Tourmaline and zircon trace the nature and timing of magmatic-hydrothermal episodes in granite-related Sn mineralization: Insights from the Libata Sn ore field

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ABSTRACT

The Bin Yauri-Libata polymetallic ore district is a Sn and Au ore-bearing district in the Zuru schist belt, Northwestern Nigeria. The Libata Sn ore field is characterized by a set of cassiterite-bearing hydrothermal veins associated with Neoproterozoic Pan-African granites affected by deformation and low-grade metamorphism. The hydrothermal alteration associated with cassiterite-bearing
quartz veins in the Libata deposit includes silicification, albitization, chloritization, and potassic alteration. In this study, geochemical and geochronological data from tourmalines and zircons from Sn bearing lodes, unmineralized and altered granites is applied to reveal the timing, fluid composition, and source of ore-forming materials for tin mineralization in the Libata ore field. Zircon trace element and Hf isotopes (εHf(t)= +4.37 to +10.85) reveal a mantle-derived source with some crustal contribution for the melts forming the Libata Sn-bearing granites. LA-ICPMS zircon U-Pb dating constrains the magmatic and hydrothermal ages to 650-646 Ma and 649-646 Ma for the Libata granites. Overlapping zircon εHf(t) and 176Hf/177Hf but distinct 176Lu/177Hf and 176Yb/177Hf ratios from magmatic and hydrothermally altered zircons reveal a magmatic source for the hydrothermal fluids which triggered cassiterite deposition in the Libata ore field. Major element chemistry constrain tourmalines from the Libata ore field as schorls that show high alkalis, low Ca contents, and moderate □ values (where □ is x-site vacancy). High Li, Zn, and Sn concentrations in tourmaline as well as Li/Sr and Ca-Fe-Mg ratios demonstrate that the tourmaline formed from granite-sourced fluid likely derived from the host Libata granites. Measured δ11B values from the Libata tourmaline range from −15.69‰ to −14.07‰. The δ11B of the mineralizing fluid is estimated to be −13.1 to −11.9‰ for the Libata tourmalines at 400-500 °C and overlaps with averages from fractionated granites worldwide. Therefore, our data show that tourmaline and zircon are useful tracers of magmatic-hydrothermal evolution in rare metal bearing granites systems.

Keywords: Tourmaline chemistry, Sn mineralization, Hydrothermally-altered zircons, Pan-African granites, B isotopes, Libata

INTRODUCTION

Tourmaline, an accessory mineral in various rock types, is common in most granitic rocks and in various types of hydrothermal ore deposits (Dutrow and Henry, 2011; Marschall and Jiang, 2011). Due to its resistance to weathering and stability over a wide range of P-T-X conditions, tourmaline typically preserves geological information about the magma or hydrothermal fluid from which it precipitated (Marks et al., 2013). Since tourmaline incorporates a large variety of elements into its crystal lattice, hydrothermal tourmaline is a robust tools for tracking the nature and
evolution of mineralizing fluids in magmatic-hydrothermal systems (Jiang et al., 2004; Zhao et al., 2021a). Similarly, boron isotopes of tourmaline are a reliable tracer for fluid–rock interactions, boron sources, and fluid evolution in ore deposit systems (Yang et al., 2015; Codeço et al., 2017; Trumbull et al., 2019; Trumbull et al., 2020).

Zircon, a prevalent accessory phase in various rock types, is of increasing geological focus due to its resilience to weathering and ability to record geochronological, isotopic, and geochemical changes in host rocks (Hoskin, 2005; Valley et al., 2010). Trace element variations in zircon track magma evolution, metamorphism, and can serve as good recorders of magmatic-hydrothermal evolution in granitic systems (Claiborne et al., 2010; Li et al., 2014). The coupled use of zircon trace element composition, zircon Lu-Hf isotopes, and high-precision zircon U-Pb geochronology have been recognized as robust tools for tracking the timing and evolution of magmatic-hydrothermal stages in granite hosted ore deposits (Li et al., 2018; Jiang et al., 2020; Vincent et al., 2021).

Sn-W bearing lodes from Nigeria have long been a source of research and economic interest due to their abundance and world-class deposit styles (Girei et al., 2019). However, most of the present and historic mining has been from deposits associated with anorogenic ring complexes in northcentral Nigeria (Kinnaird and Bowden, 1987; Melcher et al., 2015). Deposits sourced from I- and S-type granitoids, pegmatites and other vein-type Sn deposits account for only 5% of the production from Nigeria (Olade, 2021). These Sn-bearing granitoids, rare metal pegmatites, and vein-type deposits are primarily concentrated along a 500 km NE-SW trending belt (Fig. 1b) from the southwestern part of Nigeria to the Jos Plateau (Okunlola and Ocan, 2009; Adetunji et al., 2016). However, recent studies suggest a wider distribution range for the ore-bearing calc-alkaline granitic suites and pegmatites in Northwestern and Southeastern Nigeria.
(Garba, 2003; Ero and Ekwueme, 2009). The cassiterite-tourmaline assemblages in quartz from the Libata deposit are similar to other granite-related Sn deposits found in Pan-African terrains of West Africa (Kinnaird et al., 2016). However, the timing, nature, and source of ore forming materials for these Sn-bearing granites remain poorly constrained. Therefore, a comprehensive geologic, geochemical, and isotopic study of the Libata Sn deposit is crucial in constraining the nature, genetic type, and genesis of Sn-bearing granites and vein systems in Northwestern Nigeria and by extension the Pan-African suites of the Nigeria-Benin Shield.

In this study, cassiterite-bearing lodes associated with granites in northwestern Nigeria were selected to evaluate the Sn mineralization history for these granites. This study presents textural observations together with zircon U-Pb age, zircon Lu-Hf isotope, tourmaline major-trace element and boron isotopic data from barren and mineralized granites to determine the origin and timing of magmatic and hydrothermal processes that are associated with Sn mineralization in the Libata ore field.

