

1 **Revision 2**

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3 **Tourmaline chemical and boron isotopic constraints on the**
4 **magmatic-hydrothermal transition and rare-metal mineralization in alkali**
5 **granitic systems**

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7 HUAN-HUAN WU^{1,2,3,4}, HE HUANG^{1*}, ZHAO-CHONG ZHANG², SHUI-YUAN YANG⁵,

8

YONG-BAO GAO³, ADRIAN A. FINCH⁴

9 ¹ SinoProbe Laboratory, Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037,

10

P.R. China

11 ²State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences,

12

Beijing 100083, P.R. China

13 ³Xi'an Center of Mineral Resources Survey, China Geological Survey, Xi'an 710100, P.R. China

14

⁴School of Earth & Environmental Sciences, University of St Andrews, KY16 9TS, UK

15 ⁵State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences,

16

Wuhan 430074, P.R. China

17

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ABSTRACT

19 The magmatic-hydrothermal transition in granite-related rare-metal metallogenic
20 systems has received great attention, as economic rare metal (including rare earth)
21 minerals reach saturation and trigger mineralization at this stage. However, deciphering
22 the details of the melt-fluid evolution process and the distribution behavior of rare
23 metals remains difficult. Here, we applied tourmaline chemistry and B isotopes to
24 unravel processes at the magmatic-hydrothermal transition that are responsible for
25 rare-metal partitioning in the Huoshibulake (HS) and Tamu (TM) REE-Nb-mineralized
26 intrusions in Southern Tianshan, SW Central Asian Orogenic Belt. Three types of
27 tourmaline are identified in the plutons: (1) disseminated tourmaline in the granite, with
28 a brown-yellow core (HS-DB) and blue-green rim (HS-DG); (2) orbicular tourmaline,
29 with a brown-yellow core (HS-OB and TM-OB) and blue-green rim (HS-OG and
30 TM-OG); (3) vein tourmaline (HS-V and TM-V). Compositionally, all these
31 tourmalines exhibit extremely low Ca and Mg contents and are classified as schorl. The
32 substitution processes of major-element variations are dominantly caused by (Al, □)
33 (Fe, Na)₋₁ exchange vectors. Four generations of tourmaline crystallization are
34 established based on the petrographic, compositional, and B isotopes evolution of the
35 tourmaline. Firstly, the HS-DB crystals crystallized from the highly evolved residual
36 melt, and then HS-OB and TM-OB precipitated from immiscible B-rich aqueous melts
37 during the magmatic-hydrothermal transition. Subsequently, the blue-green
38 overgrowths (HS-DG, HS-OG, and TM-OG) crystallized from exsolved hydrothermal
39 fluids. Finally, the formation of HS-V and TM-V resulted from another melt pulse from

40 a deeper magma chamber. The magmatic tourmaline exhibits a narrow range of $\delta^{11}\text{B}$
41 values between -12.6 to -10.0‰, while the hydrothermal tourmaline shows
42 significantly heavier and variable $\delta^{11}\text{B}$ values ranging from -10.2 to -4.9‰. The
43 fractionation of B isotopes is reproduced by Rayleigh fractionation modeling. Lower
44 Nb and Sn contents in the orbicular tourmaline relative to those precipitated from the
45 residual melt, along with the lack of rare-metal minerals in the orbicules, indicate that
46 B-rich melt/fluid exsolution does not necessarily contribute to the rare-metal
47 mineralization. In comparison, the veins contain abundant rare-metal and REE minerals
48 in close paragenesis with fluorite, and the vein tourmaline shows high Nb and Sn
49 contents. These observations suggest that saturation of fluorite triggered the
50 precipitation of rare metals, and fluorine played a critical role in rare metal
51 concentration and mineralization. This study highlights the potential of tourmaline to
52 trace the magmatic-hydrothermal transition and provide insights into rare-metal
53 mineralization in the granitic systems.

54 **Keywords:** Multi-generation tourmaline, boron isotopes, magmatic-hydrothermal
55 transition, rare-metal mineralization

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57

INTRODUCTION

58 The magmatic-hydrothermal transition, during which the
59 crystallization/fractionation of orthomagmatic systems evolves from melt-driven
60 (magmatic) to fluid-driven (hydrothermal) processes, is still poorly understood
61 because of the transient timescale and widespread overprints by post-magmatic,
62 low-temperature alteration ([Halter and Webster, 2004](#); [Michaud and Pichavant, 2020](#)).
63 During the transition, complex melt-fluid interactions involving silicic melts, aqueous
64 melts, and hydrothermal fluids occur ([Kaeter et al., 2018](#); [Thomas et al., 2012](#)).
65 Although it has been acknowledged that rare-metal granites generally originate from
66 a fertile source with low-degree partial melting and high-degree fractional
67 crystallization contributing significantly to rare-metal enrichment ([Ballouard et al.,](#)
68 [2020](#); [Linnen et al., 2014](#); [Sheard et al., 2012](#); [Williams-Jones and Vasyukova, 2023](#)),
69 evidence increasingly points towards the magmatic-hydrothermal transition as the
70 critical stage to achieve the hyper-enrichment and mineralization of rare metals
71 ([Ballouard et al., 2016](#); [Carr et al., 2021](#); [Zhu et al., 2015](#)). However, clarifying the
72 distribution behavior of rare-metal elements and their metallogenic mechanism
73 during the transition remains challenging.

74 Tourmaline is a common borosilicate mineral in granitic systems that can
75 crystallize directly from the early magmatic stage through to the late sub-solidus fluid
76 ([Liu and Jiang, 2021](#); [Yang et al., 2015](#)). Due to its highly variable composition,
77 stability over large P-T ranges, and resistance to post-crystallization alteration,
78 tourmaline has been regarded as a reliable monitor for tracing the evolution of

79 melts/fluids composition ([Dutrow and Henry, 2011](#); [Hong et al., 2019](#); [Jiang et al.,](#)
80 [2004](#); [Slack and Trumbull, 2011](#); [van Hinsberg et al., 2011](#)). In particular, the
81 differential distribution behavior of ^{11}B and ^{10}B between melts and fluids makes boron
82 isotopes in tourmaline a potentially valuable indicator for deciphering
83 magmatic-hydrothermal processes ([Drivenes et al., 2015](#); [Qiu et al., 2021](#); [Zhao et al.,](#)
84 [2021a](#)).

85 The Atushi-Baicheng-Yuli alkaline rock belt, located in South Tianshan, is a
86 transitional zone between the Central Asian Orogenic Belt and Tarim Craton and it is
87 composed of outcrops of alkali granite, syenite, and carbonatite, some of which host
88 world-class rare-metal (Nb-REE) deposits (e.g., Boziguo'er Nb-REE deposit, [Huang](#)
89 [et al., 2018](#); the Wajilitag REE deposit, [Cheng et al., 2018](#); the Kuoketag Nb-REE
90 deposit, [Chen et al., 2002](#)). The Huoshibulake (HS) and Tamu (TM) plutons are
91 adjacent A-type granitic plutons in the Atushi district with Nb and REE
92 mineralization, characterized by a wide occurrence of economic minerals, e.g., most
93 importantly columbite, synchysite, fluocerite ([Shi et al., 2010](#)). Tourmaline occurs in
94 many forms in the plutons, including disseminated, orbicular, and veins, the latter two
95 intimately with quartz. It records a continuous evolution from the magmatic to
96 hydrothermal stages. Tourmaline-quartz orbicules occur widely in the two alkali
97 granitic plutons, a texture most commonly reported in peraluminous granitic systems
98 and considered a product of segregated B-rich melts ([Drivenes et al., 2015](#); [Harlaux et](#)
99 [al., 2020](#); [Hong et al., 2019](#); [Zhao et al., 2021a](#)). These plutons show varying degrees
100 of rare-metal mineralization in the different stages, and rare-metal minerals exhibit

101 paragenesis with specific generations of tourmaline. Consequently, the two alkali
102 plutons offer an exceptional natural laboratory for elucidating the
103 magmatic-hydrothermal transition and associated rare-metal mineralization within the
104 alkali granitic systems, from the perspective of tourmaline.

105 In this study, we carry out detailed investigations on tourmaline from the two
106 plutons, including mineral textures, chemical compositions, and B isotopes, to
107 reconstruct the magmatic-hydrothermal evolution. We further constrain the
108 distribution and precipitation of Nb and REE during the magmatic-hydrothermal
109 transition by integrating the paragenesis of economic minerals with the different types
110 of tourmaline as well as by evaluating variations of the ore-forming elements in the
111 tourmaline.

112 **GEOLOGICAL BACKGROUND**

113 The Central Asian Orogenic Belt (CAOB) is one of the largest accretionary orogens
114 in the world, sandwiched between the Siberian and European Cratons to the north and
115 the Karakum-Tarim-North China Cratons to the south. The Western Xinjiang region is
116 situated in the southwestern CAOB and can be divided into (from north to south) the
117 Altay, Junggar Block, North Tianshan Belt (NTB), Yili-Kazakhstan Block (YKB),
118 Central Tianshan Block (CTB), South Tianshan Belt (STB), and northern margin of the
119 Tarim Craton (NMTC) ([Figure 1a](#)). The STB is bounded by the Southern-Central
120 Tianshan Suture (SCTS) to the north and by the North Tarim Suture (NTS) to the south
121 and resulted from the Paleozoic closure of the Paleo-Asian Ocean and the subsequent
122 collision of Tarim Block and Southwestern CAOB. During the Early Permian, the

123 northern margin of Tarim and its adjacent areas was subjected to intracontinental
124 extension, accompanied by regional alkaline magmatism (Wei et al., 2019; Zong et al.,
125 2020). From Atushi in the west to Yuli in the east, this created a series of alkaline
126 volcanic and intrusive rocks, forming a ~1100 km long alkaline-rock belt. Several rare
127 metal deposits (e.g., Boziguo'er Nb-Ta-Zr deposit, Kuoketag Nb-Ta-Zr deposit, and
128 Wajilitag REE deposit) and rare metal mineralized plutons (e.g., Tamu
129 Nb-REE-mineralized pluton, Huoshibulake REE-mineralized pluton, and
130 Bashisuogong Nb-REE complex) have been found in the belt (Nechaev et al., 2021; Xie
131 et al., 2021), revealing significant rare-metal metallogenic potential in the area.

132 The Huoshibulake and Tamu plutons are situated in the north-east of Atushi city
133 (Figure 1a). The Huoshibulake pluton has an outcrop of 30 km² and consists of two
134 transitional units from the center outward: biotite granite and biotite K-feldspar granite
135 (Figures 1b and 2a). The Tamu pluton, located ~10 km southwest of the Huoshibulake
136 pluton (Figure 1c), shows similar petrographic features to the Huoshibulake pluton.
137 The major minerals in both plutons are alkali feldspar, quartz, biotite, and minor alkali
138 amphibole, fluorite, and tourmaline. Major economic rare metal (including REE)
139 minerals consist of monazite, columbite, synchysite, and fluocerite. Both plutons
140 exhibit high SiO₂ (74.6–78.1 wt%), Al₂O₃ (11.5–12.6 wt%), and total alkali (7.85–8.96
141 wt%) contents, while having extremely low CaO (0.10–1.22 wt%) and MgO (0.02–
142 0.22 wt%) contents (Huang et al., 2012). Multi-mineral U-Pb dating of both plutons
143 yielded an identical age of ~273 Ma, revealing the early Permian emplacement (Wu et
144 al., in preparation).

