

# “PARAÍBA”-TYPE COPPER-BEARING TOURMALINE FROM BRAZIL, NIGERIA, AND MOZAMBIQUE: CHEMICAL FINGERPRINTING BY LA-ICP-MS

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Gem-quality bright blue to green “Paraíba”-type Cu-bearing tourmaline is now known from deposits in Africa (Nigeria and Mozambique), in addition to three commercial localities in Brazil (in Paraíba and Rio Grande do Norte States). Stones from these new localities have been mixed into parcels from the original Brazilian Paraíba occurrence. The Nigerian and Mozambique tourmalines that show saturated blue-to-green colors cannot be distinguished from the Brazilian material by standard gemological testing or on the basis of semi-quantitative chemical data (obtained by EDXRF analysis). However, quantitative chemical data obtained by LA-ICP-MS show that tourmalines from the three countries can be differentiated by plotting (Ga+Pb) versus (Cu+Mn), (Cu+Mn) versus the Pb/Be ratio, and Mg-Zn-Pb. In general, the Nigerian tourmalines contained greater amounts of Ga, Ge, and Pb, whereas the Brazilian stones had more Mg, Zn, and Sb. The new Cu-bearing tourmalines from Mozambique showed enriched contents of Be, Sc, Ga, Pb, and Bi, but lacked Mg.

Copper-bearing elbaite with blue-to-green coloration is commonly called “Paraíba” tourmaline in the gem trade. This name refers to the state of Paraíba in Brazil, where such material was first discovered in the late 1980s (figure 1). Similar tourmaline was later found in the adjacent state of Rio Grande do Norte, and Brazil has been supplying limited amounts of this material to the world market for more than two decades. Today, however, Cu-bearing tourmaline is also being sourced from two countries in Africa: Nigeria and Mozambique. Cu-bearing tourmaline is priced in the gem trade according to its appearance as well as its geographic origin. The latter has stimulated the demand for origin information on identification reports issued by some gemological laboratories, and the availability of attractive Cu-bearing tourmaline from several geographic sources has complicated the origin determination of this valuable material.

In this article, we review the gemological proper-

ties and chemical composition of blue-to-green tourmalines from known localities in Brazil, Nigeria, and Mozambique that contain significant amounts of copper. We also present new chemical data determined by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) analyses of more than 198 tourmaline specimens from these three countries, and evaluate how these data can be used to determine geographic origin.

## BACKGROUND

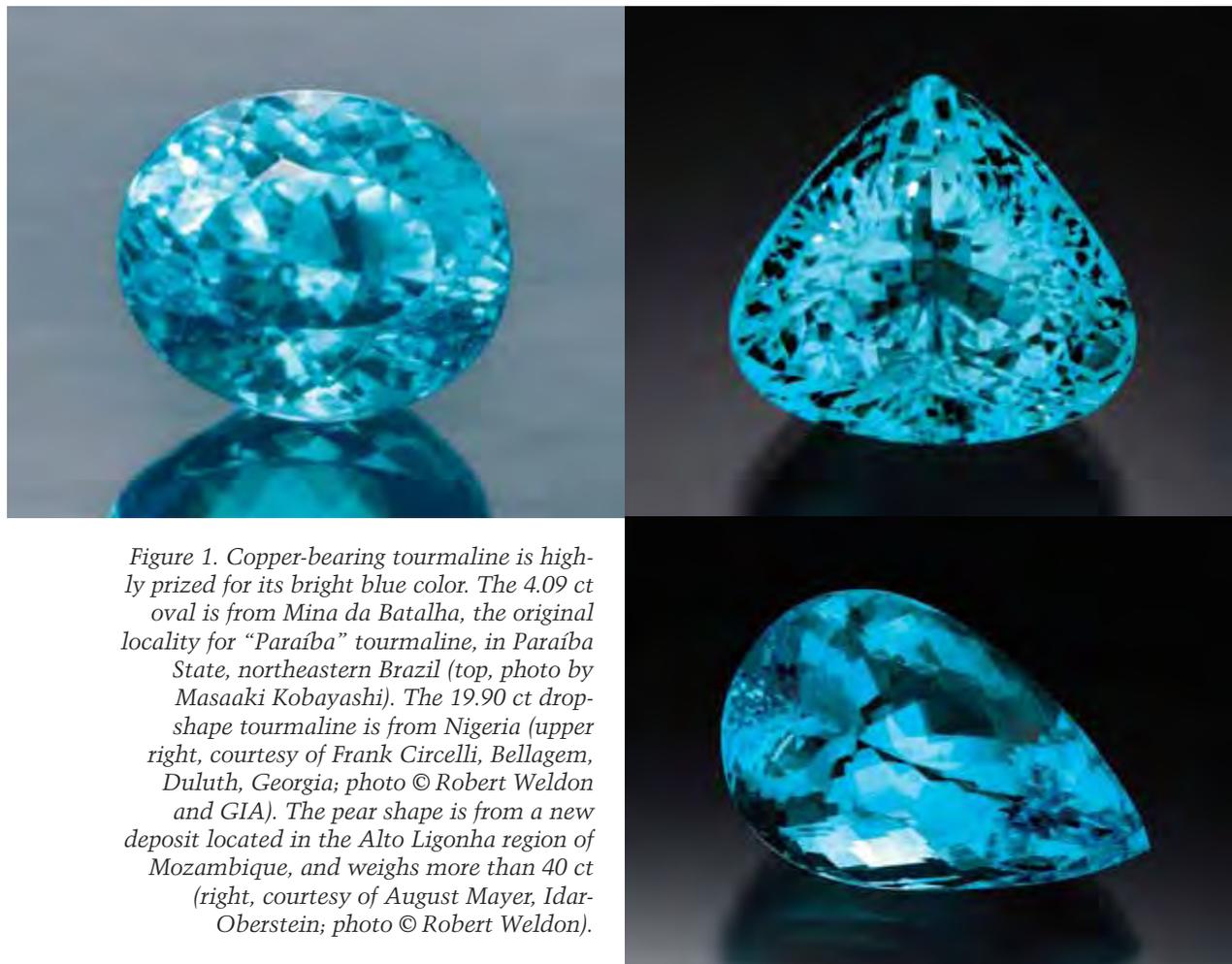
“Paraíba” tourmaline is by far the most valuable, and perhaps the most popular, of all tourmaline gem varieties. Traditionally, this trade name has been

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See end of article for About the Authors and Acknowledgments.

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*Figure 1. Copper-bearing tourmaline is highly prized for its bright blue color. The 4.09 ct oval is from Mina da Batalha, the original locality for “Paraíba” tourmaline, in Paraíba State, northeastern Brazil (top, photo by Masaaki Kobayashi). The 19.90 ct drop-shape tourmaline is from Nigeria (upper right, courtesy of Frank Circelli, Bellagem, Duluth, Georgia; photo © Robert Weldon and GIA). The pear shape is from a new deposit located in the Alto Ligonha region of Mozambique, and weighs more than 40 ct (right, courtesy of August Mayer, Idar-Oberstein; photo © Robert Weldon).*

reserved for Cu- and Mn-bearing, bright blue-to-green elbaite from Mina da Batalha, near São José da Batalha in Paraíba State, northeastern Brazil (Fritsch et al., 1990). Originally discovered in 1987, it appeared on the gem market shortly thereafter (Koivula and Kammerling, 1989). Similar but less saturated blue Cu-bearing tourmaline appeared in the gem trade during the 1990s from two mines in Rio Grande do Norte State: Mulungu and Alto dos Quintos (Karfunkel and Wegner, 1996; Shigley et al., 2001). The Mulungu mine is located 5 km north-northeast of the town of Parelhas, and Alto dos Quintos is situated about 10 km south of Parelhas. Although neither of these mines is located in Paraíba state, the tourmalines they produce are commonly referred to as “Paraíba” in the gem trade.