**GEOLOGICAL BACKGROUND**

The Nigeria basement complex forms part of the Trans-Saharan orogenic belt (Fig. 1a) extending from the Hoggar Massifs into West Africa (Cahen et al., 1984). Tectonic welding of the West African craton, Congo craton, and Pharusian belt between 700 to 590 Ma is interpreted to have formed the Trans-Saharan orogenic belt (Bute et al., 2019). The basement complex rocks of Northwestern Nigeria exhibit signatures of the Liberian, Eburnian, and Kibaran orogeny (Turner, 1983). Based on differing lithology and tectonic evolution, the Nigerian basement complex is subdivided into a western and eastern terrain (Fig. 1b; Bute et al., 2019; Ferré et al., 1996). The basement complex rocks of the eastern terrain have witnessed significantly higher grades of metamorphism than those of the western terrain and are composed of gneisses, migmatites, and
metapelites (Ferré et al., 1996; Ferré et al., 1998). The country rocks of the western terrain are
overlain by an array of N-S trending metasediments (Turner, 1983). Based on variations in
metamorphic grade and lithology, several workers have proposed two distinct sets of
metasediments, namely the “Older Metasediments” and “Younger Metasediments” (McCurry,
1971). The grade of metamorphism is highest in the Older Metasediments where amphibolite
metamorphic grade rocks, which formed around 2.5 Ga, have been reported (Turner, 1983). The
Younger Metasediments are composed of fine to coarse-grained clastic deposits in largely
undeformed structures of late Pan-African age (Turner, 1983). Extensive post-collisional (Pan-
African) granitoid plutons, generated during the main to late-stages of the Pan-African orogeny
(750-550 Ma), are widespread in the Older Metasediments of the eastern and western basement
complex terrains (Ferré et al., 1996). The basement complex rocks are further intruded by later
staged Carboniferous to early Cretaceous granites (324-141 Ma) termed “Younger Granites” to
differentiate them from the more widely distributed “Older granites” of Pan-African (750-550 Ma)
ages (Bute et al., 2019; Vincent et al., 2022).

GEOLOGY OF THE LIBATA SN ORE FIELD

The Libata area is composed of low-lying gneisses intruded by Pan-African granite
porphyries and porphyritic biotite granites. The granitic rocks also intrude biotite-muscovite
schists of the Zuru schist belt (Fig. 2a). The biotite-muscovite schists of the Zuru-Libata area show
varying degrees of metamorphism with locally well-banded textures and gradation into hornfels
(Danbatta and Garba, 2007). Two prominent Sn-bearing ore bodies have been found in the Libata
ore field (Fig. 2b). Both Sn-bearing ore bodies in the Libata ore field are quartz veins with
alteration zones bounding wall rocks. Vein 1 is a granite-hosted ore-bearing lode, while, vein 2 is
a NE-SW trending metasedimentary-hosted ore-bearing lode (Fig. 2b). Wall rock samples from
the granite-hosted vein primarily consist of quartz, plagioclase, tourmaline, and minor biotite, with
accessory albite, chlorite, and zircon (Figs. 3b; 4a). The main ore mineral is cassiterite, which is
accompanied by minor sulfides such as pyrite. Gangue minerals include chlorite, tourmaline, and
quartz. Cassiterite occurs primarily in the tourmaline-quartz veins and the adjacent tourmaline-
bearing wall rocks. Based on the above observations, mineral paragenesis from ore-bearing veins
in the Libata ore field are summarized in Fig. 5. The Libata ore field is also comprised of several
alluvial Au workings (Fig. 2b). Elsewhere, tourmaline-bearing auriferous quartz veins are hosted
in the metasediments of the Zuru schist belt (Fig. 2a) along fault zones at Bin Yauri and (Garba,
2000).

**SAMPLING AND PETROGRAPHY**

Samples for zircon geochemistry and U-Pb dating analysis were collected from two
outcrop samples representing unmineralized Pan-African granitoids (sample CR-01 – granite
porphyry) and altered wall rocks near vein 1 (sample KB-01 – altered biotite granite) from the
Libata Sn ore field. Sample locations and representative photographs of analyzed samples are
shown in Fig. 2a-b and Fig. 3a-b, respectively.

Tourmaline-bearing samples were collected from both veins 1 and 2 (Fig. 3c, e). In hand
specimens, tourmaline grains from both the granite-hosted vein (vein 1) and metasedimentary-
hosted vein (vein 2) are distributed in a matrix of quartz and micas (e.g. biotite and muscovite)
(Fig. 3c, e, h). The abundance of mica in vein 2 is higher than in vein 1 where their occurrence is
limited to halos around tourmaline grains. Within both veins, tourmaline forms local grain
aggregates bound by quartz or overgrowths on disrupted fragments of wall rock enclosed in the
vein quartz (Fig. 3b, c, e). Vein 1 tourmalines form euhedral grains that are greenish-brown under
plane-polarized light, ranging from 0.2 to 1 cm in size, disseminated in clusters within the mineral
assemblages of the ore-bearing vein. The metasedimentary-hosted vein 2 tourmalines form euhedral grains with coloration varying from orange-brown to dark green color and dark blue in PPL photomicrographs and range from 0.05 to 1 cm in size (Fig. 3f-h). Tourmaline grains from wall rock sections and quartz-vein hosted tourmaline from granite-hosted vein 1 and metasedimentary-hosted vein 2 are primarily unzoned. However, some grains show pleochroic hue and intensity suggesting zonation (Figs. 3d, 4g-h). In BSE images, tourmaline grains from vein 1 and vein 2 show light to dark zonation bands (Fig. 4a). Photomicrographs from vein 2 show higher occurrence of zoned tourmaline grains in this vein compared to the granite-hosted vein 1 (Fig. 3g-h). In both quartz-vein and wall rock alteration zones, Fe-Ti oxides, which locally contain Sn, occur in highly fractured zones within tourmaline (Fig. 3g-h). The unzoned tourmalines are coexisting or filled with mineral inclusions (e.g. pyrite and zircon) (Fig. 3f, h). Inclusions of these minerals in unzoned tourmalines are relatively free from fractures suggesting coeval deposition of sulfides, cassiterite-bearing phases, and tourmaline (Fig. 3h). Albite primarily occurs in wall rock alteration zones from both vein 1 and 2 suggesting they precipitated during pre-ore metasomatism (Figs. 3b, 3g, 4b). K-feldspar is partly replaced and co-exists with albite along wall rocks in the Libata Sn deposit (Fig. 4a). K-feldspar also crystallizes in fractures between tourmaline in granite wall rock sections from vein 1 in the Libata Sn ore field (Fig. 4b). SEM images show tourmaline-quartz-chlorite assemblages along ore-bearing structures in the Libata Sn deposit (Fig. 4d-e) with wall rock samples from vein 1 showing similar alteration assemblage to those in wall rock samples from vein 2.

RESULTS

Chemical analyses were conducted on tourmalines from the Libata Sn ore field, including tourmaline major and trace element and B isotope analysis. Additionally, zircon U-Pb dating and
Lu-Hf isotopes of zircon from sampled unaltered and altered granites were carried out. Analytical details related to samples and methods can be found in Online Material\(^1\) while the analytical results are described below.