145 **TOURMALINE OCCURRENCE AND SAMPLE DESCRIPTIONS**

146 Tourmaline is widespread and shows similar features in both the Huoshibulake and
147 Tamu plutons. Based on the textural characteristics, three distinct types of tourmaline
148 are identified: (1) disseminated subhedral to anhedral tourmaline in granite matrix; (2)
149 tourmaline in tourmaline-quartz orbicules (termed “orbicular tourmaline” in this paper);
150 and (3) tourmaline in tourmaline-quartz veins. The characteristics of these tourmalines
151 are described as follows:

152 **Disseminated tourmaline in the Huoshibulake pluton**

153 Disseminated tourmaline is found in most granite samples from the Huoshibulake
154 pluton (Figure 2b, c) but is absent in the Tamu pluton. Tourmaline grains of this type
155 are distributed within the granitic matrix as isolated subhedral to anhedral grains
156 (Figure 2d, e) or grain aggregates (Figure 2f), tens to hundreds of micrometers long,
157 commonly coexisting with quartz, biotite, and K-feldspar grains. They generally
158 contain yellow-brown (abbreviated as HS-DB, where ‘HS’, ‘D’, and ‘B’ represent
159 pluton name, texture, and color of tourmaline; similar rules apply to the abbreviations
160 used below) mantles with occasional blue-green rims (HS-DG), which are also
161 distinguished from each other by different degrees of back-scattered brightness in the
162 back-scattered electron images (BSE, Figure 2g–i). A notable phenomenon is a large
163 abundance of rare-metal minerals (e.g., zircon, monazite, columbite, synchysite,
164 fluorite) enclosed in these disseminated tourmalines (Figures 2g–i and 3a–c). These
165 rare-metal minerals are highly concentrated in close proximity to fluorite (Figure 3a–c).

166 **Tourmaline in tourmaline-quartz orbicules**

167 Tourmaline–quartz orbicules have a widespread occurrence in both Huoshibulake
168 and Tamu plutons (Figure 1b, c). The orbicules are randomly distributed and
169 commonly several to more than ten centimeters in diameter (Figure 4a, b). A typical
170 orbicule consists of a tourmaline core, a tourmaline-quartz mantle, and a leucocratic
171 rim (Figure 4b). The core consists mainly of clusters of euhedral tourmaline with minor
172 quartz grains, whereas tourmaline (~50 vol.%) is intergrown with quartz (~40 vol.%) in
173 the mantle, along with minor relicts of partially-replaced perthitic K-feldspar (~10
174 vol.%). Minor biotite, muscovite, and fluorite are also present in the orbicules, but
175 rare-metal minerals are lacking. A 0.5–1 cm wide leucocratic rim can be recognized
176 surrounding the orbicules. The fine-grained granitic-textured rim is compositionally the
177 same as the surrounding granite, but with lower proportions of mafic minerals. The
178 tourmaline in orbicules shows a sieve-like texture characterized by the intergrowth of
179 tourmaline and quartz (Figure 4c, d). Two types of tourmaline are distinguishable in
180 plane-polarized light: tourmaline at the core of the crystals shows yellow to brown
181 pleochroism (HS-OB and TM-OB), and tourmaline at the rim exhibits green to blue
182 pleochroism (HS-OG and TM-OB) (Figure 4c, d). When viewed using BSE imaging,
183 the green rims consistently show lower brightness than the brown cores (Figure 4e, f).

184 **Tourmaline in tourmaline-quartz vein**

185 Tourmaline-quartz veins are well developed in the Huoshibulake and Tamu
186 plutons, with variable widths ranging from several to tens of centimeters and lengths
187 from several to tens of meters (Figure 5a, b). Most veins exhibit near-vertical

188 orientation and are generally parallel in the same outcrop (Figure 5a). These veins are
189 composed mainly of tourmaline and quartz, with minor muscovite and fluorite (Figure
190 5c). The tourmaline from these veins (HS-V and TM-V) exhibits yellow to blue
191 pleochroism; most grains show distinct growth zonation (Figure 5d–f), which is also
192 recognizable in the BSE images (Figure 5g–i). A large number of rare-earth minerals
193 (e.g., synchysite, fluocerite, and monazite) and columbite are observed in these veins
194 (Figure 3d–f) in contrast to the orbicules. Most rare-metal minerals are precipitated as
195 inclusions in, or near, fluorite (Figure 3e, f).

196 ANALYTICAL METHODS

197 Electron probe microanalysis (EPMA)

198 The major and minor elements of tourmaline were analyzed with a JEOL
199 JXA-8230 Electron Probe Microanalyzer equipped with five wavelength-dispersive
200 spectrometers (WDS) at the Laboratory of Microscopy and Microanalysis, Wuhan
201 Microbeam Analysis Technology Co., Ltd. The samples were coated with a thin
202 conductive carbon film before analysis. The precautions suggested by Zhang and Yang
203 (2016) were used to minimize the difference in carbon film thickness between samples
204 and obtain a ca. 20 nm approximately uniform coating. Operating conditions for
205 quantitative WDS analyses involved an accelerating voltage of 15 kV, a beam current
206 of 20 nA, and a 10 μm spot size. Data were corrected online using a ZAF (atomic
207 number, absorption, fluorescence) correction procedure. The content of B was
208 calculated based on the mole ratio of B:Si = 1:2, and then involved in the ZAF
209 correction procedure. The peak counting time was 10 s for Ca, Mg, K, F, Si, Al, Ti, Na,
210 and Cl, and 20 s for Fe and Mn. The background counting time was 1/2 of the peak
211 counting time on the high- and low-energy background positions. The following

212 standards were used: diopside (Ca, Mg), microcline (K), barium fluoride (F), olivine
213 (Si), pyrope garnet (Fe, Al), jadeite (Na), halite (Cl), rutile (Ti), rhodonite (Mn).

214 **LA-ICP-MS and LA-MC-ICP-MS analysis**

215 In situ trace-element analyses of tourmaline were conducted at the State Key
216 Laboratory of Geological Processes and Mineral Resources (GPMR) in China
217 University of Geosciences (Wuhan), using a RESolution S-155 laser ablation system
218 coupled to a Thermo iCAP-Q_c inductively coupled plasma-mass spectrometer
219 (LA-ICP-MS). The U.S. Geological Survey (USGS) reference glasses (BIR-1G,
220 BCR-2G, and BHVO-2G) and the NIST SRM 612 and 610 glasses were analyzed after
221 every eight tourmaline sample spots. The ablation protocol employed a spot diameter of
222 33 μm at a 10 Hz repetition rate for 40 s. The approximate depth of ablation was 30–50
223 μm. Helium was used as the carrier gas to the ICP-MS. The isotope ²⁹Si was used as the
224 internal standard in conjunction with the Si concentrations determined by EPMA.
225 External calibration was performed using the USGS reference glasses. The NIST
226 glasses were used for correcting the signal drift. Raw data reduction was performed
227 offline using the ICPMSDataCal software (Liu et al., 2010), and to reduce the effect of
228 the signal variability with depth on the test results, the same integration interval of the
229 signal was chosen for the sample and standard.

230 Most of the in situ B isotopic compositions of tourmaline were measured at the
231 GPMR using the same laser ablation system coupled to a Nu Plasma II multicollector
232 ICP-MS. Additional analyses were conducted at the National Research Center for
233 Geoanalysis, Chinese Academy of Geological Science (CAGS), using a Neptune Plus

234 fs-LA-MC-ICP-MS (Thermon Fisher Scientific, Germany) in combination with a 343
235 nm femtosecond laser ablation system (J-100, Applied Spectra, West Sacramento, CA,
236 USA). Both analyses were carried out with a beam diameter of 50 μm and a 10 Hz
237 repetition rate. The ^{11}B and ^{10}B were collected statically and simultaneously with two
238 Faraday cups. The instrumental mass fractionation (IMF) was calibrated using the
239 sample standard bracketing (SSB) method. The international tourmaline standard IAEA
240 B4 ($\delta^{11}\text{B} = -8.71\text{‰}$; [Tonarini et al., 2003a](#)) was adopted as the external standard during
241 the two analyses. The similarity of IMF values ([Online Materials Table OM2](#))
242 determined for the chemically distinct tourmaline standards, including two in-lab
243 tourmaline reference materials used at the GPMR (schorl HS#112566 and dravite
244 HS#108796 from the Harvard Mineralogical Museum, [Dyar et al., 2001](#)) and one used
245 at the CAGS (IMR RB1, [Hou et al., 2010](#)), all demonstrate insignificant matrix effects.
246 The analytical precision is estimated to be better than 0.5‰ ($\pm 2\sigma$) based on the
247 replicated analyses of reference tourmaline during this study. More detailed
248 descriptions of the two analytical methods can be found in [Zhao et al. \(2021a\)](#) and [Long](#)
249 [et al. \(2021\)](#), respectively. Ten replicated spots were arranged to monitor the analytical
250 errors between the two labs, and the results showed near identical $\delta^{11}\text{B}$ values between
251 the two analyses (all less than 0.2‰, see details in [Online Materials Table OM2](#)).

252 RESULTS

253 Major element compositions

254 A total of 264 spots among 37 tourmaline grains were analyzed by EPMA, and the
255 results are given in [Online Materials Table OM1](#). Structural formulae were calculated

256 based on the general formula of $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, where $X = Ca^{2+}, Na^+, K^+, X_{vac}$
257 (vacancy); $Y = Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Ti^{4+}, Fe^{3+}$; $Z = Mg^{2+}, Al^{3+}, Fe^{3+}$; $T = Si^{4+}, Al^{3+}$,
258 (B^{3+}); $V = OH^-, O^{2-}$; and $W = OH^-, F^-, O^{2-}$ (Henry et al., 2011). Tetrahedral and
259 octahedral sites (T+Z+Y) were normalized to 15 cations apfu (atoms per formula unit).

260 Overall, comparable to those of tourmalines crystallized from peraluminous
261 granitic systems (e.g., Zhao et al., 2019; Zhao et al., 2022), all tourmaline samples from
262 the Huoshibulake and Tamu plutons show relatively high SiO_2 (32.50–36.03 wt%),
263 Al_2O_3 (21.77–33.21 wt%), FeO^T (13.98–24.64 wt%) contents, and low TiO_2 (0.00–2.95
264 wt%), MnO (0.00–0.15 wt%), MgO (0.00–1.19 wt%), CaO (0.00–1.69 wt%), Na_2O
265 (1.69–2.57 wt%), K_2O (0.008–0.18 wt%), F (0.00–1.24 wt%), and Cl (<0.07 wt%)
266 contents. Notably, most tourmaline shows extremely low CaO contents (mostly < 0.1
267 wt%), except for the HS-DB ones that exhibit much higher contents (0.003–1.69 wt%).
268 According to the X-site occupancy-based classification by Henry et al. (2011), all
269 tourmalines are members of the alkali series (Figure 6a). In the Al-Fe-Mg ternary
270 diagrams of Henry and Guidotti (1985), the tourmaline samples studied exhibit a
271 narrow variation and plots in the field of Li-poor granite (Figure 6b). Moreover, all
272 tourmaline is Fe-rich and Mg-poor with restricted $Mg/(Mg+Fe)$ (0.00 to 0.09) and
273 $Na/(Na+Ca)$ (0.64 to 1.00) ratios, plotting in the field of schorl series on the X
274 $[\square/(\square+Na)]$ vs. $Mg/(Mg+Fe)$ and X $[Na/(Na+Ca)]$ vs. $Mg/(Mg+Fe)$ diagrams (Figure
275 7a, b). The blue-green tourmaline (i.e., HS-DG, HS-OG, and TM-OG types) at the rim
276 exhibits significantly lower Fe and Ti contents but higher Al and X-site vacancy
277 contents compared to the yellowish-brown tourmaline (HS-DB, HS-OB, and TM-OB

278 types) in the core ([Figure 8a–d](#)). The yellowish-brown tourmaline has higher Ti
279 contents than those in blue-green ones, consistent with the suggestion by [Trumbull et al.](#)
280 ([2007](#)) that Ti content in tourmaline is the primary control for pleochroism. Most
281 tourmaline crystals from HS-DB, HS-OB, HS-V, TM-OB, and TM-V types have >3
282 apfu Fe and < 6 apfu total Al, while ones from HS-DG, HS-OG, and TM-OG mainly
283 possess < 3 apfu Fe and > 6 apfu total Al ([Figures 7d and 8a, b](#)).

