1   **Revision 1：**

2   **Tourmaline and zircon trace the nature and timing of magmatic-hydrothermal**

3   **episodes in granite-related Sn mineralization: Insights from the Libata Sn ore**

4   **field**

5   *Victor Ikechukwu Vincent[1,2], Huan Li[2]*, Musa Bala Girei[2,3,4], Michael W. Förster[5], Vandi Dlama*

6   *Kamaunji[1]*

7   *1. Faculty of Earth Sciences, China University of Geosciences, 430074, Wuhan, P.R. China*

8   *2. Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment*

9   *Monitoring, Ministry of Education, School of Geosciences and Info-Physics, Central South*

10   *University, Changsha 410083, China*

11   *3. Faculty of Earth Resources, State Key Laboratory of Geological Processes and Mineral*

12   *Resources, China University of Geosciences, Wuhan 430074, China*

13   *4. Department of Geology, Bayero University Kano, Kano State, Nigeria*

14   *5. Department of Earth and Environmental Sciences, Macquarie University, NSW 2109, Sydney,*

15   *Australia*

16   *Corresponding author (H. Li): lihuan@csu.edu.cn

17   **ABSTRACT**

18   The Bin Yauri-Libata polymetallic ore district is a Sn and Au ore-bearing district in the Zuru schist

19   belt, Northwestern Nigeria. The Libata Sn ore field is characterized by a set of cassiterite-bearing

20   hydrothermal veins associated with Neoproterozoic Pan-African granites affected by deformation

21   and low-grade metamorphism. The hydrothermal alteration associated with cassiterite-bearing

22 quartz veins in the Libata deposit includes silicification, albitization, chloritization, and potassic

23 alteration. In this study, geochemical and geochronological data from tourmalines and zircons

24 from Sn bearing lodes, unmineralized and altered granites is applied to reveal the timing, fluid

25 composition, and source of ore-forming materials for tin mineralization in the Libata ore field.

26 Zircon trace element and Hf isotopes ($\varepsilon Hf(t)$= +4.37 to +10.85) reveal a mantle-derived source

27 with some crustal contribution for the melts forming the Libata Sn-bearing granites. LA-ICPMS

28 zircon U-Pb dating constrains the magmatic and hydrothermal ages to 650-646 Ma and 649-646

29 Ma for the Libata granites. Overlapping zircon $\varepsilon Hf(t)$ and $^{176}Hf/^{177}Hf$ but distinct $^{176}Lu/^{177}Hf$ and

30 $^{176}Yb/^{177}Hf$ ratios from magmatic and hydrothermally altered zircons reveal a magmatic source for

31 the hydrothermal fluids which triggered cassiterite deposition in the Libata ore field. Major

32 element chemistry constrain tourmalines from the Libata ore field as schorls that show high alkalis,

33 low Ca contents, and moderate □ values (where □ is x-site vacancy). High Li, Zn, and Sn

34 concentrations in tourmaline as well as Li/Sr and Ca-Fe-Mg ratios demonstrate that the tourmaline

35 formed from granite-sourced fluid likely derived from the host Libata granites. Measured $\delta^{11}B$

36 values from the Libata tourmaline range from −15.69‰ to −14.07‰. The $\delta^{11}B$ of the mineralizing

37 fluid is estimated to be −13.1 to −11.9‰ for the Libata tourmalines at 400-500 °C and overlaps

38 with averages from fractionated granites worldwide. Therefore, our data show that tourmaline and

39 zircon are useful tracers of magmatic-hydrothermal evolution in rare metal bearing granites

40 systems.

41 **Keywords:** Tourmaline chemistry, Sn mineralization, Hydrothermally-altered zircons, Pan-

42 African granites, B isotopes, Libata

INTRODUCTION

44   Tourmaline, an accessory mineral in various rock types, is common in most granitic rocks

45 and in various types of hydrothermal ore deposits (Dutrow and Henry, 2011; Marschall and Jiang,

46 2011). Due to its resistance to weathering and stability over a wide range of P-T-X conditions,

47 tourmaline typically preserves geological information about the magma or hydrothermal fluid from

48 which it precipitated (Marks et al., 2013). Since tourmaline incorporates a large variety of elements

49 into its crystal lattice, hydrothermal tourmaline is a robust tools for tracking the nature and

50   evolution of mineralizing fluids in magmatic-hydrothermal systems (Jiang et al., 2004; Zhao et al.,

51   2021a). Similarly, boron isotopes of tourmaline are a reliable tracer for fluid–rock interactions,

52   boron sources, and fluid evolution in ore deposit systems (Yang et al., 2015; Codeço et al., 2017;

53   Trumbull et al., 2019; Trumbull et al., 2020).

54   Zircon, a prevalent accessory phase in various rock types, is of increasing geological focus

55   due to its resilience to weathering and ability to record geochronological, isotopic, and

56   geochemical changes in host rocks (Hoskin, 2005; Valley et al., 2010). Trace element variations

57   in zircon track magma evolution, metamorphism, and can serve as good recorders of magmatic-

58   hydrothermal evolution in granitic systems (Claiborne et al., 2010; Li et al., 2014). The coupled

59   use of zircon trace element composition, zircon Lu-Hf isotopes, and high-precision zircon U-Pb

60   geochronology have been recognized as robust tools for tracking the timing and evolution of

61   magmatic-hydrothermal stages in granite hosted ore deposits (Li et al., 2018; Jiang et al., 2020;

62   Vincent et al., 2021).

63   Sn-W bearing lodes from Nigeria have long been a source of research and economic

64   interest due to their abundance and world-class deposit styles (Girei et al., 2019). However, most

65   of the present and historic mining has been from deposits associated with anorogenic ring

66   complexes in northcentral Nigeria (Kinnaird and Bowden, 1987; Melcher et al., 2015). Deposits

67   sourced from I- and S-type granitoids, pegmatites and other vein-type Sn deposits account for only

68   5% of the production from Nigeria (Olade, 2021). These Sn-bearing granitoids, rare metal

69   pegmatites, and vein-type deposits are primarily concentrated along a 500 km NE-SW trending

70   belt (Fig. 1b) from the southwestern part of Nigeria to the Jos Plateau (Okunlola and Ocan, 2009;

71   Adetunji et al., 2016). However, recent studies suggest a wider distribution range for the ore-

72   bearing calc-alkaline granitic suites and pegmatites in Northwestern and Southeastern Nigeria

73   (Garba, 2003; Ero and Ekwueme, 2009). The cassiterite-tourmaline assemblages in quartz from

74   the Libata deposit are similar to other granite-related Sn deposits found in Pan-African terrains of

75   West Africa (Kinnaird et al., 2016). However, the timing, nature, and source of ore forming

76   materials for these Sn-bearing granites remain poorly constrained. Therefore, a comprehensive

77   geologic, geochemical, and isotopic study of the Libata Sn deposit is crucial in constraining the

78   nature, genetic type, and genesis of Sn-bearing granites and vein systems in Northwestern Nigeria

79   and by extension the Pan-African suites of the Nigeria-Benin Shield.

80   In this study, cassiterite-bearing lodes associated with granites in northwestern Nigeria

81   were selected to evaluate the Sn mineralization history for these granites. This study presents

82   textural observations together with zircon U-Pb age, zircon Lu-Hf isotope, tourmaline major-trace

83   element and boron isotopic data from barren and mineralized granites to determine the origin and

84   timing of magmatic and hydrothermal processes that are associated with Sn mineralization in the

85   Libata ore field.

GEOLOGICAL BACKGROUND

87   The Nigeria basement complex forms part of the Trans-Saharan orogenic belt (Fig. 1a)

88   extending from the Hoggar Massifs into West Africa (Cahen et al., 1984). Tectonic welding of the

89   West African craton, Congo craton, and Pharusian belt between 700 to 590 Ma is interpreted to

90   have formed the Trans-Saharan orogenic belt (Bute et al., 2019). The basement complex rocks of

91   Northwestern Nigeria exhibit signatures of the Liberian, Eburnian, and Kibaran orogeny (Turner,

92   1983). Based on differing lithology and tectonic evolution, the Nigerian basement complex is

93   subdivided into a western and eastern terrain (Fig. 1b; Bute et al., 2019; Ferré et al., 1996). The

94   basement complex rocks of the eastern terrain have witnessed significantly higher grades of

95   metamorphism than those of the western terrain and are composed of gneisses, migmatites, and

96 metapelites (Ferré et al., 1996; Ferré et al., 1998). The country rocks of the western terrain are

97 overlain by an array of N-S trending metasediments (Turner, 1983). Based on variations in

98 metamorphic grade and lithology, several workers have proposed two distinct sets of

99 metasediments, namely the "Older Metasediments" and "Younger Metasediments" (McCurry,

100 1971). The grade of metamorphism is highest in the Older Metasediments where amphibolite

101 metamorphic grade rocks, which formed around 2.5 Ga, have been reported (Turner, 1983). The

102 Younger Metasediments are composed of fine to coarse-grained clastic deposits in largely

103 undeformed structures of late Pan-African age (Turner, 1983). Extensive post-collisional (Pan-

104 African) granitoid plutons, generated during the main to late-stages of the Pan-African orogeny

105 (750-550 Ma), are widespread in the Older Metasediments of the eastern and western basement

106 complex terrains (Ferré et al., 1996). The basement complex rocks are further intruded by later

107 staged Carboniferous to early Cretaceous granites (324-141 Ma) termed "Younger Granites" to

108 differentiate them from the more widely distributed "Older granites" of Pan-African (750-550 Ma)

109 ages (Bute et al., 2019; Vincent et al., 2022).

GEOLOGY OF THE LIBATA SN ORE FIELD

111 The Libata area is composed of low-lying gneisses intruded by Pan-African granite

112 porphyries and porphyritic biotite granites. The granitic rocks also intrude biotite-muscovite

113 schists of the Zuru schist belt (Fig. 2a). The biotite-muscovite schists of the Zuru-Libata area show

114 varying degrees of metamorphism with locally well-banded textures and gradation into hornfels

115 (Danbatta and Garba, 2007). Two prominent Sn-bearing ore bodies have been found in the Libata

116 ore field (Fig. 2b). Both Sn-bearing ore bodies in the Libata ore field are quartz veins with

117 alteration zones bounding wall rocks. Vein 1 is a granite-hosted ore-bearing lode, while, vein 2 is

118 a NE-SW trending metasedimentary-hosted ore-bearing lode (Fig. 2b). Wall rock samples from

119   the granite-hosted vein primarily consist of quartz, plagioclase, tourmaline, and minor biotite, with

120   accessory albite, chlorite, and zircon (Figs. 3b; 4a). The main ore mineral is cassiterite, which is

121   accompanied by minor sulfides such as pyrite. Gangue minerals include chlorite, tourmaline, and

122   quartz. Cassiterite occurs primarily in the tourmaline-quartz veins and the adjacent tourmaline-

123   bearing wall rocks. Based on the above observations, mineral paragenesis from ore-bearing veins

124   in the Libata ore field are summarized in Fig. 5. The Libata ore field is also comprised of several

125   alluvial Au workings (Fig. 2b). Elsewhere, tourmaline-bearing auriferous quartz veins are hosted

126   in the metasediments of the Zuru schist belt (Fig. 2a) along fault zones at Bin Yauri and (Garba,

127   2000).

SAMPLING AND PETROGRAPHY

129   Samples for zircon geochemistry and U-Pb dating analysis were collected from two

130   outcrop samples representing unmineralized Pan-African granitoids (sample CR-01 – granite

131   porphyry) and altered wall rocks near vein 1 (sample KB-01 – altered biotite granite) from the

132   Libata Sn ore field. Sample locations and representative photographs of analyzed samples are

133   shown in Fig. 2a-b and Fig. 3a-b, respectively.

134   Tourmaline-bearing samples were collected from both veins 1 and 2 (Fig. 3c, e). In hand

135   specimens, tourmaline grains from both the granite-hosted vein (vein 1) and metasedimentary-

136   hosted vein (vein 2) are distributed in a matrix of quartz and micas (e.g. biotite and muscovite)

137   (Fig. 3c, e, h). The abundance of mica in vein 2 is higher than in vein 1 where their occurrence is

138   limited to halos around tourmaline grains. Within both veins, tourmaline forms local grain

139   aggregates bound by quartz or overgrowths on disrupted fragments of wall rock enclosed in the

140   vein quartz (Fig. 3b, c, e). Vein 1 tourmalines form euhedral grains that are greenish-brown under

141   plane-polarized light, ranging from 0.2 to 1 cm in size, disseminated in clusters within the mineral

142   assemblages of the ore-bearing vein. The metasedimentary-hosted vein 2 tourmalines form

143   euhedral grains with coloration varying from orange-brown to dark green color and dark blue in

144   PPL photomicrographs and range from 0.05 to 1 cm in size (Fig. 3f-h). Tourmaline grains from

145   wall rock sections and quartz-vein hosted tourmaline from granite-hosted vein 1 and

146   metasedimentary-hosted vein 2 are primarily unzoned. However, some grains show pleochroic hue

147   and intensity suggesting zonation (Figs. 3d, 4g-h). In BSE images, tourmaline grains from vein 1

148   and vein 2 show light to dark zonation bands (Fig. 4a). Photomicrographs from vein 2 show higher

149   occurrence of zoned tourmaline grains in this vein compared to the granite-hosted vein 1 (Fig. 3g-

150   h). In both quartz-vein and wall rock alteration zones, Fe-Ti oxides, which locally contain Sn,

151   occur in highly fractured zones within tourmaline (Fig. 3g-h). The unzoned tourmalines are

152   coexisting or filled with mineral inclusions (e.g. pyrite and zircon) (Fig. 3f, h). Inclusions of these

153   minerals in unzoned tourmalines are relatively free from fractures suggesting coeval deposition of

154   sulfides, cassiterite-bearing phases, and tourmaline (Fig. 3h). Albite primarily occurs in wall rock

155   alteration zones from both vein 1 and 2 suggesting they precipitated during pre-ore metasomatism

156   (Figs. 3b, 3g, 4b). K-feldspar is partly replaced and co-exists with albite along wall rocks in the

157   Libata Sn deposit (Fig. 4a). K-feldspar also crystallizes in fractures between tourmaline in granite

158   wall rock sections from vein 1 in the Libata Sn ore field (Fig. 4b). SEM images show tourmaline-

159   quartz-chlorite assemblages along ore-bearing structures in the Libata Sn deposit (Fig. 4d-e) with

160   wall rock samples from vein 1 showing similar alteration assemblage to those in wall rock samples

161   from vein 2.

162   **RESULTS**

163   Chemical analyses were conducted on tourmalines from the Libata Sn ore field, including

164   tourmaline major and trace element and B isotope analysis. Additionally, zircon U-Pb dating and

165 Lu-Hf isotopes of zircon from sampled unaltered and altered granites were carried out. Analytical

166 details related to samples and methods can be found in Online Material[1] while the analytical results

167 are described below.

