

# GEOGRAPHIC ORIGIN DETERMINATION OF PARAÍBA TOURMALINE

Yusuke Katsurada, Ziyin Sun, Christopher M. Breeding, and Barbara L. Dutrow

Vivid blue to green copper-bearing tourmalines, known as Paraíba tourmalines, are recovered from deposits in Brazil, Nigeria, and Mozambique. These tourmalines are sought after for their intense colors. Prices are based, in part, on the geographic origin of a stone, and determining provenance is thus an important aspect for Paraíba tourmaline. However, their geographic origin cannot be established by standard gemological testing and/or qualitative chemical analyses. GIA has established sophisticated criteria requiring quantitative chemical analyses to determine geographic origin for these tourmalines. These criteria were based on several hundred samples from known sources spanning the three countries. Highly accurate and precise quantitative elemental concentrations for Cu, Zn, Ga, Sr, Sn, and Pb are acquired with laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). These data can then be plotted as a function of elemental concentration for accurate geographic origin determination.

Copper-bearing gem tourmaline—recognizable by its vivid neon blue to green color—has been one of the most popular colored gemstones on the market for the nearly three decades since its debut (figures 1 and 2). It was first discovered in the state of Paraíba in northeastern Brazil in the late 1980s, and subsequently found in the neighboring state of Rio Grande do Norte (Fritsch et al., 1990; Shigley et al., 2001; Furuya, 2007). These gems became known as Paraíba tourmalines after the locality of their discovery. In the early twenty-first century, similarly colored gem-quality tourmalines were discovered in Nigeria and Mozambique (figures 3 and 4; Smith et al., 2001; Abduriyim and Kitawaki, 2005).

In the gem market, Brazilian Paraíba tourmalines are typically more highly valued than their African counterparts. While top-quality Brazilian Paraíba tourmalines tend to have more intense color, there is significant overlap in the color range for all localities. Additionally, standard gemological tests cannot definitively separate stones from these three locali-

ties. As a result, there is market demand for gemological laboratories to offer origin determination for copper-bearing tourmalines.

The most recent Laboratory Manual Harmonisation Committee (LMHC) definition of “Paraíba” tourmaline is “a blue (electric blue, neon blue, violet blue), bluish green to greenish blue, green (or yellowish green) tourmaline, of medium-light to high saturation and tone (relative to this variety of tour-

## In Brief

- Geographic origin can have a significant impact on the value of Paraíba tourmaline.
- Quantitative chemical analysis with LA-ICP-MS provides a robust tool for origin determination.
- The trace elements Cu, Zn, Ga, Sr, Sn, and Pb are the most useful discriminators for Paraíba tourmaline origin.
- In limited cases where there are no matching reference data, an “inconclusive” origin determination would be required.

maline), mainly due to the presence of copper (Cu) and manganese (Mn) of whatever geographical origin” (LMHC, 2012). This definition, widely accepted in the gem industry and at GIA, clearly

See end of article for About the Authors and Acknowledgments.

GEMS & GEMOLOGY, Vol. 55, No. 4, pp. 648–659,  
<http://dx.doi.org/10.5741/GEMS.55.4.648>

© 2019 Gemological Institute of America



*Figure 1. Faceted and polished copper-bearing tourmalines, ranging from 0.39 to 1.47 ct, from Brazil's Paraíba State. Photo by Robert Weldon/GIA; courtesy of Gerhard Becker.*



Figure 2. This 2.87 ct Paraiba tourmaline is from Brazil. Photo by Robert Weldon/GIA; courtesy of David Bindra, B&B Fine Gems.



Figure 4. A 29.34 ct Paraiba tourmaline from Mozambique. Photo by Robert Weldon/GIA; courtesy of the Granada Gallery.

mentions not only the color appearance but also the chemical elements causing the color. Iron (Fe) can

Figure 3. This 19.90 ct Paraiba tourmaline is from Nigeria. Photo by Robert Weldon/GIA.



also cause a blue coloration in tourmaline, such as the variety commonly termed indicolite (Faye et al., 1968; Mattson and Rossman, 1987). However, the bright blue color characteristic of Paraiba tourmaline is caused by Cu (Rossman et al., 1991) and easily surpasses the intensity and hue of indicolite's Fe-related blues. Many years of trace element analyses at GIA have demonstrated that Cu occurs in many gem tourmalines in the range of single-digit parts per million by weight (ppmw) to tens of ppmw concentrations. However, such low levels of Cu will not produce the Paraiba-like color; at least several hundred ppmw Cu are required for that. Merkel and Breeding (2009) noted that peaks near 700 and 900 nm in visible and near-infrared absorption spectra can be useful in assessing the contribution of Cu when the stone also contains Fe. Mn, another element mentioned by the LMHC definition, can create purple and pinkish hues when in combination with Cu, thus impacting the color appearance of Paraiba tourmaline.