284 **Trace-element compositions**

285 The trace elements of 187 spots among 29 tourmaline grains were analyzed by
286 LA-ICP-MS, all of which followed EPMA to ensure spot locations. The results are
287 listed in [Online Materials Table OM1](#). The median concentrations of most trace
288 elements range from 0.1 to 10 ppm, while Li, Zn, Ga, and Sn have the highest median
289 concentrations up to hundreds of ppm, and Sc, Sr, and Ce show median contents of tens
290 of ppm. Concentrations of some trace elements show large variations over several
291 orders of magnitude, such as Li (12.8–256 ppm), Zn (70.3–592 ppm), Sr (0.29–602
292 ppm), Nb (0.12–71.7 ppm), Sn (4.66–2542 ppm), and REE (0.25–170 ppm). In the
293 Huoshibulake pluton, the earlier tourmaline (HS-DB and HS-OB) exhibits higher Sc,
294 Ga, Sr, Sn, and Nb and lower Li concentrations than the later tourmaline (HS-DG and
295 HS-OG, [Figure 8e–j](#)). However, the latest-stage tourmaline in veins (HS-V) shows an
296 inverse trend and high Sc, Ga, Sr, Sn, and Nb abundances. Similar variations are also
297 observed in tourmaline from the Tamu pluton (i.e., TM-OG has higher Li and lower Sc,
298 Ga, Sr, Sn, and Nb contents than those of TM-OB and TM-V). All tourmaline spots
299 display large total REE abundance variations ([Figure 8k](#)). Besides, variation diagrams

300 of representative element pairs show significant positive correlations between Hf vs. Zr,
301 Ta vs. Nb, Sr vs. Sn, and Ce vs. La (Figure 9).

302 **Boron isotopic composition**

303 A total of 228 B isotopic compositions (including 10 replicated spots for checking
304 consistency) among 29 tourmaline grains were determined by LA-ICP-MS, and the
305 results are listed in Online Materials Table OM2 and plotted in Figure 10. The $\delta^{11}\text{B}$ of
306 five types of tourmaline from the Huoshibulake pluton range from -12.6 to -5.2‰,
307 falling in the range of typical granitic magmas (-20 to -5‰, Trumbull and Slack, 2018).
308 Tourmaline spots from the HS-OB, HS-DB, and HS-V types exhibit restricted ranges of
309 $\delta^{11}\text{B}$ from -11.8 to -10.2‰ (mean = -10.9‰, n = 26), -12.6 to -10.0‰ (mean = -11.1‰,
310 n = 30), and -11.7 to -10.1 ‰ (mean = -10.9‰, n = 23), respectively. In comparison,
311 blue-green tourmaline from HS-OG and HS-DG groups shows significantly higher
312 values of $\delta^{11}\text{B}$ ranging from -9.8 to -7.4‰ (mean = -8.7‰, n = 32) and -10.2 to -5.2‰
313 (mean = -8.2‰, n = 29). The $\delta^{11}\text{B}$ values of three types of tourmaline from the Tamu
314 pluton range from -12.6 to -4.9‰. Similar to the isotopic fractionation observed in the
315 Huoshibulake pluton, tourmaline grains of TM-OB and TM-V types show relatively
316 lower $\delta^{11}\text{B}$ values ranging from -12.6 to -10.0‰ (mean = -11.2‰, n = 34) and -12.2 to
317 -10.3‰ (mean = -11.3‰, n = 26), while the blue-green tourmaline grains from TM-OG
318 type have higher values ranging from -9.7 to -4.9‰ (mean = -6.8‰, n = 28).

319 **DISCUSSION**

320 **Formation of tourmaline**

321 The Huoshibulake and Tamu plutons are two adjacent A-type rare-metal granites in

322 the South Tianshan alkaline rock belt. Multi-mineral geochronological studies have
323 shown both emplaced at ~273 Ma (Zhang et al., 2010; Wu et al., in preparation). They
324 are both characterized by high SiO₂, Al₂O₃, and alkali contents, low FeO^T, MgO, and
325 CaO contents, and enrichment of large ion lithophile elements (e.g., Rb) and high
326 field-strength elements (e.g., Nb, Ta, Zr, Hf) (Zhang and Zou, 2013; Zong et al., 2020).
327 Besides, their similar whole-rock Nd isotopes and zircon Hf-O isotopes are consistent
328 with them being genetically related (Wei et al., 2019; Zhang and Zou, 2013). Combined
329 with their indistinguishable petrographic features, Huang et al. (2012) concluded that
330 they are twin plutons derived from a single deeper magma chamber in a multi-level
331 plumbing system, which ultimately originated from low-pressure partial melting of the
332 mafic lower crust.

333 A distinct characteristic of the Huoshibulake and Tamu plutons is the widespread,
334 multi-generation crystallization of tourmaline. Consistent with the whole-rock
335 composition, all types of tourmaline in the two plutons show extremely low CaO (0–
336 1.68 wt%) and MgO (0–1.19 wt%) contents, indicating their crystallization from
337 highly evolved magmatic-hydrothermal systems (Zheng et al., 2022). In the Mg-Fe
338 plot, tourmalines from the two plutons do not show any observable substitution trend of
339 MgFe₋₁ function because of low Mg contents but reveal a substitution trend consistent
340 with the FeAl₋₁ function (Figure 7c). The higher Fe and total Al contents in tourmaline
341 crystals from the yellowish-brown tourmaline (HS-DB, HS-OB, and TM-OB types)
342 than those of blue-green tourmaline (HS-DG, HS-OG, and TM-OG types) suggests that
343 Fe could be incorporated into the Z-site to substitute Al (up to 1.11 apfu in this study)

344 when Al is deficient. Conversely, Al can be incorporated into the Y-site to substitute Fe
345 (up to 0.77 apfu in this study) when Al became elevated to excess in the Z-site during
346 magmatic evolution. The charge balance is maintained by the adjustment of vacant
347 X-site or substitution between O and OH (Figure 7e). The HS-DB tourmaline in the
348 Huoshibulake pluton is disseminated interstitially between quartz and K-feldspar,
349 brown in color without fine-scale zonation (Figure 2d–f), and in some cases, the rim
350 of HS-DB tourmaline is replaced by K-feldspar with a few small irregular tourmaline
351 residues (Figure 2e), consistent with the characteristics of magmatic tourmaline in
352 other highly evolved granites (Zhao et al., 2021a; Zhao et al., 2019; Yang et al., 2015).
353 The Mg/(Mg+Fe) ratio generally decreases with magmatic differentiation (Yang et al.,
354 2015); higher Mg/(Mg+Fe) ratios of the HS-DB tourmaline compared to other
355 tourmaline types (Figure 7a, b) are consistent with earlier crystallization of the
356 HS-DB tourmaline. This is also supported by the linear relationships shown in the
357 plots of Al^{tot} vs. Fe^{tot} and Al^{tot} vs. X-site vacancy that the compositional evolution of
358 most tourmaline types in the Huoshibulake and Tamu plutons were mainly controlled
359 by exchange of $(Al, \square) (Fe, Na)_{-1}$ while the HS-DB show an exchange trend of (Al, Na)
360 $(Ca, Mg)_{-1}$ (Figure 7d–f). Thus, we conclude that the HS-DB tourmaline is of primary
361 magmatic origin.

362 Tourmaline-quartz orbicules have been widely reported in evolved peraluminous
363 granitic rocks with different tectonic settings and ages worldwide (Yang et al., 2015;
364 Trumbull et al., 2007). However, they have rarely been reported in alkali granitic
365 systems. Although a hydrothermal origin related to post-magmatic alteration has been

366 proposed in some studies (e.g., [Rozendaal and Bruwer, 1995](#)), the orbicules are more
367 commonly interpreted as crystallization products of late-magmatic, volatile-rich melts
368 in which volatile-rich phases are incapable of escaping from the magmatic system
369 ([Balen and Broska, 2011](#); [Trumbull et al., 2007](#); [Yang et al., 2015](#)). The
370 tourmaline-quartz orbicules in the Huoshibulake and Tamu plutons are isolated in the
371 granites without fracture networks or veinlets (denoting fluid pathways) connecting
372 them to the surrounding rock ([Figure 4a, b](#)). Besides, the orbicular tourmaline exhibits
373 extremely low Mg and Ca contents, inconsistent with the origination of external fluids
374 that are generally rich in Mg and Ca ([Slack, 1996](#); [Trumbull et al., 2007](#)). Some
375 trace-element pairs (e.g., Nb-Ta, [Ballouard, et al., 2016](#); Zr-Hf, [Zaraisky, et al., 2009](#))
376 show similar enrichment behaviors during magmatic-hydrothermal evolution. The
377 positive correlations of these element pairs shown in [Figure 9](#) are consistent with a
378 continuous magmatic-hydrothermal evolution trend. It has been proposed that an
379 aqueous melt phase, rich in fluxing elements (e.g., P, Li, B, and F), can separate from
380 the residual melt at the final stage of highly evolved granitic systems ([Balen and](#)
381 [Broska, 2011](#); [Thomas et al., 2005](#); [Veksler et al., 2002](#)). Evidence from both
382 experiments and melt inclusions in natural samples reveals that B has a higher affinity
383 for partitioning into such an aqueous melt compared with normal aluminosilicate melt
384 and aqueous fluid ([Thomas et al., 2003](#); [Veksler et al., 2002](#)). In our case, the similar
385 pleochroism and B isotopic compositions of the HS-OB and HS-DB tourmalines
386 allow their crystallization from compositionally and isotopically similar melts. For
387 these reasons, the tourmaline orbicules are interpreted to form from immiscible B-rich

388 aqueous melts during the magmatic-hydrothermal transition. The lower Mg/(Mg+Fe)
389 ratios of the HS-OB tourmaline relative to the HS-DB ones can be attributed to the
390 precipitation of biotite before the exsolution of the immiscible B-rich melts,
391 analogous to the scenario of Qitianling granite in South China (Yang et al., 2015).
392 Feldspar is the major Sr-bearing mineral in the Huoshibulake pluton; the lower Sr
393 contents of the HS-OB (2.82–44.8 ppm) tourmaline compared to HS-DB ones (11.9–
394 602 ppm) are consistent with the later formation of tourmaline-quartz orbicules.
395 Overgrowths of green-blue tourmaline (HS-DG, HS-OG, and TM-OG types) around
396 brown cores (HS-DB, HS-OB, and TM-OB types) show sharp changes in both
397 elemental and B isotopic compositions, precluding progressive crystallization and
398 revealing a change of the crystallization medium. Analogous characteristics have also
399 been reported in highly evolved peraluminous granites and interpreted as the
400 transition of tourmaline formation from a silicate melt-dominated to hydrothermal
401 environments (e.g., Zhao et al., 2022, Drivenes et al., 2015, Trumbull et al., 2020).
402 Compared with the brown tourmaline, the green-blue overgrowths exhibit lower Ca,
403 Na, Ti, and Fe contents and higher X-site vacancy (Figure 8a–d). The significantly
404 higher Sr and Sc and lower Li contents of the brown tourmaline than those of
405 green-blue tourmaline (Figure 8e–g) agree with the partition preference that Sr and Sc
406 strongly partition in melt while Li is highly fluid mobile (Bai and Van Groos, 1999;
407 Penniston-Dorland et al., 2012). Besides, the stronger B isotopic fractionation during
408 crystallization of tourmaline from fluids than that from melts generally causes
409 significantly heavier B isotopic compositions in hydrothermal tourmaline than in

410 magmatic tourmaline (see details in the next section), consistent with the fractionation
411 observed in this study (Figure 10). In combination with its occurrence in both
412 disseminated and orbicular tourmaline groups, the green-blue tourmaline is
413 interpreted as a hydrothermal origin and precipitated from later exsolved fluids in the
414 magmatic-hydrothermal transition.