Zircon morphology and classification

169   Zircons separated from both the granite porphyry and the altered biotite granite show

170 variable morphologies and internal textures, as shown by Cathodoluminescence (CL), reflected-,

171 and transmitted light images (Fig. 6a-c). Zircon grains mostly vary from 50 to 300 μm in diameter,

172 with length/width ratios between 1:1 and 1:3 (Fig. 6a-b). Three groups of zircons are delineated in

173 the Libata granites based on morphological and geochemical features: Group 1 zircons are

174 euhedral to anhedral, showing bright grains with concentric oscillatory zoning (Fig. 6a-b). These

175 zircon grains exhibit characteristics of magmatic zircons (Table 1). In contrast, Group 2 zircons

176 are characterized by bright residual cores surrounded by dark, jagged rims, in addition to a few

177 dark prismatic crystals (Fig. 6a-b). Group 3 zircons exhibit heterogeneous zoning patterns showing

178 un-zoned areas, rimmed zones with jagged widths/brightness likely reflective of inherited/detrital

179 zircon grains (Table 1; Fig. 6c). The zircon groups show distinct geochemical signatures based on

180 zircon discrimination plots proposed by Hoskin (2005). Group 1 zircons largely plot in the field

181 of magmatic zircons (MZ), while, Group 2 largely plot in the field of hydrothermal zircons and

182 Group 3 zircon largely plot in the magmatic zircon fields (Fig. 7a-b). Notably, zircon grains that

183 plot outside the field of magmatic zircons fall within fields of both hydrothermal zircons and

184 neocrystallized zircons. We interpret the hydrothermal zircon field as representative of original

185 magmatic zircons that have experienced modification by later hydrothermal fluids to form

186 hydrothermally altered zircons and the neocrystallized zircon field to represent hydrothermal

187 zircon grains that precipitated directly from Zr-saturated hydrothermal fluids, respectively (Geisler

188 et al., 2003; Hoskin, 2005). The zircon grains of the Libata granites are defined by two

189   morphological types, namely a "100" type crystal face that predominantly occurs in the granite

190   porphyry (sample CR-01) and only sparingly occurs in the altered biotite granite (sample KB-01),

191   and a "110" type that predominantly occurs in the KB-01 sample with minor amounts in the CR-

192   01 sample (Fig. 6a-b). The internal textures of zircons vary greatly in back-scattered electron

193   (BSE), transmitted, and reflected light images. Group 2 zircons from the granite porphyry (CR-01)

194   and altered biotite granite (KB-01) sample exhibit variable CL characteristics with dark and bright

195   colors and spongy internal textures (Fig. 6c). The Group 2, mostly "110"-type zircon grains, are

196   classified as hydrothermally altered zircons (HAZ) based on a combined analysis of zircon CL

197   images, internal textures, and geochemical characteristics of analyzed zircons in the Libata granite

198   (Table 1). In summary, eight grains from granite porphyry and seven grains from altered biotite

199   granites were recognized as HAZ types (Table 1).

200   **Zircon U-Pb geochronology**

201   Results of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

202   U−Pb dating of zircon grains are listed in Table 2. Low concordance (<90%) zircon grains were

203   excluded from the above table and concordia plots.

204   Magmatic zircon from the granite porphyry (CR-01) sample yield concordant ages of 650

205    $\pm$ 4 Ma (1 s, mean square of weighted deviate, MSWD = 0.74, n=13, Fig. 8a), comparable to

206   weighted-mean $^{206}Pb/^{238}U$ age of 650 $\pm$ 5 Ma (1 s, MSWD = 2.80, n = 13, Fig. 8a). However, a

207   single grain yields an age of 421 $\pm$ 5 Ma, which we interpret as a magmatic grain that has

208   experienced metamictization and slight Pb-loss (Fig. 6c). In contrast, Group 1 magmatic zircons

209   from the altered biotite granites (sample KB-01) yield $^{206}Pb/^{238}U$ ages of 650 $\pm$ 4 (1 s, MSWD =

210   1.40, n = 12; Fig. 8c), comparable to weighted-mean $^{206}Pb/^{238}U$ age of 650 $\pm$ 5 Ma (1 s, MSWD =

211   1.83, n = 12, Fig. 8c). Two magmatic zircon grains from the altered biotite granite show $^{206}Pb/^{238}U$

212   ages of 867 ± 5 Ma and 963 ± 7 Ma, respectively. We interpret these ages as inherited zircon ages

213   from detrital zircons (Fig. 6c).

214   Group 2 HAZ grains from the granite porphyry yield concordant ages of 650 ± 6 Ma (1 s,

215   MSWD = 0.87, n = 7, Fig. 8b), comparable to weighted-mean $^{206}Pb/^{238}U$ age of 650 ± 8 Ma (1 s,

216   MSWD = 2.70, n = 7, Fig. 8b). Contrastingly, group 2 HAZ grains from the altered biotite granite

217   yield $^{206}Pb/^{238}U$ concordant ages of 650 ± 5 Ma (1 s, MSWD = 3.20, n = 5; Fig. 8d), comparable

218   to weighted-mean $^{206}Pb/^{238}U$ age of 650 ± 5 Ma (1 s, MSWD = 6.18, n = 5, Fig. 8d).

219   **Zircon trace element compositions**

220   Trace element compositions of zircon from the studied rocks are given in Online Material[2]

221   Table OM1. Trace element concentrations vary significantly between magmatic and

222   hydrothermally altered zircon in the unmineralized and altered granites. In the granite porphyry

223   sample (CR-01), Group 1 (magmatic) zircons are characterized by low P (avg = 340 ppm), Y (avg

224   = 754 ppm), Hf (avg 9834 ppm), U (147 ppm), and ΣREE (avg = 550 ppm). In contrast, Group

225   2 hydrothermally altered zircons show higher average P (1211 ppm), Y (850 ppm), Hf (9972 ppm),

226   U (175 ppm), and ΣREE (698 ppm) values. Compared to magmatic zircon, hydrothermal zircon

227   from sample CR-01 shows flat HREE with relatively weak positive Eu anomaly (Eu/Eu* = 0.05–

228   0.07) and positive Ce anomaly (Ce/Ce* = 1.2–46.9; Fig. 8e). Trace element and REE distribution

229   for both magmatic and hydrothermally altered zircons from the altered biotite granites also show

230   moderate variation trends. HAZ grains in the altered biotite granites are characterized by high

231   values of Y (467–1351 ppm, average = 776 ppm), Hf (8250–10086 ppm, average = 9325 ppm), P

232   (443–3632 ppm, average = 1299 ppm), and ΣREE (428–944 ppm, average = 650 ppm).

233   Corresponding values from MZ in the altered biotite granites are markedly lower (P = 101–426

234   ppm, average = 237 ppm; Y = 283–2274 ppm, average = 737 ppm; Hf = 7360–10045 ppm, average

235   = 8844 ppm; ΣREE = 235–1517 ppm, average = 566 ppm). However, they exhibit negative Eu

236   anomaly (Eu/Eu* = 0.06–0.54) with weakly positive Ce anomaly (Ce/Ce* = 1.3–2.9; Fig. 8f).

237   **Zircon Lu-Hf isotopes**

238   Twenty-four representative zircon spots were selected for Hf isotopic analysis (Table 3).

239   MZ from the unmineralized granite porphyry (sample CR-01) show a narrow range of εHf(t) (+4.4

240   to +5.6), $^{176}Lu/^{177}Hf$ (0.000610–0.000756), $^{176}Yb/^{177}Hf$ (0.025232–0.032046), and variable

241    $^{176}Hf/^{177}Hf$ (0.282494–0.282534) values. On the other hand, HAZ grains from the Libata granite

242   porphyry show overlapping εHf(t) (+4.5 to +6.2) and $^{176}Hf/^{177}Hf$ (0.282502–0.282545) but higher

243    $^{176}Lu/^{177}Hf$ (0.000573–0.001012) and $^{176}Yb/^{177}Hf$ (0.023931–0.044225) values. Calculated two-

244   stage Hf model ages for the granite porphyry show Mesoproterozoic crustal Model ages (T_{DM}^{C} =

245   1311 to 1200 Ma) (Table 3). MZ in the altered biotite granite also show variable Lu-Hf-Yb isotopic

246   ratios, namely $^{176}Hf/^{177}Hf$ (0.282521–0.282591), $^{176}Lu/^{177}Hf$ (0.000554–0.000927), $^{176}Yb/^{177}Hf$

247   (0.019038–0.039216), and εHf (t) values of +5.2 to +7.9. Comparatively, HAZ grains from the

248   altered biotite granite show higher εHf (t) (+6.3 to +10.9), $^{176}Lu/^{177}Hf$ (0.000657–0.001227),

249    $^{176}Yb/^{177}Hf$ (0.028083–0.054186) but variable $^{176}Hf/^{177}Hf$ (0.282544–0.282676). Calculated two-

250   stage Hf model ages for the altered biotite granite show Mesoproterozoic to Neoproterozoic crustal

251   model ages (T_{DM}^{C} = 1254 to 900 Ma) (Table 3). Two crystals (one metamict and one inherited

252   magmatic) from our samples are characterized by variable $^{176}Hf/^{177}Hf$ ratios (0.281972–0.282529)

253   and yielding outliers of εHf (t) (−7.5 to +0.5) and T_{DM}^{C} (1378–2293 Ma). Due to the standard

254   ƒLu/Hf values (<−0.9), obtained from analyzed zircon grains in this study, calculated Hf T_{DM}^{C}

255   modal ages are considered reliable estimates of crustal residence times (Wang et al., 2016).

256   **Tourmaline EPMA data**

257   Tourmalines from the veins 1 and 2 in the Libata Sn ore field exhibit similar major

258   elemental compositions (Online Material[3] Table OM1). They have variable F (0.03–0.49 wt%),

259   CaO (0.10–1.28 wt%) and MgO (1.85–4.62 wt%), high SiO_2 (34.36–36.48 wt%), Al_2O_3 (29.93–

260   33.40 wt%), FeO (11.03–13.95 wt%), and TiO_2 (0.36–1.01 wt%), as well as low MnO (0.15–0.81

261   wt%). Based on the X-site occupancy and according to the classification of Henry et al. (2011),

262   the tourmalines from both veins belong to the alkali group (Fig. 9a). The tourmalines display a

263   large variation in Mg/(Mg + Fe) ratios from 0.2 to 0.4, with all the tourmaline samples showing

264   schorl compositions (Fig. 9b). The tourmalines also shows high total Al (6.0-6.5 apfu), moderate

265   excess Al in octahedral Y-sites (up to 0.5 apfu), moderate F contents (up to 0.3 apfu) and variable

266   X-site vacancy content (0.2 to 0.4 apfu) whereby the Na cation is dominant in the X-site (0.6–0.7;

267   Online Material[3] Table OM1). The tourmalines from vein 1 and 2 plot in the field of Li-poor

268   granitoids, pegmatites, and aplites (Fig. 9b) based on discrimination plots of Al-Fe-Mg (Henry and

269   Guidotti, 1985).

In situ tourmaline trace elements

271   Trace element compositions of tourmaline from the Libata Sn-W deposit are given in

272   Online Material[3] Table OM2. Tourmaline is overall characterized by low concentrations (< 0.1–

273   10 ppm) of Co, Ni, Cu, Rb, Y, REE, Zr, Nb, Mo, Cs, Ba, Ta, W, Pb, Bi, Th, and U, moderate

274   concentrations (10 s to 100 ppm) of Be, Sc, and Sr, and high concentrations (100s ppm to >1000

275   ppm) of Li, Sn, Ga, V, and Zn (Online Material[3] Table OM2). Multi-element normalized to average

276   continental crust values from Rudnick and Gao (2003) (Fig. 9c) show only a few elements reach

277   concentration levels at or above those of the average crust (Sn, Zn, Li, Ta, V, Co, Ni, and Sc) (Fig.

278   9c). Chondrite-normalized REE plots (Fig. 9d) overall also show low concentrations and a high

279   variability of REE distribution from the Libata tourmaline. Overall, the vein 1 tourmalines show

280   higher total REE values (avg = 11.4 ppm, standard deviation (Stdev): 5) than those from vein 2

281   (avg = 9.8 ppm, Stdev = 4) (Online Material[3] Table OM2). The tourmalines from veins 1 and 2

282   show a negative sloping pattern from light through middle REE concentrations to a slightly

283   positive sloping pattern towards the heavy REE segment, and a weakly positive Eu anomaly on

284   chondrite-normalized REE plots (Fig. 9d).

285   To identify trace element correlations in our dataset, we applied principal component

286   analysis (PCA), a multivariate statistical technique that provides dimensionality-reduction of

287   correlated variables into a reduced set of orthogonal linear combinations. This technique is

288   particularly useful for analyzing large geochemical datasets including LA-ICP-MS trace element

289   data, maximizing variance, and minimizing information loss (Winderbaum et al., 2012; Harlaux

290   et al., 2019; Codeço et al., 2021). PCA was applied on log-transformed LA-ICP-MS trace element

291   data from the Libata tourmaline (n = 49 spots). 15 variables were selected for the PCA including

292   the main trace elements (Li, Sc, V, Cr, Co, Ni, Zn, Ga, Ge, Sr, Nb, In, Sn, Pb, and Ta). Elements

293   with very low concentrations (< 1 ppm) or below the limits of detection were excluded. Results of

294   the two-dimensional projection of the two first principal components (PC1 vs. PC2), showing the

295   statistical correlations between the investigated variables on a correlation circle is given in Fig. 9e-

296   f. For the Libata tourmalines, four main groups of element correlation clusters are discriminated

297   by the PCA. Group 1 comprised of Co, Ga, Ni, Cr, Sc, and In characterizes the higher

298   concentrations in vein 1 tourmalines (Fig. 9f; Online Material[3] Table OM2). Group 2 composed

299   of Li and Zn shows the variability of vein 2 tourmalines. Overlapping concentrations in Group 3

300   and 4 (Nb-Ta and Sc-V) precludes the discrimination of distinct clusters. Some elements (i.e. Sn,

301   Ge, In, and Pb) plot individually, without correlations between each other. Trace elements show

302   overlapping concentrations between the core and rim from vein 1 and 2 and therefore preclude the

303   discrimination of distinct clusters (Online Material[3] Table OM2).

Boron isotopes

304

305   The LA–MC–ICP-MS boron isotopic data of tourmalines from our study are available in

306   Online Material[3] Table OM3 and illustrated in Fig. 10. The vein 1-type tourmalines show a narrow

307   range of $\delta^{11}B$ values between $-15.7 \pm 0.4‰$ and $-14.4 \pm 0.5‰$, with a weighted mean value of

308    $-15.0 \pm 0.2‰$ (n = 27, MSWD = 0.48) (Fig. 10a). Cores from zoned tourmaline grains from vein

309   1 show higher $\delta^{11}B$ values compared to the rims (Online Material[3] Table OM3). The vein 2

310   tourmalines show markedly higher $\delta^{11}B$ values than the vein 1 type, ranging from $-15.1 \pm 0.4‰$

311   and $-14.1 \pm 0.3‰$, with a weighted mean value of $-14.6 \pm 0.1‰$ (n = 42, MSWD = 0.49) (Fig.

312   10a). Within sample variations between core and rim in zoned tourmaline from vein 2 are typically

313   <1‰ (Fig. 4a) with cores showing higher average in $\delta^{11}B$ values compared to rims (Online

314   Material[3] Table OM3).

DISCUSSION

315

Geochemical features of zircons from the Libata Sn-W ore field

316

317   To track the degree of alteration between Group 1 and Group 2 zircons in the Libata ore

318   field, we applied the discrimination indices (LREE-I = Dy/Nd + Dy/Sm) proposed by Bell et al.

319   (2019). Magmatic zircons from the granite porphyry and altered biotite granite display higher

320   LREE-I values (sample CR-01: 4.3–95.8, average = 56.8, n = 15; sample KB-01: 23.9–81.5,

321   average = 50.1, n = 14) than corresponding HAZs (CR01: 3.3–82.6, average = 27.1, n = 8; sample

322   KB-01: 3.7–30.4, average = 21.3, n = 7) from the studied samples (Fig. 7c-d). The low LREE-I

323   values (Online Material[2] Table OM1) in the HAZ grains along with the textural alteration is

324   indicative of post-magmatic modification from fluid-zircon interactions (Bell et al., 2019).

325   Generally, trace and minor (Hf, U, Y Th, LREE, etc.) element concentrations in HAZs are

326   markedly higher than values in magmatic zircons (Hoskin, 2005; Li et al., 2014). Due to the higher

327   mobility of LREEs relative to HREEs in hydrothermal phases, LREEs are preferentially

328   incorporated into hydrothermally altered, metamict and hydrothermal zircon grains (Sheard et al.,

329   2012). In the Libata granites, hydrothermally altered zircons are enriched in LREE and ΣREE

330   when compared to magmatic zircons (Figs. 7e-f; 8e-f).