While the “Paraíba” tourmalines from these three Brazilian localities have some similarities, there are notable differences in the production from each mine. Mina da Batalha has been the source of fine blue-green and green tourmalines, with a small per-

centage of the material showing a distinct “neon” blue color. To date, the total production of copper-bearing blue-green and green elbaite from Mina da Batalha has been rather limited, although it is estimated to be at least 600 grams per year, or approximately 10,000 pieces of rough with most crystal fragments weighing less than 5 ct (M. Mizumura, pers. comm., 2005). In recent years, the tourmaline output from Mina da Batalha has dwindled in comparison to its greatest production of the best blue-to-green material, which reached 10,000–15,000 grams during the 1989–1991 period (Shigley et al., 2001). The Mulungu mine has yielded large amounts of good-quality light blue Cu-bearing elbaite (figure 2) and small quantities of blue-green and “emerald” green material. The maximum production is estimated at 1,000 grams of rough fragments per year that typically weigh less than 1 ct each. Most small pieces of rough “Paraíba” tourmaline in the Japanese market are from the Mulungu mine (M. Mizumura, pers. comm., 2005). The Alto dos Quintos mine is another source of



Figure 2. These light blue Cu-bearing tourmalines (0.41–0.50 ct) are from the Mulungu mine in Rio Grande do Norte State, Brazil. Courtesy of Hideki Sakamaki and Yuji Tsukuda; photo by Masaaki Kobayashi.

melee-size light blue Cu-bearing elbaite (figure 3), and it also produces some green material. Large pieces weighing several carats are occasionally found. Although the output of “Paraíba” tourmaline from Alto dos Quintos decreased in 2005, the mine still regularly produces small amounts of material. In recent years, the production from all three Brazilian mines has fulfilled most of the Japanese demand for “Paraíba” tourmaline (Kitawaki, 2005).

Elbaite tourmaline from western Nigeria has been known in the gem trade since 2001 (figure 4; Henricus, 2001; Smith et al., 2001; Zang et al., 2001). The material reportedly originated from a mine in the Edeko area, near Ilorin in Ibadan State, southwestern Nigeria. It exhibits a wide range of color, from light blue, violetish blue, “neon” blue, and bluish green to “emerald” green; these colors are mainly due to variations in the copper and manganese contents. The typical inclusions in this tourmaline are similar to those seen in the Brazilian material. The Nigerian production has been sporadic (Shigley et al., 2001; Furuya, 2004), and some reports indicate that most of the Cu-bearing tourmaline from Nigeria has been sold in Germany, Brazil, and Bangkok (Milisenda, 2001).

According to chemical data on Nigerian tourmalines obtained with EDXRF spectroscopy (Smith et al., 2001), electron-microprobe analysis, and LA-ICP-MS (Zang et al., 2001), major amounts of Na, Al, Si, Cu, and Mn—and minor-to-trace contents of Mg, Ca, Ti, Fe, Zn, Pb, and Bi—were reported in violet-blue, bluish green, and green crystals. The highest concentration of copper measured was 2.18 wt.% CuO, and MnO reached 2.59 wt.% in violet-blue



Figure 3. This ring is set with four Cu-bearing tourmalines (0.13–0.22 ct) from the Alto dos Quintos mine in Rio Grande do Norte State, Brazil. Courtesy of Hideki Sakamaki; photo by Masaaki Kobayashi.

samples (Zang et al., 2001). These studies indicate that there is an overlap in both the chemical composition and gemological properties between Nigerian and Brazilian copper-bearing tourmaline, so that materials from these two countries cannot be identified with these techniques alone. At the 29th International Gemological Conference in Wuhan, China, Furuya (2004) reported that there were two types of Cu-bearing tourmaline from Nigeria. Using qualita-

Figure 4. Cu-bearing elbaite from the Edeko area of western Nigeria are the center stones (3.05–3.56 ct) in these rings. This deposit, discovered in 2001, yields tourmaline with a color range similar to that of the Brazilian material. This high-copper-bearing tourmaline from Edeko is commonly referred to as Nigerian type I tourmaline by Japanese dealers. Courtesy of M. Furuya; photo by Masaaki Kobayashi.



tive EDXRF chemical analysis, he explained that light blue elbaite (which Japanese dealers refer to as *Nigerian type II tourmaline*; figure 5) from the Ofiki region in Ilorin State contained less Cu and more Pb than the high-copper-bearing Edeko material (referred to as *Nigerian type I tourmaline*), which further complicates separation of the Nigerian tourmalines from comparably colored elbaites from Brazil. For the past few years, there has been controversy over whether all of this material from Brazil and Nigeria should be called “Paraíba” tourmaline (Furuya, 2004).

In mid-2005, a new source of attractive Cu-bearing elbaite was discovered in Mozambique (Abduriyim and Kitawaki, 2005). The mining area is reportedly located in the Alto Ligonha region, approximately 100 km southwest of Nampula. A variety of colors have been produced, including blue to green (e.g., figure 6), violet, and pink. Excitement over this new source, and rumors of limited production, caused prices of faceted material to escalate at the September 2005 Hong Kong International Jewelry Fair, where the material first debuted.

Preliminary studies have indicated that the gemological properties and chemical composition of these Mozambique tourmalines resemble similarly colored tourmaline from both Brazil and Nigeria. In some early reports (Wentzell, 2004; Wentzell et al., 2005), color-change (purple in fluorescent light, gray

*Figure 5. Tourmalines from the Ofiki area of Nigeria typically have a light blue color, as shown by these stones (0.28–0.43 ct). This material has a low copper concentration, and is commonly referred to as Nigerian type II tourmaline by Japanese dealers. Courtesy of Hideki Sakamaki; photo by A. Abduriyim.*



*Figure 6. These saturated bright blue (top, 0.70–6.11 ct) and blue-green (bottom, 0.26–5.98 ct) tourmalines are from a new deposit in the Alto Ligonha region of Mozambique. All of these stones were included in this study. Courtesy of Hideki Sakamaki; photos by Masaaki Kobayashi (top); H. Kitawaki (bottom).*

to bluish green in incandescent light) tourmalines from the Moiane area in northern Mozambique were shown to contain traces of copper.

## MATERIALS AND METHODS

We examined a total of 198 samples of Cu-bearing tourmaline from Brazil, Nigeria, and Mozambique (see table 1). The Brazilian materials included 71 rough and polished samples from Mina da Batalha in colors ranging from “turquoise” blue to “neon” blue, greenish blue to bluish green, and “emerald” green; 14 light blue faceted pieces from the Mulungu mine; and 10 faceted stones from the Alto dos Quintos mine that were light blue and light “neon” blue. All of these samples were either provided by two gem importers (Glorious Gems Co. and YT Stone Co.) or

**TABLE 1.** Tourmaline specimens used in this study.<sup>a</sup>

| Sample no. and locality                        | Quantity | Color                         | Weight (ct) | Type                      |
|--|----------|-------------------------------|-------------|---------------------------|
| <b>Brazil</b>                                  |          |                               |             |                           |
| B504-T001-007 (Mina da Batalha)                | 6        | "Turquoise" blue              | 0.60–1.74   | Cabochons                 |
| B504-K001-020 (Mina da Batalha)                | 25       | "Neon" blue, intense blue     | 0.22–0.30   | Mixed rough and cut       |
| B504-BG001-040 (Mina da Batalha)               | 30       | Greenish blue to bluish green | 0.11–3.21   | Mixed rough and cut       |
| B504-G001-015 (Mina da Batalha)                | 10       | "Emerald" green               | 0.31–3.03   | Cabochons and mixed cuts  |
| B504-M001-014 (Mulungu)                        | 14       | Light blue                    | 0.40–0.50   | Mixed cuts and fancy cuts |
| B504-Q001-003 (Alto dos Quintos)               | 3        | Light blue                    | 0.12–0.30   | Fancy cuts                |
| B504-Q004-010 (Alto dos Quintos)               | 7        | Light "neon" blue             | 0.14–0.20   | Fancy cuts                |
| <b>Nigeria</b>                                 |          |                               |             |                           |
| NI001-007                                      | 7        | Light blue                    | 0.54–2.02   | Cabochons                 |
| N249-4-7                                       | 4        | Violetish blue                | 0.25–1.12   | Cabochons and mixed cuts  |
| N074-1-4, N249-1-3, NFB001-012, NI-1-6, GP-1-5 | 30       | "Neon" blue to blue           | 0.34–21.72  | Cabochons and mixed cuts  |
| NFG001-010, TEN-001-020                        | 30       | Greenish blue to bluish green | 0.23–3.20   | Mixed cuts                |
| HVE02-1-15, NFY001-005                         | 10       | "Emerald" green               | 0.18–2.45   | Mixed cuts                |
| <b>Mozambique</b>                              |          |                               |             |                           |
| MS001  | 1        | Light blue                    | 0.27        | Fancy cut                 |
| MA001-007                                      | 7        | Bright blue                   | 0.70–6.11   | Fancy cuts                |
| MVB001-002                                     | 2        | Violet-blue, pale blue        | 4.65, 1.65  | Polished flat             |
| MBG001-010                                     | 10       | Bluish green                  | 0.26–5.98   | Fancy cuts                |
| MLG001-002                                     | 2        | Light green                   | 0.46, 0.95  | Polished flat             |
| MPP001 (used for heating experiments only)     | 1        | Purplish pink                 | 2.97        | Polished flat             |
| MY001 (used for heating experiments only)      | 1        | Yellow                        | 2.15        | Polished flat             |

<sup>a</sup> Gemological examination showed that none of the samples were filled with oil or resin.