**Zircon morphology and classification**

Zircons separated from both the granite porphyry and the altered biotite granite show variable morphologies and internal textures, as shown by Cathodoluminescence (CL), reflected-, and transmitted light images (Fig. 6a-c). Zircon grains mostly vary from 50 to 300 μm in diameter, with length/width ratios between 1:1 and 1:3 (Fig. 6a-b). Three groups of zircons are delineated in the Libata granites based on morphological and geochemical features: Group 1 zircons are euhedral to anhedral, showing bright grains with concentric oscillatory zoning (Fig. 6a-b). These zircon grains exhibit characteristics of magmatic zircons (Table 1). In contrast, Group 2 zircons are characterized by bright residual cores surrounded by dark, jagged rims, in addition to a few dark prismatic crystals (Fig. 6a-b). Group 3 zircons exhibit heterogeneous zoning patterns showing un-zoned areas, rimmed zones with jagged widths/brightness likely reflective of inherited/detrital zircon grains (Table 1; Fig. 6c). The zircon groups show distinct geochemical signatures based on zircon discrimination plots proposed by Hoskin (2005). Group 1 zircons largely plot in the field of magmatic zircons (MZ), while, Group 2 largely plot in the field of hydrothermal zircons and Group 3 zircon largely plot in the magmatic zircon fields (Fig. 7a-b). Notably, zircon grains that plot outside the field of magmatic zircons fall within fields of both hydrothermal zircons and neocrystallized zircons. We interpret the hydrothermal zircon field as representative of original magmatic zircons that have experienced modification by later hydrothermal fluids to form hydrothermally altered zircons and the neocrystallized zircon field to represent hydrothermal zircon grains that precipitated directly from Zr-saturated hydrothermal fluids, respectively (Geisler et al., 2003; Hoskin, 2005). The zircon grains of the Libata granites are defined by two
morphological types, namely a “100” type crystal face that predominantly occurs in the granite porphyry (sample CR-01) and only sparingly occurs in the altered biotite granite (sample KB-01), and a “110” type that predominantly occurs in the KB-01 sample with minor amounts in the CR-01 sample (Fig. 6a-b). The internal textures of zircons vary greatly in back-scattered electron (BSE), transmitted, and reflected light images. Group 2 zircons from the granite porphyry (CR-01) and altered biotite granite (KB-01) sample exhibit variable CL characteristics with dark and bright colors and spongy internal textures (Fig. 6c). The Group 2, mostly “110”-type zircon grains, are classified as hydrothermally altered zircons (HAZ) based on a combined analysis of zircon CL images, internal textures, and geochemical characteristics of analyzed zircons in the Libata granite (Table 1). In summary, eight grains from granite porphyry and seven grains from altered biotite granites were recognized as HAZ types (Table 1).

Zircon U-Pb geochronology

Results of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U–Pb dating of zircon grains are listed in Table 2. Low concordance (<90%) zircon grains were excluded from the above table and concordia plots.

Magmatic zircon from the granite porphyry (CR-01) sample yield concordant ages of 650 ± 4 Ma (1 s, mean square of weighted deviate, MSWD = 0.74, n=13, Fig. 8a), comparable to weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ age of 650 ± 5 Ma (1 s, MSWD = 2.80, n = 13, Fig. 8a). However, a single grain yields an age of 421 ± 5 Ma, which we interpret as a magmatic grain that has experienced metamictization and slight Pb-loss (Fig. 6c). In contrast, Group 1 magmatic zircons from the altered biotite granites (sample KB-01) yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 650 ± 4 (1 s, MSWD = 1.40, n = 12; Fig. 8c), comparable to weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ age of 650 ± 5 Ma (1 s, MSWD = 1.83, n = 12, Fig. 8c). Two magmatic zircon grains from the altered biotite granite show $^{206}\text{Pb}/^{238}\text{U}$
ages of 867 ± 5 Ma and 963 ± 7 Ma, respectively. We interpret these ages as inherited zircon ages from detrital zircons (Fig. 6c).

Group 2 HAZ grains from the granite porphyry yield concordant ages of 650 ± 6 Ma (1 s, MSWD = 0.87, n = 7, Fig. 8b), comparable to weighted-mean 206Pb/238U age of 650 ± 8 Ma (1 s, MSWD = 2.70, n = 7, Fig. 8b). Contrastingly, group 2 HAZ grains from the altered biotite granite yield 206Pb/238U concordant ages of 650 ± 5 Ma (1 s, MSWD = 3.20, n = 5; Fig. 8d), comparable to weighted-mean 206Pb/238U age of 650 ± 5 Ma (1 s, MSWD = 6.18, n = 5, Fig. 8d).

Zircon trace element compositions

Trace element compositions of zircon from the studied rocks are given in Online Material Table OM1. Trace element concentrations vary significantly between magmatic and hydrothermally altered zircon in the unmineralized and altered granites. In the granite porphyry sample (CR-01), Group 1 (magmatic) zircons are characterized by low P (avg = 340 ppm), Y (avg = 754 ppm), Hf (avg = 9834 ppm), U (147 ppm), and ΣREE (avg = 550 ppm). In contrast, Group 2 hydrothermally altered zircons show higher average P (1211 ppm), Y (850 ppm), Hf (9972 ppm), U (175 ppm), and ΣREE (698 ppm) values. Compared to magmatic zircon, hydrothermal zircon from sample CR-01 shows flat HREE with relatively weak positive Eu anomaly (Eu/Eu* = 0.05–0.07) and positive Ce anomaly (Ce/Ce* = 1.2–46.9; Fig. 8e). Trace element and REE distribution for both magmatic and hydrothermally altered zircons from the altered biotite granites also show moderate variation trends. HAZ grains in the altered biotite granites are characterized by high values of Y (467–1351 ppm, average = 776 ppm), Hf (8250–10086 ppm, average = 9325 ppm), P (443–3632 ppm, average = 1299 ppm), and ΣREE (428–944 ppm, average = 650 ppm). Corresponding values from MZ in the altered biotite granites are markedly lower (P = 101–426 ppm, average = 237 ppm; Y = 283–2274 ppm, average = 737 ppm; Hf = 7360–10045 ppm, average = 237 ppm).
However, they exhibit negative Eu anomaly (Eu/Eu* = 0.06–0.54) with weakly positive Ce anomaly (Ce/Ce* = 1.3–2.9; Fig. 8f).