331   Titanium-in-zircon thermometry (Ferry and Watson, 2007) has been recognized as a

332   reliable indicator for zircon crystallization and host magma temperatures (Schiller and Finger,

333   2019; Vincent et al., 2021). However, the reliability of the Ti-in-zircon temperatures is dependent

334   on the preservation of Ti concentrations in zircon, which may become perturbed during highly

335   mobile phases that form HAZ (Fu et al., 2008; Bloch et al., 2022). For the Libata granites, the

336   application of Ti-in-zircon geothermometry to delineate crystallization temperatures of the

337   hydrothermal zircon grains is not feasible due to the markedly high Ti concentrations in

338   neocrystallized and HAZ (Online Material[2] Table OM1). However, the crystallization

339   temperatures can be derived from zircon morphology due to the large dependence of prism shapes

340   on crystallization temperatures (Pupin, 1980; Dill et al., 2012). High crystallization temperatures

341   (>800 °C) favor the growth of "100" type prims whereas moderate to low temperatures (<700 °C)

342   favor the development of "110" type prisms (Hayashi and Shinno, 1990). For the Libata granites,

343   most magmatic zircons show "100" prisms, while hydrothermal zircons generally exhibit "110"

344   prisms (Fig. 6a-b). Zircon morphology combined with Ti-in-zircon geothermometry from

345   magmatic zircons in the granite porphyry (avg. 761 ± 11 °C) and altered biotite granites (avg. 717

346   ± 12 °C) samples confirm high initial crystallization temperatures (>700 °C) for the Libata granites.

347   The dominance of "110" prims in hydrothermal zircons from the Libata ore field likely reflects

348   zircon metamictization in these grains. The presence of these "110" prisms also point to a shift

349   towards late-stage magmatic-hydrothermal conditions since metamict zircons are typically

350 crystallized from highly evolved late residual melt (Kozlik et al., 2016). Their late-stage origin and

351 typical "110" form suggests relatively low closure temperatures (<650 °C) for the hydrothermal

352 zircons (Fig. 6a-b) in the Libata granites (Jiang et al., 2019a).

Timing of magmatic-hydrothermal activities in the Libata ore field

354 The zircon U-Pb ages from our study allow for precise timing of magmatic activity in the

355 Libata Sn deposit and its implication for the magmatic-hydrothermal episodes in the Libata ore

356 field. Zircon U-Pb ages for Libata granites cluster around ~650 Ma (Table 1). Group 1 magmatic

357 zircons from the Libata granite porphyry and altered biotite granite yield U–Pb concordant ages of

358 650 ± 4 (1 s, MSWD = 0.74, n = 13), and 650 ± 4 Ma (1 s, MSWD = 1.40, n = 12), respectively

359 (Fig. 8a, c). The zircon U-Pb ages from the Libata granites (650 Ma) confirm their emplacement

360 during the peak of the Pan-African orogenic episode in western Nigerian terrain (Bute et al., 2019;

361 Ferré et al., 1996). Our zircon U-Pb ages are markedly similar to ages (642 ± 6 Ma) obtained from

362 quartz potassic syenites from southwestern Nigeria (Adetunji et al., 2016). They also overlap U-

363 Pb ages from other Pan-African suites (580-751 Ma) from the eastern and western terrain of the

364 Nigerian basement (Ferré et al., 1996; Ferré et al., 1998).

365 The utility of LA-ICP-MS U-Pb dating of hydrothermal zircons to constrain timing of

366 hydrothermal episodes have been demonstrated for Pb-Zn-Cu (Vincent et al., 2021), Au (Bao et

367 al., 2014), and Sn−W deposits (Jiang et al., 2019a; Jiang et al., 2019b). In the Libata ore field,

368 Group 2 HAZs in sample CR-01 and Sample KB-01 yield ages of 650 ± 6 Ma (1 s, MSWD = 0.87,

369 n = 7) and 650 ± 5 Ma (1 s, MSWD = 3.20, n = 5), respectively (Fig. 8b, d). In this study, the

370 concordant ages from HAZs in both the Libata granite porphyries and altered biotite granite (650

371 Ma) suggests they were modified immediately after the crystallization of the host granite intrusions.

372 **Source of melts and ore-forming materials for the Libata Sn deposit**

373   Trace element and Hf isotope variation are suitable tracers of distinct magma sources and

374 melt evolutionary history in magmatic rocks (Kemp et al., 2005). Consequently, we apply

375 discrimination ratios based on magmatic zircon trace element chemistry to constrain source(s) and

376 evolution of the Libata granitoids. Zircon U/Yb vs. Yb (Fig. 11a) show that samples from the

377 Libata ore field mostly fall in the continental zircon field and suggest a continental origin for the

378 Libata granitoids (Grimes et al., 2007). Furthermore, zircon U/Yb vs. Nb/Yb discrimination plots

379 (Fig. 11b) imply a continental arc-related tectonic regime for the Libata intrusions and suggests

380 granite emplacement in a continental margin. Applying our zircon Lu-Hf isotope data, the Libata

381 granites show high positive εHf (t) (+4.4 to +10.6, average, = +6.4; Table 3) values. These values

382 are higher than εHf (t) signatures from inherited zircons in the Libata granites (εHf (t) = -7.6) and

383 other granitoids in the Benino-Nigerian shield within the range of 656–610 Ma yielding negative

384 εHf(t) (−27.1 to −6.4) (Ganade et al., 2016). Our εHf(t) values are below depleted mantle values

385 (Fig. 12a; Table 3) showing positive εHf(t) values which rule out anataxis of local crustal rocks

386 and reflective of source rocks derived from a mantle source. Calculated Hf model ages for the

387 Libata granites (0.8–1.3 Ga) are lower than the values from other 656–610 Ma granites from the

388 Benino-Nigerian shield (1.5–3.4 Ga) suggesting, limited contamination of the primary mantle

389 melts with crustal material.

390   Lu−Hf isotopic compositions of hydrothermal zircons are distinct from signatures in

391 magmatic zircons and provide a viable tool for tracking fluid sources and evolutionary processes

392 in magmatic-hydrothermal systems (Li et al., 2018). The $^{176}Hf/^{177}Hf$ ratios are similar in the

393 magmatic and hydrothermally altered zircons from the Libata granitoids (Table 3), indicating the

394 preservation of the Hf isotopic system in zircon (Lenting et al., 2010). However, $^{176}Lu/^{177}Hf$ (up

395 to 0.0012) and $^{176}Yb/^{177}Hf$ (up to 0.055) ratios are markedly higher in HAZ compared to MZ from

396   the Libata granites (Fig. 12c-d) explained by higher mobility of Lu and Yb during hydrothermal

397   phases associated with zircon alteration (Lenting et al., 2010). The similar and broadly overlapping

398   εHf (t) values for magmatic and hydrothermally altered zircon grains from the Libata orefield

399   (Table 3) suggest that the mineralizing fluids were likely sourced from the granitic magmas.

400   The $\delta^{11}B$ values in tourmaline from the ore bearing veins in the Libata Sn ore field range

401   from -15.7 ‰ to -14.7 ‰ (Fig. 10a-b). Vein 1 tourmalines have $\delta^{11}B$ values of -15.7 to -14.4 ‰

402   (average = -15.0 ‰), whilst vein 2 tourmalines show $\delta^{11}B$ values of -15.1 to -14.1 ‰ (average =

403   -14.6 ‰). Due to limited fluid inclusion data from the Libata Sn deposit, we infer temperature

404   conditions of the primary hydrothermal fluids to derive fluid-tourmaline equilibrium temperatures.

405   Assuming crystallization temperatures of 400 to 500 °C, equilibrium fluid-tourmaline fractionation

406   at 500 °C and 400 °C are +1.9‰ and +2.7‰, respectively (Meyer et al., 2008). This suggests that

407   the $\delta^{11}B$ values of the fluids in isotopic equilibrium were -13.1 to $-12.3‰$ for the vein 1

408   tourmalines and -12.7 to $-11.9‰$ for the vein 2 tourmalines. The emplacement of vein 1 firmly

409   within the Libata granites suggests derivation of boron predominantly from magmatic fluids

410   exsolved from granitic melts. To test for a granitic fluid source, we estimate the isotopic

411   compositions of a granitic melt that produces a magmatic fluid with a $\delta^{11}B$ of -12.3 to $-13.1‰$

412   for the granite-hosted vein 1. At temperatures of 650 °C estimated for the hydrous F-rich granitic

413   melt and assuming 50:50 proportion of trigonal-tetrahedral coordination of boron in the melt

414   (Trumbull et al., 2013), a B-isotope fractionation factors of 5‰ between granitic melt and fluid is

415   calculated from molecular dynamics (Kowalski et al., 2013). This would imply $\delta^{11}B$ values of

416   -17.3 to $-18.1‰$ for the hypothetical granitic source, which falls in the range of values from

417   granites (Trumbull et al., 2020). For the metasedimentary-hosted vein 2, the markedly similar trace

418   element (Fig. 9a-d) and close overlap in boron isotopic values (Fig. 10b) with tourmalines from

419   the granite-hosted vein 1 suggests ore materials/fluids in vein 2 were sourced from either the same

420   source as the granite-hosted vein 1 or from shallow magmatic bodies. The difference between $\delta^{11}B$

421   compositions from veins 1 and 2 (Fig. 10a) may reflect differential temperature change between

422   both veins at constant fluid composition, differing $\delta^{11}B$ compositions for zoned rims and cores

423   from vein 2 or depletion in $\delta^{11}B$ during vein fluid vs. wall rock interaction in vein 2.

424   To investigate fluid sources for Sn mineralization in the Libata ore field, we used major

425   and trace element ratios in tourmaline to track source compositions for the hydrothermal fluids

426   that precipitated the Libata tourmalines. The Li/Sr ratio provides a good separator for delineating

427   tourmaline from magmatic vs metamorphic fluid origin (Harlaux et al., 2020). Compared to other

428   tourmalines hosted in granite and metamorphic rocks (e.g. amphibolites and granite gneiss),

429   tourmalines from the Libata ore field fall in the compositional field of magmatic tourmaline based

430   on Li/Sr discrimination plots (Fig. 13a-b) and are in agreement with tourmaline major element

431   compositions that fall into the field of Li-poor granitoids in the Ca-Fe-Mg diagram (Fig. 8b). The

432   composition of the Fe-rich schorls from the Libata Sn ore field are in agreement with tourmaline

433   compositions from most granitic rocks and magmatic-hydrothermal environments (Pirajno and

434   Smithies, 1992). Our results are chemically distinct from the schorl-dravite tourmalines from the

435   Bin-Yauri gold deposit whose origin has been proposed to be from metasedimentary sources

436   (Garba, 1996). This would suggest that the tourmaline from the Libata Sn veins largely formed

437   from magmatic fluids. Accordingly, our data suggests derivation of boron in the Libata ore field

438   was dominantly from magmatic fluids although we do not rule out some contribution from the

439   metasedimentary rocks in the area.

440   **Magmatic-hydrothermal evolution in the Libata Sn mineralizations**

441   The utility of HAZs as tracers of the nature and chemical compositions of hydrothermal

442   fluids associated with ore deposits have been widely recognized (Kozlik et al., 2016; Jiang et al.,

443   2019b; Vincent et al., 2021). Experimental studies and natural observations have highlighted the

444   increased mobility of incompatible elements such as Hf, Th, U, Nb, Ta, Y, P, Sn and Pb in the

445   presence of volatiles (e.g. B, F, Cl, and H_2O) (Bau, 1996; Jiang et al., 2020). These highly mobile

446   fluid-vapor phases are important in alkali-rich granitic systems (Girei et al., 2019; Girei et al., 2020;

447   Vincent et al., 2021) as well as in B-rich hydrothermal systems (Lehmann, 2020). The high F

448   concentrations in tourmaline (up to 0.5 wt.%, determined with EPMA) suggest the late-stage

449   volatile-rich fluids exsolved from the Libata granites were able to carry incompatible elements and

450   exchange them with Si and Zr from magmatic and metamict zircons through diffusion-controlled

451   alteration processes that formed HAZs in the Libata granites. Therefore, the hydrothermal fluids

452   that interacted with these zircons were likely highly enriched in U, Th, F, Y, REE, Nb, Ta, Hf, Fe,

453   and Ca and moderately enriched in P, Sn, Sc, Pb, and Ti. The Libata HAZs show coupled

454   correlation trends between U + Nb + Ta and Y + ∑REE (Fig. 14a) suggesting that many trace

455   elements have been incorporated into these zircons. Th/U ratios of HAZ in the Libata granites vary

456   between 0.4 and 0.7 (average = 0.5) and are markedly lower than those of MZ (Fig. 14b). The shift

457   in Th/U values from magmatic to HAZ is typical for ore deposits and a crucial marker for

458   delineating hydrothermal zircons (Li et al., 2014). To further track magmatic to hydrothermal

459   trends in the zircons from the Libata granites, we assessed geochemical ratios (e.g. Y/Ho and

460   Yb/Gd) that show stable behaviors in primary or anhydrous melts but vary in evolved melts that

461   are enriched in volatiles and halogens. Other studies have highlighted the stability of Y/Ho in

462   primary melts where they retain ratios close to chondritic values (Bau, 1996). However, these

463   ratios show large variations in evolved granitic systems due to increased mobility and behavior of

464   Y, Zr, Hf, and REEs during volatile-driven mobility (Bau, 1996). HAZ from our studied samples

465   mostly show elevated Y/Ho values (>28; Fig. 14c) due to complexation with halogen-rich phases

466   with a negative correlation between Y content and Y/Ho ratio present for the magmatic zircon

467   grains (Jiang et al., 2019a). Differentiation trends for the Libata granites are also traced by Yb/Gd

468   against Eu/Eu* values (Fig. 14d). Progressive oxidization conditions along with increased

469   fractionation during magmatic evolution suggests that the altered biotite granites are more evolved

470   than the granite porphyries of the Libata ore field (Lu et al., 2019). Furthermore, this trend also

471   differentiates barren from fertile granite suites with the altered biotite granites largely plotting

472   above the field synonymous with mineralized granites (Fig. 14d).

473   Geochemical (major and trace element) composition of tourmaline have been widely

474   recognized as reliable monitor of formation environment and conditions (Dutrow and Henry, 2011).

475   Moreover, these geochemical signatures have been used extensively to trace evolution in

476   magmatic-hydrothermal systems (Jiang et al., 2004; Yang et al., 2015; Codeço et al., 2020;

477   Harlaux et al., 2020). Compositions of tourmalines from Libata, plotting mostly in the schorl field

478   (Fig. 9b), with low Na contents (average 0.6 apfu) and high X-site vacancies (average 0.3 apfu),

479   suggesting precipitation from a low-salinity fluid (von Goerne et al., 2001; von Goerne et al., 2011).

480   Assuming a temperature of 500 °C, a salinity of ca. 3 wt% NaCl eq is estimated for the fluid in

481   equilibrium with the assemblage tourmaline + quartz + chlorite (von Goerne et al., 2001). REE

482   patterns of tourmaline generally reflect both the REE composition of the host rock or source as

483   well as the effects of fluid-rock interactions (Yang et al., 2015; Duchoslav et al., 2017; Hong et al.,

484   2017). Tourmalines from the Libata ore field show higher concentrations of LREEs relative to

485   HREEs (Fig. 9d) similar to trends seen in tourmalines from other magmatic-hydrothermal ore

486   systems (Marks et al., 2013; Yang et al., 2015). This enrichment trend matches REE patterns in

487   hydrothermal zircons in the Libata granites (Fig. 8e-f) suggesting that the volatile-rich late-stage

488   fluids responsible for the precipitation of the hydrothermal zircon and tourmaline in the Libata

489   orefield were enriched in LREEs relative to HREEs. Tourmaline from both ore-bearing veins in

490   the Libata ore field have relatively high Sn (>100 ppm avg) contents (Fig. 13c-d). A coupled

491   increase in Fe and Sn contents have been reported from tourmalines associated with cassiterite

492   mineralization (Harlaux et al., 2020). In both veins 1 and 2, the high contents of Fe (13 wt % avg)

493   and Sn (100 ppm avg.) are notable (Online Material[3] Table OM1 and Online Material[3] Table OM2).