Figure 7. These light blue and light "neon" blue "Paraíba" tourmalines (0.16–0.24 ct), also part of the study sample, were obtained by one of the authors at the Alto dos Quintos mine in Brazil. Photo by Masaaki Kobayashi.



collected *in situ* from the mines by the authors (see, e.g., figures 2 and 7).

The Nigerian tourmalines consisted of 31 faceted specimens in blue (including "neon" blue), greenish blue to bluish green, and "emerald" green that were

Figure 8. Shown here are some of the tourmalines (0.34–2.45 ct) from Edeko, Nigeria, that were analyzed for this study. Courtesy of Hideki Sakamaki; photo by Masaaki Kobayashi.





Figure 9. The Mozambique study samples included these light green, violet-blue, and pale blue Cu-bearing tourmaline fragments. Photos by Masaaki Kobayashi (left) and A. Abduriyim (right).

obtained by one of the authors (MF) at the October 2003 Bangkok gem fair from a rough stone dealer, Hussain Rezayee, and 50 polished samples in blue (including light blue, violetish blue, and “neon” blue), blue-green, and “emerald” green that were obtained from Nigerian miners by the two gem import companies (figure 8).

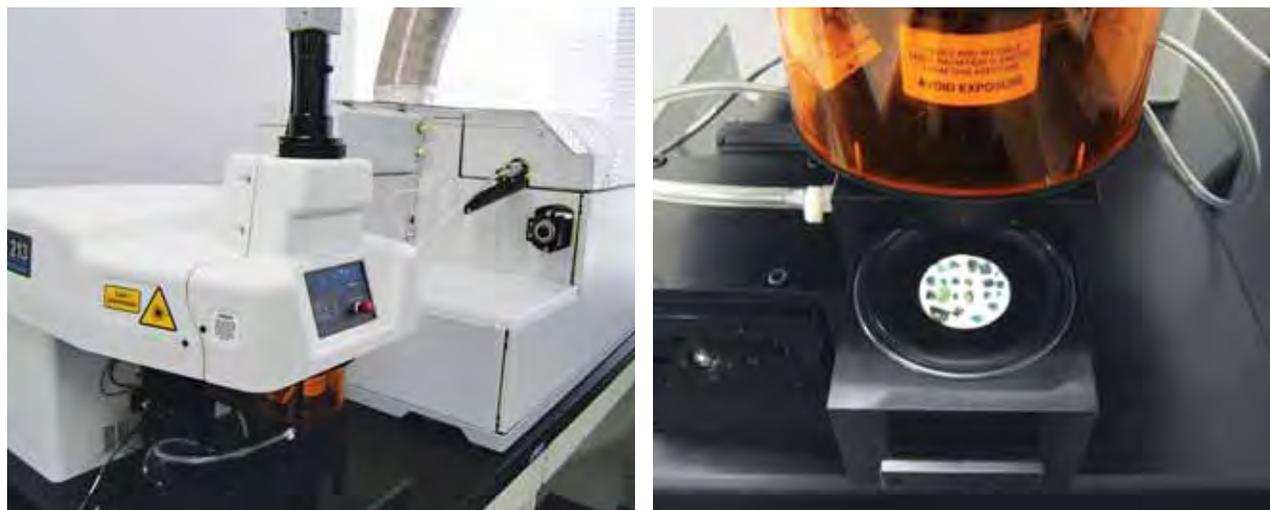
We analyzed 18 light blue, bright blue, and bluish green faceted samples of Mozambique tourmaline. We also tested four polished crystal fragments that were light violet-blue, pale blue, and light green (figure 9).

Internal features of all samples were observed with a gemological microscope. Refractive indices of all samples were measured with a standard gemological refractometer (Topcon) using a monochromatic Na-equivalent light source. Specific gravity was determined on all specimens by the hydrostatic method.

Chemical analyses of all samples were obtained by LA-ICP-MS (figure 10; table 2), which is widely used for the determination of major, minor, and trace elements in solids as well as for isotope-ratio

measurements (Jarvis and Williams, 1993; Günther and Hattendorf, 2005). The technique also has been applied to gem materials (see, e.g., Günther and Kane, 1999; Guillong and Günther, 2001). In this technique, a minute amount of the sample is vaporized by a high-energy laser beam, and the vaporized material is ionized into a plasma by a high-frequency power generator. This analytical method is capable of rapidly measuring a wide range of elements from helium to uranium, in very minute amounts (i.e., parts per million [ppm] to parts per billion [ppb] levels). The sample does not need to be placed in a vacuum with this technique, and a localized analysis of a specific area is possible with a narrow laser beam and a charge-coupling device (CCD) camera (to view the specific area). Currently, the spatial resolution (i.e., area of sample analyzed) achievable with laser ablation instruments is in the range of several micrometers, which is comparable to that of most other microbeam techniques (e.g., X-ray, electron, or proton microprobes). The measurement can be performed regardless of the condition of a sample (rough

Figure 10. The LA-ICP-MS system used in this study is shown on the left, with the laser ablation unit in the left foreground and the ICP-MS instrument behind it. The photo on the right is a close-up view of samples in the ablation chamber. Photos by Masaaki Kobayashi (left) and A. Abduriyim (right).



**TABLE 2.** Physical properties and LA-ICP-MS chemical data for Cu-bearing tourmalines from Brazil, Nigeria, and Mozambique.<sup>a</sup>

