017), conglomerate-hosted
144 paleo-placer (Tarkwa deposit; Perrouty et al. 2012), granitoid-hosted (Chirano deposit;

145 Allibone et al. 2004), intrusion-related (Morila deposit; McFarlane et al. 2011), and skarn
146 (Tongon deposit; Lawrence et al. 2017) gold deposits. Some gold deposits formed during the
147 late Eburnean tectono-thermal activity between ca. 2.09 and 2.05 Ga following docking of the
148 Archean and Paleoproterozoic domains within the southern WAC, synchronous with
149 widespread high-K and shoshonitic granites (Eglinger et al. 2017; Masurel et al. 2017).
150 Economic gold mineralization associated with this transcurrent tectonics and crust-derived
151 magmas are widespread in the western portion of the Baoulé-Mossi domain (Thébaud et al.
152 2020; Masurel et al. submitted).

153

154 **Local geology and structural framework of the Kiaka deposit**

155 The Kiaka orogenic gold deposit is located within an elongated volcano-sedimentary sequence
156 known as the Manga Fada N’Gourma greenstone belt, which extends along 250 km from
157 northeast to southwest (Hottin and Ouégrago 1976; Naba et al. 2004; Ganne et al. 2012). The
158 deposit is located at the intersection between two major structures, the Markoye Shear Zone
159 (MSZ) and a D2-related NE-trending shear zone (Fig. 1A-B; Fontaine et al. 2017). The volcano-
160 sedimentary sequence hosting the Kiaka deposit forms a NE-striking corridor, strongly dipping
161 to the northwest and commonly subparallel to the regional foliation (Fig. 1B). Host rocks
162 consist of conglomerate, metagreywacke, and metapelite, which are intercalated with garnet-
163 orthopyroxene schists and mafic rocks (Fontaine et al. 2017). Several magmatic rocks have
164 been described in the Kiaka area, such as a biotite-amphibole diorite plug dated at 2140 ± 7 Ma
165 (Fontaine et al. 2017) and an unfoliated biotite granite, dated between 2120 and 2100 Ma,
166 intruding the tonalite-trondhjemite-granodiorite (TTG) basement (Castaing et al. 2003; Vegas
167 et al. 2008; Fontaine et al. 2017). Litho-geochemical data suggest similarities between the
168 biotite-amphibole diorite and the Tenkodogo-Yamba batholith that is part of the TTG suite
169 (Naba et al. 2004).

170 Deposit-scale study suggests the existence of at least three main deformation phases reported
171 as D1_{Ki}, D2_{Ki}, and D3-4_{Ki} (Fontaine et al. 2017). The two first phases (D1_{Ki} and D2_{Ki}) occurred
172 under ductile conditions (P=550-650°C, T=6-8 kbars; Ganne et al. 2012; Fontaine et al. 2017),
173 whereas the others (D3_{Ki}-D4_{Ki}) took place at the ductile-brittle transition (P<4 kbars, T=200-
174 450°C; Fontaine et al. 2017; Ganne et al. 2012; Block et al. 2015). The D1_{Ki} phase corresponds
175 to a relic structural event marked by P1_{Ki} folds, resulting from EW to WNW-ESE compression,
176 which are preserved in low-strain domains between D2_{Ki} shear zones (Fontaine et al. 2017).
177 The S2_{Ki} regional foliation, parallel to the isoclinal P1_{Ki} folding, records a biotite-sillimanite-
178 garnet-amphibole assemblage, suggesting lower to middle amphibolite facies conditions (Fig.
179 3A).

180 At the regional scale, the NE-trending D2-related shear zones and the NS-trending MSZ are the
181 main structures controlling the emplacement of the gold mineralization at Kiaka (Fontaine et
182 al. 2017). These structures record dextral-reverse D1 motion and sinistral-reverse D2
183 reactivation (Tshibubudze et al. 2009; Tshibubudze and Hein 2013). Mineralized envelopes are
184 spatially associated with the NE-trending shear zones and some of them extend along the axial
185 plane of P2_{Ki} isoclinal folds (Fontaine et al. 2017). The sinistral-reverse D2 reactivation is
186 coeval with the emplacement of the Kiaka diorite dated at 2140 ± 7 Ma. The D3-4_{Ki} phases
187 correspond to quartz-carbonate veins that formed during reactivation along D2-related shear
188 zones and retrogression at greenschist facies conditions (Fontaine et al. 2017), likely during or
189 after the ductile-brittle transition.

190

191 **Tourmaline paragenesis and space-time relationships with gold mineralization**

192 A relative chronology between tectono-metamorphic and hydrothermal events has been
193 proposed by Fontaine et al. (2017), based on crosscutting relationships, hydrothermal

194 assemblages, and ore mineralogy, identifying two successive stages of gold mineralization and
195 associated hydrothermal alteration in the Kiaka deposit (Fig. 2):

196 (i) The first main stage corresponds to the early sulfide-rich disseminated gold
197 mineralization related to the D2_{Ki} phase, coeval with emplacement of the biotite-amphibole
198 diorite intrusion (Fig. 2). This mineralization is volumetrically the most important (>80% of the
199 orebodies) and constitutes most of the gold resources with average grades of 1-3 g/t. The ore
200 assemblage consists of 50µm-1mm large anhedral pyrrhotite (60-80%) that is commonly
201 associated with sub-millimetric (200-300 µm) pyrite (10-20%), chalcopyrite (5-10%),
202 arsenopyrite (5-10%), and rare löllingite disseminated in sericitized metagreywacke and partly
203 in metamafic volcanic rocks, containing a biotite-titanite-clinozoisite assemblage. Gold
204 probably occurs as nano-inclusions hosted in, or within, the crystal lattice of pyrite,
205 arsenopyrite, and löllingite. This stage was dated at 2157 ± 24 Ma (Re-Os on pyrrhotite; Le
206 Mignot et al. 2017; Fontaine et al. 2017).

207 (ii) The second stage is related to formation of a high-grade gold mineralization at 50-
208 60 g/t Au hosted in hydrothermal veins and breccias that formed during the D3_{Ki} to D4_{Ki} phases
209 (Fig. 2). The ore assemblage is composed of pyrrhotite, chalcopyrite, arsenopyrite, electrum,
210 native gold (2-20 µm), and tellurobismuthite, intergrown with clinozoisite, quartz, calcite, and
211 chlorite.

212 According to Fontaine et al. (2017) and new petrographic observations, two generations of
213 tourmaline are observed in the Kiaka deposit. A first generation of tourmaline (*Tur*₁) is locally
214 found as rounded detrital grains (<10 µm) in quartz-biotite metagreywacke, representing <5%
215 in volume of the host rock. *Tur*₁ is also found within garnet-biotite-chlorite-muscovite layers
216 hosted in muscovite schists (Fig. 3A-B), which are affected by the S2_{Ki} foliation and associated
217 folds, suggesting an early formation prior, or during, the D1_{Ki} stage. A second generation of
218 tourmaline (*Tur*₂) is found in the metagreywacke and metamafic volcanic rock (referred

219 subsequently as metamafic rocks) located close to or within the mineralized zones. This
220 tourmaline is found as large (typically 50-500 μm) zoned porphyroblasts containing sulfide and
221 silicate inclusions. It is locally oriented along the $S_{2\text{Ki}}$ foliation. In the metagreywacke, Tur_2 is
222 intergrown with an assemblage of biotite, clinozoisite, quartz, K-feldspar and disseminated
223 sulfides, including pyrrhotite, chalcopyrite, pyrite, and arsenopyrite (Fig. 3C-D). In the
224 metamafic rock, Tur_2 is intergrown with chlorite (Chl 1, pre- to syn- $D_{1\text{Ki}}$), biotite, titanite,
225 clinozoisite, and pyrrhotite, which are characteristics of the $D_{2\text{Ki}}$ hydrothermal assemblage.
226 Chlorite (Chl 1) inclusions oriented along an early foliation (syn- $D_{1\text{Ki}}$) within the poikiloblastic
227 Tur_2 porphyroblasts (Fig. 5), as well as a chlorite (Chl 2)-biotite assemblage (Fig. 3F), related
228 to the $D_{3\text{Ki}}$ stage and overgrown by Tur_2 , constraint the formation of Tur_2 within syn- to late-
229 $D_{2\text{Ki}}$ event. The assemblage of Chl 1 and biotite is interpreted as a relic from stage $D_{1\text{Ki}}$ that
230 was overprinted by ore stage fluids during the $D_{2\text{Ki}}$ event in replacement zones. In contrast, the
231 assemblage of titanite, clinozoisite, and pyrrhotite is considered to be earlier than $D_{3\text{Ki}}$, because
232 it is cut by chlorite (Chl 3)-calcite veins (Fig. 3E-F). Therefore, the second generation of
233 tourmaline (Tur_2) is interpreted to be of hydrothermal origin and to have formed during the
234 $D_{2\text{Ki}}$ event, coevally with formation of the Kiaka disseminated gold mineralization. In this
235 paper, a specific focus is given on Tur_2 hosted both in metagreywacke and metamafic rocks, in
236 order to determine the fluid sources and processes related to the formation of the first gold
237 event, i.e. the early sulfide-rich disseminated gold mineralization related to the $D_{2\text{Ki}}$ event.
238 Early detrital Tur_1 was not investigated because it formed before the gold mineralization and
239 thus cannot be used as a tracer of ore-forming processes and mineralizing fluids.

240

241 **SAMPLE DESCRIPTION AND ANALYTICAL METHODS**

242

243 **Sample description**

244 Representative samples of the four main lithologies of the Kiaka deposit were collected from
245 drill cores (spacing >400 m) intersecting the main orebody and alteration zones. Investigation
246 of these lithologies was carried out in order to document the hydrothermal alteration by the
247 gold-bearing fluids and to identify the presence of hydrothermal tourmaline. These lithologies
248 include:

249 (i) Muscovite schists: they are mostly located in the southern part of the deposit in
250 the footwall of the D2-related shear zone (Fig. 1). They represent 50 to 100 m thick lenses
251 intercalated between metagreywacke and metavolcanic rocks. The muscovite schists contain
252 folded tourmaline (*Tur₁*)-garnet-biotite-chlorite-muscovite layers (Fig. 3A-B) and rare
253 pyrrhotite grains. The muscovite schist sample (drill KDH75, depth 64.9 m) is located at about
254 1-2 m from the mineralized zones and is weakly hydrothermally altered.

255 (ii) Diorite: it consists of sub-vertical intrusive plugs within the metasedimentary
256 sequence in the northern part of the deposit (Fig. 1C). It is interpreted to be contemporaneous
257 with the D2_{Ki} event generating sinistral displacement along mineralized, NE-trending D2 shear
258 zones. The diorite is dominantly composed of plagioclase, amphibole, chlorite, biotite, and
259 quartz. No tourmaline was found in the diorite. Sample KDH337 (depth 44.1m) is located at
260 about 50 m from the mineralized zones and is weakly hydrothermally altered, containing rare
261 grains of pyrrhotite and chalcopyrite associated with titanite.

262 (iii) Metagreywacke: it is the dominant lithology at Kiaka and forms the southern
263 footwall of a D2-related shear zone hosting the main mineralized zone. Composed of quartz,
264 feldspar, and sillimanite with a granoblastic texture, metagreywacke locally contain
265 disseminated tourmaline grains (*Tur₂*), about 50 µm in size (Fig. 3C-D). Sample KDH29 (depth
266 311.8 m; Fig. 3C-D; Fig. 4) is from a phlogopite-rich alteration zone close to the orebody.

267 (iv) Metamafic rock: it is intercalated within the metasedimentary sequence forming
268 >50 m thick sequences dipping towards the northwest (Fig. 1). Sample KDH291 (depth 56.2

269 m; Fig. 3E-F) comes from an alteration zone in proximity to the mineralized envelope. Within
270 this zone, the metamafic rock contains porphyroblasts of hydrothermal tourmaline (*Tur*₂)
271 reaching few millimeters in size, embedded within a chloritized, fine-grained matrix, that
272 locally contains pyrrhotite, titanite and clinozoisite (Fig. 3E).