494   These high concentrations suggest that hydrothermal fluids precipitating tourmaline in the Libata

495   ore field were rich in Fe and Sn primarily transported as chloride complexes under moderate to

496   high temperature phases (Taylor and Wall, 1993; Schmidt, 2018). In granitic rocks, mica group

497   minerals (e.g., biotite) are important hosts of Sn with concentrations ranging from 10s to 100s

498   parts per million (López-Moro et al., 2017). Mineralizing fluids in Sn ore systems may become

499   enriched in tin through the breakdown of biotite during chloritization processes (Harlaux et al.,

500   2020). Elevated vanadium concentrations and the high V/Sc ratios suggest that the hydrothermal

501   fluid precipitating the tourmalines was rich in vanadium. This enrichment is likely linked to metal

502   release during biotite chloritization, as biotite is a major host of vanadium (Viswanathan et al.,

503   2012). Therefore, biotite alteration seen in the Libata granites (Fig. 4c-d) due to chloritization

504   likely triggered the coupled release of tin and vanadium into the mineralizing fluids, which then

505   substituted into the crystal lattice of tourmaline during precipitation of hydrothermal tourmalines

506   in the Libata orefield. Experimental and thermodynamic data support the transport of high

507   concentrations of tin (100s to 1000s) likely as Sn^{4+}–Cl complexes in hydrothermal fluids (Heinrich,

508   1990; Schmidt, 2018).

509   Due to their robust ability to retain geochemical signatures from several petrogenetic

510   processes, tourmaline has been found to be a potential pathfinder mineral for tin deposits (Fogliata

511   et al., 2012). Elevated trace element concentrations (typically >10s to 100s ppm) of Li, V, Ga, Zn,

512   and Sn in tourmaline grains from the Libata ore field are typical for tourmaline from granite-related

513   tin deposits (Duchoslav et al., 2017; Codeço et al., 2021). Our data suggests that the high Sn, Zn,

514   and Li concentration in tourmaline from the Libata ore field can be regarded as 'indicators' of

515   cassiterite mineralization. Accordingly, tracer signatures from tourmaline + chlorite + quartz

516   alteration assemblages associated with cassiterite-wolframite-niobium mineralization in the Pan-

517   African granites may serve as valuable indicators for other granite-associated vein-type deposits

518   in adjacent areas.

IMPLICATIONS FOR ORE GENESIS

519

520   (1) Our study constrains overlapping magmatic (~650 Ma) and magmatic-hydrothermal

521   (~650 Ma) events from the Libata granite porphyry and altered biotite granite porphyry. Our ages

522   are consistent with magmatic-mineralogenic events at the peak of the Pan African orogeny and

523   expands the known temporal range of granite-related Sn mineralization in the basement complex

524   of Nigeria.

525   (2) The abundance of metamict and hydrothermally-altered zircons hosted in the granites

526   adjoining Libata vein 1 and their components suggests that the hydrothermal fluids derived from

527   the granites likely contributed the ore forming fluids associated with Sn mineralization. The fluids

528   were enriched in volatile phases (F, Cl, and H_2O) as well as numerous trace elements such as U,

529   Y, Nb, Ta, Hf, P, and Ti.

530   (3) Trace element chemistry and B isotopes from both the granite- and metasedimentary-

531   hosted Sn-Tur veins suggests a common source for ore metals, boron and hydrothermal fluids

532   forming both veins. Our data point to magmatic-hydrothermal fluids derived from the Libata

533   granites as the source for ore materials forming the Libata deposit.

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810   **Figure Captions**

811

812   **Fig. 1.** Geological sketch map showing (a) generalized map of Africa showing the distribution of

813   rare-metal granites and rare metal-bearing pegmatites. (b) Nigeria showing distribution of Pan-

814   African granites, schist belts, and established NE-SW trending Sn-W bearing pegmatites. The

815   Raghane shear zone is a potential suture zone marking the boundary between Eastern Nigeria

816   Terrane (ENT) and Western Nigeria Terrane (WNT) adopted from Ferré et al. (1998).

817

818   **Fig. 2.** Geological map of (a) the Bin Yauri-Libata area showing the distribution of Au and Sn

819   mineralizations, and (b) the Libata Sn ore field showing the distribution of ore-bearing lodes.

820

821   **Fig. 3.** Photographs showing hand specimens and photomicrographs (PPL) of (a) deformed granite

822   porphyry; (b) altered biotite granite wall rock sample from vein 1; (c) hand specimen

823   photomicrograph of quartz vein-hosted hydrothermal tourmaline from Libata vein 1; (d) wall rock

824   from the granite-hosted vein 1 showing the occurrence of unzoned and zoned tourmaline; (e) quartz

825   vein-hosted hydrothermal tourmaline from Libata vein 2 and (f) tourmaline and zircon from wall

826   rock sections at the Libata vein 2; (g) section from quartz vein at Libata vein 2 and (h) wall rock

827   alteration zone from Libata vein 2. Abbreviation: Ab, albite; Fe-Ti oxides, iron-titanite oxides; Kfs,

828   K-feldspar; Ms, muscovite; Plg, plagioclase; Py, pyrite; Qtz, quartz; Tur, tourmaline; Zr, zircon.

829   **Fig. 4.** (a) Selected BSE-images of analyzed sections from veins 1 and 2 in the Libata ore field.

830   SEM micrographs of the bulk ore showing distinct morphologies of (b) albite grains occurring

831   with K-feldspar and quartz from wall rocks near vein 1; (c) tourmaline from vein 2 with later-stage

832   K-feldspar; (d) tourmaline-chlorite occurrence seen in vein 1; (e) chlorite-tourmaline-quartz

833   assemblage from Libata vein 1. Abbreviation: Ab, albite; Chl, chlorite; Kfs, K-feldspar; Tur,

834   tourmaline; Qtz, quartz.

835

836   **Fig. 5.** Simplified paragenesis for the Libata Sn mineralizations. The thickness of the horizontal

837   lines indicates the abundance of the mineral species.

838

839   **Fig. 6.** Selected CL-images of analyzed zircon grains from the (a) granite porphyry (CR-01) and

840   (b) altered biotite granite (KB-01). (c) Representative transmitted and reflected light images of

841   zircons, showing the distribution of fluid/mineral inclusions in the granite porphyry and altered

842   biotite granite samples.

843

Fig. 7. Magmatic-hydrothermal zircon discrimination plots of (a) SmN/LaN vs. Ce/Ce* diagram;

(b) La vs. SmN/LaN diagram. (c) Ti vs LREE-I showing LREE+Ti contamination as well as

potential contamination by Ti without substantial LREE. (d) Hf vs LREE-I showing both a positive

correlation expected for magmatic zircon grains and alteration trend for the hydrothermally altered

zircon grains. Fig. 7(c-d) adapted from Bell et al., 2019. Magmatic-hydrothermal zircon plots for

(e) ΣREE vs. ΣLREE; and (f) ΣREE vs. Eu/Eu* values in zircon grains from the Libata Sn

mineralization. Magmatic and hydrothermal fields are from Hoskin (2005).

851

Fig. 8. Zircon U-Pb concordant ages of different zircon groups in the (a-b) granite porphyry (CR-

01), and (c-d) altered biotite granite (KB-01) samples. Group 1 zircons = magmatic zircons and

Group 2 zircons = hydrothermally altered zircons. Chondrite-normalized REE patterns for the (e)

granite porphyry and (f) altered biotite granite from the Libata quartz-tourmaline-cassiterite ore

field. Normalization values for zircon/chondrite REE patterns are from Sun and McDonough

(1989).

858

Fig. 9. Chemical compositions of tourmaline from Libata (a) Ca-X□-Na+K (apfu) ternary

diagrams, after Henry et al. (2011); (b) Ca-Fe-Mg (apfu) ternary diagrams, after Henry and

Guidotti (1985). Fig. 8 (c-d). Trace element and chondrite-normalized REE compositions of

tourmalines from the Libata ore field. Fig. 8 (e-f). Principal component analysis (PCA) of LA-

ICP-MS log-transformed trace element data from the Libata tourmaline (n = 49 spot analyses, 15

variables). Trace element normalized to upper continental crust values (UCC) from Rudnick and

Gao (2003) and normalization values for chondrites are from Sun and McDonough (1989).

866

867   **Fig. 10.** Frequency histogram of boron isotopic compositions of the (a) vein 1 tourmaline and vein

868   2 tourmaline at Libata. (b) $\delta^{11}B$ values of the tourmaline in the Libata Sn deposit. The $\delta^{11}B$ data

869   for boron reservoirs are cited from Marschall and Jiang (2011). $\delta^{11}B$ data for deposits are from

870   Ludwig et al. (2011); Codeço et al. (2017); Zhang et al. (2018); Trumbull et al. (2019) and

871   Trumbull et al. (2020).

872

873   **Fig. 11.** Magmatic zircon geochemical diagrams for the Libata granites: (a) U/Yb vs. Yb, after

874   Grimes et al. (2007) and (b) $Log_{10}(U/Yb)$ vs $Log_{10}(Nb/Yb)$ after Grimes et al. (2015).

875

876   **Fig. 12.** Hafnium isotopic signatures of different types of zircons (a) age vs. $\varepsilon Hf(t)$ scattered

877   diagram for different zircons and neighboring deposits; (b) a limited age between 600 and 670 Ma

878   of (a). (c) $^{176}Hf/^{177}Hf$ vs. $^{176}Lu/^{177}Hf$ and (d) $^{176}Hf/^{177}Hf$ vs. $^{176}Yb/^{177}Hf$. Hf isotope values for the

879   Archean basement complex rocks of Western Nigeria and West Africa are from Dickin et al.

880   (1991), Ganade et al. (2016) and Petersson et al. (2018). Hf isotope values from the Benin-Nigeria

881   shield are from Ganade et al. (2016) and Petersson et al. (2018), values for the Hawal Massif are

882   from Bute et al. (2019), and values for the Brasilliano-Pan African orogeny are from Ganade et al.

883   (2014).

884

885   **Fig. 13.** (a-b) Source discrimination plots for the Libata tourmalines based on Li/Sr ratio as

886   compared to compositions of worldwide tourmaline hosted in granites and metamorphic rocks.

887   Variation diagrams of selected trace elements in tourmaline from the Libata Sn ore field. (c) Sn vs.

888   Co/La; (d) Sn vs. Zn/Nb. Data for Cornwall granites are from Duchoslav et al. (2017); Puy-les

889   Vigness gneisses are from Harlaux et al. (2019); Hutti amphibolites are from Hazarika et al. (2015);

890   Dachang granite-hosted Sn deposit are from Zhao et al. (2021b) and Baishaziling granite-hosted

891   Sn deposit are from Zhao et al. (2022). Field for tourmaline hosted in granites, metasediments and

892   metavolcanic rocks is from Harlaux et al. (2019). Field for tourmaline hosted in barren vs

893   mineralized granite from Hong et al. (2017).

894

895   **Fig. 14.** Scatter diagrams of zircon LA-ICP-MS results (ppm). (a) Y + ΣREE vs. U + Nb + Ta; (b)

896   Y + ΣREE vs. Th/U; (c) Y/Ho vs. Y.; and (d) Eu/Eu* vs. Yb/Gd. C1-Chondritic value of Y/Ho =

897   28 in (c) from Bau (1996). Dashed line at Eu/Eu* represent demarcation of field of fertile and

898   barren granites. Values for fertile and infertile Phanerozoic granites are from Lu et al. (2019).

899   **Table Caption**

900   Table 1. Major distinct characteristics of zircon types from granites in the Libata Sn-W orefield.

901   Table 2. LA-ICP-MS Zircon U-Pb data of the studied granites.

902   Table 3. Zircon in situ Lu-Hf isotopic compositions of the Libata granites.

903   **Online Material Caption**

904   Online Material[1] Description of analytical methods

905   Online Material[2] Table OM1 Zircon trace element compositions of the Libata granites

906   Online Material[3] Table OM1 Major element compositions from tourmalines in the Libata tin ore

907   district.

908   Online Material[3] Table OM2 Trace element compositions from tourmalines in the Libata tin ore

909   district.

910   Online Material[3] Table OM3 LA-ICP-MS Boron isotope analysis from the Libata Sn-W ore field.

911   Online Material[4] Table OM1 Zircon U-Pb data for standard samples GJ-1 and PLE.
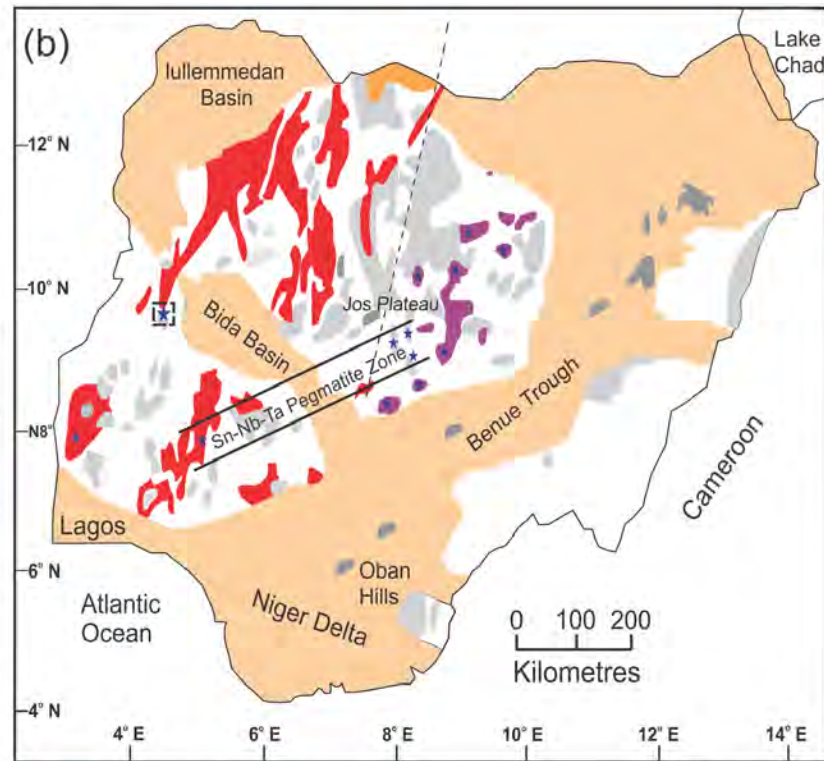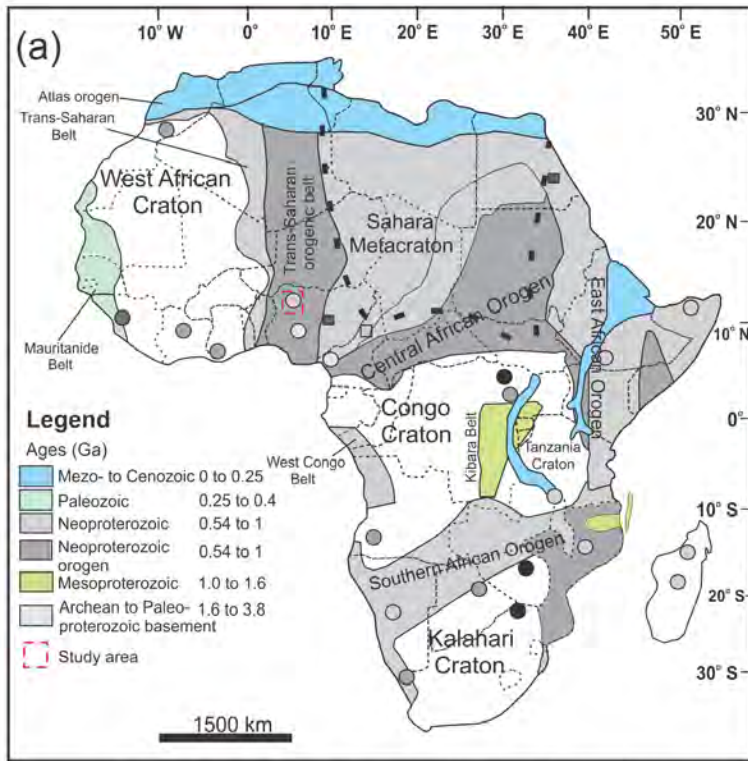
912   Online Material[4] Table OM2 Zircon trace element data for standard samples GJ-1 and PLE.