| Property/<br>chemical<br>composition | Brazil           |                           |                               |                  |                  |                               | Nigeria          |                  |
|--------------------------------------|------------------|---------------------------|-------------------------------|------------------|------------------|-------------------------------|------------------|------------------|
|                                      | Mina da Batalha  |                           |                               | Mulungu          | Alto dos Quintos | Edeko                         |                  |                  |
| Color                                | "Turquoise" blue | "Neon" blue, intense blue | Greenish blue to bluish green | "Emerald" green  | Light blue       | Light blue, light "neon" blue | Light blue       | Violetish blue   |
| No. samples                          | 6                | 25                        | 30                            | 10               | 14               | 10                            | 7                | 4                |
| <b>Properties</b>                    |                  |                           |                               |                  |                  |                               |                  |                  |
| R.I.                                 |                  |                           |                               |                  |                  |                               |                  |                  |
| $n_o$                                | 1.639–1.642      | 1.638–1.640               | 1.638–1.640                   | 1.638–1.640      | 1.639–1.640      | 1.638–1.640                   | 1.639–1.640      | 1.638–1.639      |
| $n_e$                                | 1.619–1.621      | 1.618–1.619               | 1.618–1.620                   | 1.619–1.620      | 1.619–1.621      | 1.619–1.620                   | 1.619–1.620      | 1.618–1.620      |
| Birefringence                        | 0.020–0.021      | 0.018–0.021               | 0.018–0.020                   | 0.019–0.020      | 0.019–0.020      | 0.019–0.020                   | 0.020            | 0.018–0.020      |
| S.G.                                 | 3.04–3.07        | 3.04–3.09                 | 3.06–3.08                     | 3.05–3.09        | 3.08–3.13        | 3.04–3.09                     | 3.06–3.09        | 3.08–3.09        |
| <b>Chemical composition</b>          |                  |                           |                               |                  |                  |                               |                  |                  |
| Major elements (wt.% oxide)          |                  |                           |                               |                  |                  |                               |                  |                  |
| Al <sub>2</sub> O <sub>3</sub>       | 37.85–39.25      | 37.96–39.02               | 38.30–39.74                   | 38.17–39.62      | 37.67–41.85      | 38.30–41.03                   | 39.14–41.31      | 39.98–41.09      |
| SiO <sub>2</sub>                     | 35.97–36.73      | 36.36–37.01               | 36.56–37.11                   | 36.54–37.56      | 35.96–38.47      | 36.96–38.11                   | 37.01–38.17      | 37.51–39.02      |
| B <sub>2</sub> O <sub>3</sub>        | 9.42–10.19       | 9.80–11.34                | 9.05–11.19                    | 9.57–12.62       | 8.98–9.96        | 9.05–11.19                    | 9.81–10.09       | 10.47–11.49      |
| Minor elements (wt.% oxide)          |                  |                           |                               |                  |                  |                               |                  |                  |
| Li <sub>2</sub> O                    | 1.58–1.71        | 1.60–1.74                 | 1.65–1.81                     | 1.51–1.85        | 1.61–1.71        | 1.34–1.75                     | 1.53–1.84        | 1.69–1.78        |
| Na <sub>2</sub> O                    | 1.98–2.49        | 2.20–2.35                 | 2.23–2.78                     | 1.70–2.87        | 1.75–2.47        | 1.62–2.78                     | 2.14–2.34        | 2.32–2.78        |
| MnO                                  | 0.29–0.34        | 0.02–2.96                 | 1.25–3.43                     | 0.97–2.52        | 0.15–0.58        | 0.13–0.92                     | 1.71–2.49        | 1.70–2.81        |
| <b>CuO</b>                           | <b>0.42–0.57</b> | <b>0.69–2.50</b>          | <b>0.74–2.17</b>              | <b>0.86–2.32</b> | <b>0.40–0.51</b> | <b>0.41–1.33</b>              | <b>0.48–0.95</b> | <b>0.60–2.01</b> |
| Trace elements (ppm)                 |                  |                           |                               |                  |                  |                               |                  |                  |
| Be                                   | 7–8              | 14–176                    | 14–64                         | 7–128            | 6–9              | 15–46                         | 5–6              | 5–58             |
| Mg                                   | 0.5–2            | 2–4470                    | 387–1070                      | 1000–6620        | 1–3              | 0.6–97                        | 2–8              | 2–15             |
| K                                    | 100–140          | 120–150                   | 127–280                       | 96–190           | 88–140           | 86–157                        | 120–270          | 160–240          |
| Ca                                   | 1250–1700        | 1350–7190                 | 3570–8090                     | 1680–6460        | 980–1770         | 1610–8880                     | 1160–1630        | 1480–1540        |
| Sc                                   | 0.7–1            | 1–3                       | 0.8–2                         | 2–4              | 0.6–1            | 0.6–1                         | 2–4              | 2                |
| Ti                                   | 18–41            | 9–410                     | 200–380                       | 280–880          | 16–42            | 12–220                        | 17–180           | 29–110           |
| V                                    | 0.5–0.9          | 0.2–12                    | 0.9–3                         | 2–16             | 0.6–2            | 0.2–6                         | 0.3–0.8          | 0.6–3            |
| Fe                                   | 6–41             | bdl–350                   | 580–1440                      | 1160–4260        | 12–130           | bdl–590                       | 17–97            | 38–68            |
| Zn                                   | 11–21            | 10–2490                   | 1510–9400                     | 420–12330        | 19–92            | 5–124                         | 12–88            | 11–93            |
| Ga                                   | 160–230          | 67–160                    | 49–130                        | 44–150           | 170–250          | 160–260                       | 140–210          | 190–270          |
| Ge                                   | 3–6              | 5–43                      | 7–34                          | 4–45             | 4–10             | 15–26                         | 10–22            | 13–57            |
| Sr                                   | bdl              | 0.1–4                     | 0.4–3                         | bdl–58           | bdl              | bdl–2                         | bdl              | bdl–3            |
| Nb                                   | 1–3              | bdl–3                     | 0.5–4                         | 0.5–0.6          | 1.2–3            | 0.8–7                         | 0.1–0.6          | 0.2–0.5          |
| Sn                                   | bdl–0.5          | bdl–2                     | bdl–2                         | bdl–4            | 2–5              | 3–6                           | 0.5–4            | bdl–0.8          |
| Sb                                   | bdl              | 1–22                      | 16–41                         | 0.2–22           | bdl–0.3          | 3–17                          | 0.2–2            | 0.3–5            |
| Ta                                   | 1–2              | 1–10                      | 0.2–1                         | 0.4–3            | 0.9–2            | 67–23                         | 0.3–3            | 1–2              |
| Pb                                   | 1–5              | 22–120                    | 37–242                        | 5–180            | 1–4              | 31–65                         | 18–36            | 24–130           |
| Bi                                   | 14–56            | 290–13840                 | 380–4490                      | 290–11730        | 19–79            | 78–1130                       | 44–140           | 150–880          |

<sup>a</sup> The table shows the minimum and maximum values obtained for 95 samples from Brazil, 81 tourmalines from Nigeria, and 22 specimens from Mozambique. Each sample was analyzed in three spots, using a laser repetition rate of 10 Hz and an ablation interval of 15 sec. Data for Ca and K showed poor correlation between each analysis, while the other elements showed little variation. Abbreviation: bdl = below detection limit of the LA-ICP-MS system. Detection limits (ppm) are as follows: Li (1.9), Be (0.1), B (1.5), Na (17), Mg (0.4), Al (0.7), Si (520), K (3.4), Ca (200), Sc

or polished) when using the fourth harmonic (266 nm) and the fifth harmonic (213 nm) of a tunable Nd-YAG laser or using an excimer laser (193 nm). The analysis creates a small surface crater (diameter of ~60–80 μm and depth of ~5–10 μm), so on a faceted stone the girdle is the most suitable area for testing. LA-ICP-MS is four orders of magnitude more sensitive than laser-induced breakdown spectroscopy (LIBS; Günther and Hattendorf, 2005).

We used a Merchantek UP-213A/F laser ablation system (New Wave Research) with an Agilent 7500a ICP-MS for this study (again, see figure 10). A 213 nm laser was employed with a power of 2.5 mJ and a spot size of 60 μm, using a carrier gas mixture of helium (0.50 ml/min) and argon (1.20–1.23 ml/min). The laser repetition rate was 10 Hz, with an energy density of 14.63 J/cm<sup>2</sup>, ablation interval of 15 seconds, elapsed time of 0.01 seconds, and a measure-