415 Both external fluid activity and exsolved magmatic-hydrothermal melt/fluid at the
416 latest stage of magmatic evolution could account for tourmaline-quartz veins (Zhao et
417 al., 2019). However, the extremely low Ca and Mg contents of the vein tourmaline
418 argue against an external origin involving the country rocks which mainly consist of
419 calcareous sandstone and limestone (Shuai et al., 2019). The tourmaline-quartz veins
420 in the Huoshibulake and Tamu plutons show straight and sharp boundaries with the
421 host granite (Figure 5a, b). Most of these veins have near-vertical orientation and are
422 generally parallel in the same outcrop (Figure 5a), indicating that they intruded along
423 fractures after the granites solidified. U-Pb dating of the cassiterite from the
424 tourmaline-quartz vein yields a coeval age (271 ± 4 Ma) with the host granite (275 ± 2
425 Ma), suggesting that they formed within the same magmatic event (Wu et al., in
426 preparation). Besides, the indistinguishable elemental (Figures 8 and 9) and B isotopic
427 compositions (Figure 10) of the vein tourmaline with the disseminated tourmaline
428 permit a similar origin. Based on these lines of evidence, we propose that the
429 tourmaline-quartz veins were probably the product of highly evolved, B-rich melts of
430 another magma pulse from a deeper cogenetic magma chamber which emplaced after
431 the plutons had consolidated.

432 **Boron source and variations of boron isotopes**

433 The fractionation of B isotopes in the magmatic-hydrothermal systems is
434 commonly explained by differential B coordination in different phases since ^{11}B
435 exhibits a greater tendency to trigonal coordination while ^{10}B adopts tetrahedral
436 coordination (Kakihana et al., 1977; Palmer and Swihart, 1996). Boron is
437 predominately trigonally coordinated in tourmaline and aqueous fluid (Bassett, 1976;
438 Schmidt et al., 2005); by contrast, B coordination in silicate melt is a mix of both
439 trigonal and tetrahedral coordination depending on water content, alkali/aluminum
440 ratio, and speciation of aluminum (Dingwell et al., 1996). Thus,
441 magmatic-hydrothermal processes involving phase separation (e.g., Rayleigh
442 fractionation during the crystallization of tourmaline from melts or fluids and isotopic
443 redistribution during melt/fluid exsolution) would be encoded as differential B isotopic
444 fractionation (Smith and Yardley, 1996).

445 Due to the lack of experimental determination, the B isotopic fractionation
446 between silicate melt and tourmaline was generally calculated indirectly by
447 combining fractionation between melt and fluid ($\Delta^{11}\text{B}_{\text{melt-fluid}}$) and fluid and tourmaline
448 ($\Delta^{11}\text{B}_{\text{Tur-fluid}}$) in the past decades (e.g., Zhao et al., 2021a, Maner and London, 2017).
449 However, this method has significant uncertainty since (1) the available $\Delta^{11}\text{B}_{\text{melt-fluid}}$
450 and $\Delta^{11}\text{B}_{\text{Tur-fluid}}$ data were determined by different experimental methods (Cheng et al.,
451 2022) and (2) the predicted B isotopic fractionation between granitic melt and
452 tourmaline is much more significant when compared with that observed in the natural
453 magmatic tourmaline (Kowalski and Wunder 2018; Zhao et al., 2022). Recently, Cheng

454 [et al. \(2022\)](#) reported the first set of experimental data of B isotopic fractionation
455 between granitic melt and tourmaline, which they defined as $\Delta^{11}\text{B}_{\text{melt-Tur}} = 4.51 \times$
456 $(1000/T \text{ [K]}) - 3.94$. Using the Titanium-in-quartz thermobarometer proposed by
457 [Huang and Audétat \(2012\)](#), crystallization temperatures of the magmatic tourmaline
458 paragenic with quartz from the Huoshibulake and Tamu plutons are estimated as 624–
459 825°C and 614–838°C ([Online Supplementary Material](#)). The small B isotopic
460 fractionation between melt and magmatic tourmaline ($\Delta^{11}\text{B}_{\text{melt-Tur}} = -0.26$ at 800 °C and
461 -1.23 at 600 °C) based on the empirical equation is consistent with the limited B
462 isotopic variation observed in the magmatic tourmaline groups in this study (HS-DB,
463 HS-OB, HS-V, TM-OB, and TM-V; [Figure 10](#)). With increasing B concentration in the
464 residual melt, immiscible B-rich magmatic globules could separate from coexisting
465 granitic magma to form quartz-tourmaline orbicules ([Balen and Broska, 2011](#); [Thomas](#)
466 [et al., 2005](#)). [Gurenko et al. \(2005\)](#) observed negligible fractionation between
467 coexisting immiscible B-rich melt and silicate melt. This mechanism explains the
468 similar B isotopic composition of magmatic tourmaline crystallized from silicate melt
469 (HS-DB, 12.6‰ to -10.0‰) and those from conjugated aqueous B-rich melts (HS-OB,
470 -11.8 to -10.2‰; TM-OB, -12.6‰ to -10.0‰). Considering the lightest $\delta^{11}\text{B}$ value of
471 -12.6‰, the initial $\delta^{11}\text{B}$ value of the initial melt is set as -12.3‰. The modeling in
472 [Figure 11a](#) shows that the slight rise of $\delta^{11}\text{B}$ values in the magmatic tourmaline can be
473 reproduced by the combination of increasing $\delta^{11}\text{B}$ values in the residual melt caused by
474 Rayleigh fractionation of tourmaline crystallization and the enlargement of $\Delta^{11}\text{B}_{\text{melt-Tur}}$
475 along with the decreasing temperature.

476 Both fluid exsolution and Rayleigh fractionation during the crystallization of
477 hydrothermal tourmaline cause increasing $\delta^{11}\text{B}$ values in later crystallizing
478 hydrothermal tourmaline. The experimental data reported by [Hervig et al. \(2002\)](#)
479 suggested significant B isotopic fractionation between hydrous fluids and silicate melt
480 of rhyolitic composition at high temperatures (up to -7.1% , at $750\text{ }^\circ\text{C}$ and 500 MPa).
481 [Hervig et al. \(2002\)](#) explained the remarkable $\Delta^{11}\text{B}_{\text{melt-fluid}}$ by the significant difference
482 of B coordination between melts (dominantly tetrahedral) and fluids (dominantly
483 trigonal). However, this result and explanation have been long debated since they
484 contradict the spectroscopic measurements on synthesized and natural silicate glasses
485 which show a small amount of or negligible tetrahedral B ([Schmidt et al. 2004](#); [Tonarini](#)
486 [et al., 2003b](#)). Both the experimental studies and the analysis of melt and fluid
487 inclusions in evolved granites and pegmatites have revealed that the system changes
488 from a melt-driven stage to a fluid-driven period at a near-solidus temperature of
489 $500\text{ }^\circ\text{C}$ ([Thomas et al. 2003](#); [Veksler and Thomas 2002](#)). In this study, given the
490 heaviest $\delta^{11}\text{B}$ values of -10.0% of the magmatic tourmaline and assuming the fluid
491 exsolution temperature of $500\text{ }^\circ\text{C}$, the $\delta^{11}\text{B}$ value of the latest melt would be $\sim -8.1\%$.
492 For hydrothermal tourmaline, [Meyer et al. \(2008\)](#) proposed that the B isotopic
493 fractionation between fluid and tourmaline is temperature-dependent and can be
494 calculated by $\Delta^{11}\text{B}_{\text{tour-fluid}} = -4.20 \times [1000/T (\text{K})] + 3.52$. Considering the most negative
495 $\delta^{11}\text{B}$ value recorded by HS-DG (-10.2%) and assuming the exsolution temperature of
496 500°C , the $\delta^{11}\text{B}$ value of initial hydrothermal fluid in equilibrium with the late
497 green-blue tourmaline would be about -8.3% . The near-identical estimated B isotopic

498 compositions between the residual melt and the initial fluid imply that the B isotopic
499 fractionation during fluid exsolution in this study is negligible. Alternatively, the
500 Rayleigh fractionation modeling shown in [Figure 11b](#) demonstrates that the heavy and
501 highly variable B isotopic composition of the hydrothermal green-blue tourmaline can
502 be explained by significant Rayleigh fractionation during the depletion of B in the fluid.
503 The decrease in temperature can amplify the fluid-tourmaline B isotopic fractionation,
504 and the heaviest composition (-4.9 ‰ from the TM-OG) can be achieved by ~86%
505 depletion of B in the residual fluid at 400 °C ([Figure 11b](#)).

506 In summary, the B isotopic variations in the magmatic and hydrothermal
507 tourmaline observed in the Huoshibulake and Tamu plutons can be reproduced by the
508 Rayleigh fractionation during the magmatic-hydrothermal transition. Based on the
509 discussion above, an idealized model is proposed and illustrated in [Figure 12](#).

510 **Rare-metal concentration and precipitation during the magmatic-hydrothermal** 511 **transition in granitic systems**

512 The magmatic-hydrothermal transition has been considered one of the most critical
513 stages in the granite-related metallogenic system, during which rare metals generally
514 reach their peak concentrations and precipitate as economic minerals ([Kaeter et al.,](#)
515 [2018](#); [Ballouard et al., 2020](#)). However, whether the rare metal mineralization in the
516 granitic system occurs at the melt-driven or fluid-driven stage is still widely disputed
517 ([Ballouard et al., 2016](#); [Sokół et al., 2021](#); [Yang et al., 2020](#)). Some previous studies
518 highlighted the role of high-degree fractional crystallization and suggested that the
519 ore-forming elements are highly concentrated and deposited in the residual melts at the

520 end of the magmatic period ([Borodulin et al., 2009](#); [Chevychelov et al., 2005](#)). In
521 contrast, some studies argued that melt-melt immiscibility or fluid exsolution during
522 the magmatic-hydrothermal transition could be a critical mechanism for the
523 hyper-enrichment of rare metals ([Ballouard et al., 2016](#); [Thomas and Davidson,](#)
524 [2016](#)), especially when the strongly differentiated distribution of fluxing elements is
525 involved ([Mohamed, 2013](#); [Vasyukova and Williams-Jones, 2014](#)). For instance, some
526 experimental studies suggested that Nb, Ta, and REE can form complexes with ligands
527 (e.g., F⁻, Cl⁻) through which they can be effectively concentrated in aqueous melts or
528 hydrothermal fluids ([Migdisov and Williams-Jones, 2014](#); [Timofeev et al., 2015](#);
529 [Zaraisky et al., 2010](#)). However, little direct evidence from the natural systems has been
530 found to confirm the trace element distribution behavior during the latest melt-fluid
531 interaction in the granitic systems.