Zircon Lu-Hf isotopes

Twenty-four representative zircon spots were selected for Hf isotopic analysis (Table 3). MZ from the unmineralized granite porphyry (sample CR-01) show a narrow range of εHf(t) (+4.4 to +5.6), $^{176}$Lu/$^{177}$Hf (0.000610–0.000756), $^{176}$Yb/$^{177}$Hf (0.025232–0.032046), and variable $^{176}$Hf/$^{177}$Hf (0.282494–0.282534) values. On the other hand, HAZ grains from the Libata granite porphyry show overlapping εHf(t) (+4.5 to +6.2) and $^{176}$Hf/$^{177}$Hf (0.282502–0.282545) but higher $^{176}$Lu/$^{177}$Hf (0.000573–0.001012) and $^{176}$Yb/$^{177}$Hf (0.023931–0.044225) values. Calculated two-stage Hf model ages for the granite porphyry show Mesoproterozoic crustal Model ages ($T_{DMC}^C = 1311$ to 1200 Ma) (Table 3). MZ in the altered biotite granite also show variable Lu-Hf-Yb isotopic ratios, namely $^{176}$Hf/$^{177}$Hf (0.282521–0.282591), $^{176}$Lu/$^{177}$Hf (0.000554–0.000927), $^{176}$Yb/$^{177}$Hf (0.019038–0.039216), and εHf (t) values of +5.2 to +7.9. Comparatively, HAZ grains from the altered biotite granite show higher εHf (t) (+6.3 to +10.9), $^{176}$Lu/$^{177}$Hf (0.000657–0.001227), $^{176}$Yb/$^{177}$Hf (0.028083–0.054186) but variable $^{176}$Hf/$^{177}$Hf (0.282544–0.282676). Calculated two-stage Hf model ages for the altered biotite granite show Mesoproterozoic to Neoproterozoic crustal model ages ($T_{DMC}^C = 1254$ to 900 Ma) (Table 3). Two crystals (one metamict and one inherited magmatic) from our samples are characterized by variable $^{176}$Hf/$^{177}$Hf ratios (0.281972–0.282529) and yielding outliers of εHf (t) (−7.5 to +0.5) and $T_{DMC}^C$ (1378–2293 Ma). Due to the standard $f$/Lu/Hf values (<−0.9), obtained from analyzed zircon grains in this study, calculated Hf $T_{DMC}^C$ modal ages are considered reliable estimates of crustal residence times (Wang et al., 2016).

Tourmaline EPMA data

Tourmalines from the veins 1 and 2 in the Libata Sn ore field exhibit similar major elemental compositions (Online Material Table OM1). They have variable F (0.03–0.49 wt%),
CaO (0.10–1.28 wt%) and MgO (1.85–4.62 wt%), high SiO$_2$ (34.36–36.48 wt%), Al$_2$O$_3$ (29.93–33.40 wt%), FeO (11.03–13.95 wt%), and TiO$_2$ (0.36–1.01 wt%), as well as low MnO (0.15–0.81 wt%). Based on the X-site occupancy and according to the classification of Henry et al. (2011), the tourmalines from both veins belong to the alkali group (Fig. 9a). The tourmalines display a large variation in Mg/(Mg + Fe) ratios from 0.2 to 0.4, with all the tourmaline samples showing schorl compositions (Fig. 9b). The tourmalines also shows high total Al (6.0-6.5 apfu), moderate excess Al in octahedral Y-sites (up to 0.5 apfu), moderate F contents (up to 0.3 apfu) and variable X-site vacancy content (0.2 to 0.4 apfu) whereby the Na cation is dominant in the X-site (0.6–0.7; Online Material Table OM1). The tourmalines from vein 1 and 2 plot in the field of Li-poor granitoids, pegmatites, and aplites (Fig. 9b) based on discrimination plots of Al-Fe-Mg (Henry and Guidotti, 1985).

**In situ tourmaline trace elements**

Trace element compositions of tourmaline from the Libata Sn-W deposit are given in Online Material Table OM2. Tourmaline is overall characterized by low concentrations (< 0.1–10 ppm) of Co, Ni, Cu, Rb, Y, REE, Zr, Nb, Mo, Cs, Ba, Ta, W, Pb, Bi, Th, and U, moderate concentrations (10 s to 100 ppm) of Be, Sc, and Sr, and high concentrations (100s ppm to >1000 ppm) of Li, Sn, Ga, V, and Zn (Online Material Table OM2). Multi-element normalized to average continental crust values from Rudnick and Gao (2003) (Fig. 9c) show only a few elements reach concentration levels at or above those of the average crust (Sn, Zn, Li, Ta, V, Co, Ni, and Sc) (Fig. 9c). Chondrite-normalized REE plots (Fig. 9d) overall also show low concentrations and a high variability of REE distribution from the Libata tourmaline. Overall, the vein 1 tourmalines show higher total REE values (avg = 11.4 ppm, standard deviation (Stdev): 5) than those from vein 2 (avg = 9.8 ppm, Stdev = 4) (Online Material Table OM2). The tourmalines from veins 1 and 2...
show a negative sloping pattern from light through middle REE concentrations to a slightly
positive sloping pattern towards the heavy REE segment, and a weakly positive Eu anomaly on
chondrite-normalized REE plots (Fig. 9d).

To identify trace element correlations in our dataset, we applied principal component
analysis (PCA), a multivariate statistical technique that provides dimensionality-reduction of
correlated variables into a reduced set of orthogonal linear combinations. This technique is
particularly useful for analyzing large geochemical datasets including LA-ICP-MS trace element
data, maximizing variance, and minimizing information loss (Winderbaum et al., 2012; Harlaux
et al., 2019; Codeço et al., 2021). PCA was applied on log-transformed LA-ICP-MS trace element
data from the Libata tourmaline (n = 49 spots). 15 variables were selected for the PCA including
the main trace elements (Li, Sc, V, Cr, Co, Ni, Zn, Ga, Ge, Sr, Nb, In, Sn, Pb, and Ta). Elements
with very low concentrations (< 1 ppm) or below the limits of detection were excluded. Results of
the two-dimensional projection of the two first principal components (PC1 vs. PC2), showing the
statistical correlations between the investigated variables on a correlation circle is given in Fig. 9e-
f. For the Libata tourmalines, four main groups of element correlation clusters are discriminated
by the PCA. Group 1 comprised of Co, Ga, Ni, Cr, Sc, and In characterizes the higher
concentrations in vein 1 tourmalines (Fig. 9f; Online Material\textsuperscript{3} Table OM2). Group 2 composed
of Li and Zn shows the variability of vein 2 tourmalines. Overlapping concentrations in Group 3
and 4 (Nb-Ta and Sc-V) precludes the discrimination of distinct clusters. Some elements (i.e. Sn,
Ge, In, and Pb) plot individually, without correlations between each other. Trace elements show
overlapping concentrations between the core and rim from vein 1 and 2 and therefore preclude the
discrimination of distinct clusters (Online Material\textsuperscript{3} Table OM2).
**Boron isotopes**

The LA–MC–ICP-MS boron isotopic data of tourmalines from our study are available in Online Material\(^3\) Table OM3 and illustrated in Fig. 10. The vein 1-type tourmalines show a narrow range of \(\delta^{11}\text{B} \) values between \(-15.7 \pm 0.4\%o\) and \(-14.4 \pm 0.5\%o\), with a weighted mean value of \(-15.0 \pm 0.2\%o\) (\(n = 27, \text{MSWD} = 0.48\)) (Fig. 10a). Cores from zoned tourmaline grains from vein 1 show higher \(\delta^{11}\text{B} \) values compared to the rims (Online Material\(^3\) Table OM3). The vein 2 tourmalines show markedly higher \(\delta^{11}\text{B} \) values than the vein 1 type, ranging from \(-15.1 \pm 0.4\%o\) and \(-14.1 \pm 0.3\%o\), with a weighted mean value of \(-14.6 \pm 0.1\%o\) (\(n = 42, \text{MSWD} = 0.49\)) (Fig. 10a). Within sample variations between core and rim in zoned tourmaline from vein 2 are typically \(<1\%o\) (Fig. 4a) with cores showing higher average in \(\delta^{11}\text{B} \) values compared to rims (Online Material\(^3\) Table OM3).