| Nigeria (cont.)     |                               |                  | Mozambique   |                  |                        |                  |                  |
|---------------------|-------------------------------|------------------|--------------|------------------|------------------------|------------------|------------------|
| Edeko (cont.)       |                               |                  | Alto Ligonha |                  |                        |                  |                  |
| "Neon" blue to blue | Greenish blue to bluish green | "Emerald" green  | Light blue   | Bright blue      | Violet-blue, pale blue | Bluish green     | Light green      |
| 30                  | 30                            | 10               | 1            | 7                | 2                      | 10               | 2                |
| 1.638–1.640         | 1.639–1.641                   | 1.639–1.640      | 1.639        | 1.638–1.639      | 1.639                  | 1.639–1.640      | 1.639            |
| 1.618–1.621         | 1.620–1.621                   | 1.619–1.620      | 1.619        | 1.618–1.620      | 1.620                  | 1.619–1.620      | 1.619, 1.620     |
| 0.018–0.021         | 0.019–0.021                   | 0.019–0.020      | 0.020        | 0.018–0.019      | 0.019                  | 0.020–0.021      | 0.019, 0.020     |
| 3.04–3.09           | 3.06–3.10                     | 3.07–3.09        | 3.08         | 3.07–3.09        | 3.07, 3.08             | 3.06–3.09        | 3.09, 3.10       |
| 40.60–42.97         | 39.14–42.31                   | 38.66–41.62      | 39.53        | 39.49–41.52      | 39.20–40.23            | 37.18–38.69      | 38.16–38.81      |
| 39.43–41.96         | 36.33–39.74                   | 36.95–39.02      | 37.64        | 37.83–39.44      | 37.10–38.67            | 36.81–38.26      | 37.80–38.47      |
| 9.80–11.03          | 10.47–12.31                   | 9.03–11.52       | 11.84        | 8.73–9.42        | 9.11–10.23             | 9.81–12.22       | 8.56–9.01        |
| 1.80–1.93           | 1.65–1.99                     | 1.40–2.02        | 1.68         | 1.37–2.07        | 1.33–1.46              | 1.75–1.88        | 1.35–1.47        |
| 2.32–2.60           | 2.07–3.03                     | 2.40–2.80        | 2.21         | 1.87–2.66        | 2.15–2.27              | 1.78–2.89        | 2.00–2.14        |
| 1.71–6.06           | 1.83–3.96                     | 2.81–5.05        | 3.55         | 0.03–0.40        | 2.62–3.04              | 3.28–4.81        | 3.09–3.36        |
| <b>0.60–3.20</b>    | <b>0.89–2.15</b>              | <b>1.03–2.36</b> | <b>1.19</b>  | <b>0.26–0.51</b> | <b>0.33–0.40</b>       | <b>2.08–3.21</b> | <b>0.16–0.26</b> |
| 6–52                | 9–110                         | 5–89             | 7            | 71–300           | 29–33                  | 24–96            | 38–42            |
| 4–38                | 13–64                         | 61–86            | 4            | bdl–3            | bdl–0.4                | bdl–7            | 7–9              |
| 130–260             | 130–290                       | 300–360          | 230          | 93–130           | 140–150                | 210–240          | 130–170          |
| 1620–5590           | 1710–6850                     | 2240–5350        | 1670         | 1640–9230        | 4680–5060              | 1900–6130        | 1900–2460        |
| 2–3                 | 0.8–2                         | 1–2              | 8            | 2–6              | 1–2                    | 9–15             | 4–11             |
| 27–450              | 280–610                       | 370–870          | 140          | 11–46            | 8–11                   | 19–1190          | 27–30            |
| 0.3–0.6             | 0.7–2                         | 1–2              | 1            | 0.3–0.9          | 0.4–0.8                | 0.8–5            | 1–2              |
| 50–660              | 200–1990                      | 650–3910         | 150          | bdl–490          | 100–110                | 36–790           | 2450–2960        |
| 57–270              | 95–1310                       | 700–1690         | 110          | bdl              | 4–7                    | 250–980          | 36–45            |
| 130–210             | 88–290                        | 180–300          | 300          | 160–370          | 210–250                | 180–260          | 200–220          |
| 9–34                | 12–47                         | 19–62            | 22           | 12–29            | 6–12                   | 26–65            | 10–13            |
| bdl–4               | 0.1–6                         | 0.1–3            | 0.1          | 0.1–2            | 0.5–0.7                | 0.2–2            | 0.9–2            |
| 0.1–0.4             | 0.6–2                         | 0.9–1            | 0.6          | 0.2–2            | 3–4                    | 0.4–3            | 0.4              |
| 0.6–1               | bdl–0.4                       | 0.4–1            | bdl          | bdl              | 5–6                    | bdl              | 36–39            |
| 0.4–7               | 8–14                          | 3–14             | 0.5          | 14–54            | 5–6                    | 5–11             | 11–13            |
| bdl–3               | bdl–3                         | 0.9–2            | 2            | 0.3–5            | 2–3                    | 2–8              | 0.9–1            |
| 38–750              | 56–350                        | 38–420           | 32           | 90–210           | 61–78                  | 250–710          | 21–23            |
| 270–10540           | 1030–4470                     | 44–2590          | 92           | 3340–19480       | 1300–1460              | 1090–7910        | 2080–2800        |

(0.3), Ti (0.8), V (0.13), Cr (14), Mn (0.3), Fe (7), Cu (0.3), Zn (2.0), Ga (0.2), Ge (0.5), Sr (0.03), Nb (0.02), Sn (0.4), Sb (0.04), Ta (0.01), Pb (0.1), and Bi (0.01). H<sub>2</sub>O cannot be measured by LA-ICP-MS, but this value was reported as 3.13 wt.% by Fritsch et al. (1990). Fluorine and chlorine were not measured in this study.

ment time of 40 seconds. Thus, it was possible to detect the signal of all isotope ratios (atomic mass/atomic number of 2–260) and achieve an analytical precision of RSD (relative standard deviation) of less than 10%. However, Mg, Si, K, and Fe occasionally have higher RSDs in tourmaline due to the interference from a material matrix and polyatomic ions such as <sup>24</sup>Mg (<sup>12</sup>C<sup>12</sup>C), <sup>28</sup>Si (<sup>12</sup>C<sup>16</sup>O), <sup>39</sup>K (<sup>23</sup>Na<sup>16</sup>O), <sup>56</sup>Fe (<sup>40</sup>Ar<sup>16</sup>O<sup>+</sup>, <sup>40</sup>Ca<sup>16</sup>O, <sup>28</sup>Si<sup>28</sup>Si).

During laser ablation sampling, matrix-matched calibration is necessary to avoid problems associated with elemental fractionation (i.e., the ablated mass composition is not the same as the actual sample composition). In this study, quantitative analysis was performed by calculating a concentration conversion factor for each element, and a glass reference material (NIST SRM 612; Pearce et al., 1996) was used as an external standard of known isotopic

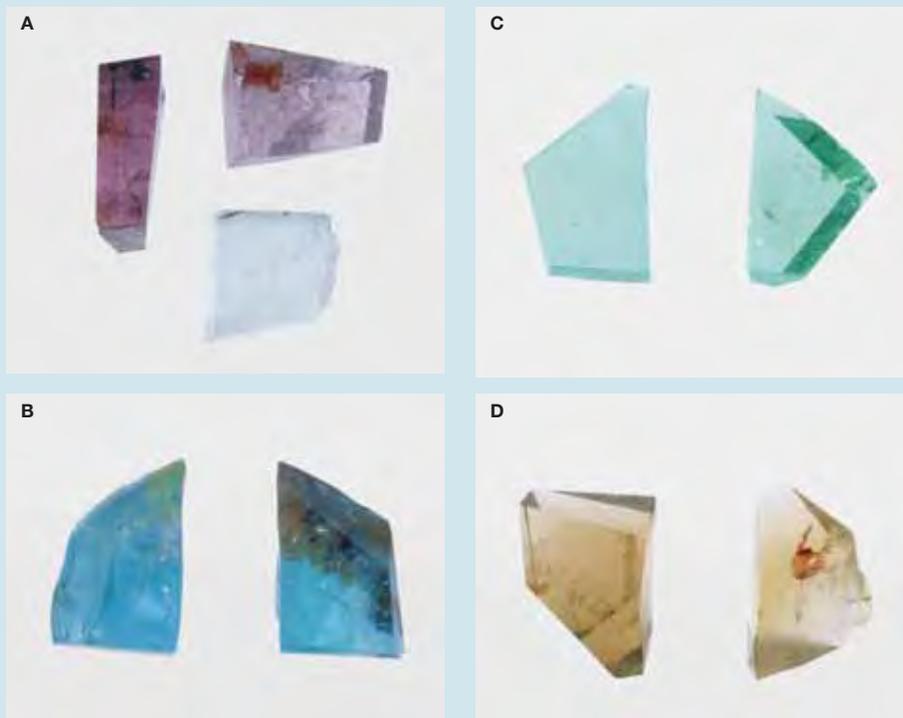
## BOX A: COLOR MODIFICATION WITH HEAT TREATMENT OF SOME MOZAMBIQUE TOURMALINES

It is estimated that 80% of the production of Brazilian Cu-bearing tourmaline does not show bright blue to greenish blue “Paraíba” colors until it has undergone heat treatment. Low to moderate temperatures are used (e.g., 350–550°C in Koivula and Kammerling, 1990; 550°C in Fritsch et al., 1990). Heating is also performed on Nigerian violet and violet-blue tourmaline (Zang et al., 2001). The color can be changed from purplish red to “emerald” green, greenish blue to “neon” blue, and violet blue to “neon” blue (Fritsch et al., 1990; Bernardes, 1999; Shigley et al., 2001). The chromophores Mn and Cu in particular play an important role in the cause of color and the color modification of “Paraíba” tourmaline.

To investigate the effect of heat treatment on the newly discovered Cu-bearing tourmaline from Mozambique, we selected four representative polished fragments (purplish pink, violet-blue, light green, and yellow; see figure A-1). The purplish pink fragment was cut into three sections, with one retained as a control and the other two subjected to progressively higher temperatures. All of the other fragments were cut into two sections, with one of each retained as a color control and the others heat treated. We buried the sections to be

treated in aluminum powder within a crucible. We then heated the crucible in an electric furnace in an oxidizing atmosphere. The temperature was carefully controlled, and heating was performed (and the samples checked) at two-hour intervals at 300, 350, 400, 450, and 500°C. The furnace was then turned off, and the samples cooled to about 60–70°C within one hour.