Because standard gemological properties and microscopic observations (e.g., mineral and fluid inclusions, fracture patterns, growth tubes) are not conclusive in distinguishing geographic origin for Paraiba tourmaline, other methods must be used. Quantitative chemical analyses of minor and trace elements have been collected and presented herein for Brazilian, Nigerian, and Mozambican material as used for locality determination (e.g., Shigley et al., 2001; Breeding et al., 2007; Laurs et al., 2008). Com-

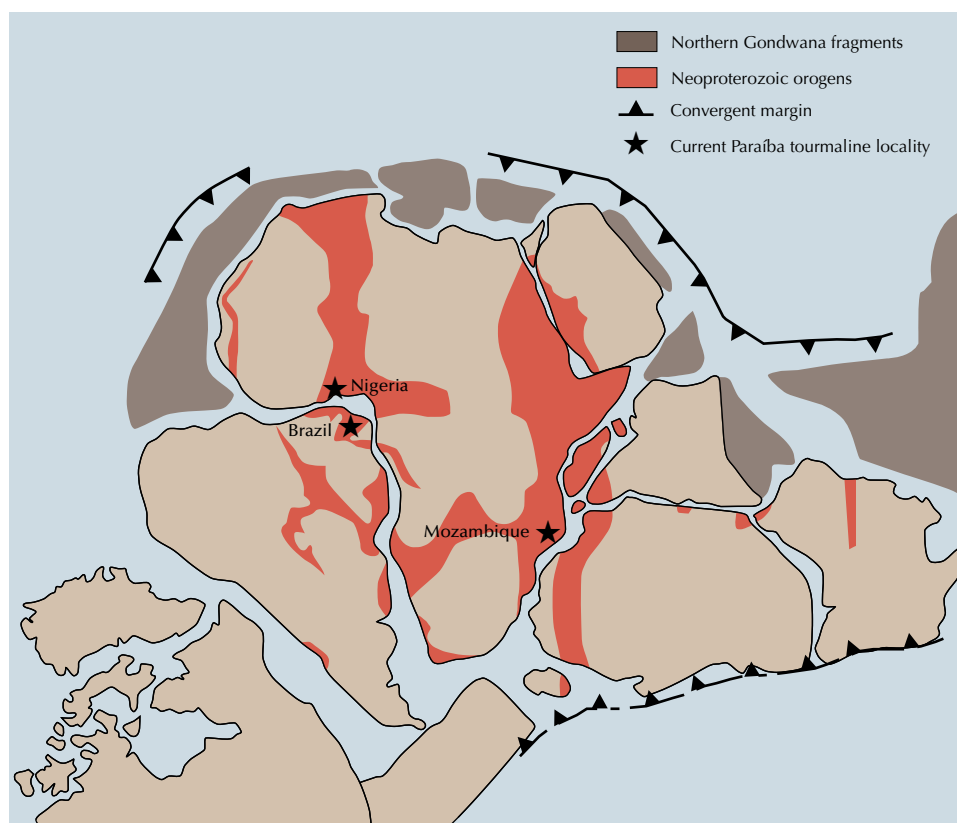


Figure 5. Overview of the Brasiliano–Pan-African orogeny (shown as Neoproterozoic orogens) in the Gondwana supercontinent (540 Ma) and locations of current Paraíba tourmaline sources. Modified from Kröner and Stern (2004).

parative studies of chemical data have also been carried out and discussed for the purpose of origin determination by several authors (Abduriyim et al., 2006; Peretti et al., 2009; Okrusch et al., 2016). For GIA’s lab service of Paraíba tourmaline origin determination, we have established an analytical and calculation protocol that utilizes major, minor, and trace element data obtained by LA-ICP-MS on reference samples from known localities.

### PARAÍBA TOURMALINE GEOGRAPHIC LOCALITIES: A BRIEF SUMMARY

Most of Brazil’s Paraíba tourmaline mining sites are primary deposits in pegmatites that intruded quartzites or metaconglomerates between 530 and 480 million years ago (Ma) (Beurlen et al., 2011). Nigerian and Mozambican mines occur as secondary deposits where the tourmalines are recovered from alluvium rather than the original host rock (e.g., Laurs et al., 2008; Milisenda, 2018a). Paraíba tourmaline’s microscopic inclusions and gemological properties, however, are similar among the deposits on both continents, suggesting a very similar geological formation for copper-bearing tourmalines collected from primary and secondary deposits.

The regional geology of northeastern Brazil and western Nigeria primarily consists of igneous and metamorphic rocks related to the Brasiliano–Pan-African orogeny that occurred 650 to 480 Ma. In Mozambique, the tourmaline host rocks are pegmatites that intruded around 500 Ma, during or after the East African orogeny, which involved the agglomeration of landmasses and continental collision that formed the Gondwana supercontinent (Kröner and Stern, 2004; figure 5).

Brazilian copper-bearing tourmaline was formed by direct crystallization from a hydrous melt, rich in boron and lithium with an unusual concentration of copper, at the early stage of pegmatite formation in the quartz core and prior to the appearance of secondary lepidolite and other late hydrothermal minerals (e.g., Beurlen et al., 2011). The origin of the copper in Brazilian Paraíba tourmaline localities is still an open question, but some researchers have attributed it to copper enrichment of the host pegmatites or pegmatite-independent hydrothermal activity (Beurlen et al., 2011 and references therein). Laurs et al. (2008) discussed the alluvial paleoplacer deposit origin of Mozambican materials, and Pezzotta (2018) proposed a residual alluvial origin from field observations. The lack of copper-rich tourma-

line in pegmatites located in the upstream area of Mozambique's Paraíba tourmaline mines leaves the copper source unknown. Further field study is necessary to better understand the source of copper in Mozambican Paraíba tourmalines.

## MATERIALS AND METHODS

GIA's Paraíba tourmaline reference samples comprise a range of stones collected by researchers directly from the mines (Shigley et al., 2001; Laurs et al., 2008; Hsu, 2018); borrowed from personal and museum collections (some established before the discovery of the African mines, thus certifying that the stones are Brazilian); or obtained from highly trusted dealers specializing in tourmaline from particular sources (see the table 1 footnote for details). The GIA reference data comes from 151 samples from Brazil, 116 elbaite and 17 liddicoatite samples from Mozambique, and 17 samples from Nigeria.