532 The characteristics of B-rich melt/fluid exsolution in this study provide a unique
533 insight into the rare metal mineralization during the magmatic-hydrothermal transition.
534 In the Huoshibulake pluton, HS-DB tourmaline (interpreted as early magmatic)
535 exhibits high Nb (2.25–71.7 ppm, with an average of 21.7 ppm) and Ta (0.52–31.6
536 ppm, with an average of 9.20 ppm) contents. In comparison, those of HS-OB type
537 crystallized from immiscible aqueous melt and HS-DG and HS-OG crystallized from
538 exsolved fluid have significantly lower Nb and Ta contents ([Figure 8j](#)). The
539 compositional variations of tourmaline are consistent with the petrographic
540 observations, that is, columbite is commonly observed and paragenetic with
541 disseminated tourmaline while absent in the tourmaline–quartz orbicules. It is thereby

542 inferred that Nb and Ta reached peak concentrations during the latest magmatic stage
543 but were depleted in the exsolved aqueous B-rich melt/fluid in the Huotoushan case.
544 Similar compositional variations were also reported in tourmaline from the Shangbao
545 Nb-Ta granite, South China (Zhao et al., 2021b). Unfortunately, the REE contents in
546 the different types of tourmaline from the two mineralized plutons exhibit low and
547 variable contents (Figure 8k), providing limited information about their evolution and
548 participation preference to melts or fluids. However, rare-earth minerals (e.g.,
549 monazite, fluocerite, and synchysite) are commonly observed in the granite matrix
550 (Figure 3a–c) and the tourmaline-quartz veins (Figure 3d–f) but are rare in
551 tourmaline-quartz orbicules, precluding the extraction effect of REE during the
552 aqueous B-rich melt/fluid exsolution. The Sn content in tourmaline has been widely
553 employed to predict Sn mineralization potential due to its high partition coefficient
554 (Hong et al., 2017; Qiu et al., 2021). In our case, tourmaline from the orbicules
555 (HS-OB and HS-OG) and rim of disseminated tourmaline (HS-DG) show
556 significantly lower Sn contents compared to the HS-DB (Figure 8i), also arguing
557 against the Sn enrichment in the B-rich melt and fluid phases during their exsolution.
558 From this perspective, B-rich melt/fluid exsolution does not necessarily contribute to
559 rare-metal mineralization.

560 As discussed above, the tourmaline-quartz orbicules resulted from exsolved
561 B-rich melts in the late-stage crystallization of the Huoshibulake and Tamu granitic
562 magmas, and the tourmaline-quartz veins represent another B-rich melt pulse from a
563 deeper cogenetic magma chamber; both of them are regarded as the products of

564 magmatic-hydrothermal transition. However, a notable phenomenon is that the veins
565 exhibit considerably higher Nb, Ta, Sn, and REE on both bulk rock and tourmaline
566 scales (except for REE in tourmaline) with a higher abundance of rare-metal minerals
567 compared to the orbicules. These rare-metal minerals show close paragenesis with
568 fluorite; especially for acicular synchysite that only occurs as inclusions in fluorite
569 (Figure 3d–f), linking fluorite saturation with REE and Nb precipitation. The
570 relevance of fluorine and rare metals is also supported by the significantly higher
571 whole-rock F, Nb, and Σ REE contents (1.10 wt%, 233 ppm, and 831 ppm,
572 respectively, Wu et al., in preparation) of the tourmaline-quartz vein compared to
573 those of the tourmaline-quartz orbicule (0.20 wt%, 84.9 ppm, and 208 ppm,
574 respectively). These lines of evidence indicate that the timing when fluorite reaches
575 saturation is a critical factor determining the concentration and precipitation of rare
576 metals during the magmatic-hydrothermal process. Fluorine is considered an
577 important agent for transporting Nb and REE as fluoride species (Williams-Jones et
578 al., 2000; Ruberti et al., 2008). Thus, the saturation of fluorite can cause rapid
579 depletion of the complexing ligand and simultaneously trigger the precipitation of
580 these rare metals (Smith and Henderson, 2000). During the crystallization of the
581 Huoshibulake and Tamu plutons, fluorite saturation occurred at the relatively early
582 stage of the magmatic-hydrothermal transition and resulted in the disseminated
583 crystallization of rare metals in the granite matrix; in contrast, fluorine in the parental
584 magmas of the tourmaline-quartz veins was concentrated and fluorite did not reach
585 saturation until their emplacement, leading to the veined rare-metal mineralization

586 after B-rich melts exsolution.

587 **IMPLICATIONS**

588 This study recognizes four generations of tourmaline formed from late magmatic,
589 through magmatic-hydrothermal transition, to late hydrothermal stages in the
590 Huoshibulake and Tamu alkali granites. The petrographic, compositional, and B
591 isotopic variations recorded by the tourmaline provide valuable information for
592 re-establishing the magmatic-hydrothermal processes. This study highlights the use of
593 tourmaline as a tracer to unravel the magmatic-hydrothermal transition and related
594 rare-metal mineralization in granitic systems. For instance, the differential rare-metal
595 abundances between tourmalines from orbicules and veins are in good accordance
596 with rare-metal mineral abundance. These observations, together with the close
597 paragenesis of ore minerals and fluorite, further decode the critical role of fluorite
598 saturation in rare-metal enrichment and mineralization during the transition. It is also
599 important to note that when employing the compositional index of tourmaline (e.g.,
600 Sn, which has been commonly used) to evaluate metallogenic potential, extra
601 attention should be paid to the mineral structure and multi-generation crystallization.

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615

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- 921

922

FIGURE CAPTIONS

923 Figure 1 **(a)** Geological map of the South Tianshan Belt and the northern margin of the
924 Tarim Craton, modified from [Gao et al. \(2011\)](#) and [Huang et al. \(2015\)](#). **(b)** Simplified
925 geological map of the Huoshibulake pluton. **(c)** Simplified geological map of the Tamu
926 pluton.

927

928 Figure 2 **(a–c)** Field photo showing the contact relationship between the Huoshibulake
929 pluton and the surrounding rock. **(b and c)** Photographs of hand specimens of
930 disseminated tourmaline, showing dispersed tourmaline crystals in the Huoshibulake
931 K-feldspar biotite granite and biotite granite, respectively. **(d and e)** Plane polarized
932 light photomicrographs of sub- to euhedral tourmaline, with brown-yellow pleochroism
933 at the core and blue-green pleochroism at the rim. **(f)** Plane polarized light
934 photomicrograph of anhedral tourmaline aggregate. **(g–i)** BSE images of disseminated
935 tourmaline. Orange circles and blue circles with numbers show the analyzed location
936 and $\delta^{11}\text{B}$ values for boron isotopic analysis, respectively. Tur = tourmaline, Qz = quartz,
937 Kfs = K-feldspar, Pl = plagioclase, Bt = biotite, Flr = fluorite, Mnz = monazite, Zrn =
938 zircon, Clb = columbite.

939

940 Figure 3 BSE images of disseminated tourmaline from the Huoshibulake pluton **(a–c)**
941 and vein tourmaline from the Huoshibulake **(d)** and the Tamu **(e and f)** plutons showing
942 the close paragenesis between fluorite and rare-metal minerals. **(a)** Typical
943 disseminated tourmaline with abundant inclusions of columbite, fluorite, and monazite;

944 **(b)** a strongly mineralized area with abundant fluocerite and synchysite showing
945 paragenesis with fluorite; **(c)** anhedral columbite and abundant acicular synchysite
946 included in a fluorite grain; **(d)** a large amount of rare-earth minerals (synchysite,
947 fluocerite, and monazite) and columbite deposited in a F-rich domain; **(e and f)**
948 columbite and acicular synchysite crystallized in fluorite droplets. Tur = tourmaline, Qz
949 = quartz, Kfs = K-feldspar, Ms = muscovite, Flr = fluorite, Mnz = monazite, Clb =
950 columbite, Fert = fluocerite, Zrn = zircon, Syn = synchysite.

951

952 Figure 4 **(a and b)** Photographs of outcrops of tourmaline-quartz orbicules from the
953 Huoshibulake and Tamu plutons, showing typical core-mantle-rim texture. **(c and d)**
954 Plane polarized light photomicrograph of sieve-like tourmaline intergrown with quartz,
955 showing the yellow-brown core and blue-green rim. **(e and f)** BSE images of orbicular
956 tourmaline with dark cores and light rims. Orange circles and blue circles with numbers
957 show the analyzed location and $\delta^{11}\text{B}$ values for boron isotope, respectively. Tur =
958 tourmaline, Qz = quartz, Flr = fluorite, Mnz = monazite.

959

960 Figure 5 Photographs showing texture, mineralogy, and B isotopic characteristics of
961 tourmaline-quartz veins in the Huoshibulake and Tamu plutons. **(a and b)**
962 Near-parallel tourmaline-quartz veins outcrops; **(c)** hand specimen photo showing the
963 sub- to euhedral tourmaline intergrowth with quartz and fluorite; **(d–f)** plane polarized
964 light photomicrograph of tourmaline grains with growth zonation and near identical B
965 isotopic compositions. Tourmaline grains **(d)** are sectioned oblique to the c axis, and **(e**

966 **and f)** parallel to the c axis. Orange circles and blue circles with numbers show the
967 analyzed location and $\delta^{11}\text{B}$ values for boron isotope, respectively. **(g–i)** Representative
968 BSE images showing the concentric zoning in tourmaline hosted in the veins. Tur =
969 tourmaline, Qz = quartz, Flr = fluorite.

970

971 Figure 6 **(a)** Classification diagrams based on X-site occupancy (modified after [Henry](#)
972 [et al. 2011](#)) and **(b)** Al-Fe-Mg ternary diagrams (modified after [Henry and Guidotti,](#)
973 [1985](#)) of tourmaline from the Huoshibulake and Tamu plutons showing compositional
974 variations of tourmaline from various source rocks. 1 = Li-rich granitoid pegmatites
975 and aplites, 2 = Li-poor granitoids and their associated pegmatites and aplites, 3 =
976 Fe^{3+} -rich quartz-tourmaline rocks (hydrothermally altered granites), 4 = metapelites
977 and metapsammities coexisting with an Al-saturating phase, 5 = metapelites and
978 metapsammities not coexisting with an Al-saturating phase, 6 = Fe^{3+} -rich
979 quartz-tourmaline rocks, calc-silicate rocks, and metapelites, 7 = low-Ca
980 metaultramafics and Cr, V-rich sediments, 8 = metacarbonates and metapyroxenites.
981 M1 = $\text{Fe}^{3+}\text{Al}_1$ and $(\text{Fe}^{2+}, \text{OH}^-)(\text{Al}, \text{O}^{2-})_{-1}$, M2 = $(\text{Mg}, \text{OH}^-)(\text{Al}, \text{O}^{2-})_{-1}$. HS =
982 Huoshibulake pluton, TM = Tamu pluton, DB = yellow-brown core of disseminated
983 tourmaline, DG = blue-green rim of disseminated tourmaline, OB = yellow-brown core
984 of orbicular tourmaline, OG = blue-green rim of orbicular tourmaline, V = vein
985 tourmaline.

986

987 Figure 7 **(a and b)** Classification of tourmaline from the Huoshibulake and Tamu

988 plutons (modified after [Trumbull and Chaussidon, 1999](#); [Henry and Dutrow, 2012](#)); (**c–**
989 **f**) Chemical discrimination diagrams for tourmaline from the Huoshibulake and Tamu
990 plutons, showing their compositional evolution trends and exchange vectors (modified
991 after [Henry and Dutrow 1990, 2012](#)). Abbreviations are same as Figure 6.

992

993 Figure 8 Box plots showing comparisons of selected major element (apfu, **a–d**) and
994 trace element (ppm, **e–k**) compositions in different tourmaline types from the
995 Huoshibulake and Tamu plutons. The “N” values in the table are numbers of analyzed
996 spots. Abbreviations are same as Figure 6.

997

998 Figure 9 Trace element variation diagrams of tourmaline from the Huoshibulake and
999 Tamu plutons, showing the positive correlations between different element pairs.
1000 Abbreviations are same as Figure 6.

1001

1002 Figure 10 Box plots showing variations of boron isotopic compositions in different
1003 types of tourmaline. Abbreviations are same as Figure 6.

1004

1005 Figure 11 Modeling of B isotopic fractionation between (**a**) melt and tourmaline and
1006 (**b**) fluid and tourmaline. The initial $\delta^{11}\text{B}$ values of the melt and aqueous fluid are set
1007 as -12.3‰ and -8.3‰, respectively. See text for details. The violin plots show the
1008 ranges of B isotopic compositions of different tourmaline types. Abbreviations are
1009 same as Figure 6.