**DISCUSSION**

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

To track the degree of alteration between Group 1 and Group 2 zircons in the Libata ore field, we applied the discrimination indices (LREE-I = Dy/Nd + Dy/Sm) proposed by Bell et al. (2019). Magmatic zircons from the granite porphyry and altered biotite granite display higher LREE-I values (sample CR-01: 4.3–95.8, average = 56.8, \(n = 15\); sample KB-01: 23.9–81.5, average = 50.1, \(n = 14\)) than corresponding HAZs (CR01: 3.3–82.6, average = 27.1, \(n = 8\); sample KB-01: 3.7–30.4, average = 21.3, \(n = 7\)) from the studied samples (Fig. 7c-d). The low LREE-I values (Online Material\(^2\) Table OM1) in the HAZ grains along with the textural alteration is indicative of post-magmatic modification from fluid-zircon interactions (Bell et al., 2019). Generally, trace and minor (Hf, U, Y Th, LREE, etc.) element concentrations in HAZs are markedly higher than values in magmatic zircons (Hoskin, 2005; Li et al., 2014). Due to the higher
mobility of LREEs relative to HREEs in hydrothermal phases, LREEs are preferentially incorporated into hydrothermally altered, metamict and hydrothermal zircon grains (Sheard et al., 2012). In the Libata granites, hydrothermally altered zircons are enriched in LREE and ΣREE when compared to magmatic zircons (Figs. 7e-f; 8e-f).

Titanium-in-zircon thermometry (Ferry and Watson, 2007) has been recognized as a reliable indicator for zircon crystallization and host magma temperatures (Schiller and Finger, 2019; Vincent et al., 2021). However, the reliability of the Ti-in-zircon temperatures is dependent on the preservation of Ti concentrations in zircon, which may become perturbed during highly mobile phases that form HAZ (Fu et al., 2008; Bloch et al., 2022). For the Libata granites, the application of Ti-in-zircon geothermometry to delineate crystallization temperatures of the hydrothermal zircon grains is not feasible due to the markedly high Ti concentrations in neocrystallized and HAZ (Online Material Table OM1). However, the crystallization temperatures can be derived from zircon morphology due to the large dependence of prism shapes on crystallization temperatures (Pupin, 1980; Dill et al., 2012). High crystallization temperatures (>800 °C) favor the growth of “100” type prisms whereas moderate to low temperatures (<700 °C) favor the development of “110” type prisms (Hayashi and Shinno, 1990). For the Libata granites, most magmatic zircons show “100” prisms, while hydrothermal zircons generally exhibit “110” prisms (Fig. 6a-b). Zircon morphology combined with Ti-in-zircon geothermometry from magmatic zircons in the granite porphyry (avg. 761 ± 11 °C) and altered biotite granites (avg. 717 ± 12 °C) samples confirm high initial crystallization temperatures (>700 °C) for the Libata granites. The dominance of “110” prisms in hydrothermal zircons from the Libata ore field likely reflects zircon metamictization in these grains. The presence of these “110” prisms also point to a shift towards late-stage magmatic-hydrothermal conditions since metamict zircons are typically
crystallized from highly evolved late residual melt (Kozlik et al., 2016). Their late-stage origin and typical “110” form suggests relatively low closure temperatures (<650 °C) for the hydrothermal zircons (Fig. 6a-b) in the Libata granites (Jiang et al., 2019a).

**Timing of magmatic-hydrothermal activities in the Libata ore field**

The zircon U-Pb ages from our study allow for precise timing of magmatic activity in the Libata Sn deposit and its implication for the magmatic-hydrothermal episodes in the Libata ore field. Zircon U-Pb ages for Libata granites cluster around ~650 Ma (Table 1). Group 1 magmatic zircons from the Libata granite porphyry and altered biotite granite yield U–Pb concordant ages of 650 ± 4 (1 s, MSWD = 0.74, n = 13), and 650 ± 4 Ma (1 s, MSWD = 1.40, n = 12), respectively (Fig. 8a, c). The zircon U-Pb ages from the Libata granites (650 Ma) confirm their emplacement during the peak of the Pan-African orogenic episode in western Nigerian terrain (Bute et al., 2019; Ferré et al., 1996). Our zircon U-Pb ages are markedly similar to ages (642 ± 6 Ma) obtained from quartz potassic syenites from southwestern Nigeria (Adetunji et al., 2016). They also overlap U-Pb ages from other Pan-African suites (580-751 Ma) from the eastern and western terrain of the Nigerian basement (Ferré et al., 1996; Ferré et al., 1998).

The utility of LA-ICP-MS U-Pb dating of hydrothermal zircons to constrain timing of hydrothermal episodes have been demonstrated for Pb-Zn-Cu (Vincent et al., 2021), Au (Bao et al., 2014), and Sn–W deposits (Jiang et al., 2019a; Jiang et al., 2019b). In the Libata ore field, Group 2 HAZs in sample CR-01 and Sample KB-01 yield ages of 650 ± 6 Ma (1 s, MSWD = 0.87, n = 7) and 650 ± 5 Ma (1 s, MSWD = 3.20, n = 5), respectively (Fig. 8b, d). In this study, the concordant ages from HAZs in both the Libata granite porphries and altered biotite granite (650 Ma) suggests they were modified immediately after the crystallization of the host granite intrusions.
Source of melts and ore-forming materials for the Libata Sn deposit

Trace element and Hf isotope variation are suitable tracers of distinct magma sources and melt evolutionary history in magmatic rocks (Kemp et al., 2005). Consequently, we apply discrimination ratios based on magmatic zircon trace element chemistry to constrain source(s) and evolution of the Libata granitoids. Zircon U/Yb vs. Yb (Fig. 11a) show that samples from the Libata ore field mostly fall in the continental zircon field and suggest a continental origin for the Libata granitoids (Grimes et al., 2007). Furthermore, zircon U/Yb vs. Nb/Yb discrimination plots (Fig. 11b) imply a continental arc-related tectonic regime for the Libata intrusions and suggests granite emplacement in a continental margin. Applying our zircon Lu-Hf isotope data, the Libata granites show high positive εHf (t) (+4.4 to +10.6, average, = +6.4; Table 3) values. These values are higher than εHf (t) signatures from inherited zircons in the Libata granites (εHf (t) = -7.6) and other granitoids in the Benino-Nigerian shield within the range of 656–610 Ma yielding negative εHf(t) (−27.1 to −6.4) (Ganade et al., 2016). Our εHf(t) values are below depleted mantle values (Fig. 12a; Table 3) showing positive εHf(t) values which rule out anataxis of local crustal rocks and reflective of source rocks derived from a mantle source. Calculated Hf model ages for the Libata granites (0.8–1.3 Ga) are lower than the values from other 656–610 Ma granites from the Benino-Nigerian shield (1.5–3.4 Ga) suggesting, limited contamination of the primary mantle melts with crustal material.