273

274 **Scanning electron microscopy**

275 Mineralogical observations of tourmaline were carried out using transmitted-light microscopy
276 and scanning electron microscopy (SEM) at the GeoRessources laboratory (Nancy, France).
277 Tourmaline grains were investigated using a Hitachi S-4800 and a JEOL J7600F scanning
278 electron microscopes, both equipped with SDD-type energy-dispersive X-ray spectrometers
279 (EDS). Backscattered electron (BSE) images were acquired on carbon-coated polished thin
280 sections with an acceleration voltage of 15 kV, adjusting the image contrast to reveal internal
281 zoning within the tourmaline grains. SEM was used to characterize the internal textures of
282 tourmaline and to select representative grains for the *in situ* chemical and isotopic analyses.

283

284 **Electron probe microanalysis**

285 Major and minor element composition of tourmaline was determined using a Cameca SX100
286 electron microprobe analyzer (EMPA) equipped with five wavelength-dispersive X-ray
287 spectrometers (WDS) at the GeoRessources laboratory (Nancy, France). Analyses were
288 performed with the following operating conditions: beam current of 20 nA, acceleration voltage
289 of 15 kV, and beam diameter of 1 µm. Counting times on element peaks and backgrounds were
290 16 sec and 8 sec, respectively, for Si, Al, K, Ca, Fe, Mg, Mn, Ti, and 30 sec and 15 sec,
291 respectively, for Na, Cr, and Cl. The following standards and monochromators were used for
292 the EMPA measurements: albite (Si, Na on TAP), olivine (Mg on TAP), corundum (Al on
293 TAP), orthoclase (K on LPET), andradite (Ca on PET), ilmenite (Ti on LPET, Mn on LIF),

294 hematite (Fe on LIF), and vanadinite (Cl on LPET). Detection limits are approximately 330
295 ppm for Si, 300 ppm for Al, 1000 ppm for Fe, 265 ppm for Mg, 250 ppm for Ti, 365 ppm for
296 Mn, 515 ppm for Na, 370 ppm for Ca, 200 ppm for K, and 140 ppm for Cl. Structural formulae
297 of tourmaline were calculated using the WinTcac software (Yavuz et al. 2014) normalizing to
298 15 cations in Y+Z+T sites and assuming stoichiometric 3 atoms for B and 4 atoms for OH+F,
299 based on the general formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where X = Na⁺, Ca²⁺, K⁺, or vacancy
300 site; Y = Fe²⁺, Mg²⁺, Mn²⁺, Al³⁺, Li⁺, Fe³⁺, or Cr³⁺; Z = Al³⁺, Fe³⁺, Ti⁴⁺, Mg²⁺, or Cr³⁺; T = Si⁴⁺,
301 Al³⁺, or B³⁺; V = OH⁻, O²⁻; and W = OH⁻, F⁻, or O²⁻ (Henry et al. 2011). Chemical compositions
302 of tourmaline are reported in weight per cent (wt.%) oxides and the structural formulae are
303 expressed in atoms per formula unit (apfu) (ESM Table 2). X-ray elemental maps were acquired
304 with a 15 kV accelerating voltage, a 100 nA beam current, and a 1 μm^2 electron beam (Fig. 6).
305 The elements Na, Si, Mg, Al, Ca, Ti, and Fe were measured with dwell times of 300 msec each
306 and an acquisition step of 10 μm , for a total map size of 2900 x 3890 μm .

307

308 **Secondary ion mass spectrometry**

309 Boron isotopic composition of tourmaline was measured by secondary ion mass spectrometry
310 (SIMS) using a Cameca IMS 1280-HR instrument at the CRPG-CNRS (Vandoeuvre-lès-
311 Nancy, France). Analyses were performed on gold-coated polished thin sections that were
312 previously investigated by SEM and EMPA, with a 20 nA beam of primary ions O⁻ accelerated
313 at 13 kV with an ellipsoid ablation spot of 20 μm long axis. The secondary ions ¹⁰B⁺ and ¹¹B⁺
314 were accelerated at 10 kV and were measured in mono-collection with the axial Faraday cup
315 with a mass resolution power $M/\Delta M = 2000$. Each calculated isotopic ratio ¹¹B/¹⁰B corresponds
316 to 30 cycles of measurement with counting times of 8 sec per cycle on mass 10 and of 4 sec per
317 cycle on mass 11. For each spot, a pre-sputtering of 60 sec was applied immediately before
318 each analysis for surface cleaning. Instrumental mass fractionation (IMF) was determined and

319 corrected using two tourmaline reference materials corresponding to dravite (Harvard #108796)
320 and schorl (Harvard #112566) described by Dyar et al. (2001) and Leeman and Tonarini (2001).
321 Each standard was measured several times during the analytical SIMS session following a
322 standard-sample bracketing procedure. The summary of the B isotope analyses on the
323 tourmaline reference materials measured by SIMS is reported in ESM Table 1. The matrix
324 effect was corrected using the dravite Harvard #108796 reference material because the
325 tourmaline samples analyzed in this work have dravitic composition. After correction of IMF,
326 the measured $^{11}\text{B}/^{10}\text{B}$ ratios were reported in $\delta^{11}\text{B}$ notation (in ‰) relative to the NIST SRM
327 951, whose $^{11}\text{B}/^{10}\text{B}$ ratio is 4.04362 (Catanzaro et al. 1970). The external error (2σ) is about
328 0.13‰ over 28 analyses for the dravite Harvard #108796 and 0.26‰ over 14 analyses for the
329 schorl Harvard #112566. The external error used is that of the dravite Harvard #108796. The
330 total error is the quadratic sum of the internal and external errors and range between 0.2 and
331 1.2‰ (2σ) on the tourmaline samples with a median value of 0.3‰ (2σ).

332

333 **Multi-collector – inductively coupled plasma – mass spectrometry**

334 Whole-rock boron content and isotopic compositions of the muscovite schist and diorite were
335 measured using a Thermo Scientific Neptune multi-collector – inductively coupled plasma –
336 mass spectrometer (MC-ICP-MS) at the LhyGeS (Université de Strasbourg-EOST, France).
337 The B extraction procedure was adapted from Lemarchand et al. (2012) and is summarized as
338 follows: 10 mg of powdered sample were mixed with 250 mg of analytical grade K_2CO_3 in a
339 12 mL PtAu 05 crucible and placed in a muffle furnace at 950°C for 45 min. After cooling, the
340 fusion residue was dissolved in 35 mL of bidistilled HCl 0.2N. Boron was then purified from a
341 0.5 mL aliquot by a two-step chemical procedure using the cation exchange resin Biorade
342 AG50WX12 and the B-specific resin Amberlite IRA743. The recovered solution was
343 simultaneously analyzed for both B concentration and isotope ratios using the standard-sample-

344 standard bracketing method. The operational settings for B analyses by MC-ICP-MS are
345 described in details by Roux et al. (2015). Accuracy has been verified by repeated analyses of
346 solution and rock standards (ERM AE120 = -20.1‰; ERM AE121 = +20.0‰; NRC NASS5
347 = +39.8‰; GSJ JB2 = +7.2‰). Total B contamination is 15 ng and the analytical uncertainties
348 are 5% and 0.4‰ (2σ) for B concentration and isotope ratios, respectively.

349

350 **RESULTS**

351

352 **Petrography and textural features of tourmaline**

353 Hydrothermal tourmaline (*Tur*₂) hosted in metagreywacke (sample KDH29-311.8 m; 1.08 g/t
354 Au) ranges in size from 20 to 400 μm with euhedral to sub-euhedral shapes (Fig. 3C-D; Fig. 4).
355 No foliation is clearly preserved in this sample. A metamorphic recrystallization can be
356 observed whereas *Tur*₂ and biotite seem to represent a mineral equilibrium assemblage and to
357 be part of the same hydrothermal D2_{Ki} event. In addition, pyrrhotite and pyrite are characteristic
358 of the assemblage of the low-grade disseminated ore in the Kiaka deposit. The tourmaline grains
359 in the metagreywacke sample occasionally host micro-inclusions of apatite, quartz and
360 pyrrhotite oriented along intra-grain fractures. At microscopic scale, tourmaline has light green
361 to brownish colors in polarized light and is greenish in crossed polarized light. The grains
362 appear homogeneous without core-rim zoning on BSE images (Fig. 4). Nine representative
363 tourmaline grains were selected for *in situ* chemical and isotopic analyses.

364 Hydrothermal tourmaline (*Tur*₂) hosted in metamafic rock (sample KDH291-56.2 m; 0.05 g/t
365 Au) is characterized by euhedral to sub-euhedral habit and is commonly millimetric in size (Fig.
366 3E). Under the microscope, poikiloblastic tourmaline porphyroblasts have light yellow to beige
367 colors in polarized light and are yellow-brownish in crossed polarized light. Three
368 representative millimetre-size tourmaline grains intergrown with the biotite-titanite-clinozoisite

369 D2_{Ki} assemblage were selected for the *in situ* chemical and isotopic analyses (Fig. 5). Those
370 three grains show different crystal orientation relative to the thin section plane, and their internal
371 zoning and compositional variations were investigated in detail. The first tourmaline grain
372 (Grain 1) shows an oblique section relative to the c-axis of about 3 mm wide, the second (Grain
373 2) shows a transversal section relative to the c-axis of about 9 mm in length, and the third (Grain
374 3) shows an oblique section relative to the c-axis (Fig. 5). The poikiloblastic tourmaline
375 porphyroblasts host numerous sulfide inclusions (<100 μm up to 0.1 mm in size), including
376 pyrrhotite, chalcopyrite and pyrite, as well as accessory clinozoisite, biotite, amphibole, and
377 chlorite (Chl 2) (Fig. 2). At the grain scale, tourmaline hosted in metamafic rock shows a core-
378 rim zoning on BSE images (Fig. 5C). The core represents the main part of the grains and shows
379 a patchy zoning with dark to medium grey contrasts on BSE images. The rim forms a 100-300
380 μm thick overgrowth in optical continuity with the core and shows brighter contrasts on BSE
381 images. No dissolution textural evidence between core and rim was observed. X-ray elemental
382 maps show intra-crystalline chemical zoning for Al, Fe, Mg, Ca, and Ti (Fig. 6). The rim is
383 marked by higher Fe contents relative to the core, which is Mg-rich. The intra-grain variation
384 in Ca, Ti, and Al, corresponds to the patchy zoning within the core related to the primary crystal
385 growth of tourmaline.

386

387 **Chemical composition of tourmaline**

388 Chemical compositions and structural formulae of representative tourmaline grains (*Tur2*) from
389 the Kiaka deposit are reported in the ESM Table 2. Overall, tourmaline compositions show
390 relatively large variations in major elements for FeO (4.65-7.68 wt.%), MgO (7.10-9.52 wt.%),
391 Al₂O₃ (29.59-35.20 wt.%), and relatively small variations in minor elements for Na₂O (1.41-
392 1.70 wt.%), CaO (0.58-2.10 wt.%), MnO (<0.1 wt.%), and TiO₂ (0.19-1.51 wt.%). The

393 measured K₂O and Cl values are very low (up to 0.14 wt.%), close to or below the EMPA limits
394 of detection.