For the past decade, GIA has chemically analyzed copper-bearing tourmaline samples by LA-ICP-MS. Two instruments have been used to collect this chemical data (with great care in calibrating the instruments to ensure that the data are internally consistent). A Thermo Fisher X-series II ICP-MS coupled with a New Wave Research UP-213 laser ablation unit was used initially, with National Institute of Standards and Technology (NIST) 610 and 612 references used for external calibration. Ablation was achieved using a 55 µm diameter laser spot size, a fluence of around 10 J/cm<sup>2</sup>, and a 15 Hz repetition rate. <sup>11</sup>B was initially selected as an internal standard, although for comparison with data collected later the analyses were reprocessed with <sup>29</sup>Si as the internal standard. Between 2014 and 2017, the LA-ICP-MS systems at GIA were upgraded to those currently in place, including a Thermo Fisher iCAP Qc ICP-MS coupled with an Elemental Scientific Lasers NWR213 laser ablation system. With this upgrade, data for most of the reference stones were recollected in order to ensure internal consistency of data collected on client stones using the new system. At the same time, data processing protocols were revised, with <sup>29</sup>Si used as an internal standard and U.S. Geological Survey glasses GSD-1G, GSE-1G, and NIST 610 as external standards. Ablation is currently achieved using a 55 µm diameter laser spot size, a fluence of around 10 J/cm<sup>2</sup>, and a 20 Hz repetition rate. The isotopes routinely measured include <sup>23</sup>Na, <sup>24</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>39</sup>K, <sup>43</sup>Ca, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>69</sup>Ga, <sup>88</sup>Sr, <sup>118</sup>Sn, and <sup>206</sup>Pb.

**TABLE 1.** Paraíba tourmaline samples used in this study.

Origin	Species <sup>a</sup>	Number of samples tested
Brazil <sup>b</sup>	Elbaite	151
Nigeria <sup>c</sup>	Elbaite	17
Mozambique <sup>d</sup>	Elbaite	116
Mozambique <sup>e</sup>	Liddicoatite	17

<sup>a</sup>F cannot be determined using LA-ICP-MS. Therefore, only hydroxyl end members are shown.

<sup>b</sup>Brazilian samples include mine-collected stones from the states of Paraíba and Rio Grande do Norte, stones from Shane McClure's personal collection and GIA collections that were acquired prior to the discovery of African sources, and stones provided by Hussain Rezayee and Chico Bank.

<sup>c</sup>Nigerian samples include stones obtained directly from local miners and provided to GIA by Bill Barker, William Larson, and Hussain Rezayee.

<sup>d</sup>Mozambican samples include stones obtained directly from local miners and provided to GIA by Bill Barker, Blue Sheppard, William Larson, and Hussain Rezayee.

<sup>e</sup>Mozambican liddicoatite samples are those reported in Katsurada and Sun (2017).

To date, results obtained from the two different standards sets, instruments, and operating conditions have not varied in the overall values of the trace elements used for discrimination. As a result, we have combined the data acquired from both old and new LA-ICP-MS systems for presentation. Both data sets for the elements selected in this study show a close overlap.

## DISCRIMINATION DIAGRAMS FOR REFERENCE SAMPLES

**Major Elements.** Tourmaline is a supergroup mineral because of the large number of species under that classification. Overall, it is a complex boron-aluminum cyclosilicate mineral. The generalized formula can be written as XY<sub>3</sub>Z<sub>6</sub>(T<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>V<sub>3</sub>W, with the primary occupancies of X = Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, vacancy; Y = Fe<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Li<sup>+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ti<sup>4+</sup>; Z = Al<sup>3+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Cr<sup>3+</sup>; T = Si<sup>4+</sup>, Al<sup>3+</sup>, B<sup>3+</sup>; B = B<sup>3+</sup>; V = OH<sup>-</sup>, O<sup>2-</sup>; W = OH<sup>-</sup>, F<sup>-</sup>, O<sup>2-</sup> (Henry et al., 2011). The majority of gem-quality tourmaline is elbaite or fluor-elbaite, followed by solid solutions of dravite and uvite<sup>1</sup>. While most Paraíba tourmalines are elbaites, in 2010 copper-bearing liddicoatite<sup>1</sup> appeared in the market (Karampelas and Klemm,

<sup>1</sup>elbaite = Na(Li<sub>1.5</sub>Al<sub>1.5</sub>)Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>OH

fluor-elbaite = Na(Li<sub>1.5</sub>Al<sub>1.5</sub>)Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>F

dravite = NaMg<sub>3</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>OH

fluor-uvite = CaMg<sub>3</sub>(Al<sub>5</sub>Mg)Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>F

fluor-liddicoatite = Ca(Li<sub>2</sub>Al)Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>F

Note: While uvite and liddicoatite exist only as the fluor-dominant species listed above, the common names are used for simplicity.

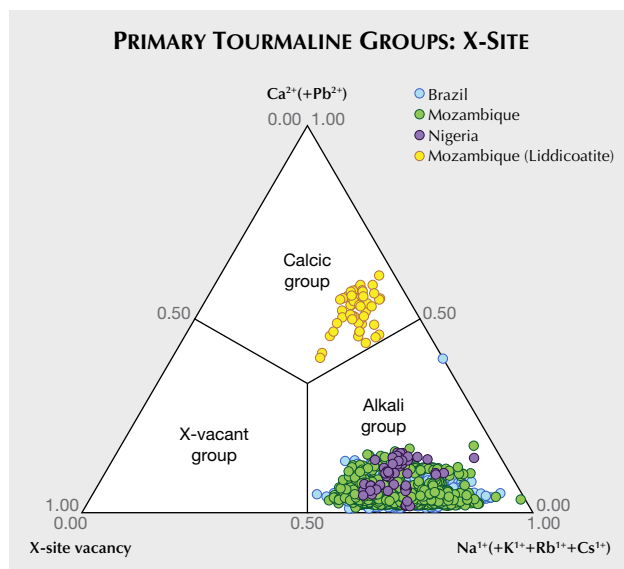


Figure 6. Ternary diagram displaying the primary tourmaline groups based on X-site occupancy of copper-bearing elbaite samples from GIA's reference collection and copper-bearing liddicoatite samples reported in Katsurada and Sun (2017). From Henry et al. (2011).