Lu–Hf isotopic compositions of hydrothermal zircons are distinct from signatures in magmatic zircons and provide a viable tool for tracking fluid sources and evolutionary processes in magmatic-hydrothermal systems (Li et al., 2018). The $^{176}$Hf/$^{177}$Hf ratios are similar in the magmatic and hydrothermally altered zircons from the Libata granitoids (Table 3), indicating the preservation of the Hf isotopic system in zircon (Lenting et al., 2010). However, $^{176}$Lu/$^{177}$Hf (up to 0.0012) and $^{176}$Yb/$^{177}$Hf (up to 0.055) ratios are markedly higher in HAZ compared to MZ from...
the Libata granites (Fig. 12c-d) explained by higher mobility of Lu and Yb during hydrothermal phases associated with zircon alteration (Lenting et al., 2010). The similar and broadly overlapping εHf (t) values for magmatic and hydrothermally altered zircon grains from the Libata orefield (Table 3) suggest that the mineralizing fluids were likely sourced from the granitic magmas.

The δ^{11}B values in tourmaline from the ore bearing veins in the Libata Sn ore field range from −15.7 ‰ to −14.7 ‰ (Fig. 10a-b). Vein 1 tourmalines have δ^{11}B values of −15.7 to −14.4 ‰ (average = −15.0 ‰), whilst vein 2 tourmalines show δ^{11}B values of −15.1 to −14.1 ‰ (average = −14.6 ‰). Due to limited fluid inclusion data from the Libata Sn deposit, we infer temperature conditions of the primary hydrothermal fluids to derive fluid-tourmaline equilibrium temperatures. Assuming crystallization temperatures of 400 to 500 °C, equilibrium fluid-tourmaline fractionation at 500 °C and 400 °C are +1.9‰ and +2.7‰, respectively (Meyer et al., 2008). This suggests that the δ^{11}B values of the fluids in isotopic equilibrium were −13.1 to −12.3‰ for the vein 1 tourmalines and −12.7 to −11.9‰ for the vein 2 tourmalines. The emplacement of vein 1 firmly within the Libata granites suggests derivation of boron predominantly from magmatic fluids exsolved from granitic melts. To test for a granitic fluid source, we estimate the isotopic compositions of a granitic melt that produces a magmatic fluid with a δ^{11}B of −12.3 to −13.1‰ for the granite-hosted vein 1. At temperatures of 650 °C estimated for the hydrous F-rich granitic melt and assuming 50:50 proportion of trigonal-tetrahedral coordination of boron in the melt (Trumbull et al., 2013), a B-isotope fractionation factors of 5‰ between granitic melt and fluid is calculated from molecular dynamics (Kowalski et al., 2013). This would imply δ^{11}B values of −17.3 to −18.1‰ for the hypothetical granitic source, which falls in the range of values from granites (Trumbull et al., 2020). For the metasedimentary-hosted vein 2, the markedly similar trace element (Fig. 9a-d) and close overlap in boron isotopic values (Fig. 10b) with tourmalines from
the granite-hosted vein 1 suggests ore materials/fluids in vein 2 were sourced from either the same
source as the granite-hosted vein 1 or from shallow magmatic bodies. The difference between δ11B
compositions from veins 1 and 2 (Fig. 10a) may reflect differential temperature change between
both veins at constant fluid composition, differing δ11B compositions for zoned rims and cores
from vein 2 or depletion in δ11B during vein fluid vs. wall rock interaction in vein 2.

To investigate fluid sources for Sn mineralization in the Libata ore field, we used major
and trace element ratios in tourmaline to track source compositions for the hydrothermal fluids
that precipitated the Libata tourmalines. The Li/Sr ratio provides a good separator for delineating
tourmaline from magmatic vs metamorphic fluid origin (Harlaux et al., 2020). Compared to other
tourmalines hosted in granite and metamorphic rocks (e.g. amphibolites and granite gneiss),
tourmalines from the Libata ore field fall in the compositional field of magmatic tourmaline based
on Li/Sr discrimination plots (Fig. 13a-b) and are in agreement with tourmaline major element
compositions that fall into the field of Li-poor granitoids in the Ca-Fe-Mg diagram (Fig. 8b). The
composition of the Fe-rich schorls from the Libata Sn ore field are in agreement with tourmaline
compositions from most granitic rocks and magmatic-hydrothermal environments (Pirajno and
Smithies, 1992). Our results are chemically distinct from the schorl-dravite tourmalines from the
Bin-Yauri gold deposit whose origin has been proposed to be from metasedimentary sources
(Garba, 1996). This would suggest that the tourmaline from the Libata Sn veins largely formed
from magmatic fluids. Accordingly, our data suggests derivation of boron in the Libata ore field
was dominantly from magmatic fluids although we do not rule out some contribution from the
metasedimentary rocks in the area.

Magmatic-hydrothermal evolution in the Libata Sn mineralizations

The utility of HAZs as tracers of the nature and chemical compositions of hydrothermal
fluids associated with ore deposits have been widely recognized (Kozlik et al., 2016; Jiang et al.,
2019b; Vincent et al., 2021). Experimental studies and natural observations have highlighted the increased mobility of incompatible elements such as Hf, Th, U, Nb, Ta, Y, P, Sn and Pb in the presence of volatiles (e.g. B, F, Cl, and H₂O) (Bau, 1996; Jiang et al., 2020). These highly mobile fluid-vapor phases are important in alkali-rich granitic systems (Girei et al., 2019; Girei et al., 2020; Vincent et al., 2021) as well as in B-rich hydrothermal systems (Lehmann, 2020). The high F concentrations in tourmaline (up to 0.5 wt.%, determined with EPMA) suggest the late-stage volatile-rich fluids exsolved from the Libata granites were able to carry incompatible elements and exchange them with Si and Zr from magmatic and metamict zircons through diffusion-controlled alteration processes that formed HAZs in the Libata granites. Therefore, the hydrothermal fluids that interacted with these zircons were likely highly enriched in U, Th, F, Y, REE, Nb, Ta, Hf, Fe, and Ca and moderately enriched in P, Sn, Sc, Pb, and Ti. The Libata HAZs show coupled correlation trends between U + Nb + Ta and Y + ∑REE (Fig. 14a) suggesting that many trace elements have been incorporated into these zircons. Th/U ratios of HAZ in the Libata granites vary between 0.4 and 0.7 (average = 0.5) and are markedly lower than those of MZ (Fig. 14b). The shift in Th/U values from magmatic to HAZ is typical for ore deposits and a crucial marker for delineating hydrothermal zircons (Li et al., 2014). To further track magmatic to hydrothermal trends in the zircons from the Libata granites, we assessed geochemical ratios (e.g. Y/Ho and Yb/Gd) that show stable behaviors in primary or anhydrous melts but vary in evolved melts that are enriched in volatiles and halogens. Other studies have highlighted the stability of Y/Ho in primary melts where they retain ratios close to chondritic values (Bau, 1996). However, these ratios show large variations in evolved granitic systems due to increased mobility and behavior of Y, Zr, Hf, and REEs during volatile-driven mobility (Bau, 1996). HAZ from our studied samples mostly show elevated Y/Ho values (>28; Fig. 14c) due to complexation with halogen-rich phases.
with a negative correlation between Y content and Y/Ho ratio present for the magmatic zircon
grains (Jiang et al., 2019a). Differentiation trends for the Libata granites are also traced by Yb/Gd
against Eu/Eu* values (Fig. 14d). Progressive oxidization conditions along with increased
fractionation during magmatic evolution suggests that the altered biotite granites are more evolved
than the granite porphyries of the Libata ore field (Lu et al., 2019). Furthermore, this trend also
differentiates barren from fertile granite suites with the altered biotite granites largely plotting
above the field synonymous with mineralized granites (Fig. 14d).