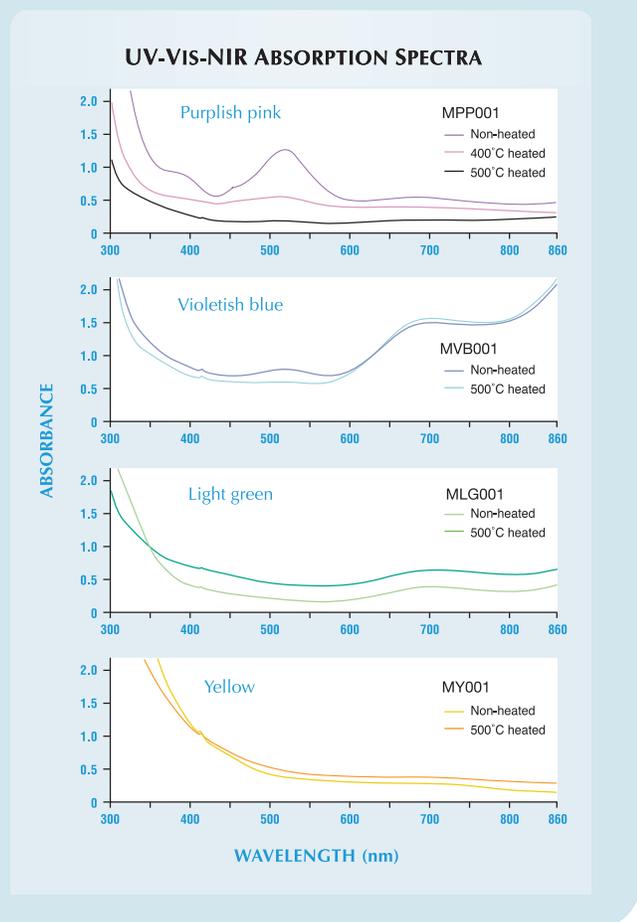
The purplish pink specimen lightened slightly at 400°C, and its counterpart faded to colorless at 500°C (figure A-1). Pink coloration related to Mn<sup>3+</sup> absorption at about 515 nm disappeared when the manganese was reduced to Mn<sup>2+</sup> during heat treatment (figure A-2). Heating of a light violet-blue specimen resulted in “neon” blue coloration at 500°C. This violet-blue sample exhibited a broad band centered at about 690 nm that is related to Cu<sup>2+</sup>; the band remained unchanged after heating, though a broad band related to Mn<sup>3+</sup> absorption centered at about 515 nm was removed. The color of a light green sample intensified slightly with heating, whereas a yellow specimen remained unchanged by the heating process. No significant changes were seen in the visible-range absorption spectra of the light green and yellow samples after heating to 500°C, but the absorption peaks did shift toward the ultraviolet.



*Figure A-1. Four polished fragments of Cu-bearing Mozambique tourmaline were cut into sections, with one section of each retained as the control color and the other(s) subjected to heating experiments. (A) The purplish pink sample started to fade at 400°C (top right), and at 500°C the material was colorless (bottom right). (B) The light violet-blue specimen became “neon” blue (right) after heating to 500°C. (C) The green fragment became only slightly more intense (right) with heating to 500°C. (D) The yellow sample was not improved by heating. Before they were sliced for the heating experiments, the samples weighed 2.97 ct, 4.65 ct, 0.95 ct, and 2.15 ct, respectively. Photos by Masaaki Kobayashi.*

From these preliminary experiments, it appears that not all color varieties of Mozambique Cu-bearing tourmaline can be improved by heat treatment at these conditions. However, if the proper starting materials are selected, heating may yield favorable color modification. Because exposure to heat can damage some stones, especially those with liquid inclusions and pre-existing fractures, it is critical that the starting material is carefully selected and the temperature controlled precisely.

Figure A-2. These UV-Vis-NIR spectra of Cu-bearing Mozambique tourmalines of various colors show absorption characteristics before and after the samples were heated in an oxidizing atmosphere. The purplish pink sample (MPP001) exhibits a decrease in  $Mn^{3+}$  absorption at about 515 nm, when this element was reduced to  $Mn^{2+}$  as the temperature increased from 400°C to 500°C. The violetish blue sample (MVB001) exhibits a broad band centered at about 690 nm that is related to  $Cu^{2+}$ ; the band remained unchanged after heating, although the sample turned “neon” blue when heated to 500°C. No significant changes are seen in the absorption spectra of the light green (MLG001) and yellow (MY001) samples after heating to 500°C.



composition to calculate the mass of measured isotopic ratios in the tourmaline samples. The contents of major and minor elements were calculated in weight percent (wt.%) oxides, while the trace elements are reported in parts per million by weight. Three analytical runs were performed on separate locations on each sample (on the girdle of the faceted stones), and average data are reported for each sample in table 2. Detection limits of  $3\sigma$  (standard deviations) were calculated for 26 selected elements that were analyzed 10 times in empty runs, and are reported in the footnote to table 2.

To investigate the effects of heat treatment on the new Mozambique Cu-bearing tourmaline, we conducted experiments on four representative crystal fragments (purplish pink, violet-blue, light green, and yellow, as described in table 1) using an Advantec model FUH712PA electric furnace. UV-visible spectroscopic analyses were conducted with a Shimadzu UV-2450 spectrophotometer on both heated and unheated sections of each crystal fragment (see box A).

## RESULTS AND DISCUSSION

**Gemological Properties.** The physical properties of our Cu-bearing tourmaline samples are reported in table 2 and summarized below. The refractive indices of 95 samples from Brazil were  $n_o=1.638-1.642$  and  $n_e=1.618-1.621$ , birefringence was 0.018–0.021, and S.G. values varied from 3.04 to 3.13. The R.I. values mostly fell within the ranges reported for Cu-bearing elbaite tourmalines from Brazil (e.g., Mina da Batalha—Fritsch et al., 1990; Mulungu—Shigley et al., 2001; and Alto dos Quintos—Milisenda, 2005), but our range of S.G. values was slightly higher.

The gemological properties of the 81 tourmaline samples from Edeko, Nigeria, were: R.I.— $n_o=1.638-1.641$  and  $n_e=1.619-1.620$ ; birefringence—0.018–0.021; S.G.—3.04–3.10. These values are consistent with data reported for similar Nigerian material by Smith et al. (2001). All specimens exhibited typical tourmaline inclusions, such as two-phase liquid-gas inclusions, healed fractures, “feathers,” and crystals (e.g., mica, figure 11). Fritsch et al. (1990), Koivula et al. (1992), Cassedanne (1996), and Shigley et al. (2001) reported that similar features were common in “Paraíba” tourmalines from Brazil.

It is notable, however, that most of the Nigerian tourmalines (all of which were faceted) displayed thin yellowish brown needle-like growth tubes oriented parallel to the optic axis (figure 12).



Figure 11. The mica inclusions seen in this Nigerian tourmaline formed transparent hexagonal platelets. Photomicrograph by Makoto Okano; magnified 50 $\times$ .

We observed these growth tubes most frequently in the blue tourmalines, but they also were seen in a few of the green samples. The Brazilian and Mozambique faceted samples showed few of these yellowish brown growth tubes, but some were distributed near the surface of crystal fragments from both countries; their coloration is possibly due to iron-oxide staining. In faceted stones, these tubes may be indicative of tourmalines from Nigeria. Interestingly, four of our Nigerian specimens also contained inclusions of native copper (identified by LA-ICP-MS) that appeared brownish yellow with magnification (figure 13). A distinct yellow reflectance in the apparent metallic luster was visible when the stones were viewed with a fiber-optic light source. Thin platelets and scattered grains of the native copper, ranging from 10 to 150  $\mu\text{m}$  long in varying thicknesses, were observed in orientations parallel to the *c*-axis. Koivula et al. (1992) and Brandstätter and Niedermayr (1994) reported seeing platelet-like native copper inclusions in some tourmalines from Mina da Batalha, Paraíba, but only one of our samples from this locality contained these inclusions.

Gemological properties obtained for our 22 Mozambique tourmaline samples were: R.I.— $n_o=1.638\text{--}1.640$  and  $n_e=1.618\text{--}1.620$ ; birefringence— $0.018\text{--}0.021$ ; and S.G.— $3.06\text{--}3.10$ . These properties fell within the ranges listed for elbaite tourmaline from Brazil and Nigeria (table 2; see also Fritsch et al., 1990). The internal features consisted of the liq-



Figure 12. Most of the Nigerian tourmalines contained yellowish brown growth tubes. Photomicrograph by A. Abduriyim; magnified 40 $\times$ .

uid inclusions, two-phase liquid-gas inclusions, and healed fractures that are commonly seen in tourmaline; no particles of native copper were observed.

**Chemical Analysis.** The chemical data for the Cu-bearing tourmalines from Brazil, Nigeria, and Mozambique are summarized in table 2. For the purposes of this article, these results are described below for each of three color groups: “Paraíba” blue, blue-green, and “emerald” green.