395 Tourmaline hosted in the metamafic rock (sample KDH291-56.2 m) belongs to the alkali-group
396 and plots within the compositional field of Al-poor and Fe³⁺-rich metasedimentary rocks in the
397 Al-Fe-Mg diagram (Fig. 7F). Tourmaline has a dravite composition with Mg/(Fe+Mg) = 0.67-
398 0.77 and X_{vacancy}/(X_{vacancy}+Na) = 0.11-0.29 (Fig. 7A). It has moderate contents of Ca (0.10-0.64
399 apfu), Na (0.50-0.70 apfu), and Al (5.55-6.27 apfu). No correlation is found between the Ca
400 and Ti contents (0.04-0.19 apfu) and the color zoning of tourmaline in polarized light. The core
401 and rim show minor compositional variations that are principally marked by variations of the
402 Fe/Mg ratio, as also seen on X-ray elemental maps (Fig. 6). The chemical variations for
403 tourmaline hosted in the metamafic rock are mostly due to the Mg₊₁Fe₋₁ and □Al₊₁(NaMg)₋₁
404 exchange vectors, with possible contribution of the (AlO)₊₁(MgOH)₋₁ deprotonation vector
405 (Fig. 7).

406 Tourmaline hosted in the metagreywacke (sample KDH29-311.8 m) has a distinct chemical
407 composition compared to the metamafic rock-hosted tourmaline. Tourmaline belongs to the
408 alkali-group with a dravite composition and plots into the compositional field of Al-rich
409 metasedimentary rocks in the Al-Fe-Mg diagram (Fig. 7F). It differs mainly from tourmaline
410 hosted in the metamafic rock by lower contents of Ca (0.16-0.22 apfu), Mg (1.75-1.89 apfu),
411 and Na (0.45-0.54 apfu), and by higher contents of X-vacancy (0.25-0.35 apfu), and Al (6.37-
412 6.72 apfu). Tourmaline has dravite composition with Mg/(Fe+Mg) = 0.68-0.73 and
413 X_{vacancy}/(X_{vacancy}+Na) = 0.32-0.44. Variations of tourmaline compositions are mostly explained
414 by the Mg₊₁Fe₋₁ and □Al₊₁(NaMg)₋₁ exchange vectors joining the dravite to foitite endmembers
415 (Fig. 7B-C).

416

417 **Boron isotope composition of the host rocks and tourmaline**

418 Whole-rock boron isotope analyses were carried out on representative samples of unaltered
419 diorite (sample KDH337-44.1) and muscovite schist (sample KDH75-64.9) collected outside
420 the mineralized envelopes. Boron concentration and isotope analyses yielded reproducible
421 values for each sample (Table 1). The diorite has a B content of 5.6 ppm with an average $\delta^{11}\text{B}$
422 value of -13.9‰ ($n = 2$), whereas the muscovite schist contains 71 ppm B and has an average
423 $\delta^{11}\text{B}$ value of -29.2‰ ($n = 2$). Because the samples are devoid of hydrothermal alteration and
424 the isotopic data are reproducible, the whole-rock boron isotope compositions are considered
425 to be representative of each rock precursor.

426 *In situ* boron isotope compositions of tourmaline hosted in the metagreywacke (sample KDH29-
427 311.8 m) and the metamafic rock (sample KDH291-56.2 m) are shown in Fig. 8 and Table 2.
428 The full range of $\delta^{11}\text{B}$ values of tourmaline extends from -25.12‰ to -15.10‰ ($n = 49$) and
429 overlaps the lower $\delta^{11}\text{B}$ range of tourmaline hosted in orogenic gold deposits worldwide ($\delta^{11}\text{B}$
430 = -24‰ to $+19\text{‰}$; Fig. 8). Tourmaline hosted in the metamafic rock has heavier boron isotopic
431 composition ($\delta^{11}\text{B} = -19.6\text{‰}$ to -15.1‰ ; mean = -17.8‰ ; mode $\sim -19.5\text{‰}$; $n = 31$) compared
432 to tourmaline hosted in the metagreywacke ($\delta^{11}\text{B} = -25.1\text{‰}$ to -22.0‰ ; mean = -24.2‰ ; mode
433 $\sim -24.0\text{‰}$; $n = 18$). Isotopic analyses of single tourmaline grains reveal $\delta^{11}\text{B}$ variations up to
434 4.7‰ from core to rim, but show no systematic $\delta^{11}\text{B}$ variation related to sector and patchy
435 zoning. No correlation was found between the chemical and boron isotopic composition of
436 tourmaline.

437

438 **DISCUSSION**

439

440 **Chemical composition of tourmaline as a monitor of fluid-rock interactions**

441 Tourmaline grains hosted in the metamafic rock and the metagreywacke belong to the dravite
442 series, but they differ by their chemical and boron isotopic compositions. Tourmaline hosted in

443 the metamafic rock is Al-poor (5.75-6.27 apfu), Fe-rich (0.63-1.05 apfu) and Mg-rich (2.00-
444 2.30 apfu), whereas tourmaline hosted in metagreywacke is Al-rich (6.37-6.72 apfu), Fe-poor
445 (0.65-0.83 apfu) and Mg-poor (1.75-1.89 apfu). This is consistent with the whole-rock contents
446 of Al₂O₃, Fe₂O₃ and MgO in metamafic rock and metagreywacke, respectively (Table 1;
447 Fontaine et al. 2017), which suggests a host rock control on the chemical composition of
448 tourmaline (except for boron), as proposed by other studies (e.g. van Hinsberg et al. 2011;
449 Hazarika et al. 2015; 2016; Kalliomäki et al. 2017; Harlaux et al. 2019). In addition, metamafic
450 rock-hosted tourmaline has lower X-vacancy contents (0.08-0.24 apfu) and higher Na+Ca
451 contents (0.76-0.92 apfu), whereas metagreywacke-hosted tourmaline has higher X-vacancy
452 contents (0.25-0.35 apfu) and lower Na+Ca contents (0.65-0.75 apfu). This is also consistent
453 with the higher whole-rock contents of CaO, Na₂O and K₂O in the metamafic rock compared
454 to metagreywacke (Table 1; Fontaine et al. 2017). In the X-vacancy vs. Al total and Fe vs. Al
455 diagrams (Fig. 7C, D), metamafic rock-hosted tourmaline shows large Al variations (5.75-6.27
456 apfu) reflecting the (AlO)₊₁(MgOH)₋₁ deprotonation exchange vector, whereas metagreywacke
457 tourmaline has higher Al and X-vacancy contents projecting along the □Al₊₁(NaMg)₋₁ exchange
458 vector.

459 These variations may reflect variable degrees of interaction between the hydrothermal fluid and
460 the host rocks. For comparison, syn-ore hydrothermal tourmaline from orogenic gold deposits
461 in the Loulo Gold District in Mali (Lambert-Smith et al. 2016) shows large variations of the
462 Mg/(Fe+Mg) ratio (0.27-0.96) and have lower Ca contents (0.01-0.09 apfu) and higher Na
463 contents (0.62-0.89) compared to hydrothermal tourmaline from Kiaka (Fig. 7). The
464 composition of the X-site in tourmaline is dominantly controlled by the Na and Ca
465 concentrations in the coexisting aqueous fluid, being therefore a function of the fluid salinity
466 (von Goerne et al. 2001, 2011; Dutrow and Henry 2016, 2018). The relative high contents of
467 Na (0.45-0.70 apfu, average = 0.61 apfu) and Ca (0.10-0.37 apfu, average = 0.24 apfu) and the

468 relative low contents of X-vacancy (0.08-0.35 apfu, average = 0.15 apfu) in hydrothermal
469 tourmaline (*Tur₂*) suggest that the fluid was of low to moderate salinity. The tourmaline-bearing
470 ore assemblage is interpreted to have formed during the D2_{Ki} stage at temperatures of 371-
471 413°C based on chlorite (Chl 2) thermometry (Fontaine et al. 2017). Additionally, arsenopyrite
472 in contact with pyrrhotite and löllingite in quartz-biotite metagreywacke contains 35.4-36.5
473 atm% of As, yielding temperatures of 360-475°C (Fontaine et al. 2017). Assuming a median
474 temperature of 400°C and an average Na = 0.6 apfu in tourmaline, a salinity of ca. 3 wt.% NaCl
475 equiv can be estimated for the fluid in equilibrium with the assemblage tourmaline + quartz +
476 chlorite (von Goerne et al. 2001). Tourmaline precipitation from hydrothermal fluids requires
477 acidic to near-neutral conditions (pH <6) that favor the formation of stable trigonal complexes
478 [B(OH)₃] in the fluid (Morgan and London 1989; Henry and Dutrow 1996). The development
479 of pervasive sericitization associated with disseminated tourmaline and clinozoisite in the
480 metagreywacke (Fontaine et al. 2017) suggests that the fluid was moderately acidic. The
481 composition of tourmaline from Kiaka is dominantly controlled by the Fe²⁺₊₁Mg²⁺₋₁ and
482 □Al₊₁(NaMg)₋₁ exchange vectors with no contribution of the Fe³⁺₊₁Al³⁺₋₁ homovalent
483 substitution (Fig. 7), which suggests low Fe³⁺/Fe²⁺ ratios and reduced fluid conditions. These
484 arguments suggest that hydrothermal tourmaline (*Tur₂*) likely formed from moderately high
485 temperature (ca. 400°C), moderately acidic, reduced, and low-salinity hydrothermal fluids and
486 that its chemical composition (except for B, Na and Ca) was buffered by the host rock during
487 fluid-rock interactions.

488

489 **Origin of fluids and boron for formation of the Kiaka gold deposit**

490 The source of boron and mineralizing fluids at Kiaka can be discussed in terms of proximal vs.
491 distal, as well as magmatic vs metamorphic origin. In the metagreywacke and the metamafic
492 rock, the boron budget is largely dominated by hydrothermal tourmaline (*Tur₂*), which is the

493 main boron-bearing mineral in those rocks. Considering that basalts have typically very low
494 boron contents (Table 1; <0.1 to 5 ppm; Leeman and Sisson 1996; Marschall 2018), it is
495 unlikely that the boron required to form *Tur*₂ in the metamafic rock was derived from the
496 basaltic precursor. The metagreywacke contains two generations of tourmaline: one generation
497 is detrital (*Tur*₁), being part of the mineral assemblage of the protolith, whereas the other one is
498 hydrothermal (*Tur*₂), being formed during the D2_{KI} event. As detrital *Tur*₁ remained stable in
499 the metagreywacke during the prograde and retrograde metamorphism, it seems unlikely that
500 *Tur*₁ was a viable source of boron for formation of *Tur*₂, even if we cannot definitively exclude
501 the potential destabilization of *Tur*₁ in deep-seated metagreywacke lithologies.

502 We may also exclude the diorite as a proximal boron source because of its low boron content
503 (B = 5.6 ppm, Table 1) and its absence of significant hydrothermal alteration, arguing against
504 the release of boron-rich magmatic fluids or post-magmatic hydrothermal alteration. Another
505 possible candidate could be the younger unfoliated biotite granites that have intruded the TTG
506 basement between ca. 2120 Ma and 2100 Ma (Vegas et al. 2008; Baratoux et al. 2011). These
507 granitic rocks emplaced through transcurrent shearing along the Manga Fada N’Gourma
508 greenstone belt and the related amphibolite-facies metamorphism attributed to contact
509 metamorphism (Naba et al. 2004; Vegas et al. 2008) has been dated at 2105 ± 30 Ma (Pb-Pb on
510 zircon; Castaing et al. 2003). However, none of these granitic rocks has been described in the
511 district of Kiaka and no granite intercept was found in the investigated drill cores.

512 A proximal origin of boron-rich fluids may therefore be discarded. The boron isotope
513 compositions of hydrothermal tourmaline (*Tur*₂) from Kiaka ($\delta^{11}\text{B} = -25.1\text{‰}$ to -15.1‰ ; Fig.
514 8) fall outside the typical $\delta^{11}\text{B}$ range for tourmaline hosted in granitic rocks (-15‰ to $+5\text{‰}$;
515 Marschall and Jiang 2011; Trumbull and Slack 2018), although they partly overlap with the
516 $\delta^{11}\text{B}$ range of tourmaline from granite-related veins (-22‰ to -3‰ ; Fig. 8).