Geochemical (major and trace element) composition of tourmaline have been widely
recognized as reliable monitor of formation environment and conditions (Dutrow and Henry, 2011).
Moreover, these geochemical signatures have been used extensively to trace evolution in
magmatic-hydrothermal systems (Jiang et al., 2004; Yang et al., 2015; Codeço et al., 2020;
Harlaux et al., 2020). Compositions of tourmalines from Libata, plotting mostly in the schorl field
(Fig. 9b), with low Na contents (average 0.6 apfu) and high X-site vacancies (average 0.3 apfu),
suggesting precipitation from a low-salinity fluid (von Goerne et al., 2001; von Goerne et al., 2011).
Assuming a temperature of 500 °C, a salinity of ca. 3 wt% NaCl eq is estimated for the fluid in
equilibrium with the assemblage tourmaline + quartz + chlorite (von Goerne et al., 2001). REE
patterns of tourmaline generally reflect both the REE composition of the host rock or source as
well as the effects of fluid-rock interactions (Yang et al., 2015; Duchoslav et al., 2017; Hong et al.,
2017). Tourmalines from the Libata ore field show higher concentrations of LREEs relative to
HREEs (Fig. 9d) similar to trends seen in tourmalines from other magmatic-hydrothermal ore
systems (Marks et al., 2013; Yang et al., 2015). This enrichment trend matches REE patterns in
hydrothermal zircons in the Libata granites (Fig. 8e-f) suggesting that the volatile-rich late-stage
fluids responsible for the precipitation of the hydrothermal zircon and tourmaline in the Libata
orefield were enriched in LREEs relative to HREEs. Tourmaline from both ore-bearing veins in the Libata ore field have relatively high Sn (>100 ppm avg) contents (Fig. 13c-d). A coupled increase in Fe and Sn contents have been reported from tourmalines associated with cassiterite mineralization (Harlaux et al., 2020). In both veins 1 and 2, the high contents of Fe (13 wt % avg) and Sn (100 ppm avg.) are notable (Online Material\textsuperscript{3} Table OM1 and Online Material\textsuperscript{3} Table OM2). These high concentrations suggest that hydrothermal fluids precipitating tourmaline in the Libata ore field were rich in Fe and Sn primarily transported as chloride complexes under moderate to high temperature phases (Taylor and Wall, 1993; Schmidt, 2018). In granitic rocks, mica group minerals (e.g., biotite) are important hosts of Sn with concentrations ranging from 10s to 100s parts per million (López-Moro et al., 2017). Mineralizing fluids in Sn ore systems may become enriched in tin through the breakdown of biotite during chloritization processes (Harlaux et al., 2020). Elevated vanadium concentrations and the high V/Sc ratios suggest that the hydrothermal fluid precipitating the tourmalines was rich in vanadium. This enrichment is likely linked to metal release during biotite chloritization, as biotite is a major host of vanadium (Viswanathan et al., 2012). Therefore, biotite alteration seen in the Libata granites (Fig. 4c-d) due to chloritization likely triggered the coupled release of tin and vanadium into the mineralizing fluids, which then substituted into the crystal lattice of tourmaline during precipitation of hydrothermal tourmalines in the Libata orefield. Experimental and thermodynamic data support the transport of high concentrations of tin (100s to 1000s) likely as Sn\textsuperscript{4+}–Cl complexes in hydrothermal fluids (Heinrich, 1990; Schmidt, 2018).

Due to their robust ability to retain geochemical signatures from several petrogenetic processes, tourmaline has been found to be a potential pathfinder mineral for tin deposits (Fogliata et al., 2012). Elevated trace element concentrations (typically >10s to 100s ppm) of Li, V, Ga, Zn,
and Sn in tourmaline grains from the Libata ore field are typical for tourmaline from granite-related tin deposits (Duchoslav et al., 2017; Codeço et al., 2021). Our data suggests that the high Sn, Zn, and Li concentration in tourmaline from the Libata ore field can be regarded as ‘indicators’ of cassiterite mineralization. Accordingly, tracer signatures from tourmaline + chlorite + quartz alteration assemblages associated with cassiterite-wolframite-niobium mineralization in the Pan-African granites may serve as valuable indicators for other granite-associated vein-type deposits in adjacent areas.

**IMPLICATIONS FOR ORE GENESIS**

1. Our study constrains overlapping magmatic (~650 Ma) and magmatic-hydrothermal (~650 Ma) events from the Libata granite porphyry and altered biotite granite porphyry. Our ages are consistent with magmatic-mineralogenic events at the peak of the Pan African orogeny and expands the known temporal range of granite-related Sn mineralization in the basement complex of Nigeria.

2. The abundance of metamict and hydrothermally-altered zircons hosted in the granites adjoining Libata vein 1 and their components suggests that the hydrothermal fluids derived from the granites likely contributed the ore forming fluids associated with Sn mineralization. The fluids were enriched in volatile phases (F, Cl, and H₂O) as well as numerous trace elements such as U, Y, Nb, Ta, Hf, P, and Ti.

3. Trace element chemistry and B isotopes from both the granite- and metasedimentary-hosted Sn-Tur veins suggests a common source for ore metals, boron and hydrothermal fluids forming both veins. Our data point to magmatic-hydrothermal fluids derived from the Libata granites as the source for ore materials forming the Libata deposit.
ACKNOWLEDGEMENTS

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**Figure Captions**

**Fig. 1.** Geological sketch map showing (a) generalized map of Africa showing the distribution of rare-metal granites and rare metal-bearing pegmatites. (b) Nigeria showing distribution of Pan-African granites, schist belts, and established NE-SW trending Sn-W bearing pegmatites. The Raghane shear zone is a potential suture zone marking the boundary between Eastern Nigeria Terrane (ENT) and Western Nigeria Terrane (WNT) adopted from Ferré et al. (1998).