2010). Because calcium (Ca) is the dominant cation in the X-site for liddicoatites, they are easily distinguished based on major element analyses.  $\text{Cu}^{2+}$  in

copper-bearing tourmaline is considered to be located in the Y-site (e.g., Ertl et al., 2013).

The normalization method established by Sun et al. (2019) allows for the accurate calculation of tourmaline stoichiometry from LA-ICP-MS analyses, with the exception of the fluor- and oxy-species. A ternary diagram of X-site composition of reference samples shows that there are two different primary groups for the Paraíba tourmalines: alkali and calcic groups (figure 6). Based on Y-site (Li-dominant) occupancy, the species are determined as elbaite and (fluor-)liddicoatite species.

**Minor/Trace Elements.** Among the minor and trace element concentrations measured, Cu, Zn, Ga, Sr, Sn, and Pb proved to be the most useful discriminators for Paraíba tourmaline geographic origin determination. The ranges, averages, and associated standard deviations of the concentration of these six elements for different localities are summarized in table 2. Brazilian samples have higher Cu (approximately 11400 ppmw on average, compared to less than 2000 ppmw for their African counterparts), but light-colored stones may have lower Cu concentration (figure 7A, B, and F). Nigerian samples have higher Sr (approx-

**TABLE 2.** Generalized trace element profiles of Paraíba tourmalines in parts per million weight (ppmw).

	Brazil					
	Cu	Zn	Ga	Sr	Sn	Pb
Range	119–38800	bdl–33400	38.4–281	bdl–48.9	bdl–1610	0.62–1360
Average	11400	4640	115	1.12	4.95	40.1
Median	10900	1070	109	0.51	bdl	26.1
	Mozambique					
	Cu	Zn	Ga	Sr	Sn	Pb
Range	193–5720	bdl–633	170–701	bdl–34.7	bdl–48.8	5.91–244
Average	1850	29.2	361	0.43	5.40	37.1
Median	1640	3.00	363	0.11	5.02	11.1
	Nigeria					
	Cu	Zn	Ga	Sr	Sn	Pb
Range	736–2780	1.66–2900	94.0–181	6.53–159	bdl–22.5	42.1–1180
Average	1550	386	131	73.0	3.10	611
Median	1500	24.9	124	72.8	1.88	616
	Mozambique (Liddicoatite)					
	Cu	Zn	Ga	Sr	Sn	Pb
Range	1330–2980	bdl–33.4	242–465	0.70–4.21	14.8–43.2	404–819
Average	1830	0.80	346	3.07	25.6	625
Median	1570	bdl	351	3.20	25.1	644
Detection limits (ppmw)	0.029–0.60	0.013–0.97	0.006–0.30	0.001–0.090	0.013–1.13	0.001–0.45