517 A magmatic-hydrothermal origin of the fluid can be excluded, because (i) no contemporaneous
518 granitic intrusion is found nearby the Kiaka deposit, (ii) age constraints exclude the diorite plug
519 as a magmatic source of boron, and, to a lesser extent, (iii) the mineralization is hosted in thick
520 metasedimentary-metavolcanic units. A meta-evaporitic fluid origin ($\delta^{11}\text{B} = +5\text{‰}$ to $> +30\text{‰}$)
521 can also be ruled out. In contrast, the B isotope values of *Tur*₂ are compatible with those of
522 tourmaline hosted in metasedimentary rocks ($\delta^{11}\text{B} = -26\text{‰}$ to $+1\text{‰}$; Nakano and Nakamura
523 2001; Bebout and Nakamura 2003; Marschall and Jiang 2011; Berryman et al. 2017; Fig. 8).
524 Despite the general diachronism observed from east to west in the southern WAC (Parra-Avila
525 et al. 2017), comparison with the Loulo Mining District in Mali is of interest. Lambert-Smith
526 et al. (2016) have used geochemistry and boron isotopy of tourmaline to discriminate fluid
527 source regions. The $\delta^{11}\text{B}$ values in syn-ore tourmaline indicate a dominant fluid contribution
528 from clastic metasediments and carbonate rocks, suggesting metamorphic devolatilization in
529 the host terrane as the most likely process that produced the ore-forming fluids. It seems likely
530 for the Kiaka deposit that hydrothermal tourmaline crystallized from a boron-rich metamorphic
531 fluid, of distal origin, derived from deep-seated metasediments.

532 Boron isotope compositions of tourmaline hosted in the metamafic rock ($\delta^{11}\text{B} = -19.6\text{‰}$ to -
533 15.1‰) and the metagreywacke ($\delta^{11}\text{B} = -25.1\text{‰}$ to -22.0‰) show a significant difference of
534 $\delta^{11}\text{B}$ values (up to 10‰), which suggests variable degrees of interactions between the boron-
535 rich hydrothermal fluid and the host rocks, as also supported by the chemical compositions of
536 tourmaline. The muscovite schists may represent a potential source for the boron-rich fluids
537 because they have a relatively high B content (71 ppm, Table 1), which is commonly associated
538 with micas (Leeman and Sisson 1996; Nakano and Nakamura 2001; Trumbull and Slack 2018).
539 Muscovite breakdown reactions in metapelitic rocks at $P \leq 4$ kbar and $T \leq 650^\circ\text{C}$ (Thompson
540 1982; Vielzeuf and Holloway 1988; Spear et al. 1999) can produce a low-salinity, reduced, and
541 boron-rich metamorphic fluid (Moran et al. 1992; Henry and Dutrow 1996; Nakano and

542 Nakamura 2001; Kawakami and Ikeda 2003). In order to evaluate whether hydrothermal
543 tourmaline could have formed from boron-rich fluids derived from devolatilization of
544 muscovite schists at depth, we calculated the tourmaline-fluid B isotope fractionation according
545 to the Rayleigh fractionation model of Marschall et al. (2009) and using the fractionation factors
546 of Meyer et al. (2008). Considering a temperature of 650°C for the muscovite breakdown
547 reaction, an average $\delta^{11}\text{B} = -29.2\text{‰}$ for the muscovite schist (Table 1), and a muscovite-fluid
548 boron isotopic fractionation of -7.7‰ (Wunder et al. 2005), we estimated a $\delta^{11}\text{B} = -21.5\text{‰}$ for
549 the expelled metamorphic fluid. At 650°C, the minimum boron content of this fluid would be
550 about 1.0 to 2.5 wt.% B_2O_3 (London 2011). The evolution of the B isotopic composition of this
551 fluid during its ascent through metamorphic rocks at amphibolite facies conditions was
552 calculated using the fractionation for a stepwise decreasing temperature from 650 to 350°C
553 following the model of Büttner et al. (2016). Considering an initial fluid composition of $\delta^{11}\text{B} =$
554 -21.5‰ at 650°C, progressive fractionation by removing 60 to 90% of boron from the fluid (F
555 $= 0.1\text{--}0.4$) results in a shift towards higher $\delta^{11}\text{B}$ values of -19.6‰ to -14.9‰ (Fig. 9).
556 Tourmaline precipitating from this fluid would acquire $\delta^{11}\text{B}$ compositions comprised between
557 -20‰ and -18‰ . At 400°C, a representative temperature for Tur_2 formation at Kiaka, the fluid
558 would have a $\delta^{11}\text{B} = -16.3\text{‰}$ and the corresponding tourmaline would acquire a $\delta^{11}\text{B} = -19.1\text{‰}$
559 (Fig. 7). These $\delta^{11}\text{B}$ values fall into the range of $\delta^{11}\text{B} = -25.1\text{‰}$ to -15.1‰ (average = -20.1‰)
560 measured for hydrothermal tourmaline from Kiaka. The differences of $\delta^{11}\text{B}$ values between
561 tourmaline hosted in the metagreywacke (average = -24.2‰) and the metamafic rock (average
562 = -17.8‰) are interpreted to reflect variable degrees of interactions, at constant temperature
563 (ca. 400°C), between the host rocks of initially distinct isotopic compositions and the boron-
564 rich metamorphic fluid.

565 In summary, hydrothermal tourmaline (Tur_2) from Kiaka formed through moderately high-
566 temperature fluid-rock interactions between boron-rich metamorphic fluids and the country

567 rocks, resulting in the local uptake of Al, Fe, and Mg required for tourmaline formation. We
568 propose that the source of the boron-rich fluids was derived from muscovite schists similar to
569 those exposed at Kiaka but located at a deeper level in the metamorphic nappe. The present
570 results indicate that neither proximal country rocks of the Kiaka deposit nor ascending granitic
571 magmas could be viable sources of fluids and boron. However, the isotopic data are consistent
572 with fluids and boron being issued from devolatilization of deep-seated muscovite schists
573 during the D_{2Ki} event, which relates to the prograde-to-peak amphibolite facies regional
574 metamorphism. This interpretation is supported by mineral-equilibria modelling suggesting that
575 exhumation of metasediments can produce important amounts of metamorphic fluids at
576 temperatures near 500°C (Vry et al. 2010).

577

578 **CONCLUSIONS**

579 In the Kiaka orogenic gold deposit, hydrothermal tourmaline (*Tur*₂) is commonly associated
580 with the proximal alteration assemblage in the host rocks. Mineralogical observations suggest
581 that deposition of *Tur*₂ was synchronous with the early sulfide-rich disseminated gold
582 mineralization coeval with the D_{2Ki} phase, corresponding to the regional prograde-to-peak
583 metamorphism. Hydrothermal tourmaline hosted in metamafic rock and metagreywacke has a
584 dravite composition, but shows variable major element contents, mainly in Al, Mg, and Fe, thus
585 suggesting a host rock buffering. Boron isotope compositions of tourmaline range between -
586 25.1‰ and -15.1‰, with differences between tourmaline hosted in the metamafic rock ($\delta^{11}\text{B} =$
587 -19.6‰ to -15.1‰) and tourmaline hosted in the metagreywacke ($\delta^{11}\text{B} = -25.1\text{‰}$ to -22.0‰).
588 Modeling of tourmaline-fluid boron isotope fractionation argue for a metamorphic origin of the
589 mineralizing fluids that were produced during devolatilization of deep-seated muscovite schists.
590 We propose that hydrothermal tourmaline (*Tur*₂) and the synchronous disseminated gold
591 mineralization resulted from moderately high-temperature (ca. 400°C) interactions between a

592 boron-rich hydrothermal fluid and the metamorphic host rocks at recorded amphibolite facies
593 conditions.

594

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906 **Figure captions**

907

908 **Figure 1. A.** Location and geological setting of the Kiaka orogenic gold deposit in the West
909 African Craton (modified after Castaing et al. 2003; Naba et al. 2004; Milési et al. 2004; Vegas
910 et al. 2008; Ganne et al. 2012). The Kénéma Man domain (Archean nucleus) and the Baoulé-
911 Mossi domain (Paleoproterozoic juvenile crust) form two domains separated by the Sassandra
912 Fault (SF). Volcano-sedimentary belts include Banfora (BA), Houndé (HO), Boromo (BO),
913 Lawra (LW), Goren (GO), Bui (BU), Ashanti (AS) and Sefwi (SW), Haute Comoé basin (HC),
914 and Manga Fada-N’Gourma belt (MFG). These belts are separated into dark green for mafic
915 volcanics rocks and light green for volcano-sedimentary rocks and intermediate to felsic
916 igneous rocks (Baratoux et al. 2011). A spatial association is found between gold deposits of
917 the Baoulé-Mossi domain and major tectonic structures such as the Grenville-Ferkessedougou-
918 Bobo-Dialouso (GFBF), Ouango-Fitini (OF) and Markoye (MSZ; this study) shear zones. For
919 interpretation of the colors, the reader is referred to the web version of this article. **B.** Geology
920 of the Manga Fada-N’Gourma greenstone belt with MSZ (thick black lines) and location of the
921 Kiaka gold deposit (Fontaine et al. 2017). **C.** Local geology of the Kiaka deposit showing the
922 location of the drillholes and cross-sections. Mineralized envelopes are projected at surface
923 from drillhole data (modified from Fontaine et al. 2017). **D.** NW-striking section 6100 showing
924 the location of the diorite plug.

925

926 **Figure 2.** Paragenetic sequence of the Kiaka gold deposit and relationships with the structural
927 events and hydrothermal alteration.

928

929 **Figure 3.** Mineralogical and textural features of tourmaline in the alteration zones of the Kiaka
930 gold deposit. **A & B.** Muscovite schist containing folded garnet-biotite-chlorite-muscovite layer

931 with detrital tourmaline (*Tur₁*) (sample KDH75-64.9). **C & D.** Metagreywacke composed of
932 quartz, plagioclase, and biotite, containing disseminated tourmaline and clinozoisite (sample
933 KDH29-311.8). **E & F.** Metamafic rock-hosted tourmaline porphyroblasts (*Tur₂*) associated
934 with D_{2K_i} biotite-clinozoisite-titanite-pyrrhotite alteration assemblage and crosscut by chlorite
935 (Chl 3)-calcite D_{4K_i} veinlet (sample KDH291-56.2). Mineral abbreviations: Bt=biotite,
936 Cal=calcite, Chl=chlorite, Czo=clinozoisite, Kfs=K-feldspar, Grt=garnet, Ms=moscovite,
937 Qtz=quartz, Pl=plagioclase, Po=pyrrhotite, Ttn=titanite, Tur=tourmaline.

938

939 **Figure 4.** Petrography of hydrothermal tourmaline (*Tur₂*) hosted in metagreywacke (sample
940 KDH29-311.8). **A.** Backscattered electron images of euhedral grains of hydrothermal
941 tourmaline in an assemblage of quartz, biotite, K-feldspar, and pyrrhotite. Note the
942 homogeneity of the tourmaline grains. **B.** Plane-polarized transmitted-light photomicrograph of
943 hydrothermal tourmaline grains.

944

945 **Figure 5.** Petrography of metamafic rock-hosted hydrothermal tourmaline (*Tur₂*)
946 porphyroblasts (sample KDH291-56.2). **A.** Global view of the three studied tourmaline
947 porphyroblasts (Grain 1, Grain 2, and Grain 3) observed by plane-polarized transmitted light
948 (x150) and **B.** interpretation sketch below (modified after Fontaine et al. 2017). The
949 hydrothermal assemblage is cut by a D_{4K_i} calcite-chlorite vein. **C.** Backscattered electron image
950 of a tourmaline porphyroblast (Grain 2) showing complex zoning and numerous sulfide
951 inclusions.

952

953

954 **Figure 6.** X-ray elemental maps of a poikilitic tourmaline porphyroblast (*Tur₂*, Grain 2) hosted
955 in metamafic rock (sample KDH291-56.2). **A** and **B** show the tourmaline grain in transmitted

956 light (TL) and backscattered electrons (BSE) (same as Figure 5C). Relative intensities of the
957 elements Fe, Mg, Al, Ca, Na, and Ti (C, D, E, F, and G) are shown with count/sec. scales.