913   Online Material[4] Table OM3 Trace element analytical results of standard sample BCR-2G, BIR-

914   1G and BVHO-2G.

915   **Supplementary Figure captions**

916

917   Supplementary Figure 1. Zircon U-Pb concordia for standard zircon samples GJ-1 and the
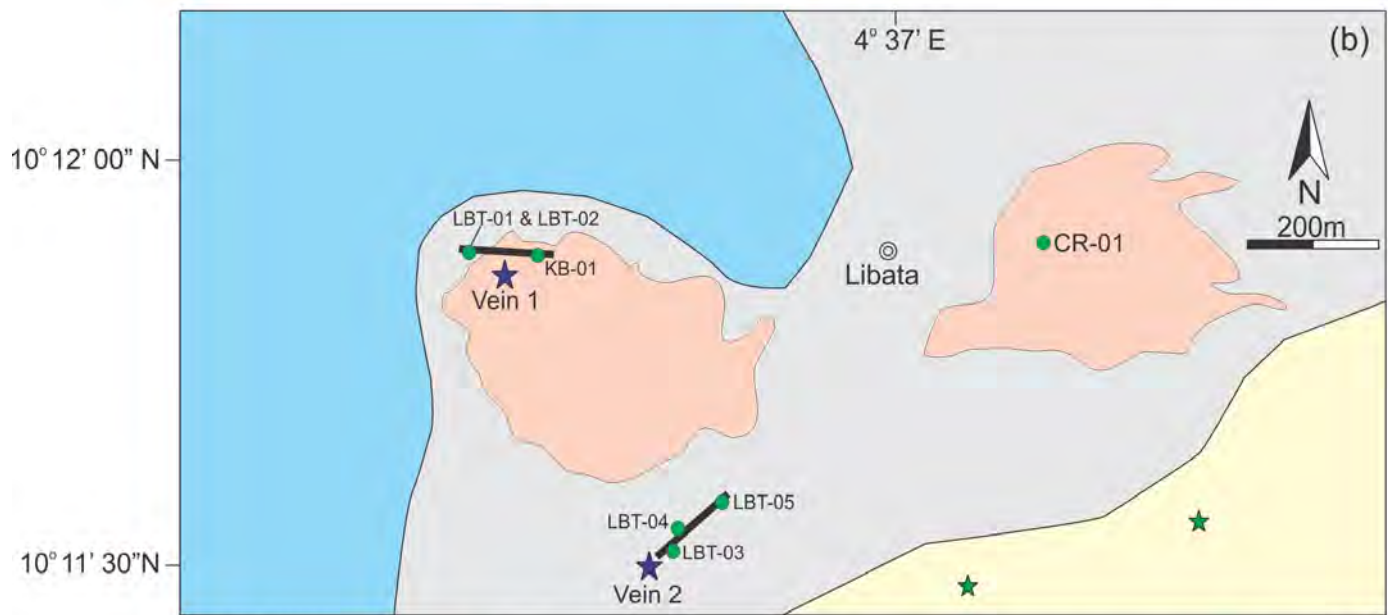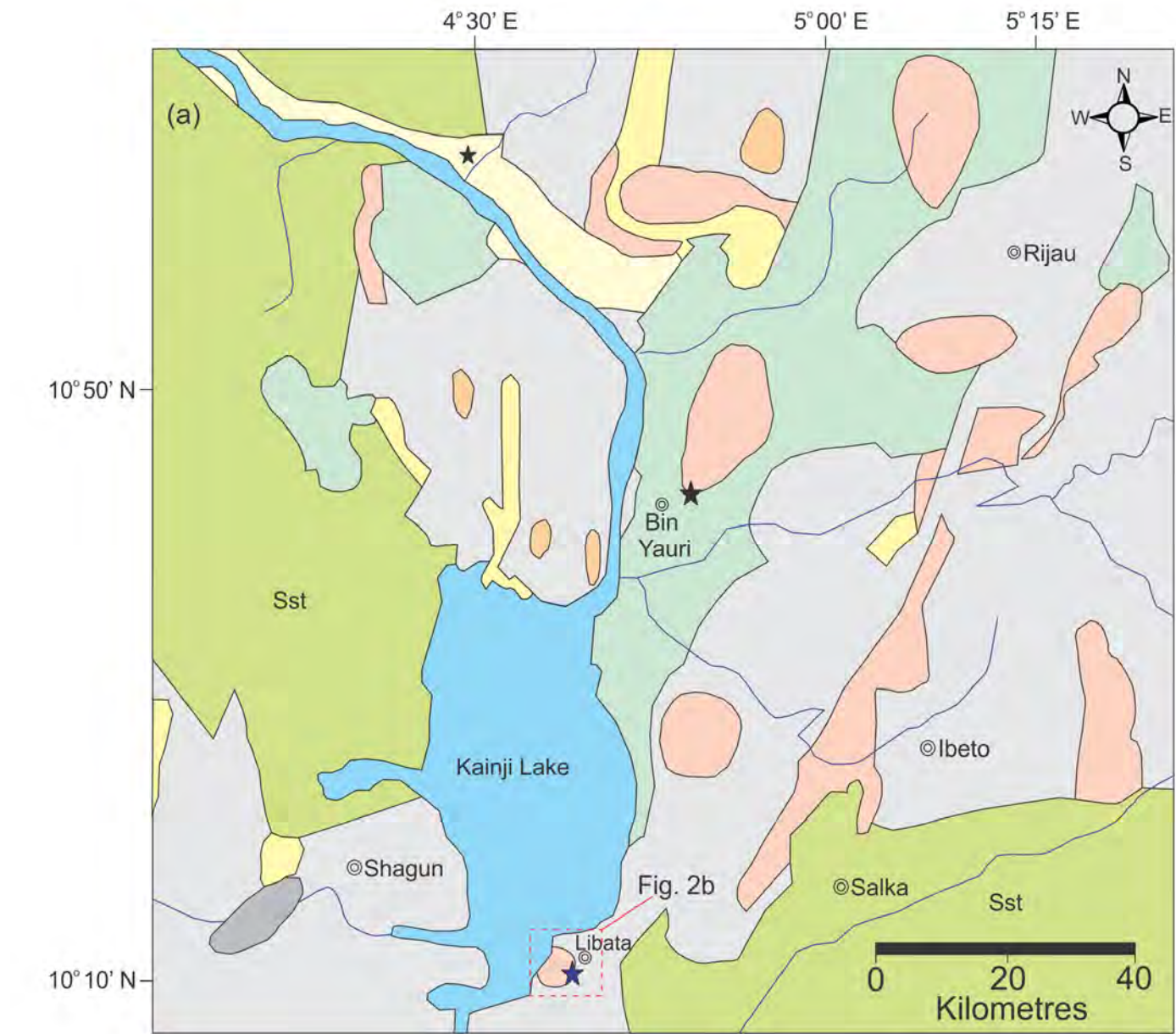
918   Plesovice (PLE).

Figure 1

Figure 2

(a) CR-01 Granite porphyry

(b) KB-01 Altered biotite granite

(c) Vein 1 Quartz-hosted tourmaline

(d) Pl, Tur, Qtz, Optical zoning, Tur, Tur, 0.5 mm

(e) Vein 2 Quartz-hosted tourmaline, Centimeter

(f) Pl, Zr, Tur, 0.5 mm

(g) Ab, Qtz, Zoned Tur, Fe-Ti oxides, Tur, 0.5 mm

(h) Kfs, Qtz, Fe-Ti oxides, Py, Tur, Unzoned Tur, Ms, 0.5 mm

Figure 3

a

Vein 1 tourmaline

500μm

-15.69
-15.30
-15.05
-15.45

-14.92
-15.05

LIB Tur-01   LIB Tur-02

Vein 2 tourmaline

-14.54
-14.83
-14.64
-14.11
-14.07
-14.33
-14.57
-14.80

LIB Tur-03   LIB Tur-04

○ B isotope (50 μm)   ○ Trace element spot (44 μm)

(b)

kfs   qtz   ab   kfs

100μm

(c)

tur   kfs

100μm

(d)

tur   chl

200μm

(e)