Figure 13. These brownish yellow-appearing metallic inclusions in Nigerian tourmaline were identified as native copper by LA-ICP-MS. The copper platelets are oriented parallel to the *c*-axis of the tourmaline. Photomicrograph by A. Abduriyim; magnified 60 $\times$ .



*“Paraíba” Blue.* Included in this color group are light blue, violetish blue, “turquoise” blue, “neon” blue, and blue tourmalines. The 31 Mina da Batalha tourmalines in this color range were “turquoise” blue, “neon” blue, and intense blue. These samples consistently contained 18 minor and trace elements (Li, B, Be, Na, Mg, K, Ca, Sc, Ti, V, Mn, Fe, Cu, Zn, Ga, Ge, Pb, Bi). Other trace elements such as Sr, Nb, Sn, and Sb were above the detection limits in some specimens. Generally, our Mina da Batalha “turquoise” blue specimens had lower Cu and Mn contents than in the other colors (i.e., up to 0.57 wt.% CuO and 0.34 wt.% MnO). Our “neon” blue and intense blue specimens contained more Cu and Mn than previously has been reported for blue elbaite tourmaline from Mina da Batalha (up to 2.50 wt.% CuO and 2.96 wt.% MnO; see table 3)

By comparison, our Nigerian “Paraíba” blue tourmaline showed more Cu and Mn than these specimens from Mina da Batalha. The latter samples contained limited amounts of the trace elements Ga, Ge, and Pb, while Be and Zn were relatively abundant.

The 14 specimens of Brazilian Mulungu tourmaline analyzed for this study were all light blue, and they contained relatively low levels of Cu and Mn (mostly below 0.51 wt.% CuO and 0.58 wt.% MnO). The Cu contents of our samples were a little higher than the level reported for a blue sample by Shigley et al. (2001): 0.44 wt.% CuO (table 3). The trace elements Sc, Ga, Ge, Nb, Sn, and Pb were consistently detectable, but contents of K, Ti, Ge, and Pb were low compared to our samples of light blue tourmaline from Nigeria.

Three light blue specimens from Alto dos

Quintos, Brazil, were quite similar in color to Mulungu tourmaline, with seven specimens of lighter “neon” blue color. Most analyzed elements for these Alto dos Quintos stones were in good agreement with those of the Mulungu specimens, except that Ca, Bi, Sb, Ta, and Pb showed higher values.

The Nigerian specimens analyzed in this color group were violetish blue, “neon” blue, and light blue; they contained 0.48–3.20 wt.% CuO and 1.70–6.06 wt.% MnO. The light blue tourmalines revealed the lowest Cu and Mn contents (<0.95 wt.% CuO, <2.49 wt.% MnO), and four violetish blue specimens showed almost the same range of Cu (0.60–2.01 wt.% CuO) as reported in violet-blue Nigerian tourmalines by Zang et al. (2001; table 3). The transition-metal elements Ti, V, and Fe were at trace levels, but Cr was characteristically below the detection limits of our instrument (<13.7 ppm). Other trace elements (Mg, Ti, Fe, Ca, K, Zn, Ga, Ge, Pb, and Bi) were usually present in significant concentrations in all the “Paraíba” blue Nigerian tourmalines, in agreement with Zang et al. (2001). Of the light elements, Li<sub>2</sub>O was between 1.53 and 1.93 wt.%, while B<sub>2</sub>O<sub>3</sub> had a wider range (9.80–11.49 wt.%), and Be was detected only in trace amounts.

The bright blue specimens of Mozambique tourmaline showed amounts of Al and Si comparable to those of Cu-bearing elbaite from Nigeria and Brazil. However, the Cu and Mn contents of most Mozambique samples were lower than in samples from Nigeria and Brazil. They ranged from 0.26 to 0.51 wt.% CuO and 0.03 to 0.40 wt.% MnO. The trace amounts of Be, Ca, Sr, Sb, Pb, and Bi were higher than those found in “Paraíba” blue tourmalines

**TABLE 3.** Contents of Cu and Mn in “Paraíba” blue, blue-green, and “emerald” green tourmaline from Brazil and Nigeria, as reported in the literature.

| Samples and Cu/Mn content | Brazil                                 |            |                 |                                |            |                                    | Nigeria    |                                 |
|---------------------------|--|------------|-----------------|--------------------------------|------------|------------------------------------|------------|---------------------------------|
|                           | Mina da Batalha (Fritsch et al., 1990) |            |                 | Mulungu (Shigley et al., 2001) |            | Alto dos Quintos (Milisenda, 2005) |            | Edeko (Zang, 2001)              |
| Color                     | “Paraíba” blue (blue)                  | Blue-green | “Emerald” green | “Paraíba” blue (light blue)    | Blue-green | “Paraíba” blue (light blue, blue)  | Blue-green | “Paraíba” blue (violetish blue) |
| No. samples               | 1                                      | 3          | 1               | 1                              | 5          | 10                                 | 2          | 3                               |
| Oxides (wt.%)             |  |            |                 |                                |            |                                    |            |                                 |
| CuO                       | 0.72                                   | 1.08–2.37  | 2.38            | 0.44                           | 0.41–0.69  | 0.32–1.52                          | 1.28, 1.48 | 0.51–2.18                       |
| MnO                       | 2.30                                   | 0.85–1.48  | 2.16            | 0.42                           | 0.79–3.15  | 0.11–2.53                          | 2.44       | 2.13–2.59                       |

from other localities, and Mg, Zn, and Sn were below the detection limits of our LA-ICP-MS system in most of the Mozambique samples. One specimen (MS001) of light blue color had significantly higher Cu and Mn contents than our light blue tourmalines from Nigeria and Rio Grande do Norte. Subsequent analyses of two polished crystal fragments (MVB001-002, violetish blue and pale blue) revealed the highest concentration of Cu measured in Mozambique tourmalines of similar color (up to 0.40 wt.% CuO), as well as enriched Mn (up to 3.04 wt.% MnO). Notably high amounts of Ca and Bi—and low levels of Ti, Zn, and Ge—were detected in these two specimens, while Mg was below or near the detection limit (<0.40 ppm).

**Blue-Green.** This color series consists of greenish blue to bluish green samples. We measured slightly higher contents of Al and Si in the Nigerian tourmalines compared to those from the other localities. The transition-metal elements Mn, Fe, and Ti strongly correlated to blue-green color, especially in

Nigerian tourmaline with the stronger coloration. Most of the Brazilian tourmalines were notably enriched in Mg, Zn, and Sb, and depleted in Ga, Ge, and Pb, while the highest Bi content was found in blue-green samples from both Brazil and Nigeria.

The Cu and Mn contents were especially noteworthy in the bluish green to greenish blue tourmalines from Mozambique, which contained much more of these elements (up to 3.21 wt.% CuO and 4.81 wt.% MnO) than did the samples from the other two countries. Although the trace elements Sc, Ga, and Pb in most of the specimens from Mozambique were higher than in equivalently colored tourmaline from Nigeria and Brazil, only minute amounts of Mg were detected in a few of the Mozambique stones.

**“Emerald” Green.** In the “emerald” green Nigerian tourmalines analyzed, most compositions overlapped those of the blue-green series from this area. However, the amounts of Ti, Mn, Fe, Cu, and Bi dif-