958

959 **Figure 7.** Chemical compositions of hydrothermal tourmaline (*Tur*₂) hosted in metamafic rock
960 (sample KDH291-56.2) and metagreywacke (sample KDH29-311.8). **A.** Binary diagram
961 $X_{\text{vacancy}}/(X_{\text{vacancy}}+\text{Na})$ vs. $\text{Mg}/(\text{Fe}+\text{Mg})$, indicating that *Tur*₂ belongs to domain dravite/oxy-
962 dravite. **B.** Binary diagram Fe vs. Mg, showing low Mg composition for metagreywacke-hosted
963 *Tur*₂, and a richer Mg content for *Tur*₂ hosted in metamafic volcanic rock. **C.** Binary diagram
964 X_{vacancy} vs. Al, showing a dravite-schorl composition for metamafic rock tourmaline, and a
965 composition closer to foitite/magnesio-foitite for metagreywacke tourmaline. **D.** Binary
966 diagram Fe vs Al, highlighting higher Al content for metagreywacke tourmaline compared to
967 metamafic rock tourmaline. **E.** Ternary diagram Ca- X_{vacancy} -(Na+K) illustrating the belonging
968 of *Tur*₂, for both lithologies, to the alkali group. **F.** Ternary diagram Al-Fe-Mg. The numbered
969 fields in the Al-Fe-Mg diagram correspond to the compositional range of tourmaline hosted in
970 different rock types as defined by Henry and Guidotti (1985): 1- Li-rich granitoids, pegmatites
971 and aplites; 2- Li-poor granitoids, pegmatites and aplites; 3- Fe³⁺-rich quartz-tourmaline rocks
972 (hydrothermally altered granitoids); 4- Al-rich metapelites and metapsammites; 5- Al-poor
973 metapelites and metapsammites; 6- Fe³⁺-rich quartz-tourmaline rocks, calc-silicate rocks and
974 metapelites; 7- Low-Ca meta-ultramafic rocks and Cr-V-rich metasediments; 8-
975 Metacarbonates and metapyroxenites.

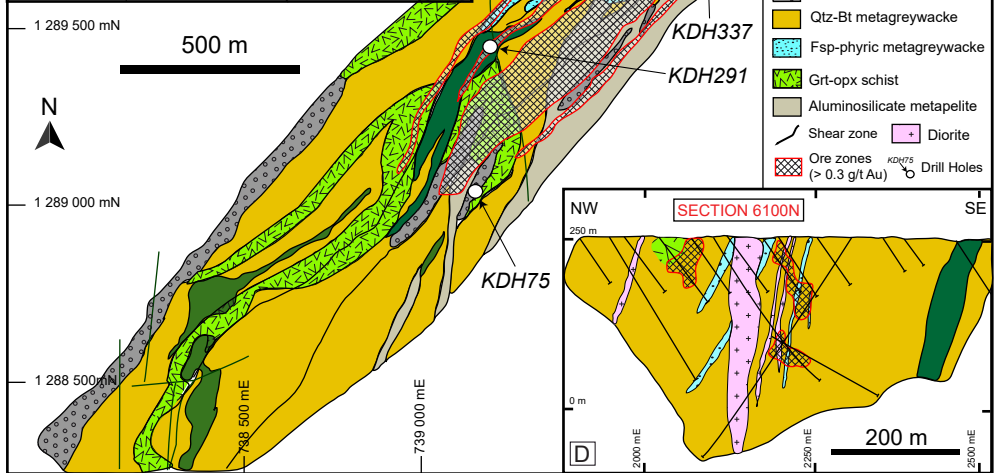
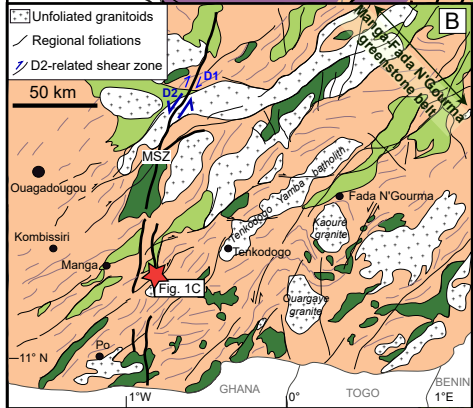
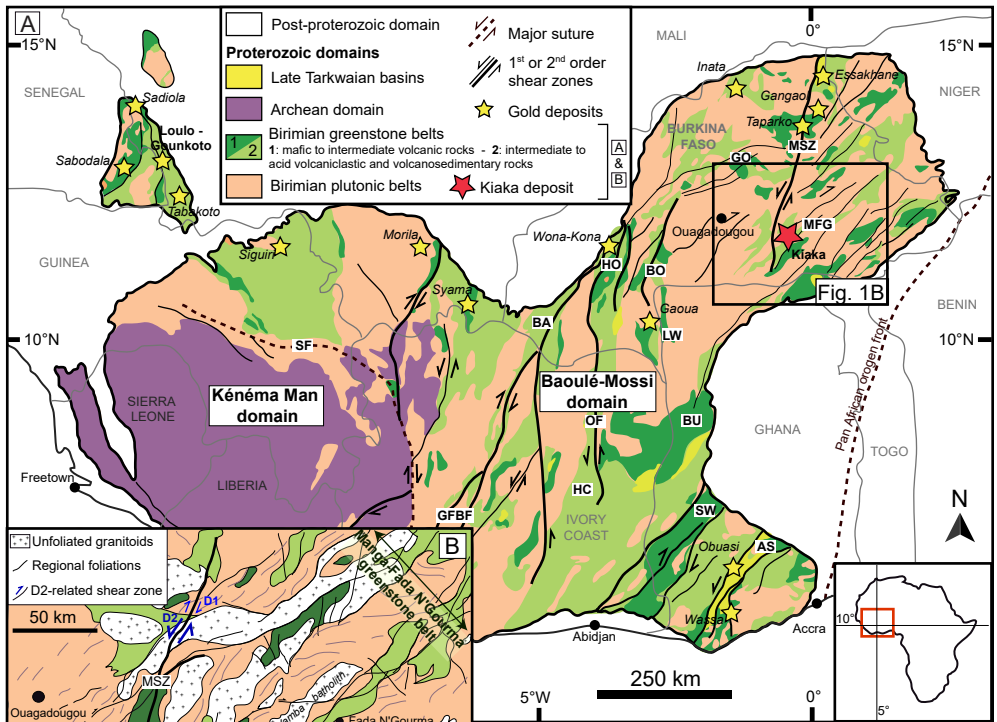
976 **Figure 8.** Boron isotope compositions of hydrothermal tourmaline (*Tur*₂) from the Kiaka gold
977 deposit. **A.** Histogram showing the $\delta^{11}\text{B}$ distribution of tourmaline hosted in metamafic rock
978 (sample KDH291-56.2) and metagreywacke (sample KDH29-311.8) compared to the whole-
979 rock $\delta^{11}\text{B}$ compositions of the diorite (sample KDH337-44.1) and the muscovite schist (sample
980 KDH75-64.9). **B.** $\delta^{11}\text{B}$ compositional range of tourmaline from orogenic gold deposits

981 worldwide. Data are compiled from (1) Lambert-Smith et al. (2016); (2) Molnár et al. (2016);
982 (3) Krienitz et al. (2008); (4, 5) Jiang et al. (2002); (6) Beaudoin et al. (2013); (7, 8, 9) Baksheev
983 et al. (2015). C. $\delta^{11}\text{B}$ compositional range of tourmaline hosted in variable lithologies
984 worldwide (Marschall and Jiang 2011; Trumbull and Slack 2018).

985

986

987 **Figure 9.** Boron isotope fractionation curves between tourmaline and fluid for a stepwise
988 decreasing temperature from 650 to 350°C (after Büttner et al. 2016). The isotopic composition
989 of fluid and tourmaline are calculated for a starting initial fluid composition of $\delta^{11}\text{B} = -21.5\text{‰}$
990 using the Rayleigh fractionation model of Marschall et al. (2009) and the temperature-
991 dependent tourmaline-fluid fractionation values of Meyer et al. (2008).



Deformation	D1	SYN-D2	LATE-D2	D3	D4
Metamorphism	Prograde	Prograde (7.5 kbar; 550°C) Diorite emplacement and shearing		D3 _{K1} -D4 _{K1} events Retrograde Reactivation of D2 shearzones	
Tourmaline generation					
<i>Tur1</i> : Detrital Rounded, brown to blue ^{1,2} <u>with Grt, Bt and Ms</u>					
<i>Tur2</i> : Hydrothermal Euhedral brown, inclusion-poor ¹ Poikiloblastic mm and inclusion-rich ³	<u>with Ap, Qtz and Po inclusions</u>		<u>with Po, Ccp, Chl, Czo and Act inclusions</u>		
Mineralization					
Po ± (Py, Ccp) disseminations in Bt replacement zones (1-3 g/t Au) ¹	—————				
Apy ± (Lo) disseminations and Qz veinlets ¹	—————				
Po ± (Py) in calc-silicate hydrothermal breccia	-----				
Visible Au in Qtz-carbonate veinlets (50-60 g/t Au)	—————				
Alteration					
Biotitization ^{1,3}	—————				
Calc-silicate alteration ³	-----				
Tourmalinization ^{1,3}	—————				
Sericitization	-----				
Chloritization ³	<u>Chl1</u> -----	-----			<u>Chl2</u> ----- <u>Chl3</u> -----
Carbonatation	-----				