tur   chl   qtz

500μm

Figure 4

	Stage:	Early	Main	Late
Paragenesis:				
Albite				
Tourmaline				
Quartz				
K-feldspar				
Chlorite				
Cassiterite				
Pyrite				
Zircon				
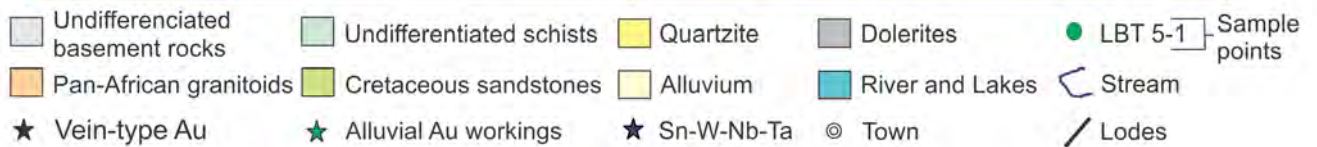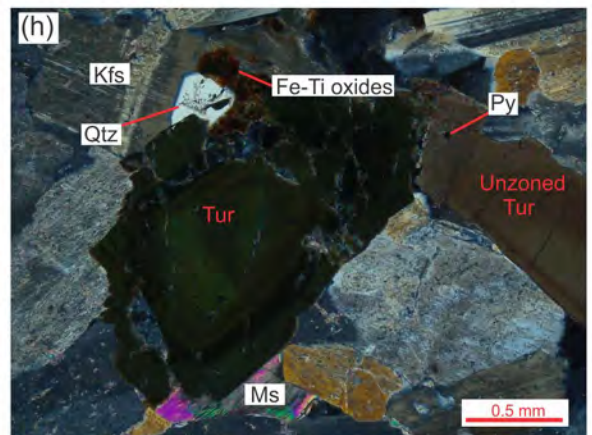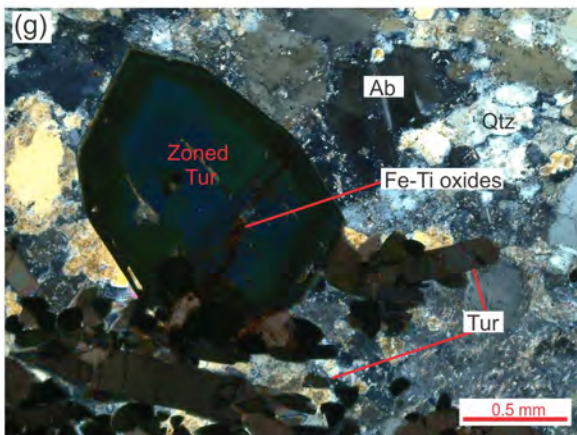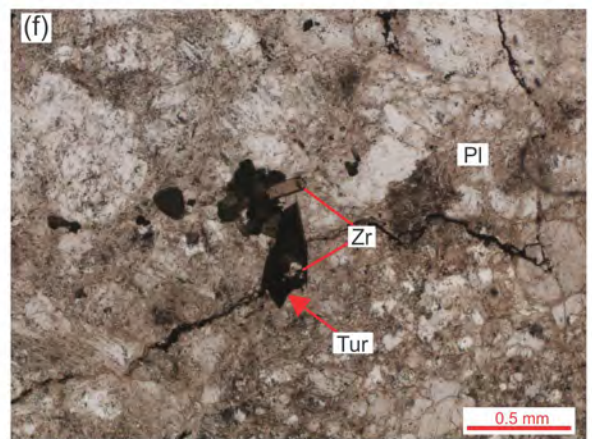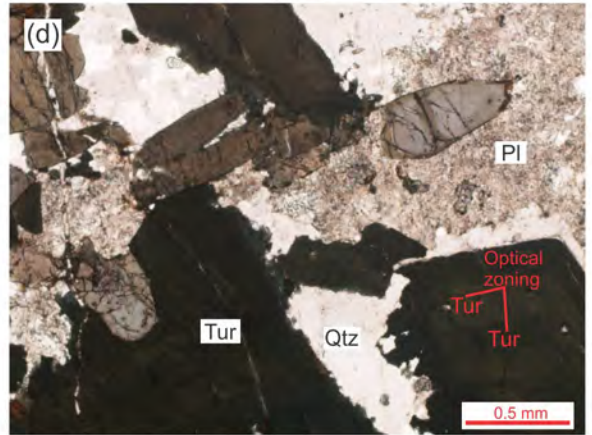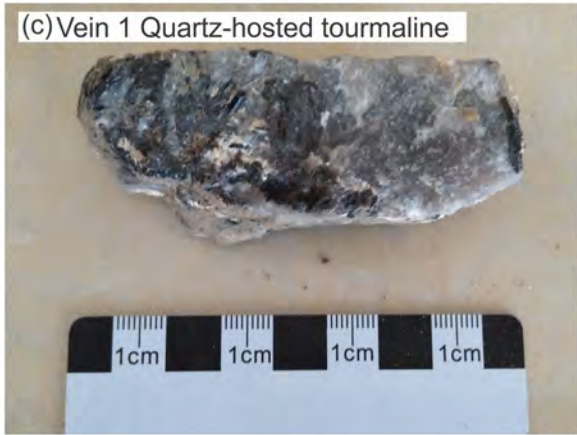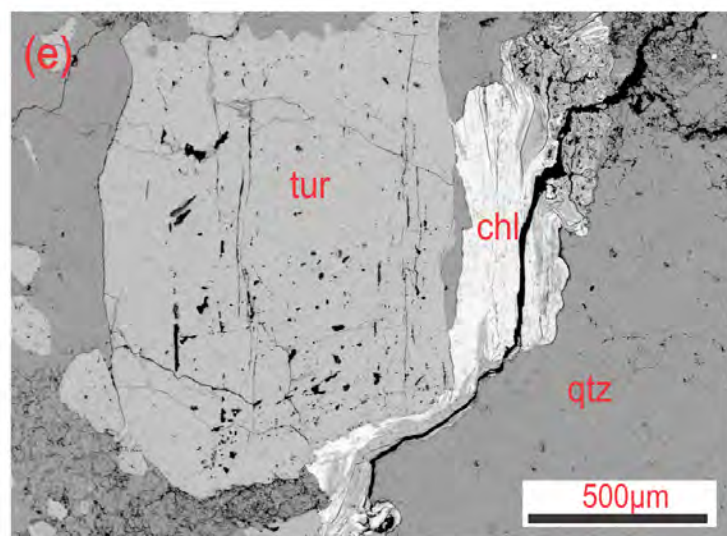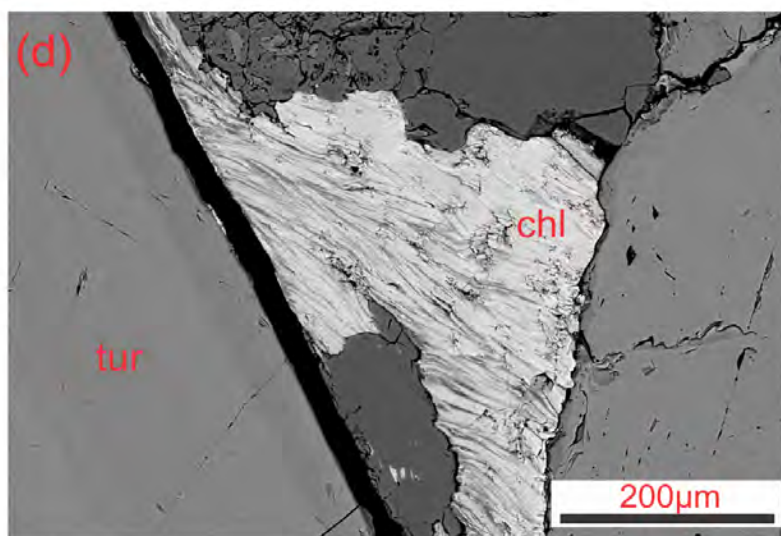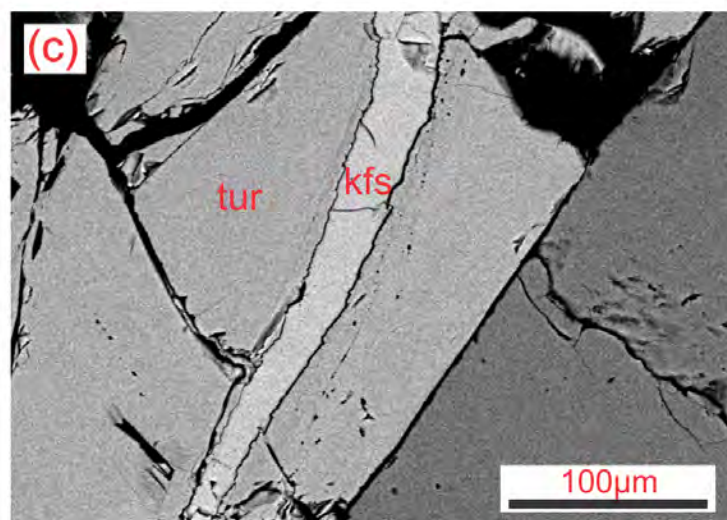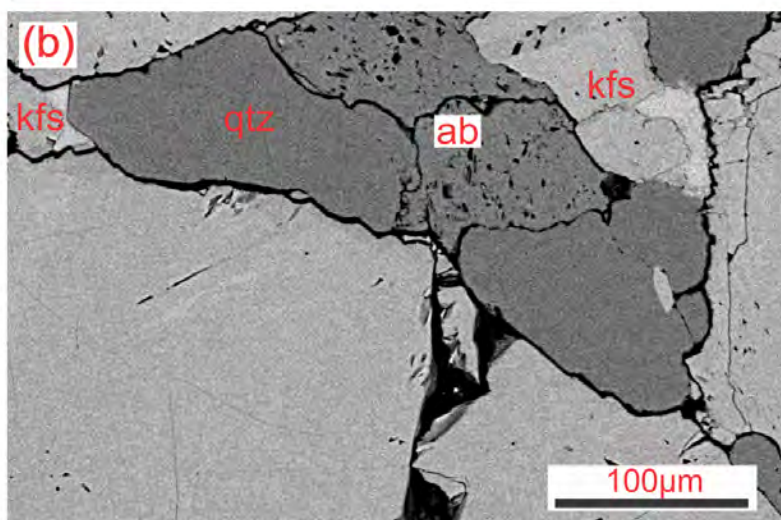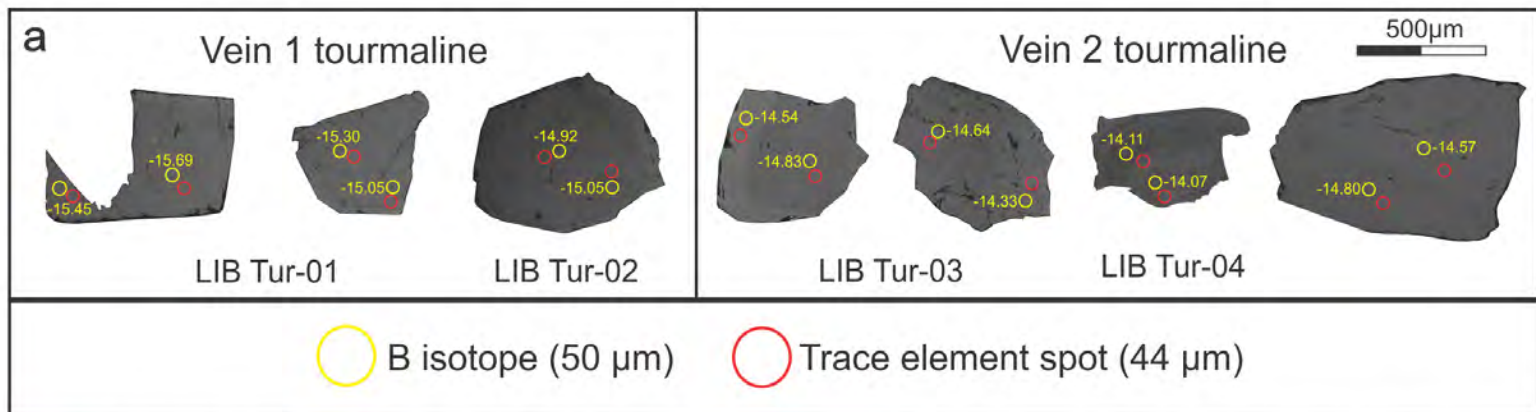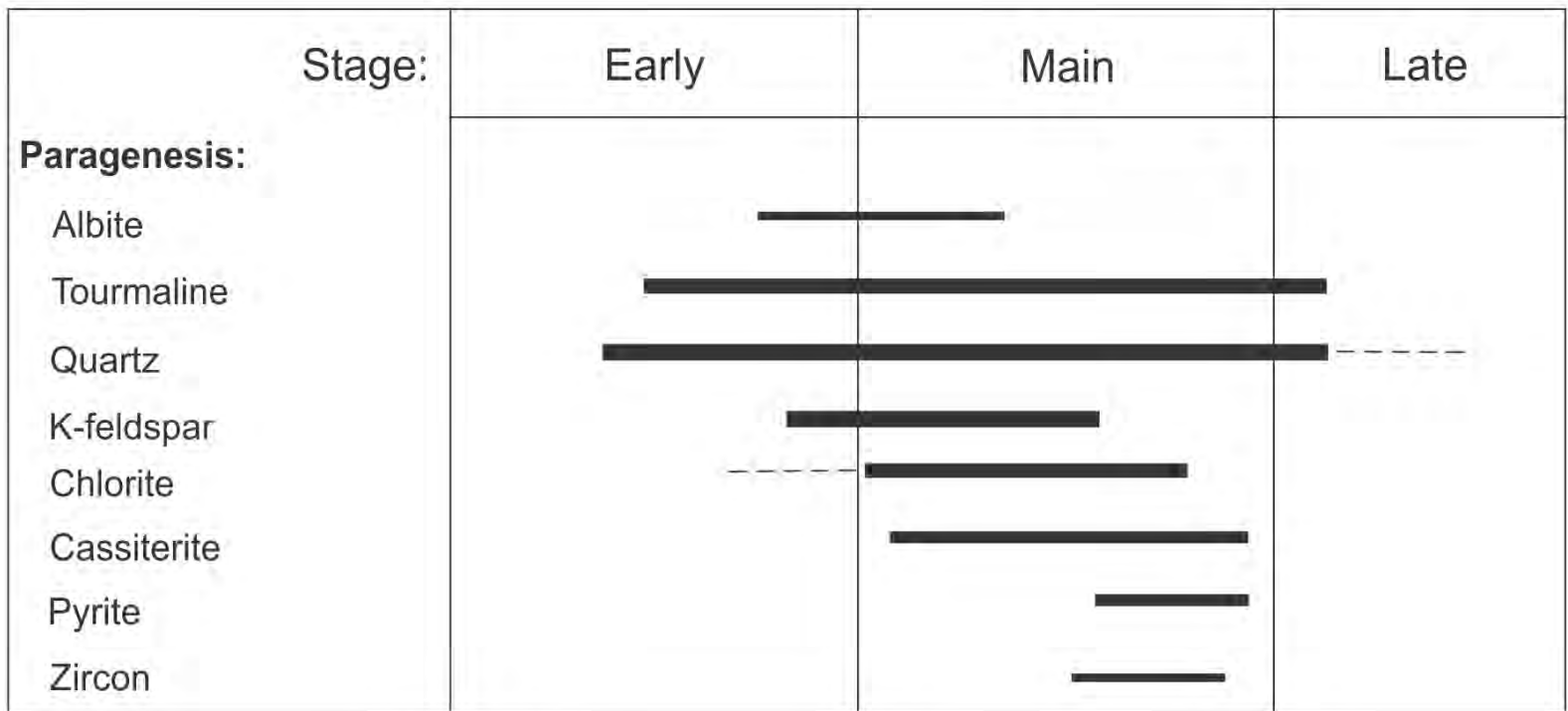
━━━━ Abundant   ──── Minor   -------Trace