\*bdl = below the detection limit of the LA-ICP-MS analysis

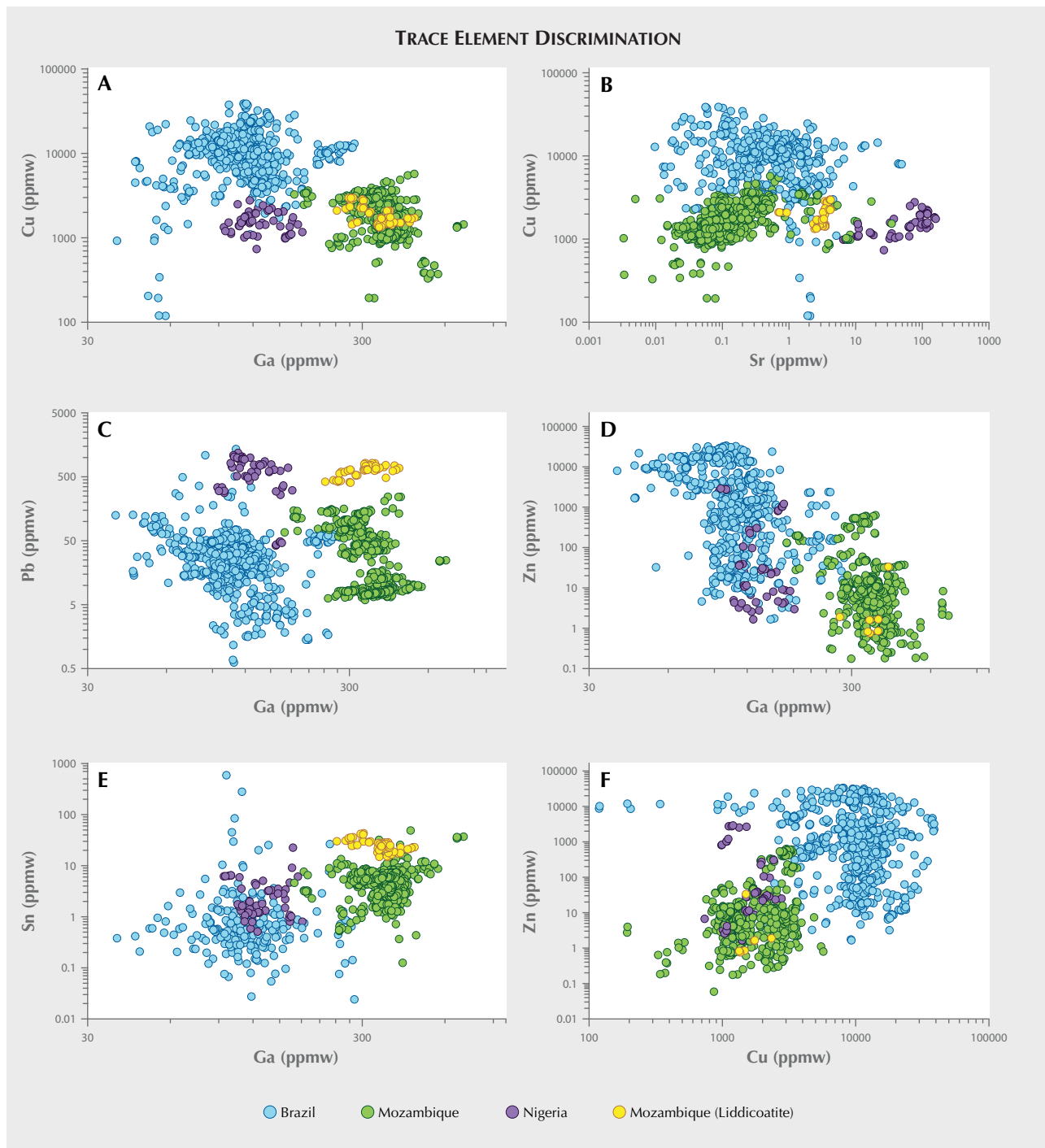


Figure 7. Diagrams displaying the concentration for selected elements used to discriminate localities: (A) Cu-Ga, (B) Cu-Sr, (C) Pb-Ga, (D) Zn-Ga, (E) Sn-Ga, and (F) Zn-Cu.

mately 73 ppmw on average, compared to less than 4 ppmw elsewhere) and higher Pb (approximately 611 ppmw on average, compared to less than 50 ppmw for Brazilian and Mozambican elbaite samples); see figure 7B and C. Mozambican samples generally show

higher Ga (both elbaite and liddicoatite are approximately 361 ppmw on average, compared to around 100 ppmw for other localities); see figure 7A, C, D, and E. High Zn (>1000 ppm) is limited to Brazilian samples, but Zn values below 1000 ppmw are not

helpful discriminators (figure 7D and F). Most of the Nigerian samples contain high Sr and Pb (figure 7B and C). Any single pair of certain elements is insufficient to determine the geographic origin, but the *combination* of these elemental discriminators provides a robust tool for origin determination. In general, the results presented here are comparable to those in previous studies (e.g., Abduriyim et al., 2006; Peretti et al., 2009; Okrusch et al., 2016).

Using GIA's reference data, four selected case studies for origin determination are shown in box A. Although most Paraíba tourmaline origin determinations are as straightforward as these case studies, some stones cannot be separated clearly, as some plot in overlapping locality fields and are not easily distinguished. When data plot in the middle of overlapping ranges for many element pairs, a definitive locality origin cannot be concluded. Such an example is shown as Case 4 in box A.

## DISCUSSION

Geographic origin can be conclusively and accurately determined for the vast majority of Paraíba tourmalines based on their trace element profiles, allowing this service to be offered for Paraíba tourmaline in the gem and jewelry market, such as the fine-color Brazilian stones in figure 8. Nonetheless, there are some cases where an "inconclusive" call is warranted when the trace element profiles are ambiguous or contradictory. There are three reasons for the ambiguity:

1. From time to time the laboratory examines Paraíba tourmalines that do not seem to match the trace element profiles of any stones in GIA's reference collection. Obtaining reference samples with reliable provenance that match these unknown stones is currently a priority of GIA's field gemology department; see Vertriest et al. (2019), pp. 490–511 of this issue.
2. New chemical discriminators may be needed. Statistical approaches such as discriminant analysis or multivariate statistics may provide additional mechanisms to evaluate the certainty of the locality determination and reduce "inconclusive" calls.
3. Chemical zoning in tourmaline may complicate interpretations. Color zoning is common in cuprian tourmaline and has been studied with electron probe microanalysis and LA-ICP-MS. In these studies, trace element concentrations correlate with color in naturally zoned samples (e.g., Laurs et al., 2008; Peretti et al., 2009). It is possible that the limits of chemical zoning of Paraíba tourmaline have not been included in the original fields for localities. Ideally, potential chemical zoning should be known before conducting LA-ICP-MS analysis so that all of the compositions can be captured. In tourmaline, however, chemical zoning may not include chromophores and may not be visually recognizable.



*Figure 8. Brazilian Paraíba tourmalines with exceptional color, ranging from 2.59 ct to 3.68 ct. Photo by Robert Weldon/GIA; courtesy of the Dr. Edward J. Gübelin Collection.*

## BOX A: CASE STUDIES OF TYPICAL RESULTS

Examples of geographic origin determination for typical stones from Brazil, Nigeria, and Mozambique are shown in Cases 1–3. These stones were examined by GIA. Photographs and weights of the samples used for these case studies are shown in figure A-1. Three spots on each stone were analyzed by LA-ICP-MS; the results are listed in table A-1. Cases 1, 2, and 3 plotted in the typical ranges for Brazil, Mozambique, and Nigeria, respectively (see figure A-2). These three cases represent the vast majority of stones submitted to the laboratory whose origin can be easily concluded based on trace element chemistry as determined by the described procedures.