1010

1011 Figure 12 Idealized scenarios showing the formation of the different types of
1012 tourmaline. Generation I: during the late-stage crystallization of the plutons, B
1013 reached saturation and crystallized as disseminated tourmaline. Generation II: with
1014 continuous crystallization, the immiscibility of B-rich aqueous melts resulted in the
1015 crystallization of orbicular tourmaline. Generation III: exsolved fluids formed the
1016 overgrowths of tourmaline at the rims of the earlier magmatic tourmaline. Generation
1017 IV: another pulse of B-rich aqueous melts intruded into fractures of the consolidated
1018 granite. Abbreviations are same as Figure 6.

1019

Figure 1

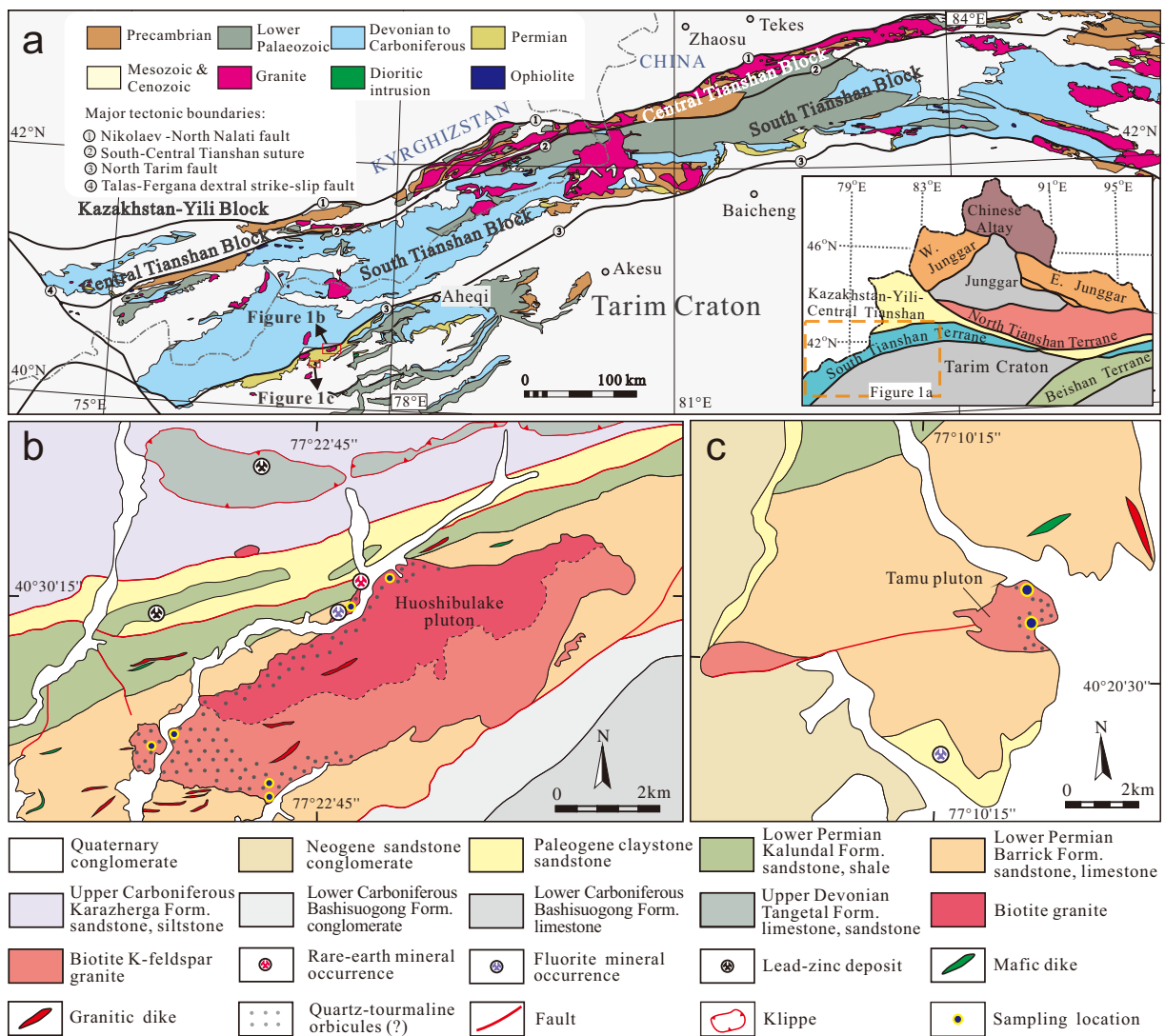


Figure 2

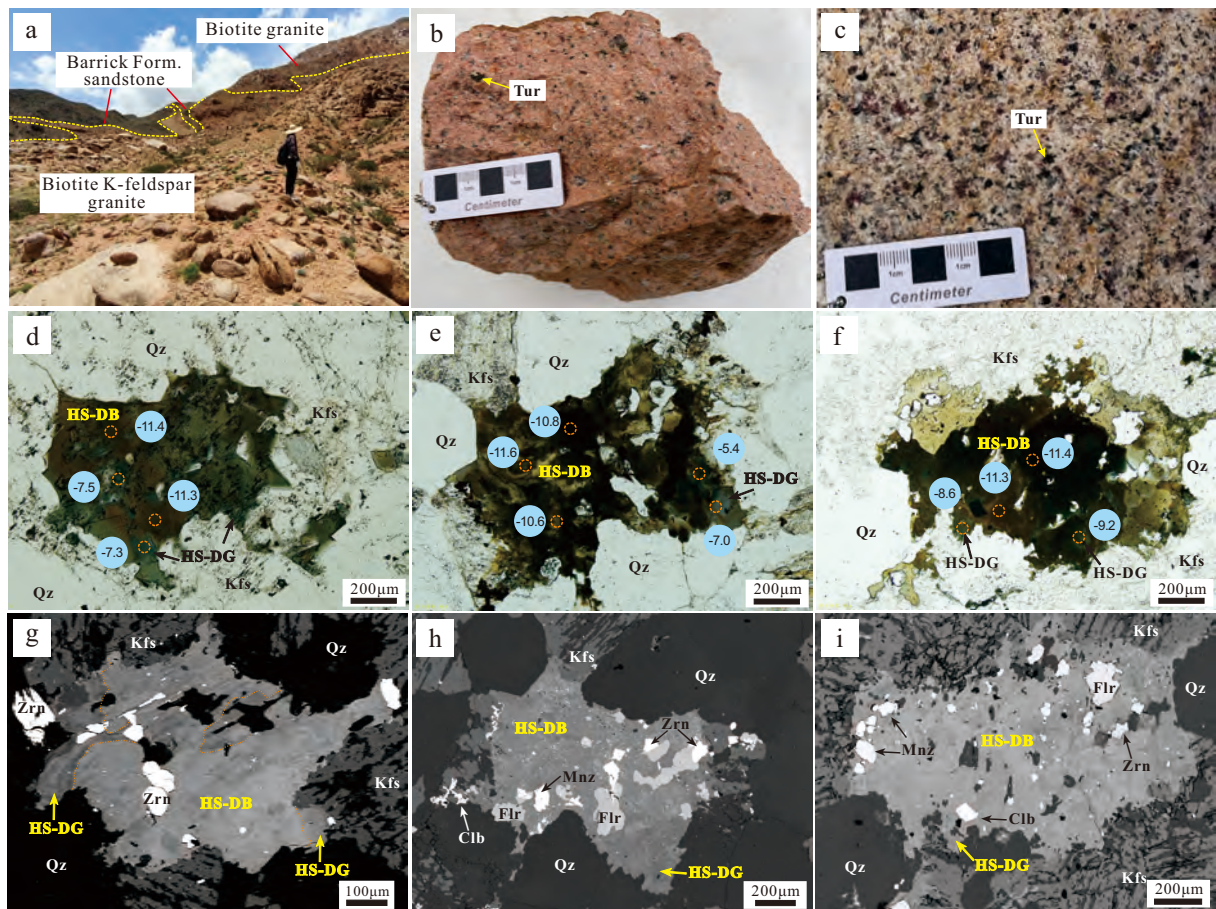


Figure 3

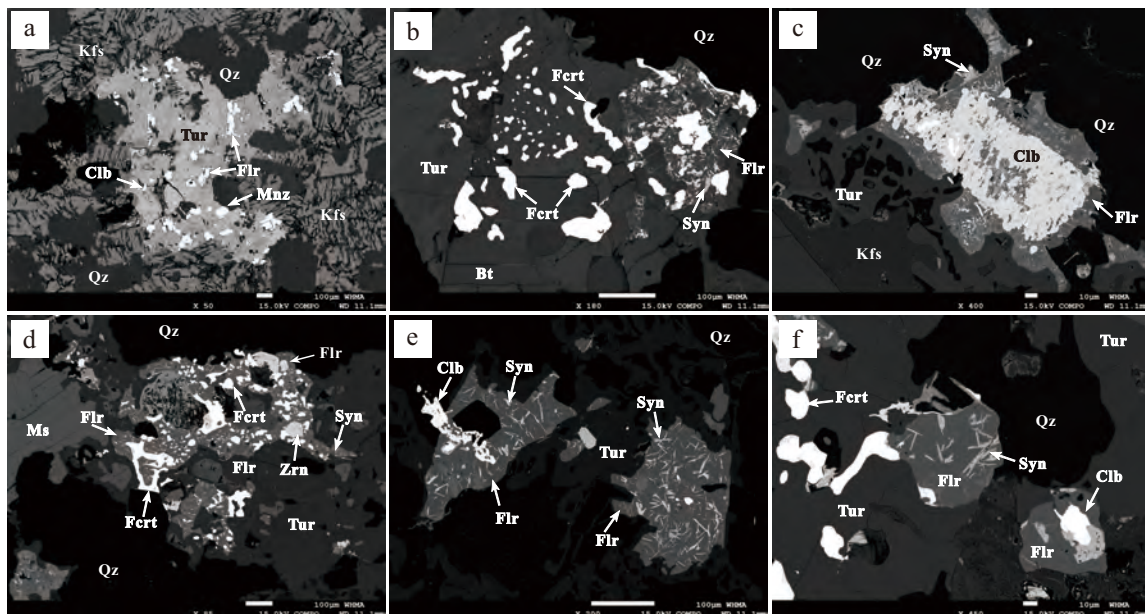


Figure 4