**Fig. 2.** Geological map of (a) the Bin Yauri-Libata area showing the distribution of Au and Sn mineralizations, and (b) the Libata Sn ore field showing the distribution of ore-bearing lodes.
**Fig. 3.** Photographs showing hand specimens and photomicrographs (PPL) of (a) deformed granite porphyry; (b) altered biotite granite wall rock sample from vein 1; (c) hand specimen photomicrograph of quartz vein-hosted hydrothermal tourmaline from Libata vein 1; (d) wall rock from the granite-hosted vein 1 showing the occurrence of unzoned and zoned tourmaline; (e) quartz vein-hosted hydrothermal tourmaline from Libata vein 2 and (f) tourmaline and zircon from wall rock sections at the Libata vein 2; (g) section from quartz vein at Libata vein 2 and (h) wall rock alteration zone from Libata vein 2. Abbreviation: Ab, albite; Fe-Ti oxides, iron-titanite oxides; Kfs, K-feldspar; Ms, muscovite; Plg, plagioclase; Py, pyrite; Qtz, quartz; Tur, tourmaline; Zr, zircon.

**Fig. 4.** (a) Selected BSE-images of analyzed sections from veins 1 and 2 in the Libata ore field. SEM micrographs of the bulk ore showing distinct morphologies of (b) albite grains occurring with K-feldspar and quartz from wall rocks near vein 1; (c) tourmaline from vein 2 with later-stage K-feldspar; (d) tourmaline-chlorite occurrence seen in vein 1; (e) chlorite-tourmaline-quartz assemblage from Libata vein 1. Abbreviation: Ab, albite; Chl, chlorite; Kfs, K-feldspar; Tur, tourmaline; Qtz, quartz.

**Fig. 5.** Simplified paragenesis for the Libata Sn mineralizations. The thickness of the horizontal lines indicates the abundance of the mineral species.

**Fig. 6.** Selected CL-images of analyzed zircon grains from the (a) granite porphyry (CR-01) and (b) altered biotite granite (KB-01). (c) Representative transmitted and reflected light images of zircons, showing the distribution of fluid/mineral inclusions in the granite porphyry and altered biotite granite samples.
Fig. 7. Magmatic-hydrothermal zircon discrimination plots of (a) SmN/LaN vs. Ce/\textit{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) $\Sigma$REE vs. $\Sigma$LREE; and (f) $\Sigma$REE vs. Eu/Eu* values in zircon grains from the Libata Sn mineralization. Magmatic and hydrothermal fields are from Hoskin (2005).

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).

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).
Fig. 10. Frequency histogram of boron isotopic compositions of the (a) vein 1 tourmaline and vein 2 tourmaline at Libata. (b) $\delta^{11}$B values of the tourmaline in the Libata Sn deposit. The $\delta^{11}$B data for boron reservoirs are cited from Marschall and Jiang (2011). $\delta^{11}$B data for deposits are from Ludwig et al. (2011); Codeço et al. (2017); Zhang et al. (2018); Trumbull et al. (2019) and Trumbull et al. (2020).

Fig. 11. Magmatic zircon geochemical diagrams for the Libata granites: (a) U/Yb vs. Yb, after Grimes et al. (2007) and (b) $\log_{10}(U/Yb)$ vs $\log_{10}(Nb/Yb)$ after Grimes et al. (2015).

Fig. 12. Hafnium isotopic signatures of different types of zircons (a) age vs. $\varepsilon$Hf(t) scattered diagram for different zircons and neighboring deposits; (b) a limited age between 600 and 670 Ma 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 Archean basement complex rocks of Western Nigeria and West Africa are from Dickin et al. (1991), Ganade et al. (2016) and Petersson et al. (2018). Hf isotope values from the Benin-Nigeria shield are from Ganade et al. (2016) and Petersson et al. (2018), values for the Hawal Massif are from Bute et al. (2019), and values for the Brasilliano-Pan African orogeny are from Ganade et al. (2014).

Fig. 13. (a-b) Source discrimination plots for the Libata tourmalines based on Li/Sr ratio as compared to compositions of worldwide tourmaline hosted in granites and metamorphic rocks. Variation diagrams of selected trace elements in tourmaline from the Libata Sn ore field. (c) Sn vs. Co/La; (d) Sn vs. Zn/Nb. Data for Cornwall granites are from Duchoslav et al. (2017); Puy-les-Vigness gneisses are from Harlaux et al. (2019); Hutti amphibolites are from Hazarika et al. (2015);
Dachang granite-hosted Sn deposit are from Zhao et al. (2021b) and Baishaziling granite-hosted Sn deposit are from Zhao et al. (2022). Field for tourmaline hosted in granites, metasediments and metavolcanic rocks is from Harlaux et al. (2019). Field for tourmaline hosted in barren vs mineralized granite from Hong et al. (2017).

**Fig. 14.** Scatter diagrams of zircon LA-ICP-MS results (ppm). (a) Y + ΣREE vs. U + Nb + Ta; (b) Y + ΣREE vs. Th/U; (c) Y/Ho vs. Y.; and (d) Eu/Eu* vs. Yb/Gd. C1-Chondritic value of Y/Ho = 28 in (c) from Bau (1996). Dashed line at Eu/Eu* represent demarcation of field of fertile and barren granites. Values for fertile and infertile Phanerozoic granites are from Lu et al. (2019).

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

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

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

**Online Material Caption**
Online Material1 Description of analytical methods

Online Material2 Table OM1 Zircon trace element compositions of the Libata granites

Online Material3 Table OM1 Major element compositions from tourmalines in the Libata tin ore district.

Online Material3 Table OM2 Trace element compositions from tourmalines in the Libata tin ore district.
Online Material 3 Table OM3 LA-ICP-MS Boron isotope analysis from the Libata Sn-W ore field.

Online Material 4 Table OM1 Zircon U-Pb data for standard samples GJ-1 and PLE.

Online Material 4 Table OM2 Zircon trace element data for standard samples GJ-1 and PLE.

Online Material 4 Table OM3 Trace element analytical results of standard sample BCR-2G, BIR-1G and BVHO-2G.

Supplementary Figure captions

Supplementary Figure 1. Zircon U-Pb concordia for standard zircon samples GJ-1 and the Plesovice (PLE).
Figure 1
Figure 4
Figure 5

Paragenesis:

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

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<td>100-150 μm</td>
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<td>Subhedral &amp; anhedral</td>
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<td>Dominant {110} prism face</td>
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<td>High intensity</td>
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<td>Variable with zoned and unzoned grains</td>
<td>Variable with zoned and unzoned grains</td>
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<td>Mostly ancient magmatic melt (distinct zircon ages)</td>
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Table 2. LA-ICP-MS Zircon U-Pb data for the studied granites.

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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

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Note:
MZ = Magmatic zircon.
MTZ = Metamict zircon
HAZ = Hydrothermally-altered zircon.
IZ = Inherited zircon