Figure 5

a Sample CR-01 — Magmatic — Magmatic-hydrothermal — 200μm

1 — "100" 657 Ma
3 — 642 Ma
16 — 662 Ma
6 — "110" 657 Ma
15 — 656 Ma

b Sample KB-01 — Magmatic — Magmatic-hydrothermal — 100μm

Late mag rim — Early mag core

3 — 647 Ma
17 — 656 Ma
14 — 567 Ma
7 — "110" 667 Ma
16 — 634 Ma
13 — 654 Ma

c Metamict — 100μm — Inherited/Detrital — 100μm

7 — 421 Ma
7 — 591 Ma
18 — 963 Ma
14 — "100" 867 Ma

d — 200μm — 100μm

Sample CR-01 — MI — FI
MI — FI — Sample KB-01

U-Pb spot (32 μm)   Lu-Hf spot (44 μm) 635 Ma concordant 635 Ma disconcordant

MI Mineral Inclusion   FI Fluid Inclusion

Figure 6

Figure 7

Figure 8
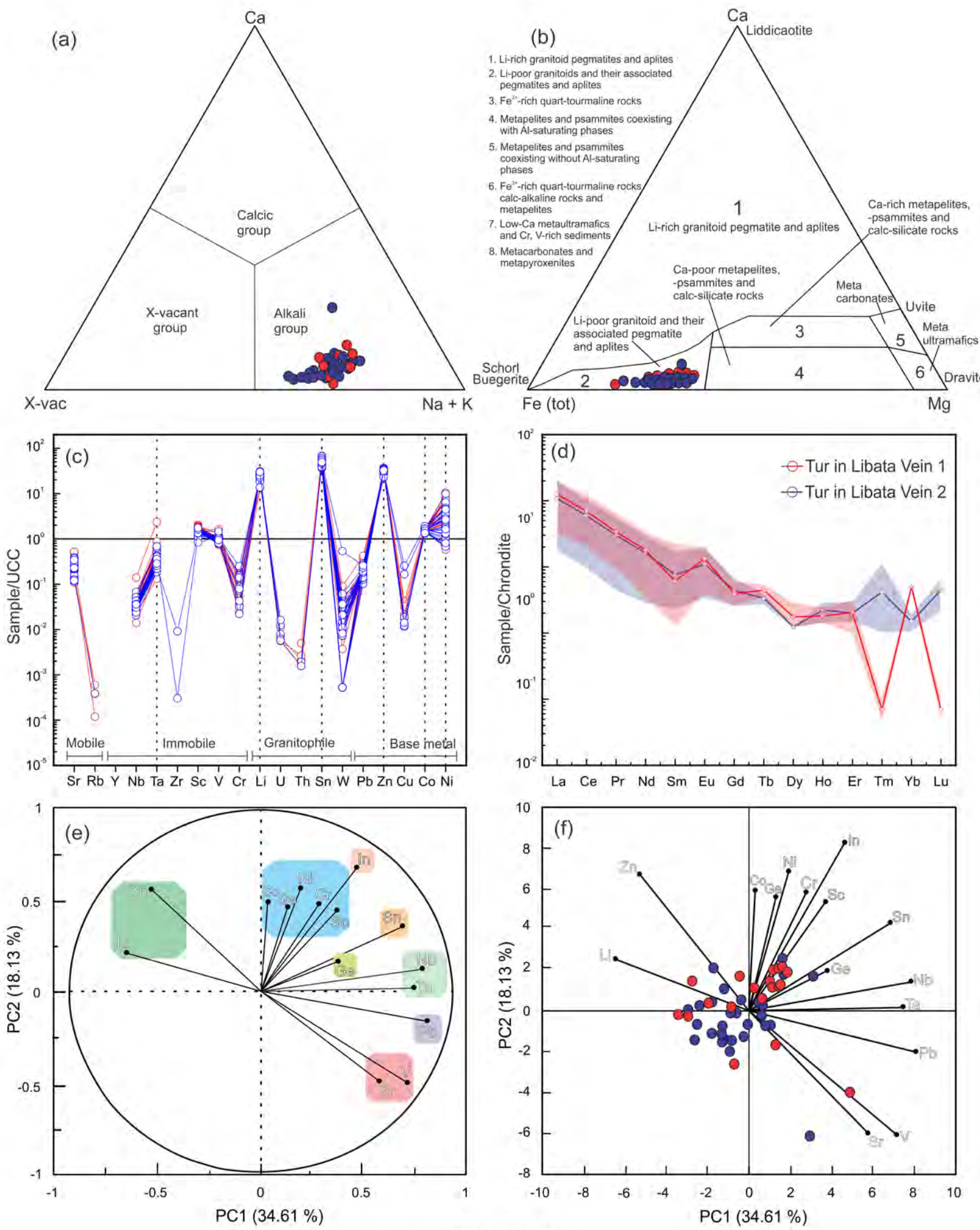
Figure 9

Figure 10
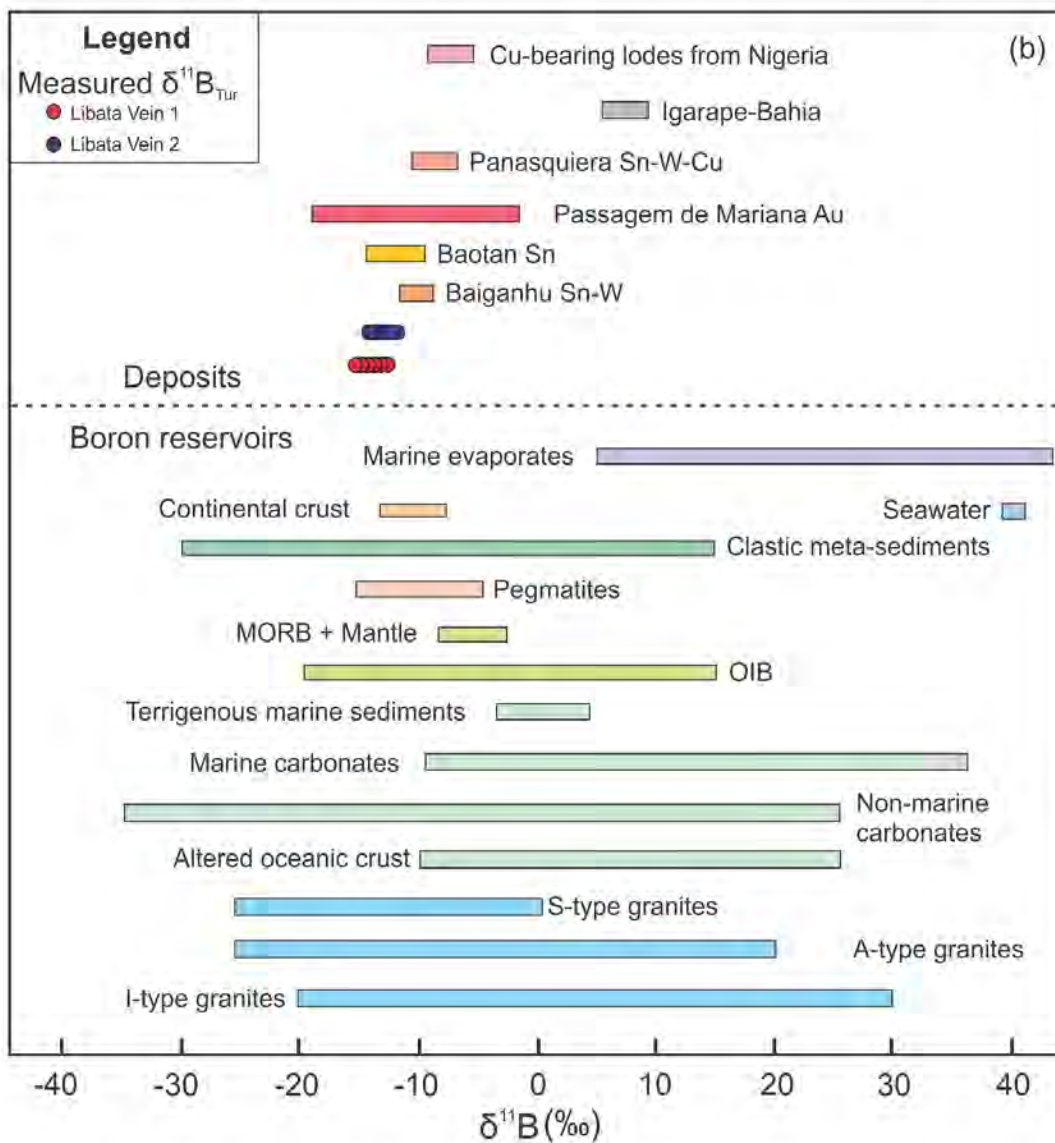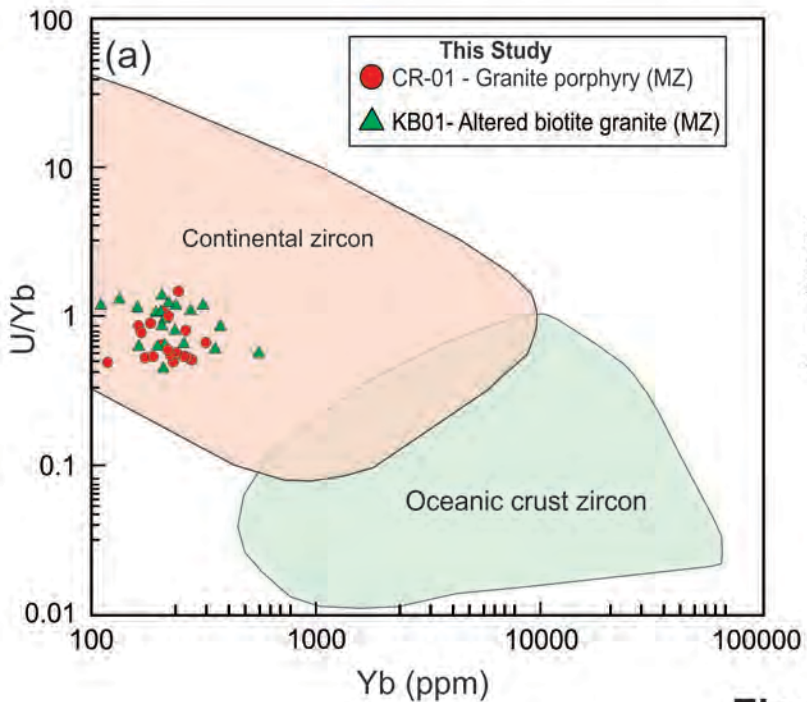
Figure 11
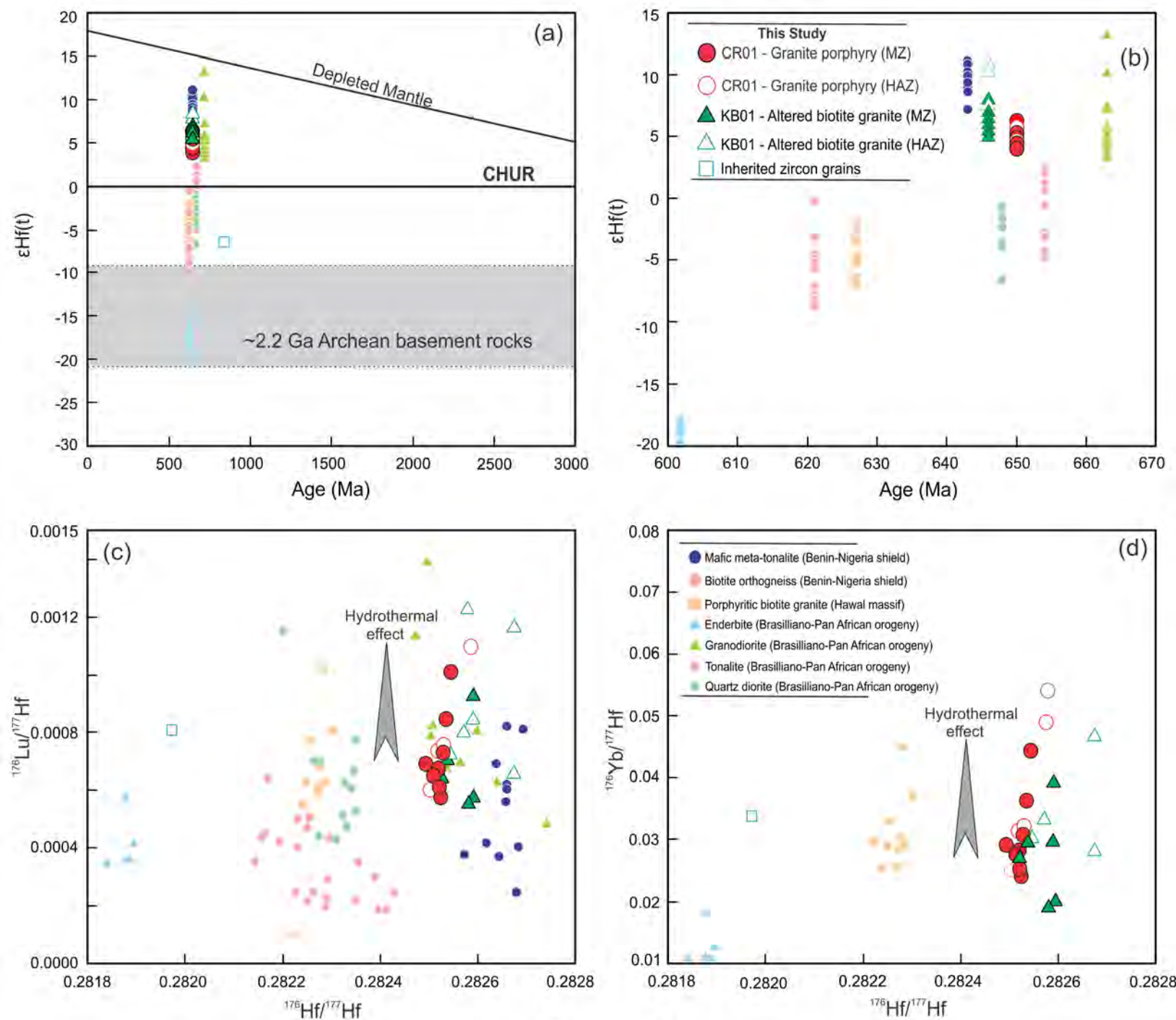
Figure 12
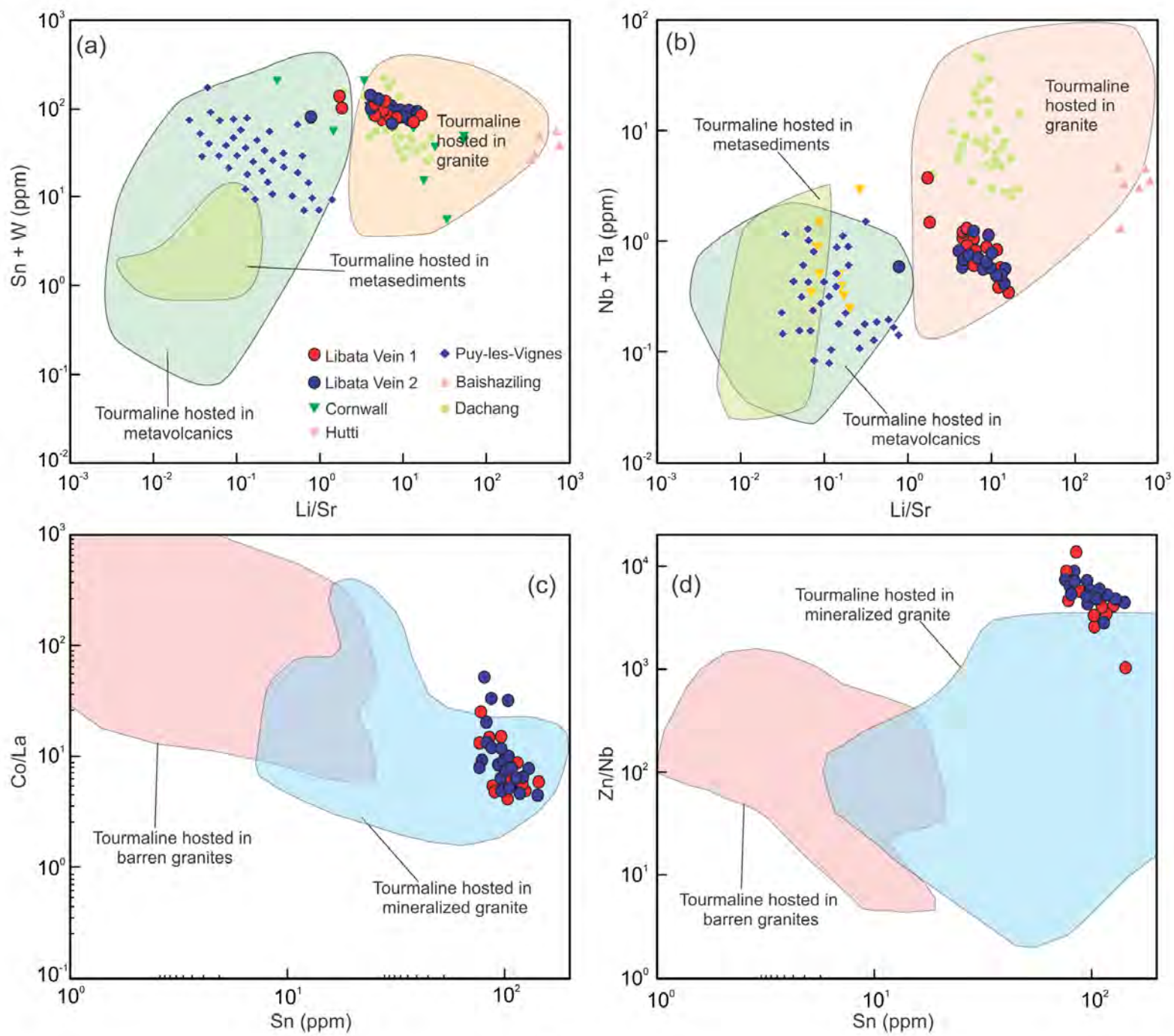
Figure 13

Figure 14
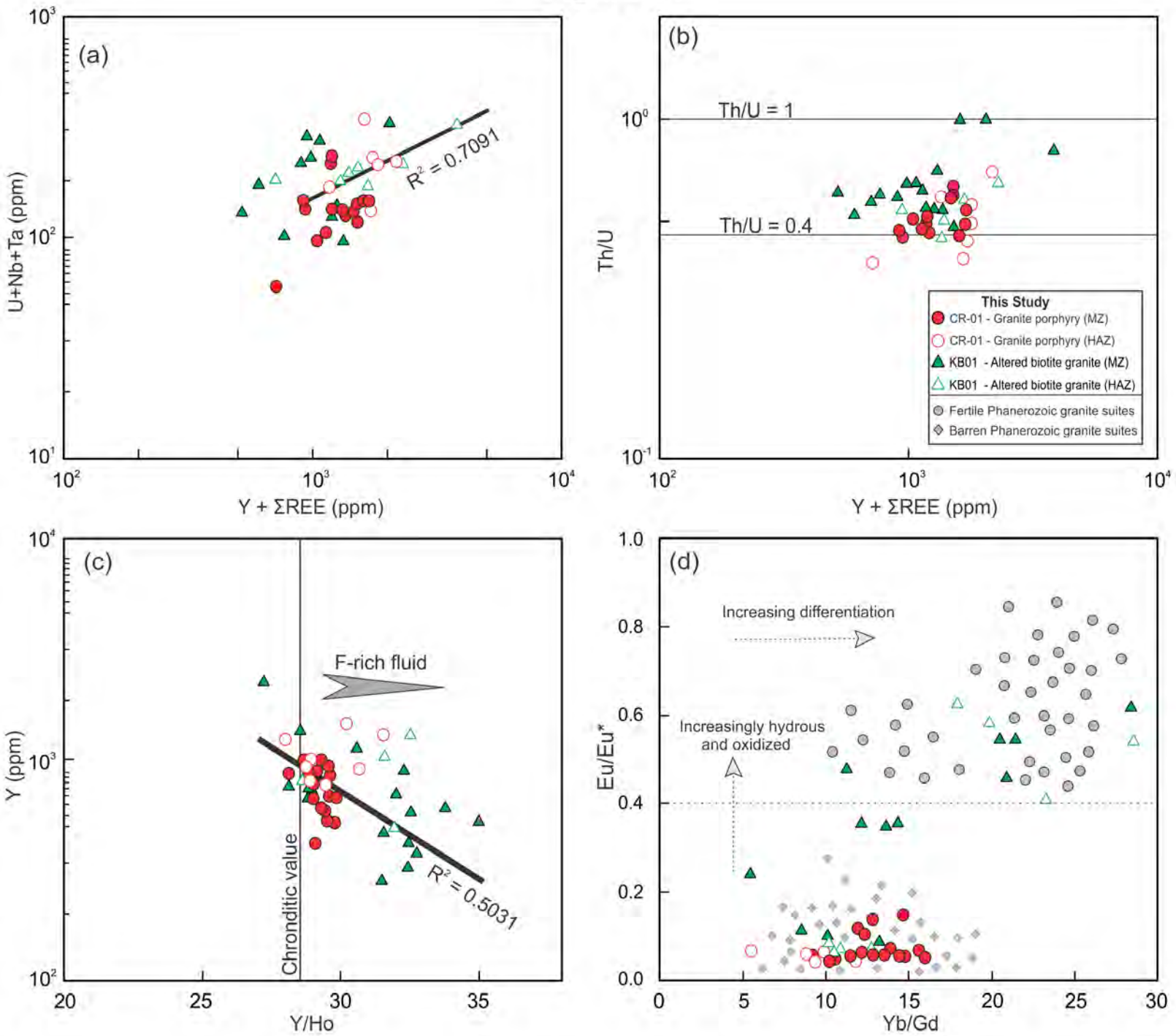
Table 1. Major distinct characteristics of zircon types from granites in the Libata Sn orefield