Occasionally the laboratory examines stones, such as the one in Case 4 (figure A-1), that do not match any of the data in GIA's reference database. The trace ele-

ment profile of this stone based on three LA-ICP-MS analyses did not plot in the known trace element ranges for any established Paraíba tourmaline localities. While the origin of most Paraíba tourmalines examined by GIA can be easily established using trace element chemistry, inevitably a small number fall into this zone between two localities in compositional spaces that are completely devoid of reference data. These stones were clearly unearthed from some mine in the world, likely in any of the three Paraíba tourmaline localities. Despite efforts to obtain reliable reference stones that match these questionable tourmaline compositions, we are unable to identify the origin of these stones. Consequently, the only possible origin determination for these questionable cases is "inconclusive."

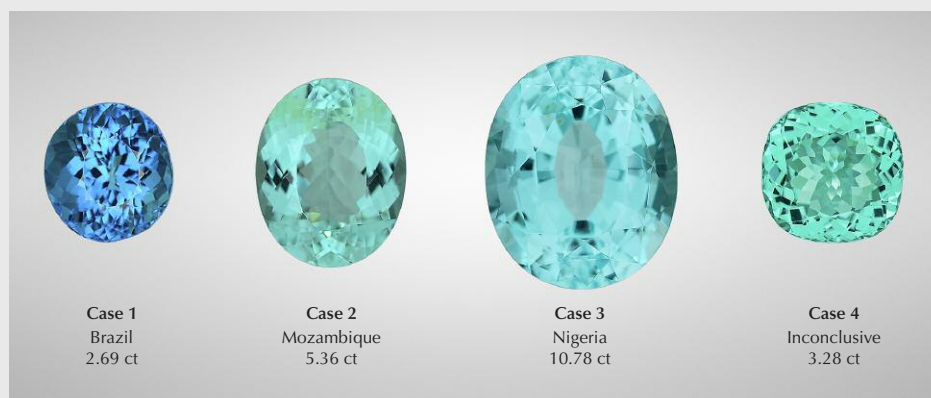


Figure A-1. Photos and weights of the stones from Cases 1, 2, 3, and 4. LA-ICP-MS identified their origin as Brazil, Mozambique, Nigeria, and "inconclusive," respectively.

TABLE A-1. Concentration of selected elements (in ppmw) for Cases 1–4.

	Cu	Zn	Ga	Sr	Sn	Pb	Results
Case 1, Spot 1	17120	71.3	78.1	0.57	0.21	31.2	Brazil
Case 1, Spot 2	17150	73.8	77.7	0.55	0.27	31.8	Brazil
Case 1, Spot 3	16930	72.2	76.3	0.62	0.24	31.6	Brazil
Case 2, Spot 1	1810	2.80	348	0.61	3.78	102	Mozambique
Case 2, Spot 2	1800	3.08	356	0.62	3.93	106	Mozambique
Case 2, Spot 3	1750	3.05	340	0.61	3.76	105	Mozambique
Case 3, Spot 1	1510	480	141	130	16.9	451	Nigeria
Case 3, Spot 2	1440	550	138	129	16.2	414	Nigeria
Case 3, Spot 3	1370	1030	137	132	18.4	433	Nigeria
Case 4, Spot 1	6230	8.06	253	10.3	0.47	233	Inconclusive
Case 4, Spot 2	6400	8.14	277	10.5	0.28	256	Inconclusive
Case 4, Spot 3	6420	8.31	271	10.3	0.35	246	Inconclusive
Detection limits (ppmw)	0.029–0.60	0.013–0.97	0.006–0.30	0.001–0.090	0.013–1.13	0.013–1.13	

### TRACE ELEMENT DISCRIMINATION



Figure A-2. Elemental concentrations from LA-ICP-MS analyses, plotted in Cu-Ga and Pb-Ga diagrams. Four case studies are shown for typical stones from Brazil (Case 1), Mozambique (Case 2), and Nigeria (Case 3), as well as an example of a stone whose trace element profile would require an “inconclusive” origin determination (Case 4).

As noted earlier, liddicoatite can also be found in the Paraíba tourmaline market. Katsurada and Sun (2017) reported that the origin of the copper-bearing liddicoatite was unknown at the time of publication. Subsequently the source was identified as Maraca, Mozambique (Milisenda and Müller, 2017). For the purpose of Paraíba tourmaline origin determination, if the LA-ICP-MS analyses identify a cuprian tourmaline as liddicoatite, the stone's origin is conclusively Mozambique.

Copper-bearing tourmalines are reported to occur in various colors, including pink, purple, violet, blue, and green (e.g., Laurs et al., 2008). Heat treatment is known to improve the color of cuprian tourmaline by changing the valence state of manganese ions from trivalent ( $Mn^{3+}$ ) to divalent ( $Mn^{2+}$ ), consequently reducing  $Mn^{3+}$  absorption in the visible range. This change can remove the purple and pink components of some stones, resulting in blue to green colors consistent with the Paraíba designation. Unfortunately, heat treatment is not always detectable. Appearance of a pink halo around tube-like inclusions, called "pink sleeves," has been used as evidence of an unheated stone (Koivula et al., 2009). However, these features can remain in heated samples (S.F. McClure, pers. comm., 2017). Therefore, the colors of Paraíba tourmalines should always be considered to be potentially modified by heat treatment. One possible avenue of future research would be to study the trace element signatures of the various colors of Paraíba tourmaline, but of course this is complicated by the prevalence of heat treatment in most stones.