——— Major
 ----- Minor
 ----- Rare

¹ mainly in aluminosilicate-bearing metapelites and quartz-biotite metagreywacke

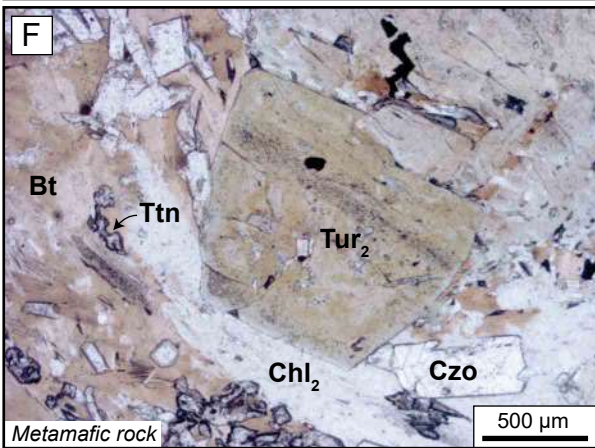
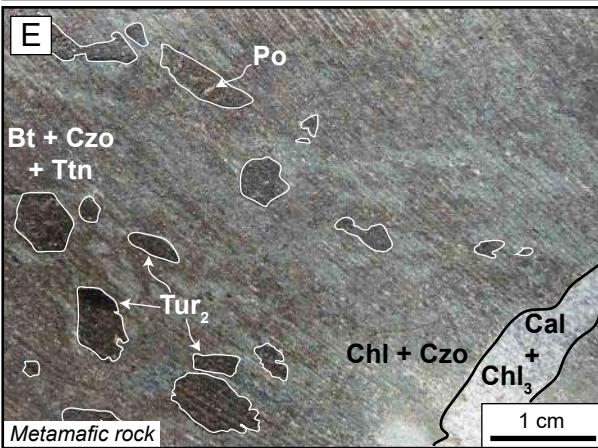
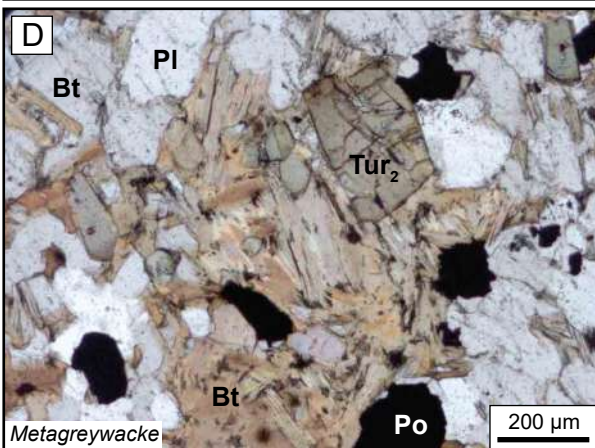
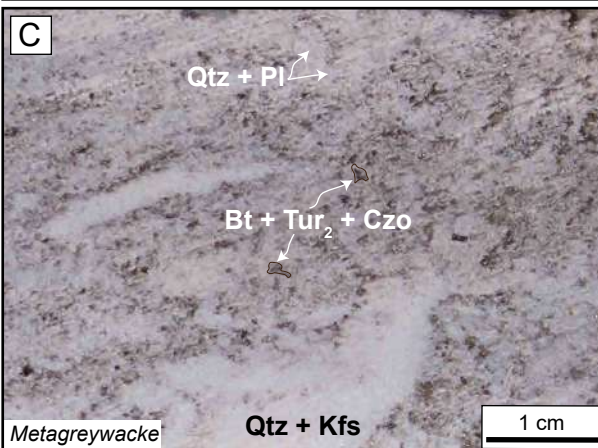
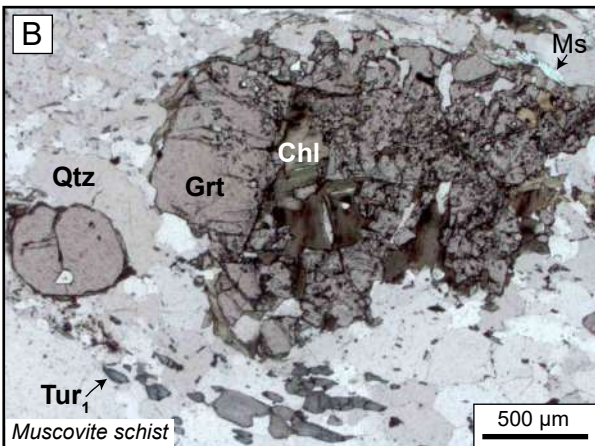
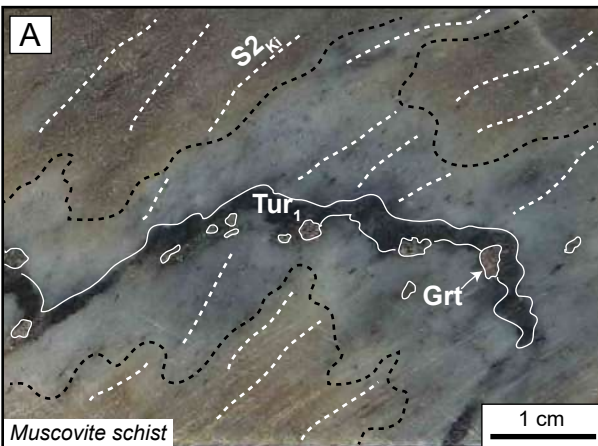
² mainly in quartz-muscovite schist

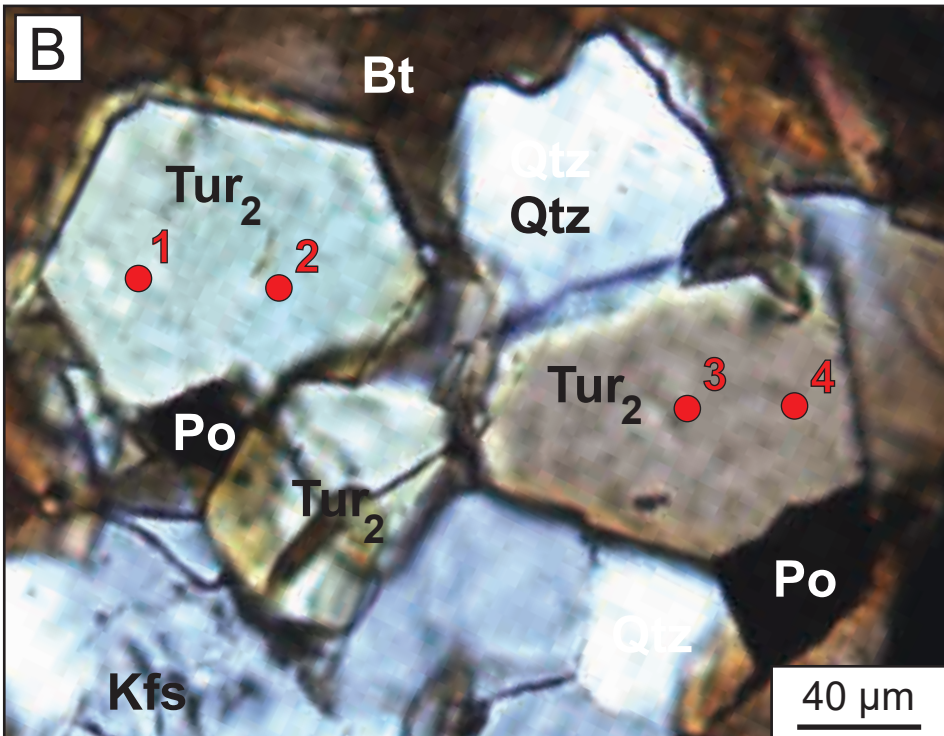
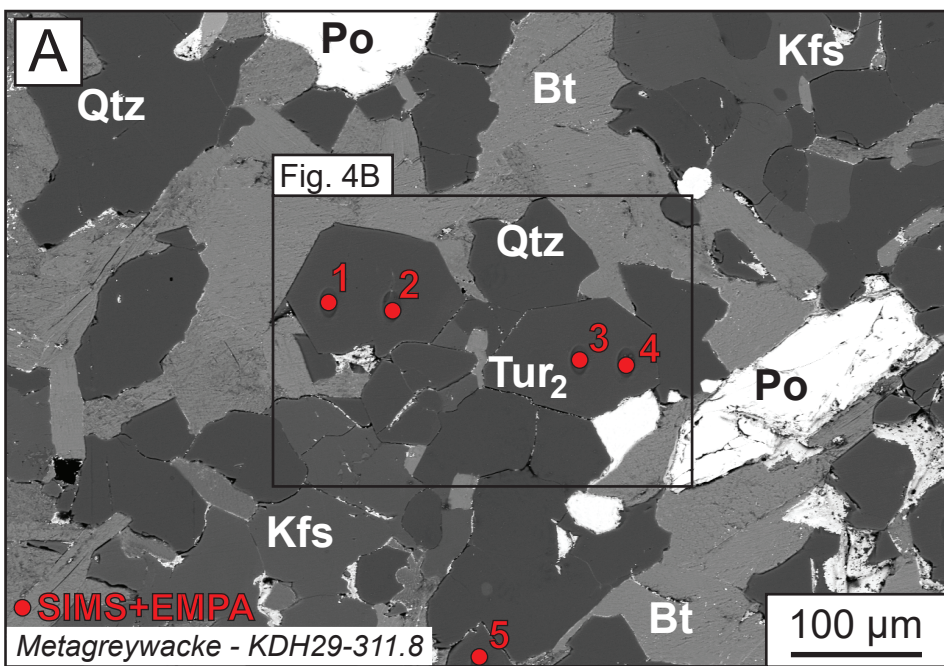
³ mainly in metamafic rock

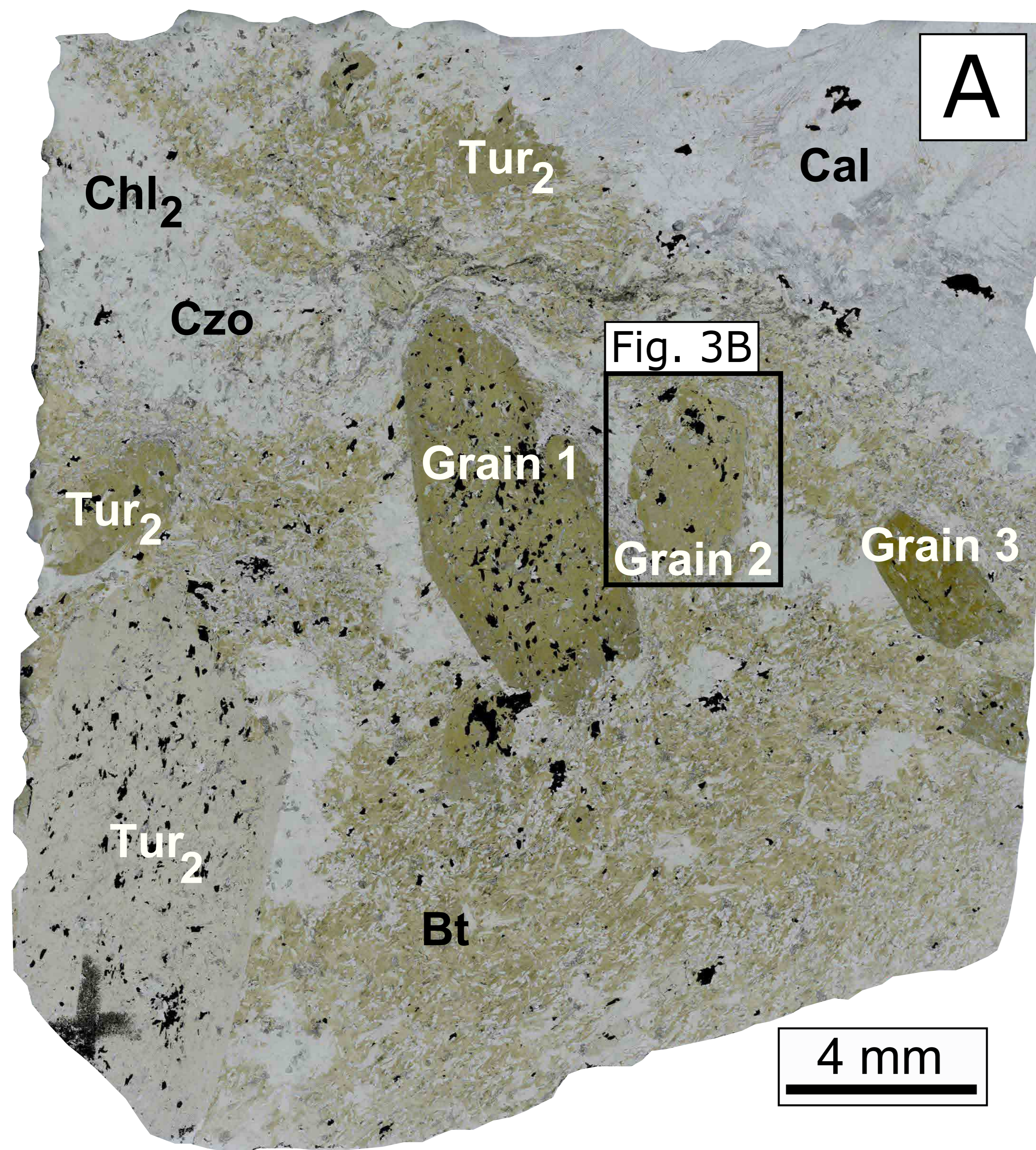
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Visible Au in Qtz-carbonate veinlets (50-60 g/t Au)	—————		—————		
Alteration					
Biotitization ^{1,3}	—————		- - - - -		
Calc-silicate alteration ³	- - - - -		—————		
Tourmalinization ^{1,3}	—————		- - - - -		
Sericitization	- - - - -		- - - - -		
Chloritization ³	<u>Chl₁</u> - - - - -		- - - - - <u>Chl₂</u>		- - - - - <u>Chl₃</u>
Carbonatation	- - - - -		- - - - -		