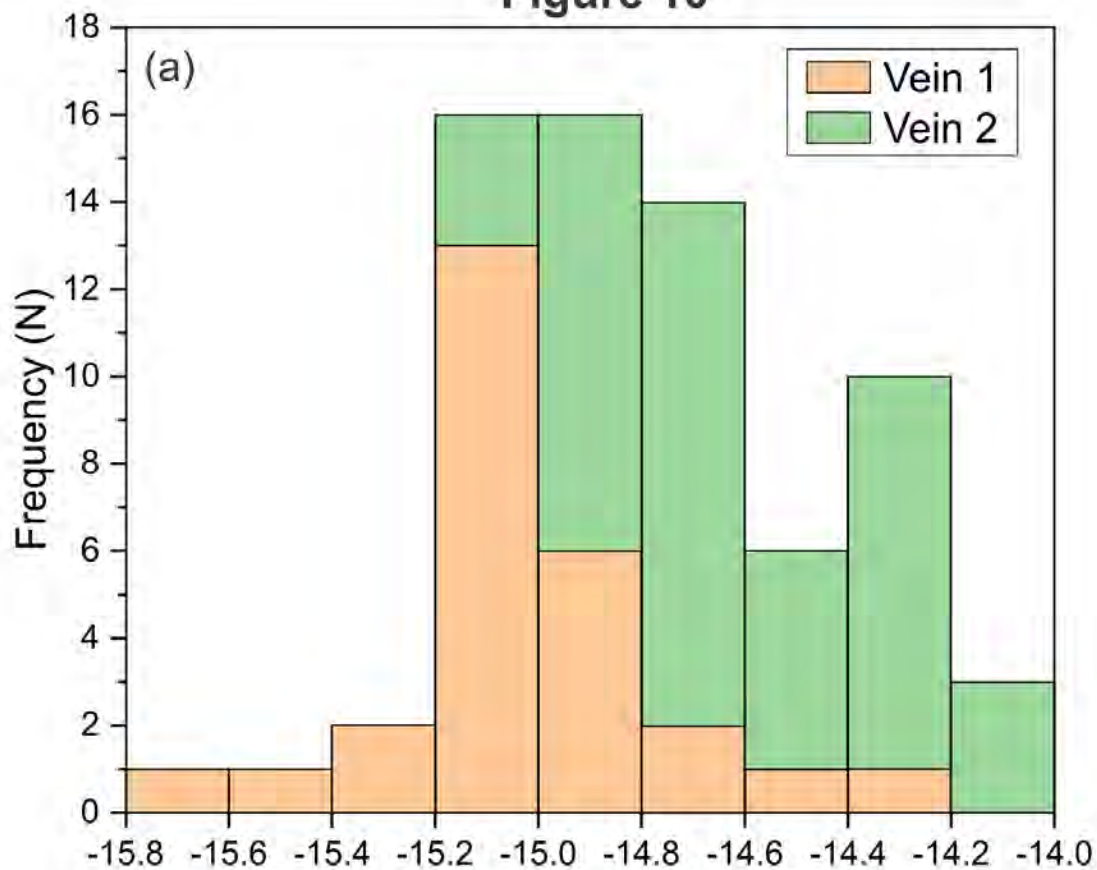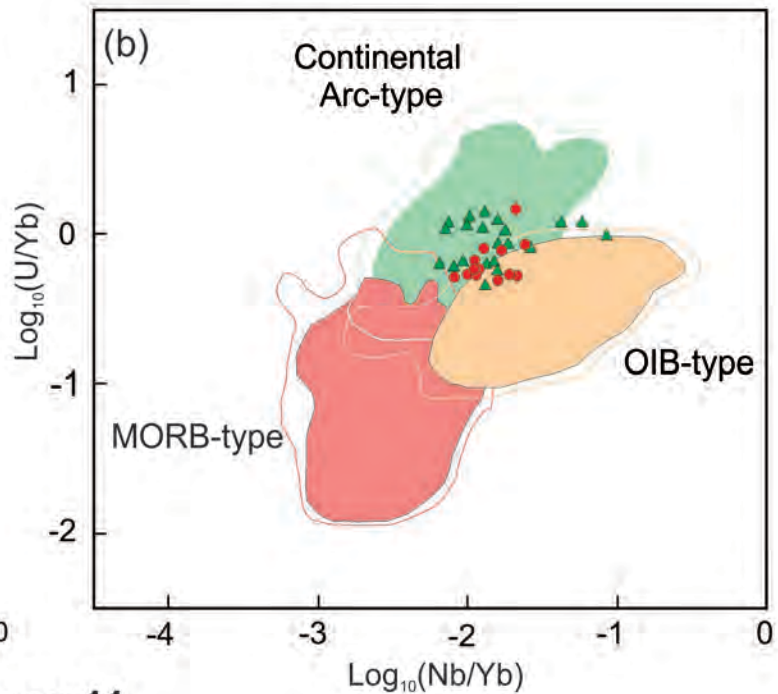| Character/type	Magmatic	Hydrothermally-altered	Inherited
Size	50-300 μm	50-200 μm	100-150 μm
Morphology	Euhedral & anhedral Dominant {100} with minimal {110} prism face	Euhedral & subeuhedral Dominant {110} prism face	Subhedral & anhedral Dominant {100} prism face
Optical appearance	Transparent and colorless	Murky-brown opaque	Transparent and colorless
CL appearance	High intensity Clear zoned texture	Low intensity Variable with zoned and unzoned grains	High intensity Variable with zoned and unzoned grains
Formation mechanism	Early- and late-stage magmatic melt	Early magmatic melt and altered by hydrothermal fluid	Mostly ancient magmatic melt (distinct zircon ages)
Internal structure	Inclusion-poor Fracture-poor	Inclusion-rich Fracture-rich Spongy texture	Inclusion-poor Fracture-poor
Geochemical feature	Moderate negative Eu anomaly Strong positive Ce anomaly Depleted in LREE Low common Pb content	Strong negative Eu anomaly Flat Ce anomaly trends Strongly enriched in U, Th, Y, REE, Nb Moderately enriched in Ti, Sc, Pb, Hf, Ta High common Pb content & varying degree of radiogenic Pb loss	Moderate negative Eu anomaly Strong Ce anomaly Depleted in LREE Low common Pb content
Zircon grain U-Pb ages	~650 Ma	~650 Ma	>800 Ma
Lu-Hf isotope signature	+4.4 to +7.9	+4.5 to +10.6	-7.63

Table 2. LA-ICP-MS Zircon U-Pb data for the studied granites.

Sample No	Type	Isotopic ratios						Apparent age (Ma)						Concordance
		$^{207}Pb/^{206}Pb$	1σ	$^{207}Pb/^{235}U$	1σ	$^{206}Pb/^{238}U$	1σ	$^{207}Pb/^{206}Pb$	1σ	$^{207}Pb/^{235}U$	1σ	$^{206}Pb/^{238}U$	1σ	
Sample CR-01 (Granite porphyry)														
LIB CR01-01	MZ	0.0586	0.0016	0.8697	0.0244	0.1073	0.0010	550	54.62	635	13.27	657	6.08	96%
LIB CR01-02	MZ	0.0639	0.0016	0.9178	0.0239	0.1039	0.0009	739	53.70	661	12.68	637	5.15	96%
LIB CR01-03	HAZ	0.0619	0.0017	0.8942	0.0232	0.1047	0.0009	672	60.02	649	12.43	642	5.00	98%
LIB CR01-04	HAZ	0.0627	0.0013	0.9197	0.0185	0.1059	0.0007	698	42.59	662	9.78	649	4.31	97%
LIB CR01-05	HAZ	0.0622	0.0015	0.9003	0.0206	0.1049	0.0008	680	50.00	652	11.01	643	4.85	98%
LIB CR01-06	HAZ	0.0579	0.0016	0.8617	0.0243	0.1073	0.0008	528	52.77	631	13.26	657	4.89	95%
LIB CR01-07	MZ	0.0611	0.0022	0.8821	0.0313	0.1049	0.0009	643	79.62	642	16.91	643	5.55	99%
LIB CR01-08	MZ	0.0610	0.0018	0.9090	0.0257	0.1082	0.0009	639	62.95	657	13.69	662	5.39	99%
LIB CR01-10	MZ	0.0637	0.0018	0.9291	0.0265	0.1054	0.0009	731	59.25	667	13.95	646	5.47	96%
LIB CR01-11	HAZ	0.0617	0.0014	0.9025	0.0200	0.1057	0.0008	661	48.15	653	10.68	648	4.71	99%
LIB CR01-13	MZ	0.0590	0.0017	0.8711	0.0249	0.1066	0.0010	569	61.87	636	13.53	653	5.64	97%
LIB CR01-14	HAZ	0.0595	0.0016	0.8806	0.0239	0.1072	0.0009	583	59.25	641	12.90	656	5.00	97%
LIB CR01-15	HAZ	0.0624	0.0014	0.9248	0.0208	0.1071	0.0009	687	46.29	665	11.00	656	5.54	98%
LIB CR01-16	MZ	0.0619	0.0018	0.9272	0.0265	0.1081	0.0009	672	61.11	666	13.95	662	5.18	99%
LIB CR01-18	MZ	0.0626	0.0017	0.9155	0.0247	0.1058	0.0009	694	57.40	660	13.11	648	5.13	98%
LIB CR01-19	MZ	0.0613	0.0017	0.8816	0.0237	0.1041	0.0009	650	57.40	642	12.80	638	5.43	99%
LIB CR01-20	MZ	0.0643	0.0019	0.9274	0.0260	0.1045	0.0009	754	56.48	666	13.69	641	5.09	96%
LIB CR01-22	MZ	0.0648	0.0019	0.9478	0.0271	0.1059	0.0008	769	61.11	677	14.14	649	4.71	95%
LIB CR01-23	MZ	0.0592	0.0027	0.8588	0.0372	0.1059	0.0012	576	99.99	629	20.33	649	7.19	97%
LIB CR01-24	HAZ	0.0624	0.0019	0.9346	0.0304	0.1081	0.0010	700	58.33	670	15.94	662	5.97	98%
LIB CR01-25	MZ	0.0612	0.0019	0.9198	0.0281	0.1087	0.0009	656	66.66	662	14.88	665	5.12	99%
Sample KB-01 (Potassic altered granite)														
LIB KB01-01	MZ	0.0621	0.0024	0.9131	0.0335	0.1066	0.0012	676	87.95	659	17.81	653	6.71	99%
LIB KB01-02	MZ	0.0624	0.0026	0.8971	0.0369	0.1043	0.0011	687	90.73	650	19.78	639	6.57	98%
LIB KB01-03	MZ	0.0626	0.0019	0.9135	0.0261	0.1057	0.0010	694	69.44	659	13.85	647	5.67	98%
LIB KB01-04	HAZ	0.0671	0.0020	0.9750	0.0272	0.1049	0.0009	843	56.48	691	13.98	643	5.46	92%

LIB KB01-05	MZ	0.0672	0.0026	0.9874	0.0358	0.1070	0.0011	843	81.48	697	18.31	655	6.33	93%
LIB KB01-06	MZ	0.0654	0.0020	0.9359	0.0274	0.1035	0.0012	787	64.81	671	14.38	635	6.92	94%
LIB KB01-07	HAZ	0.0516	0.0082	0.9456	0.1583	0.1091	0.0018	333	264.78	676	82.64	667	10.45	98%
LIB KB01-10	HAZ	0.0606	0.0022	0.9376	0.0294	0.1074	0.0011	633	79.62	672	15.40	658	6.58	97%
LIB KB01-11	MZ	0.0597	0.0018	0.8716	0.0266	0.1053	0.0010	591	66.66	636	14.44	646	5.97	98%
LIB KB01-12	MZ	0.0609	0.0018	0.8881	0.0262	0.1052	0.0011	635	62.95	645	14.08	645	6.60	99%
LIB KB01-13	HAZ	0.0596	0.0023	0.9413	0.0308	0.1067	0.0010	591	83.32	674	16.10	654	5.75	97%
LIB KB01-14	IZ	0.0663	0.0019	0.8419	0.0230	0.0919	0.0008	817	61	832	12.67	867	4.97	90%
LIB KB01-15	MZ	0.0592	0.0016	0.8625	0.0227	0.1049	0.0009	576	59.25	631	12.40	643	5.18	98%
LIB KB01-16	HAZ	0.0611	0.0019	0.8759	0.0261	0.1034	0.0009	643	66.66	639	14.13	634	5.30	99%
LIB KB01-17	MZ	0.0606	0.0023	0.8996	0.0333	0.1071	0.0011	633	79.62	652	17.80	656	6.18	99%
LIB KB01-18	IZ	0.0693	0.0019	1.5511	0.0404	0.1612	0.0013	906	55.56	951	16.10	963	7.26	98%
LIB KB01-19	MZ	0.0586	0.0025	0.8903	0.0374	0.1097	0.0013	554	92.58	647	20.10	671	7.63	96%
LIB KB01-20	HAZ	0.0613	0.0024	0.9312	0.0346	0.1099	0.0011	650	85.17	668	18.18	672	6.27	99%
LIB KB01-21	MZ	0.0629	0.0026	0.9223	0.0382	0.1062	0.0014	706	89.65	664	20.18	651	8.13	98%
LIB KB01-22	MZ	0.0617	0.0020	0.8902	0.0287	0.1043	0.0011	661	70.36	646	15.42	640	6.68	98%
LIB KB01-23	HAZ	0.0628	0.0018	0.9111	0.0253	0.1048	0.0009	702	61.11	658	13.47	642	5.25	97%
LIB KB01-24	MZ	0.0631	0.0016	0.9243	0.0235	0.1058	0.0011	722	55.55	665	12.40	648	6.59	97%
LIB KB01-25	MZ	0.0606	0.0017	0.9101	0.0251	0.1084	0.0010	633	61.10	657	13.36	664	5.62	99%

Note:

MZ = Magmatic zircon.

HAZ = Hydrothermally-altered zircon.

IZ = Inherited zircon

All of these abbreviations are also applied to the tables below.

Table 3. Zircon in situ Lu-Hf isotopic compositions for the Libata granites

Spot No	Type	$^{176}Lu/^{177}Hf$	$^{176}Yb/^{177}Hf$	$^{176}Hf/^{177}Hf$	$\pm1\sigma$	Age (Ma)	$\varepsilon Hf(t)$	TDM(Ma)	TDM2(Ma)	fLu/Hf
Sample CR-01 (Granite porphyry)										
CR-01-01	MZ	0.000691	0.029189	0.282494	0.000013	657	4.37	1063	1311	-0.98
CR-01-02	MZ	0.000756	0.032046	0.282531	0.000012	637	5.21	1013	1242	-0.98
CR-01-03	HAZ	0.000573	0.023931	0.282525	0.000013	642	5.17	1017	1249	-0.98
CR-01-04	HAZ	0.000673	0.028206	0.282519	0.000012	643	4.94	1028	1264	-0.98
CR-01-05	HAZ	0.000735	0.031256	0.282519	0.000011	657	5.24	1029	1256	-0.98
CR-01-06	HAZ	0.000600	0.024872	0.282502	0.000014	648	4.50	1049	1296	-0.98
CR-01-07	MTZ	0.000730	0.030653	0.282529	0.000014	421	0.47	1015	1378	-0.98
CR-01-08	HAZ	0.000845	0.036266	0.282534	0.000013	656	5.69	1012	1227	-0.97
CR-01-09	MZ	0.000610	0.025232	0.282522	0.000014	665	5.56	1022	1242	-0.98
CR-01-10	MZ	0.000720	0.030418	0.282534	0.000014	638	5.34	1009	1235	-0.98
CR-01-11	MZ	0.000654	0.027413	0.282514	0.000013	657	5.10	1034	1265	-0.98
CR-01-12	MZ	0.001012	0.044225	0.282545	0.000014	665	6.21	1000	1201	-0.97
Sample KB-01 (Potassic altered granite)										
KB-01-01	MZ	0.000706	0.029589	0.282539	0.000016	653	5.85	1001	1214	-0.98
KB-01-02	HAZ	0.001162	0.046562	0.282676	0.000017	643	10.31	819	923	-0.97
KB-01-03	HAZ	0.001227	0.054186	0.282579	0.000015	655	7.10	958	1137	-0.96
KB-01-04	MZ	0.000716	0.030064	0.282544	0.000015	667	6.34	994	1194	-0.98
KB-01-05	HAZ	0.000657	0.028083	0.282676	0.000013	658	10.85	808	901	-0.98
KB-01-06	HAZ	0.000797	0.033398	0.282572	0.000014	654	7.01	958	1142	-0.98
KB-01-07	MZ	0.000574	0.019880	0.282593	0.000013	656	7.90	922	1087	-0.98
KB-01-08	IZ	0.000804	0.033752	0.281972	0.000012	963	-7.53	1791	2293	-0.98
KB-01-09	MZ	0.000639	0.026938	0.282521	0.000015	651	5.20	1025	1254	-0.98
KB-01-10	MZ	0.000554	0.019038	0.282580	0.000013	640	7.09	940	1126	-0.98
KB-01-11	HAZ	0.000843	0.029512	0.282590	0.000012	642	7.39	933	1108	-0.97
KB-01-12	MZ	0.000927	0.039216	0.282591	0.000012	664	7.85	934	1096	-0.97

Note:

MZ = Magmatic zircon.

MTZ = Metamict zircon

HAZ = Hydrothermally-altered zircon.

IZ = Inherited zircon