Different approaches have been proposed for determination of origin. These techniques include, in part, using isotopic compositions of boron and lithium (Shabaga et al., 2010; Ludwig et al., 2011), photoluminescence spectra (Milisenda, 2018b), and laser-induced breakdown spectroscopy (LIBS) with multivariate statistics (Dutrow et al., 2019). These approaches may be helpful as additional techniques to enhance chemical fingerprinting and facilitate origin determination.

## CONCLUSIONS

Based on GIA's database containing more than 300 Paraíba tourmaline samples with known provenance, geographic origin determinations can be made using a variety of minor/trace element data when collected by highly precise and accurate methods. In the modern gemological laboratory, the weight of the origin determination rests overwhelmingly on trace element analysis by LA-ICP-MS. Paraíba tourmalines from Brazil, Mozambique, and Nigeria can, in most cases, be identified by their unique fingerprints of concentrations of trace elements such as Sr, Cu, Zn, Ga, Sn, and Pb. Additionally, the more recent find of Paraíba tourmaline belonging to the liddicoatite species can be identified through major element analysis. However, in a few cases "inconclusive" origin determinations may result when their trace element profiles do not match with any reference samples of known provenance. By improving the database with additional reference samples and conducting further research on analytical methods and statistical analyses, fewer Paraíba tourmalines will require an "inconclusive" call.

### ABOUT THE AUTHORS

*Dr. Katsurada is a senior staff gemologist at GIA in Tokyo. Mr. Sun is a research associate, and Dr. Breeding is a senior research scientist, at GIA in Carlsbad, California. Dr. Dutrow is the Williams Distinguished Alumni professor at Louisiana State University in Baton Rouge and a GIA governor.*

### ACKNOWLEDGMENTS

*Thorough and thoughtful peer reviews by Professor Darrell Henry at Louisiana State University, Dr. Claudio Milisenda at DSEF German Gem Lab, and an anonymous reviewer greatly improved the manuscript. Dr. Aaron Palke provided timely and important feedback. We thank Bill Barker, William Larson, Hus-sain Rezayee, Shane McClure, Chico Bank, Blue Sheppard, and the GIA Museum for providing many of the reference samples for this study. This paper benefited from National Science Foundation funding to BD (grant number EAR-1551434).*