 Major
 Minor
 Rare

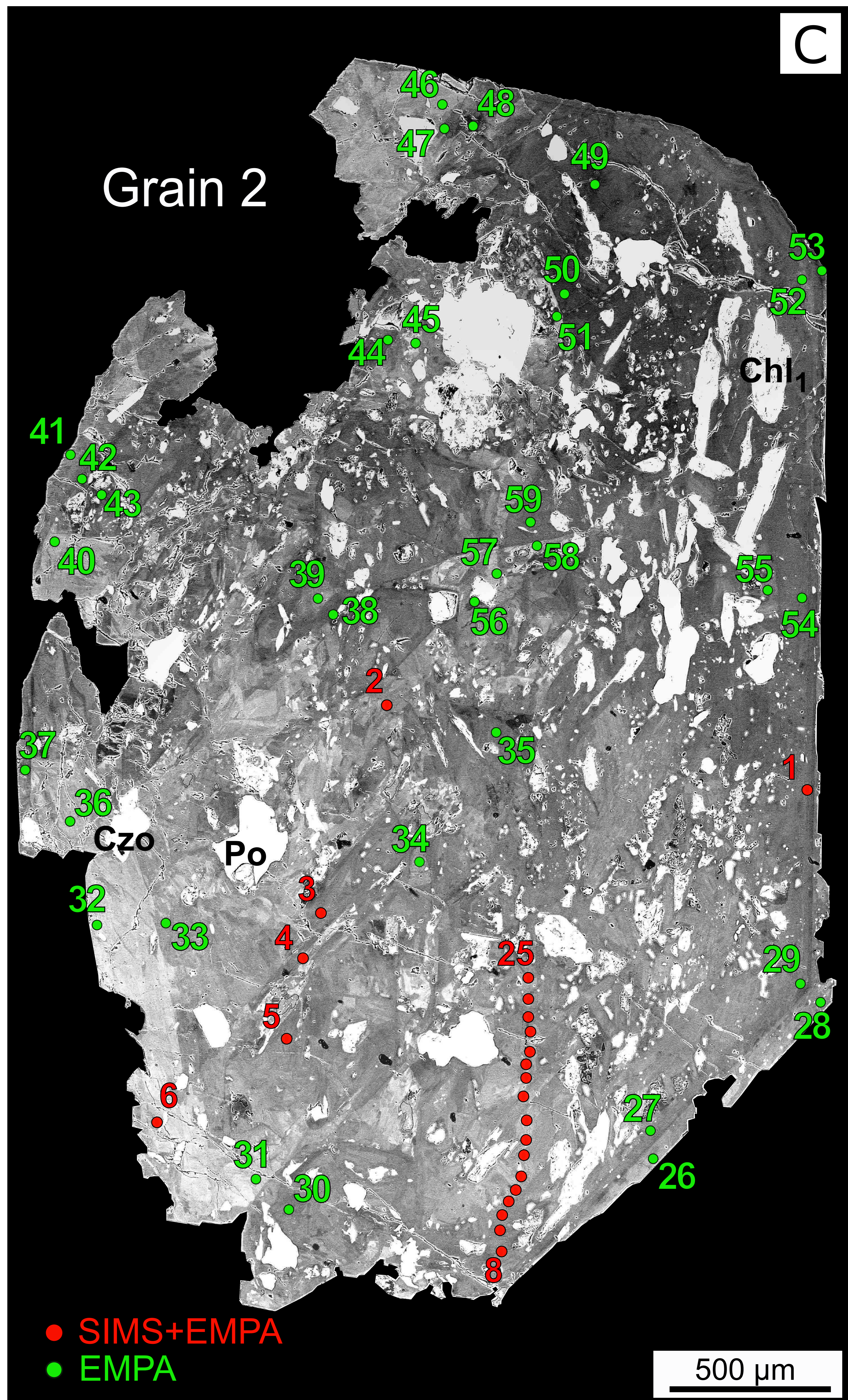
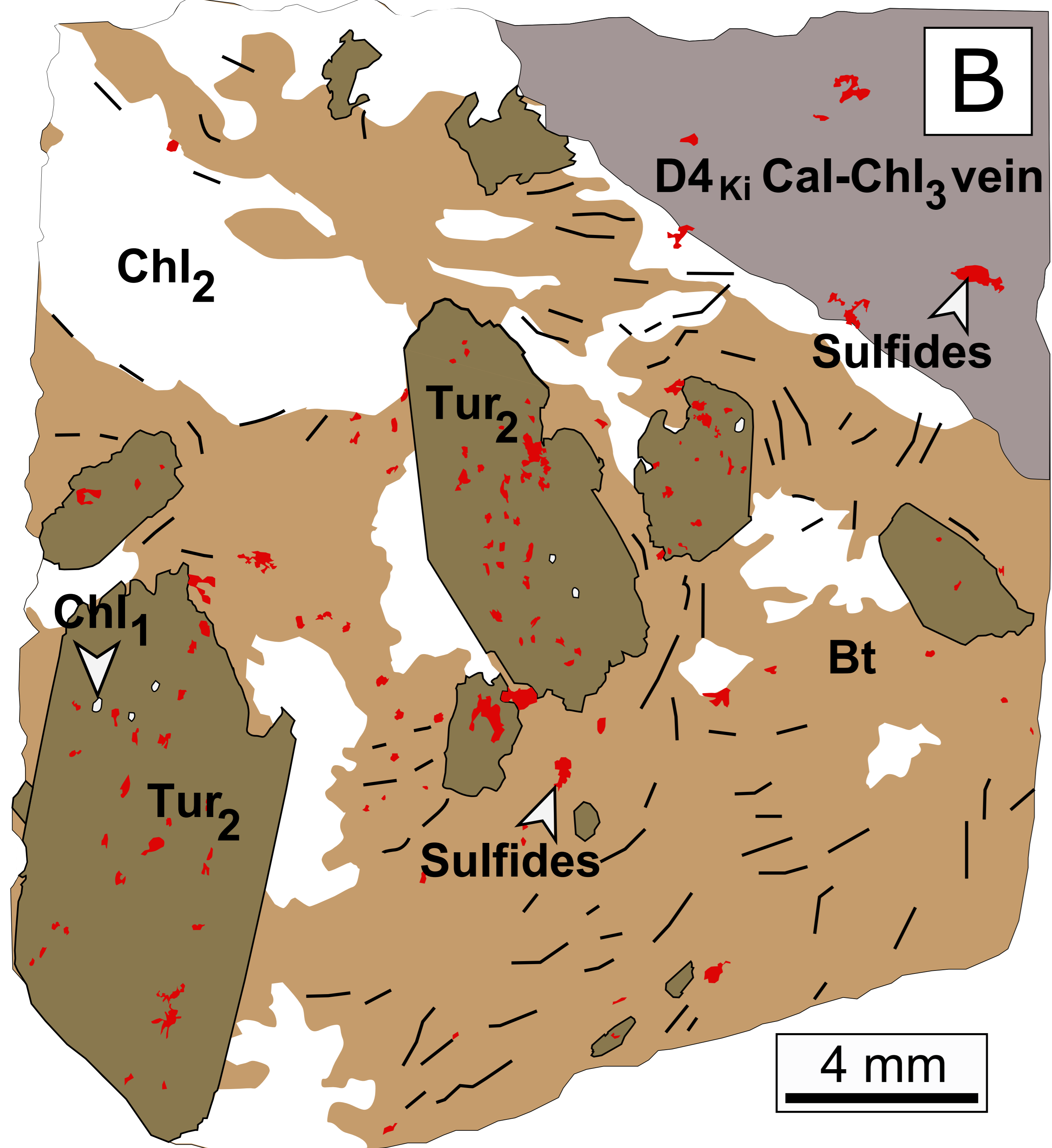
¹ mainly in aluminosilicate-bearing metapelites and quartz-biotite metagreywacke
² mainly in quartz-muscovite schist
³ mainly in metamafic rock

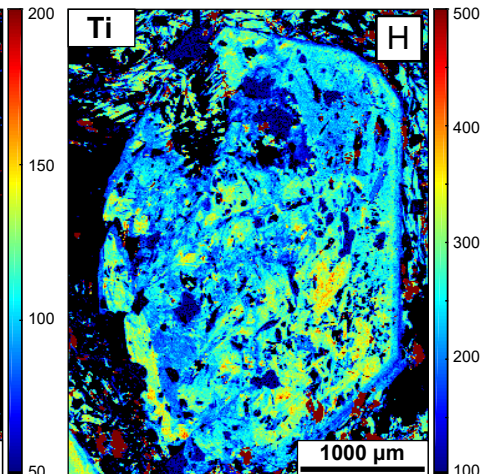
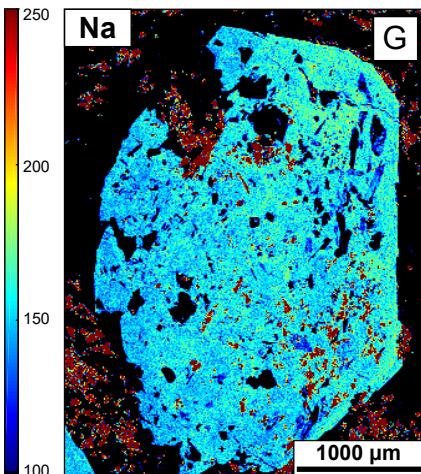
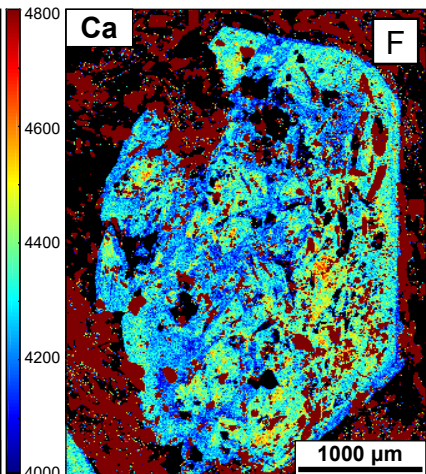
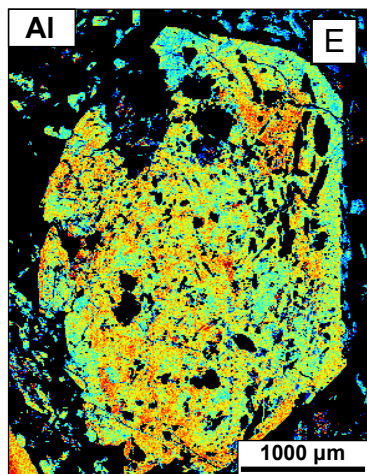
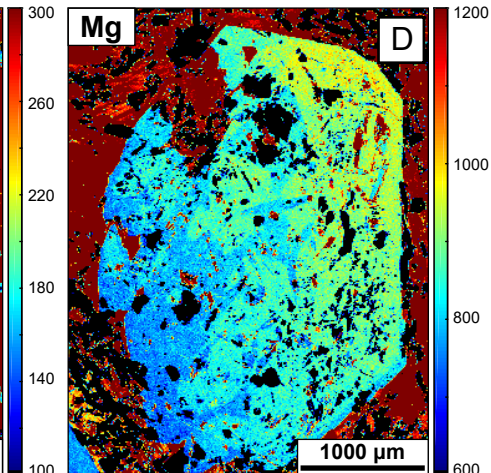
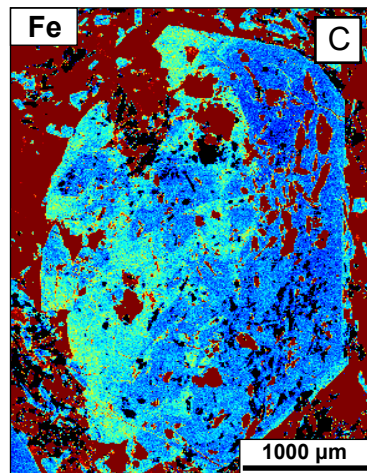
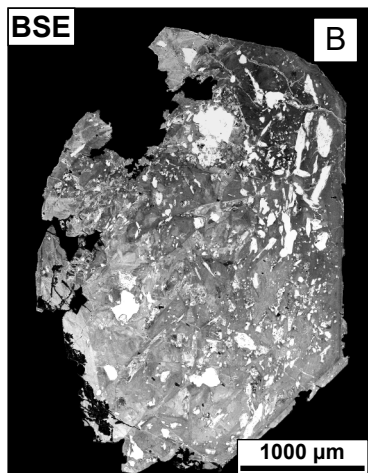
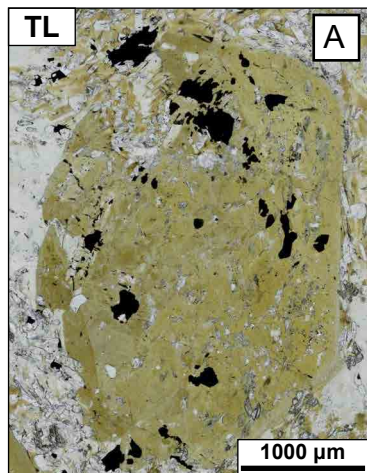