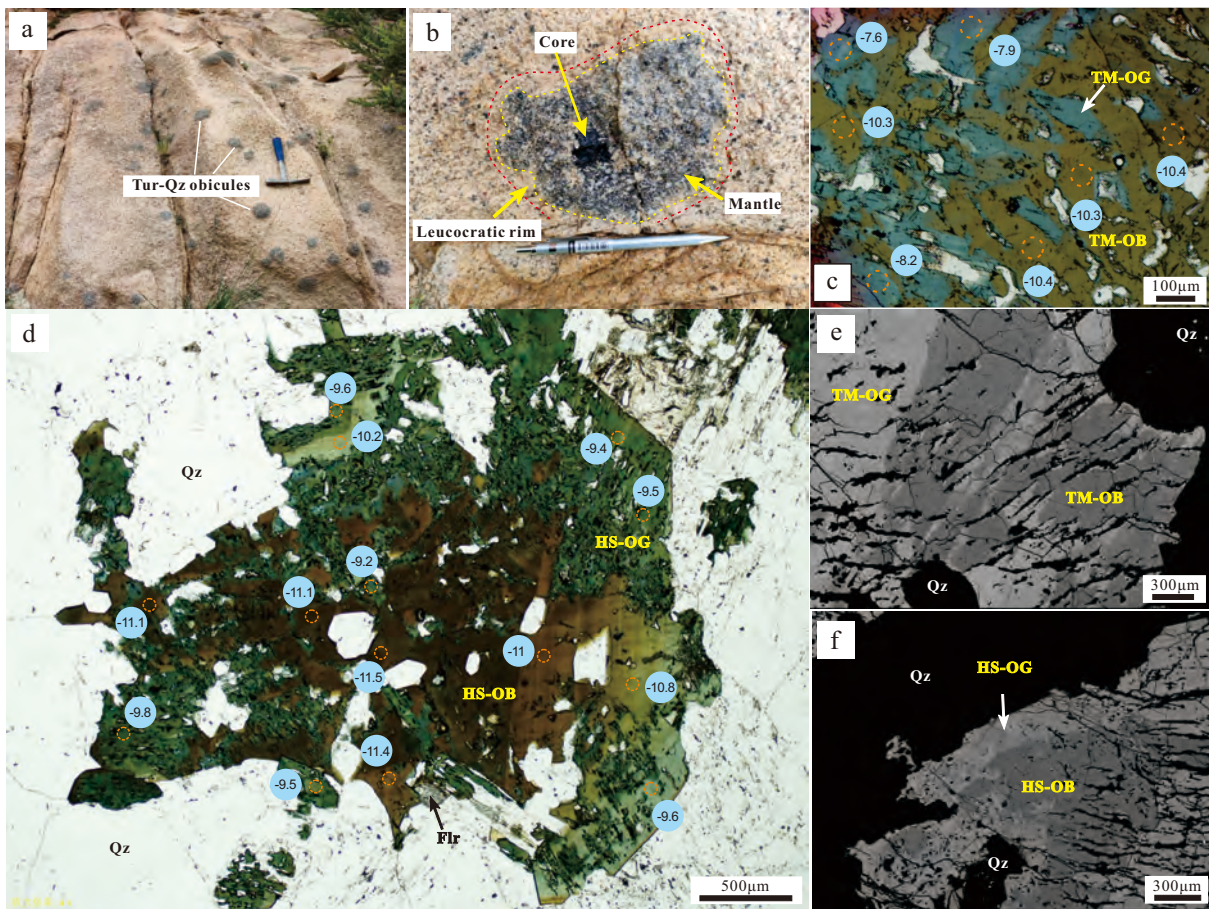


Figure 5

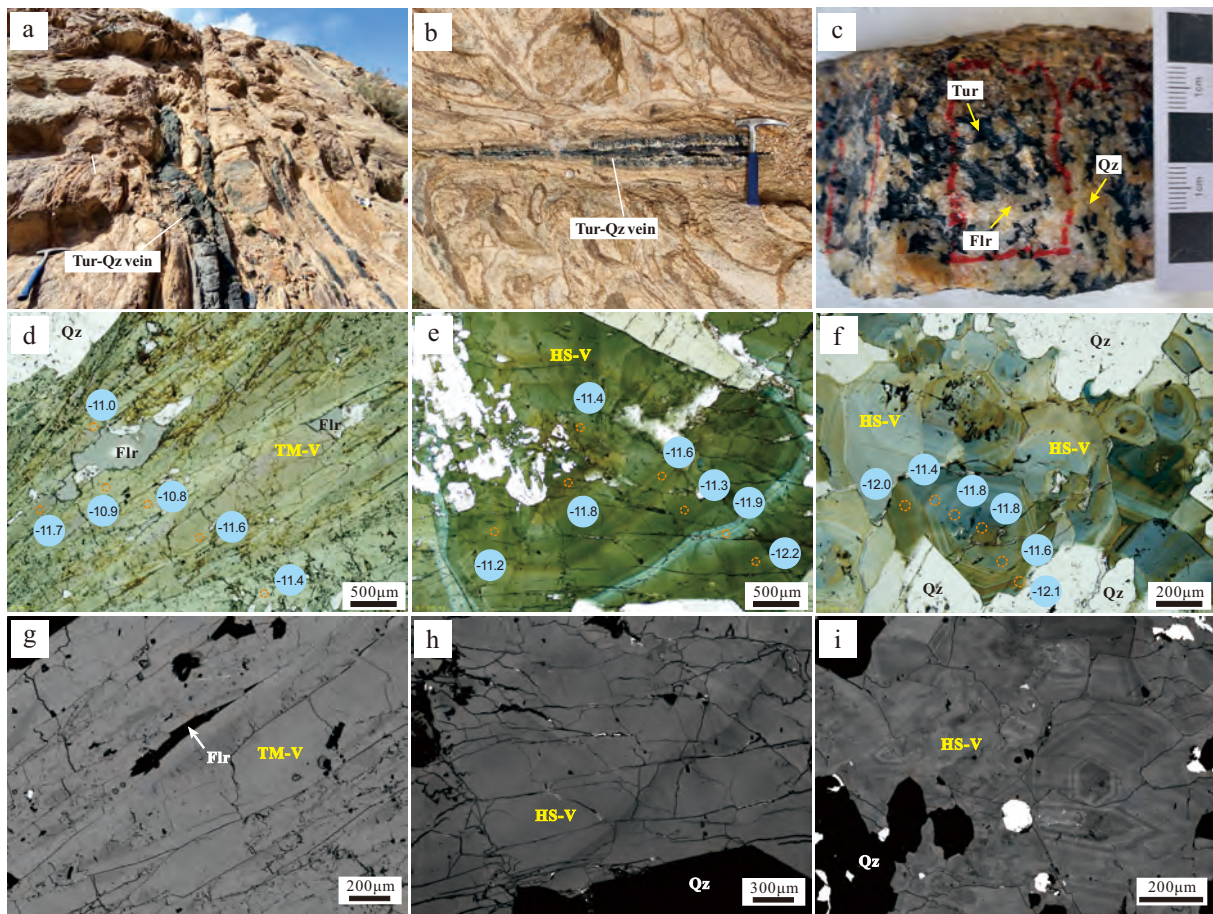


Figure 6

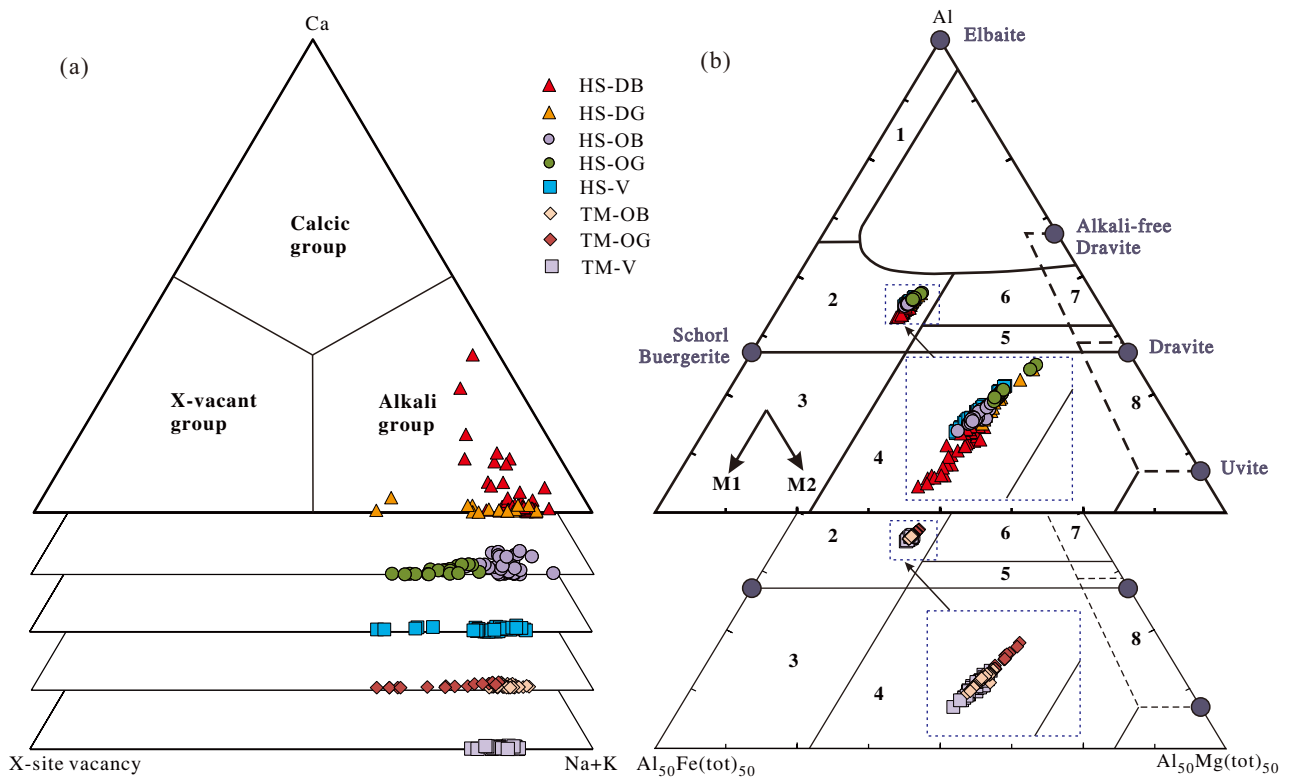


Figure 7

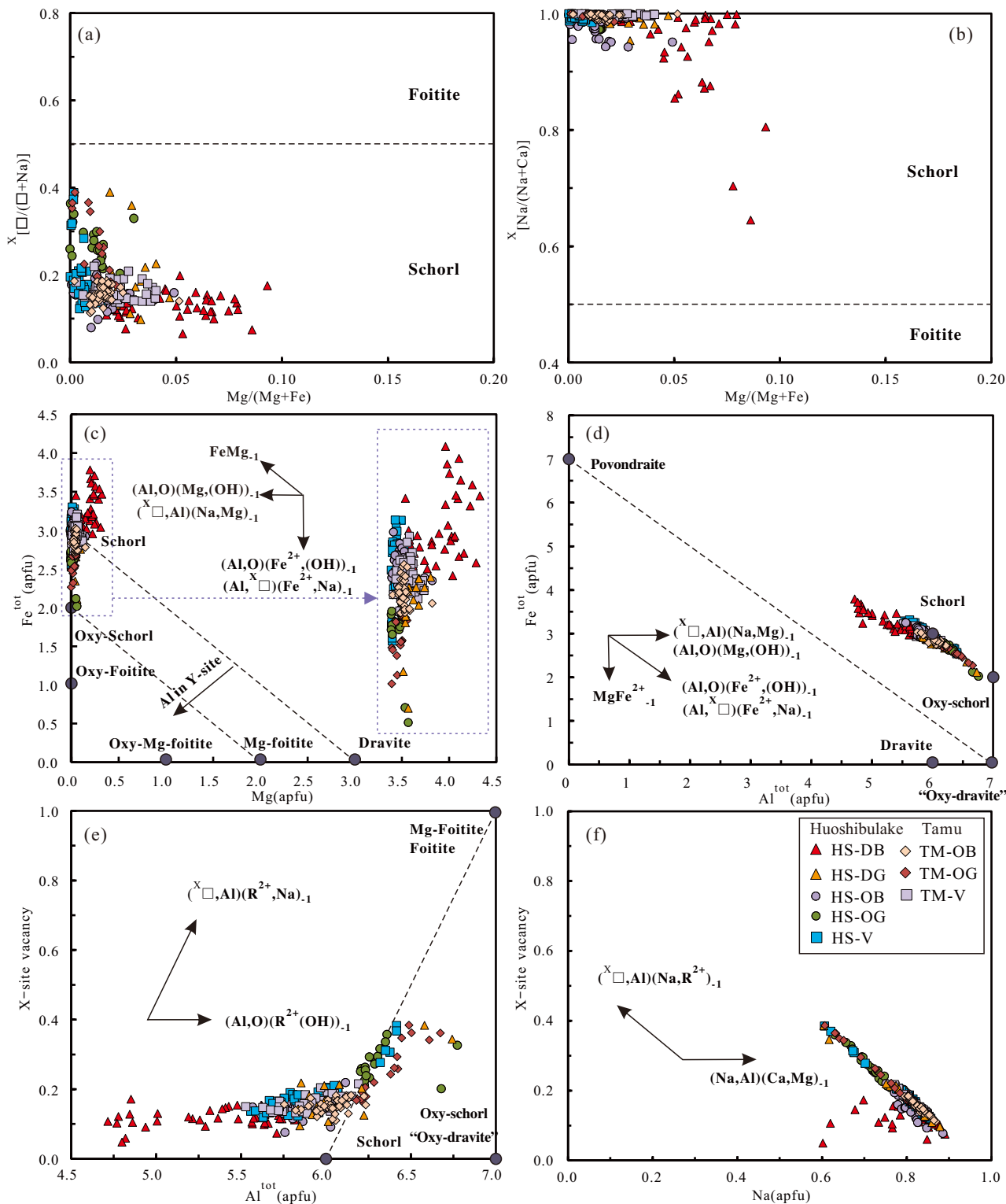


Figure 8

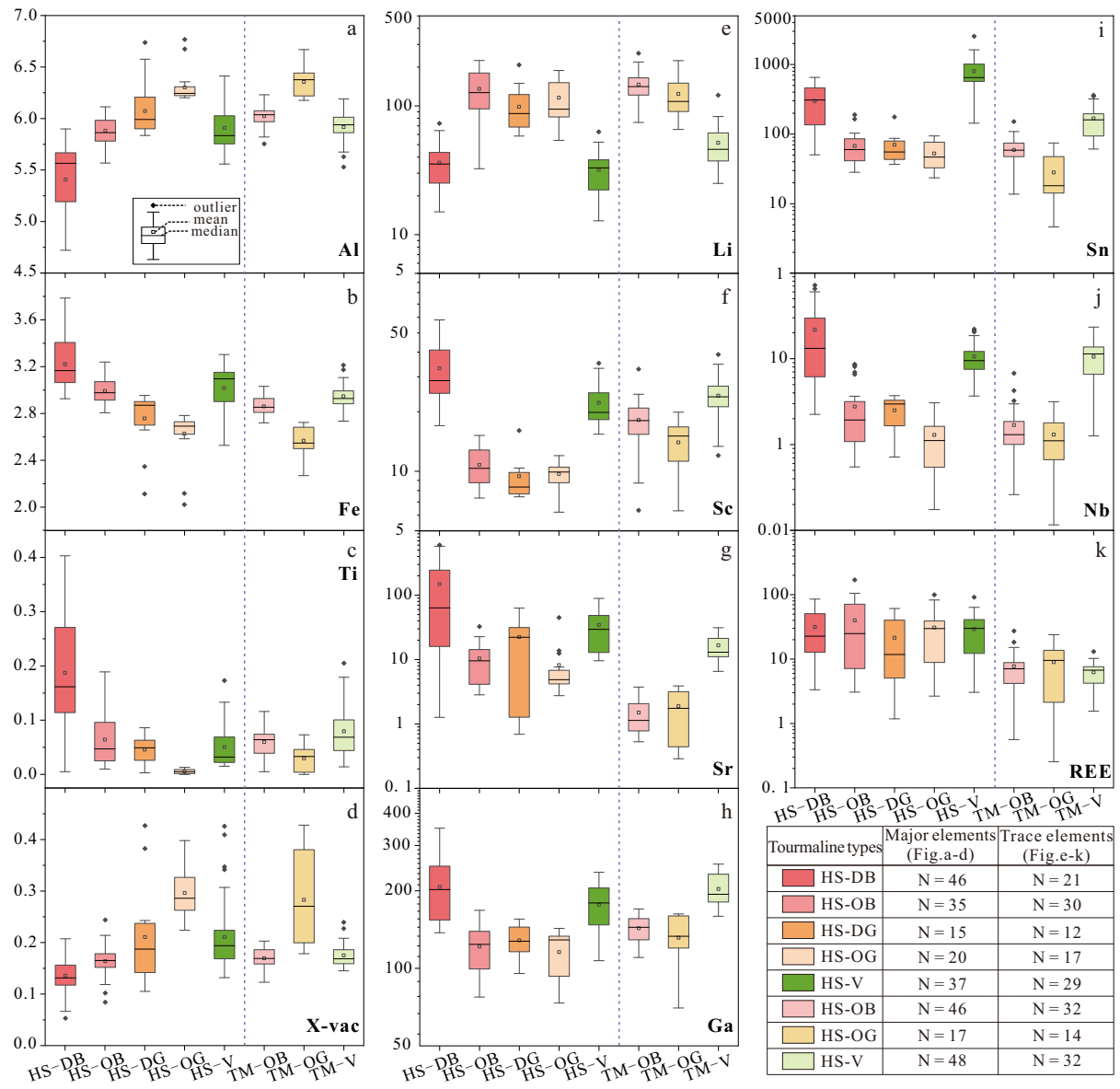


Figure 9

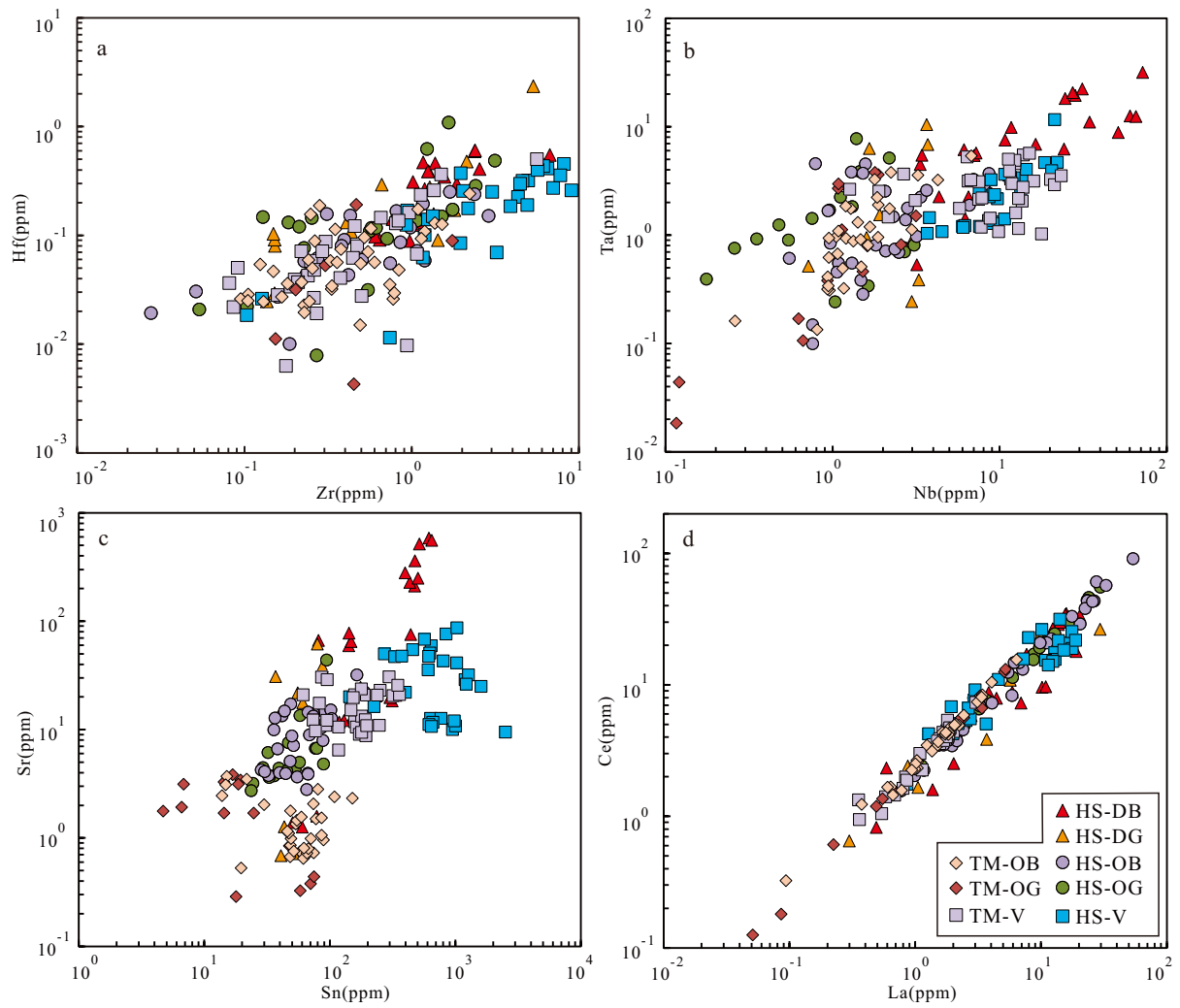


Figure 10

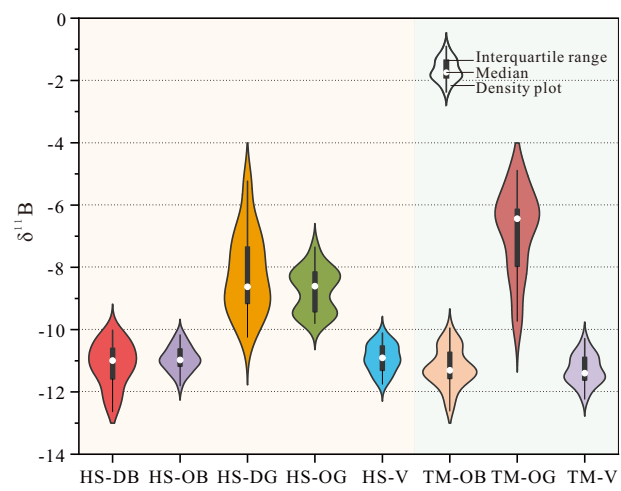


Figure 11

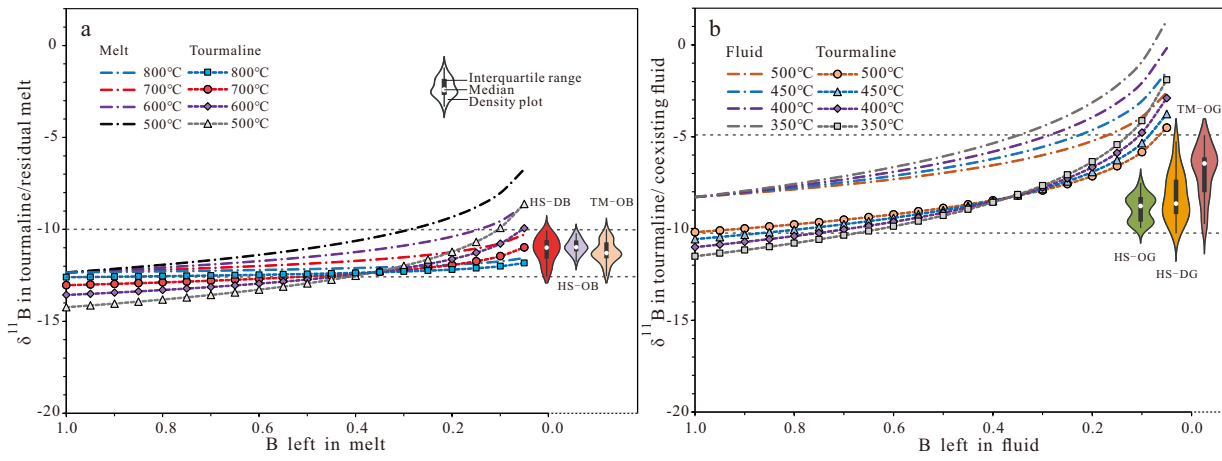


Figure 12