## REFERENCES

- Abduriyim A., Kitawaki H. (2005) Gem News International: Cu- and Mn-bearing tourmaline—More production from Mozambique. *G&G*, Vol. 41, No. 4, pp. 360–361.
- Abduriyim A., Kitawaki H., Furuya M., Schwarz D. (2006) “Paraíba”-type copper-bearing tourmaline from Brazil, Nigeria, and Mozambique: Chemical fingerprinting by LA-ICP-MS. *G&G*, Vol. 42, No. 1, pp. 4–21, <http://dx.doi.org/10.5741/GEMS.42.1.4>
- Beurlen H., de Moura O.J.M., Soares D.R., Da Silva M.R.R., Rhede D. (2011) Geochemical and geological controls on the genesis of gem-quality “Paraíba tourmaline” in granitic pegmatites from northeastern Brazil. *Canadian Mineralogist*, Vol. 49, No. 1, pp. 277–300, <http://dx.doi.org/10.3749/canmin.49.1.277>
- Breeding C.M., Rockwell K., Laurs B.M. (2007) Gem News International: New Cu-bearing tourmaline from Nigeria. *G&G*, Vol. 43, No. 4, pp. 384–385.
- Dutrow B.L., Farnsworth-Pinkerton S., Henry D.J., McMillan N.J., Niepagen N. (2019) Copper-bearing tourmaline sources: Evidence from laser-induced breakdown spectroscopy (LIBS) and electron microprobe analyses (EMP). Geological Society of America Abstracts with Programs, p. 51.
- Ertl A., Giester G., Schüssler U., Brätz H., Okrusch M., Tillmanns E., Bank H. (2013) Cu- and Mn-bearing tourmalines from Brazil and Mozambique: Crystal structures, chemistry and correlations. *Mineralogy and Petrology*, Vol. 107, No. 2, pp. 265–279, <http://dx.doi.org/10.1007/s00710-012-0234-6>
- Faye G.H., Manning P.G., Nickel E.H. (1968) The polarized optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite: Ferrous-ferric electronic interaction as a source of pleochroism. *American Mineralogist*, Vol. 53, No. 7-8, pp. 1174–1201.
- Fritsch E., Shigley J.E., Rossman G.R., Mercer M.E., Muhlmeister S.M., Moon M. (1990) Gem-quality cuprian-elbaite tourmalines from São José da Batalha, Paraíba, Brazil. *G&G*, Vol. 26, No. 3, pp. 189–205, <http://dx.doi.org/10.5741/GEMS.26.3.189>
- Furuya M. (2007) Copper-bearing tourmalines from new deposits in Paraíba State, Brazil. *G&G*, Vol. 43, No. 3, pp. 236–239, <http://dx.doi.org/10.5741/GEMS.43.3.236>
- Henry D.J., Novák M., Hawthorne F.C., Ertl A., Dutrow B.L., Uher P., Pezzotta F. (2011) Nomenclature of the tourmaline-super-group minerals. *American Mineralogist*, Vol. 96, No. 5–6, pp. 895–913, <http://dx.doi.org/10.2138/am.2011.3636>
- Hsu T. (2018) Paraíba tourmaline from Brazil: The neon-blue burn. *InColor*, No. 39, pp. 42–50.
- Karampelas S., Klemm L. (2010) Gem News International: “Neon” blue-to-green Cu- and Mn-bearing liddicoatite tourmaline. *G&G*, Vol. 46, No. 4, pp. 323–325.
- Katsurada Y., Sun Z. (2017) Cuprian liddicoatite tourmaline. *G&G*, Vol. 53, No. 1, pp. 34–41, <http://dx.doi.org/10.5741/GEMS.53.1.34>
- Koivula J.I., Nagle K., Shen A.H., Owens P. (2009) Solution-generated pink color surrounding growth tubes and cracks in blue to blue-green copper-bearing tourmalines from Mozambique. *G&G*, Vol. 45, No. 1, pp. 45–47, <http://dx.doi.org/10.5741/GEMS.45.1.44>
- Kröner A., Stern R.J. (2004) Pan-African orogeny. *Encyclopedia of Geology*, Vol. 1, Elsevier, Amsterdam, pp. 1–12, <http://dx.doi.org/10.1016/B0-12-369396-9/00431-7>
- Laboratory Manual Harmonisation Committee (LMHC) (2012) LMHC Information Sheet #6: “Paraíba tourmaline” Version 7, [https://static1.squarespace.com/static/5fbfb7e6cc8fed3bb9293bf3/t/5bfe92a90e2e72555d61eec3/1543410345434/LMHC+Information+Sheet\\_6\\_V7\\_2012.pdf](https://static1.squarespace.com/static/5fbfb7e6cc8fed3bb9293bf3/t/5bfe92a90e2e72555d61eec3/1543410345434/LMHC+Information+Sheet_6_V7_2012.pdf)
- Laurs B.M., Zwaan J.C., Breeding C.M., Simmons W.B., Beaton D., Rijdsdijk K.F., Befi R., Falster A.U. (2008) Copper-bearing (Paraíba-type) tourmaline from Mozambique. *G&G*, Vol. 44, No. 1, pp. 4–30, <http://dx.doi.org/10.5741/GEMS.44.1.4>
- Ludwig T., Marschall H.R., Pogge von Strandmann P.A.E., Shabaga B.M., Fayak M., Hawthorne F.C. (2011) A secondary ion mass spectrometry (SIMS) re-evaluation of B and Li isotopic compositions of Cu-bearing elbaite from three global localities. *Mineralogical Magazine*, Vol. 75, No. 4, pp. 2485–2494, <http://dx.doi.org/10.1180/minmag.2011.075.4.2485>
- Mattson S.M., Rossman G.R. (1987) Fe<sup>2+</sup>-Fe<sup>3+</sup> interactions in tourmaline. *Physics and Chemistry of Minerals*, Vol. 14, pp. 163–171, <http://dx.doi.org/10.1007/BF00308220>
- Merkel P.B., Breeding C.M. (2009) Spectral differentiation between copper and iron colorants in gem tourmalines. *G&G*, Vol. 45, No. 2, pp. 112–119, <http://dx.doi.org/10.5741/GEMS.45.2.112>
- Milisenda C.C. (2018a) Paraíba tourmaline revisited. *InColor*, No. 39, pp. 34–41.
- Milisenda C.C. (2018b) Gemstones and photoluminescence. *G&G*, Vol. 54, No. 3, p. 258.
- Milisenda C.C., Müller S. (2017) REE photoluminescence in Paraíba type tourmaline from Mozambique. Abstract Proceedings, 35th International Gemmological Conference, Windhoek, Namibia, pp. 71–73.
- Okrusch M., Ertl A., Schüssler U., Tillmanns E., Brätz H., Bank H. (2016) Major- and trace-element composition of Paraíba-type tourmaline from Brazil, Mozambique and Nigeria. *Journal of Gemmology*, Vol. 35, No. 2, pp. 120–139.
- Peretti A., Bieri W.P., Reusser E., Hametner K., Günther D. (2009) Chemical variations in multicolored “Paraíba-type” tourmalines from Brazil and Mozambique: Implications for origin and authenticity determination. *Contributions to Gemology*, Vol. 9, pp. 1–77.
- Pezzotta F. (2018) Mozambique Paraíba tourmaline deposits—an update. *InColor*, No. 39, pp. 52–56.
- Rossman G.R., Fritsch E., Shigley J.E. (1991) Origin of color in cuprian elbaite from São José da Batalha, Paraíba, Brazil. *American Mineralogist*, Vol. 76, pp. 1479–1484.
- Shabaga B.M., Fayak M., Hawthorne F.C. (2010) Boron and lithium isotopic compositions as provenance indicators of Cu-bearing tourmalines. *Mineralogical Magazine*, Vol. 74, No. 2, pp. 241–255, <http://dx.doi.org/10.1180/minmag.2010.074.2.241>
- Shigley J.E., Cook B.C., Laurs B.M., de Oliveira Bernardes M. (2001) An update on “Paraíba” tourmaline from Brazil. *G&G*, Vol. 37, No. 4, pp. 260–276, <http://dx.doi.org/10.5741/GEMS.37.4.260>
- Smith C.P., Bosshart G., Schwarz D. (2001) Gem News International: Nigeria as a new source of copper-manganese-bearing tourmaline. *G&G*, Vol. 37, No. 3, pp. 239–240.
- Sun Z., Palke A.C., Breeding C.M., Dutrow B.L. (2019) A new method for determining gem tourmaline species by LA-ICP-MS. *G&G*, Vol. 55, No. 1, pp. 2–17, <http://dx.doi.org/10.5741/GEMS.55.1.2>
- Vertriest W., Palke A.C., Renfro N.D. (2019) Field gemology: Building a research collection and understanding the development of gem deposits. *G&G*, Vol. 55, No. 4, pp. 490–511, <http://dx.doi.org/10.5741/GEMS.55.4.490>