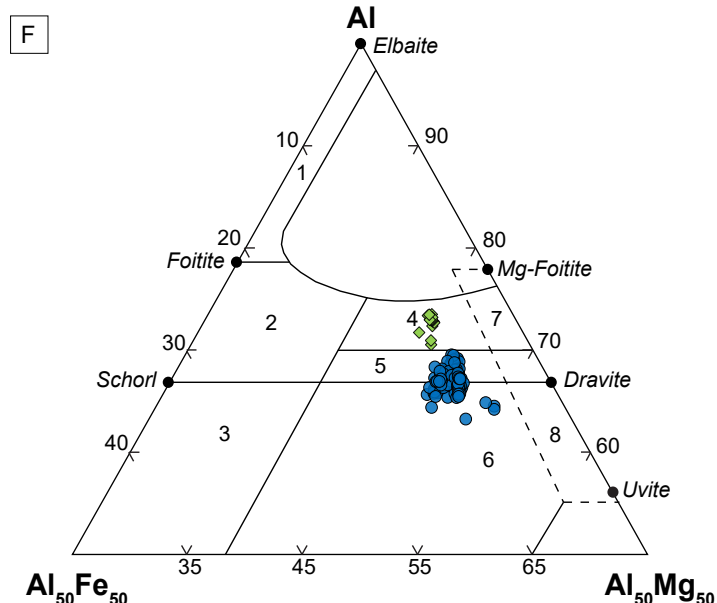
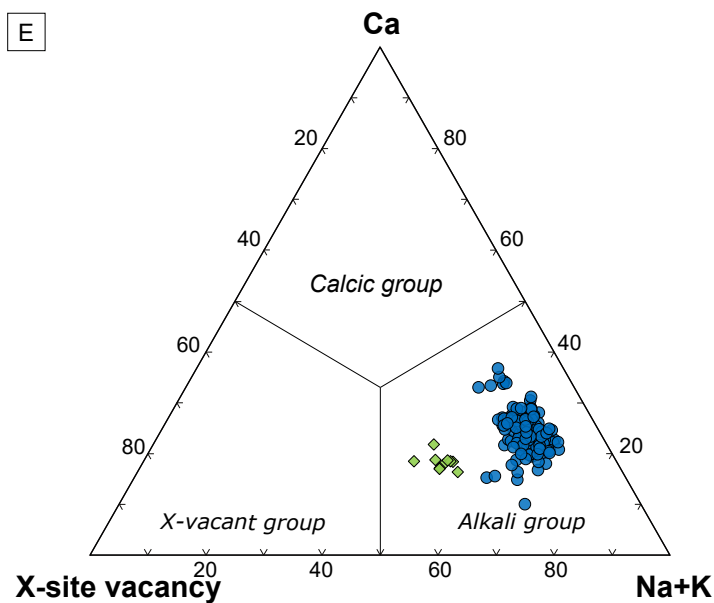
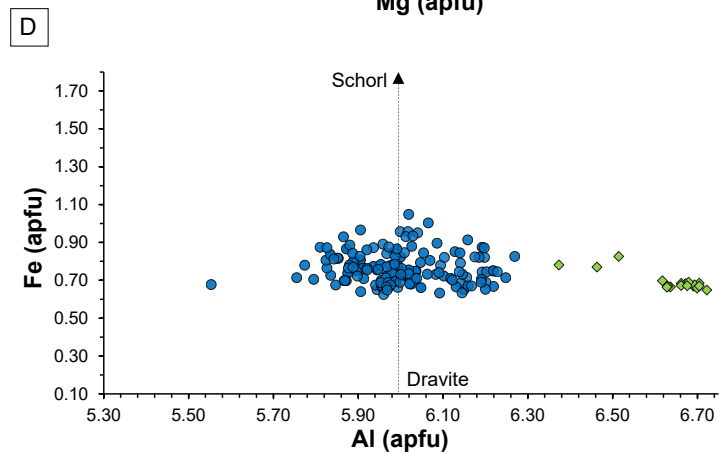
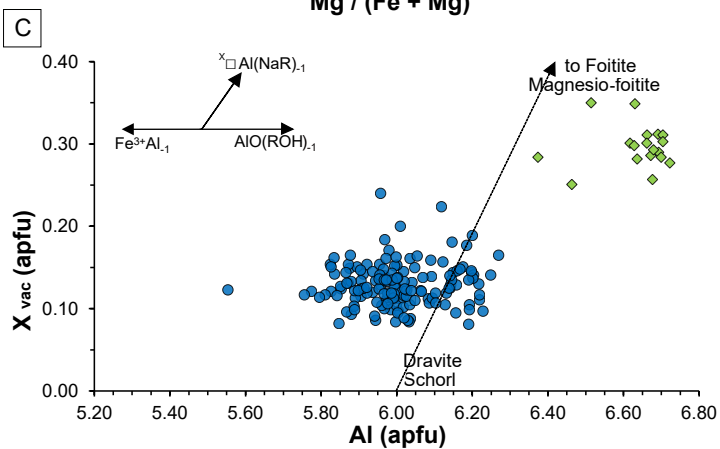
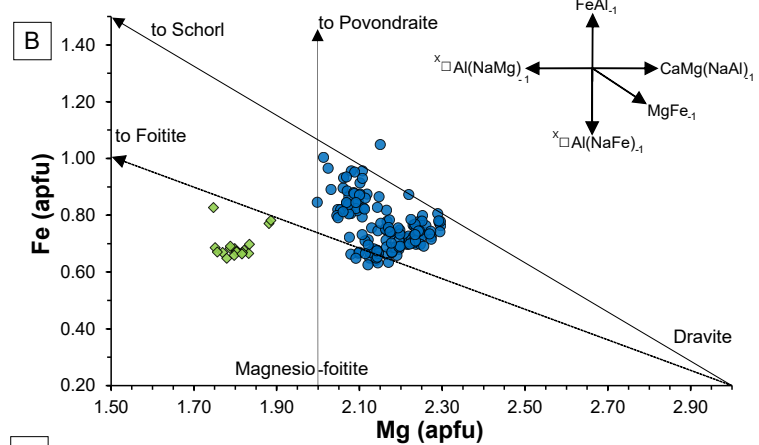
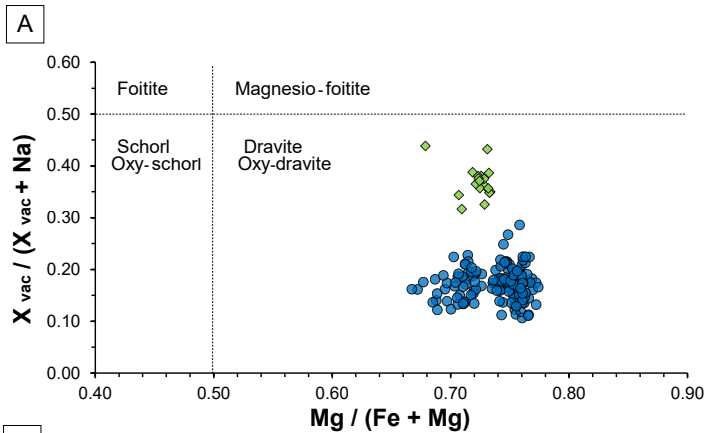




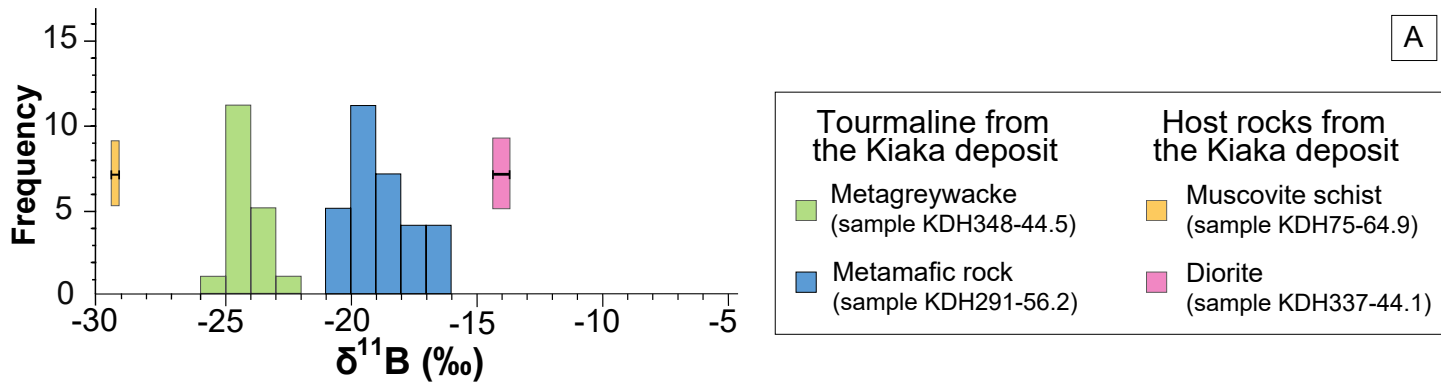
Metamafic rock - KDH291-56.2



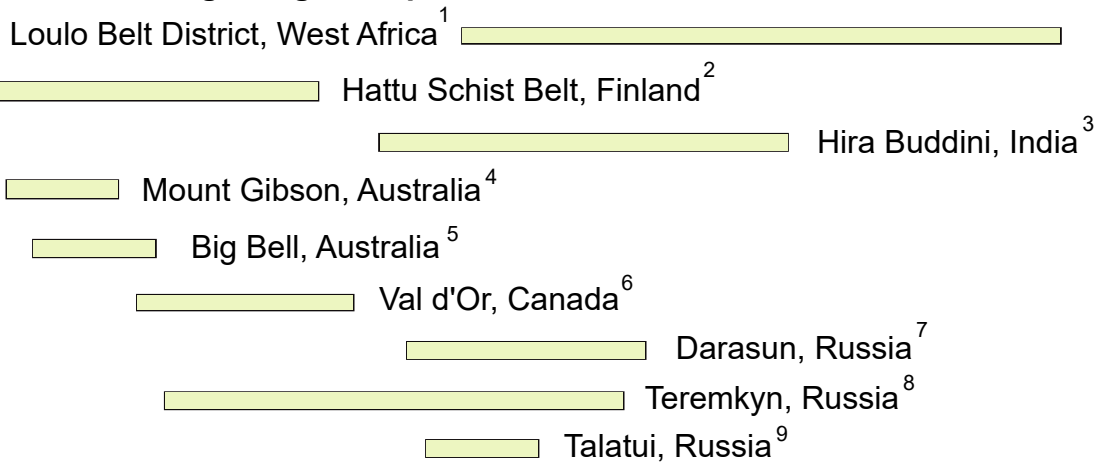




● Metamafic rock (sample KDH291-56.2) ◆ Metagreywacke (sample KDH29-311.8)



$\delta^{11}\text{B}$ of tourmaline from orogenic gold deposits



$\delta^{11}\text{B}$ of tourmaline hosted in...