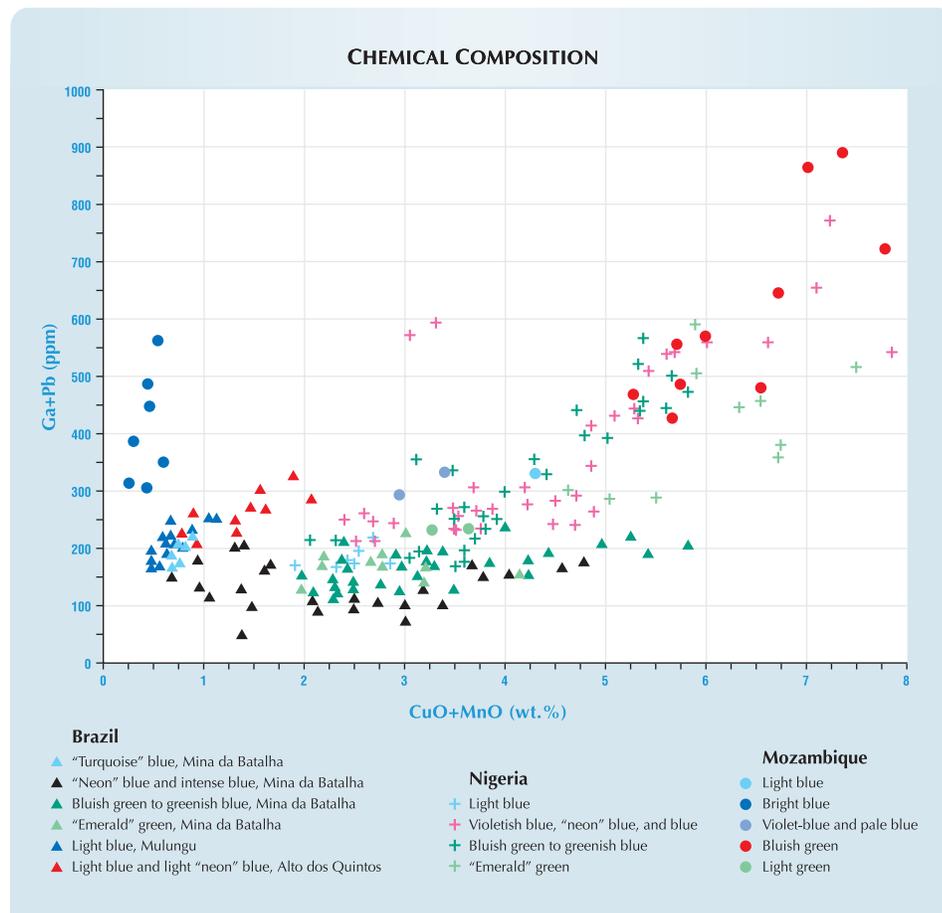


Figure 14. Chemical data obtained by LA-ICP-MS on all 198 samples are plotted according to CuO+MnO versus Ga+Pb in this diagram. The Nigerian tourmalines commonly had higher CuO+MnO and Ga+Pb values. The Brazilian samples showed some discrete populations compared to the Nigerian tourmalines, with lower Cu, Mn, and Pb contents overall. The bright blue Mozambique tourmalines had some of the lowest Cu and Mn contents, but these elements (together with Pb) were enriched in the blue-green tourmalines from this locality. Relatively high levels of Ga+Pb also were typical of the Mozambique samples.

ferred between the two color groups. As expected, the contents of the chromophores Ti, Mn, and Fe were highest in our “emerald” green specimens and lowest in the light blue samples. Notably, the “emerald” green specimens from Mina da Batalha typically contained much more Mg and Zn than those from Nigeria. None of our Mozambique samples displayed a distinct “emerald” green color; rather, they were light green. Our two light green specimens (MLG001-002) revealed much lower Cu than was detected in “Paraíba” blue material from the same locality, as well as in Nigerian and Brazilian samples from all three color series. These light green samples also contained low amounts of Mg, Ti, Zn, and Pb, and enriched Sn.

**Chemical Fingerprinting.** To evaluate the usefulness of chemical data for separating the tourmalines from the various localities, we plotted two different combinations of minor and trace elements (figures 14 and 15) in light of the chemical trends noted above.

The tourmalines from Nigeria and from all three localities in Brazil are relatively distinct in the diagrams. As seen in figure 14, by plotting Ga+Pb versus CuO+MnO it is possible to separate the tourmalines according to the three color series: “Paraíba” blue, blue-green, and “emerald” green. The light blue Nigerian samples show some overlap with blue-green and “emerald” green Mina da Batalha specimens. However, the tourmalines of similar light blue color from Mulungu and Alto dos Quintos, as well as “turquoise” blue samples from Mina da Batalha, define an area of lower Cu and Mn contents.

The Mozambique tourmalines show distinct variations in their composition according to color. The seven bright blue stones fall into a very limited field that is characterized by low concentrations of CuO+MnO (<1 wt.%) and enriched Ga+Pb (>300 ppm; figure 14). These tourmalines can be clearly differentiated from the Nigerian and Brazilian stones on this basis. The Mozambique light blue and bluish

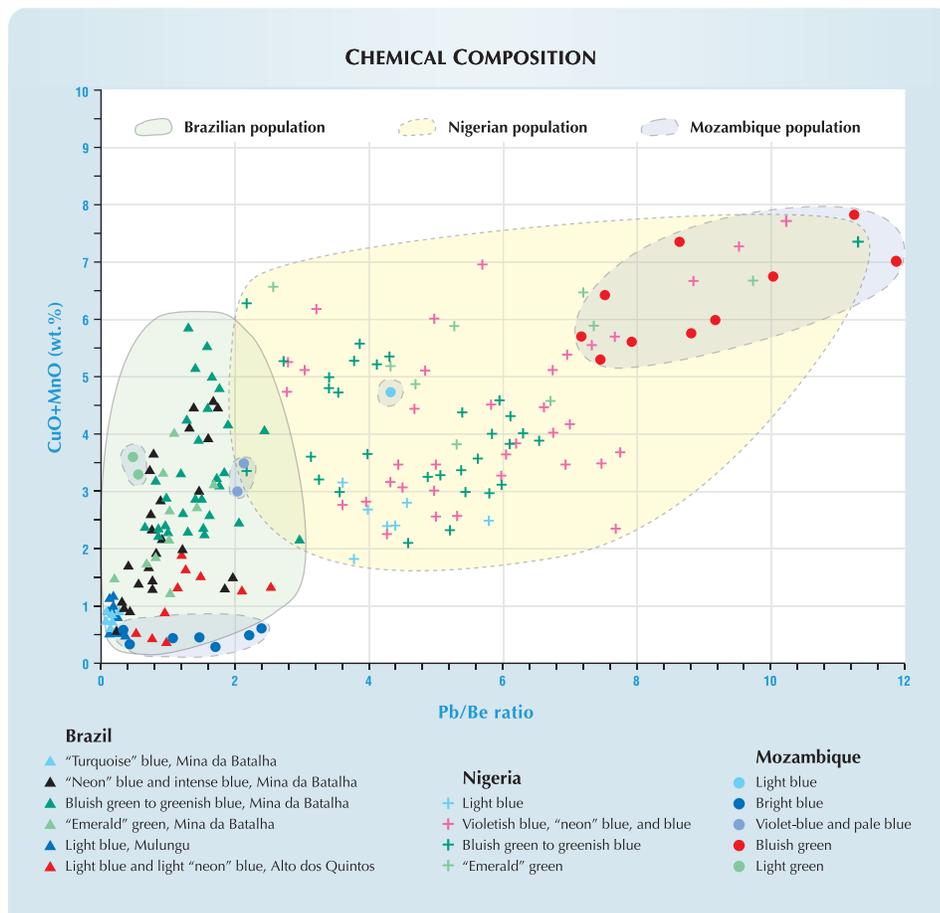


Figure 15. In this plot of CuO+MnO versus the ratio Pb/Be, there is clear separation of most Nigerian and Brazilian specimens, but a few blue-green from these localities show minor overlap. The Mozambique samples overlap the Nigerian and Brazilian fields in various places according to color.

green tourmalines are characterized by higher concentrations of CuO+MnO (>4 wt.%) and a similar concentration of Ga+Pb (>300 ppm), which is distinctly higher than Brazilian stones but overlaps the Nigerian samples. The data for the four crystal fragments of Mozambique tourmaline (light green, violetish blue, and pale blue) show lower concentrations of CuO+MnO (<4 wt.%). The violetish blue sample is distinct from "Paraíba" blue material from the Brazilian localities, but it overlaps samples of the same color from Nigeria. Although the composition of the two light green fragments overlap the Brazilian and Nigerian blue-green and "emerald" green samples in figure 14, they are chemically distinct in their very low CuO contents.

The CuO+MnO versus Pb/Be diagram (figure 15) is more effective at separating the Nigerian and Brazilian tourmalines. The Pb/Be ratio for the Brazilian tourmalines is usually less than 3, whereas this ratio for Nigerian tourmalines is typically much higher (3 to 11). A few blue-green specimens from Nigeria show a very small overlap with similarly colored Mina da Batalha tourmaline.

The blue-green tourmalines from Mozambique had the highest values of Cu, Mn, Ga, and Pb in this

study. However, the points representing these 10 samples lie in fields that almost completely overlap the Nigerian blue-green and "emerald" green stones. The lowest ratios of Pb/Be in the Mozambique tourmalines were found in the low Cu- and high Mn-bearing violetish blue and light green fragments, as well as in the lowest Cu- and Mn-bearing bright blue samples; they overlap the Brazilian population in figure 15.

According to the data from this study, the chemical fingerprinting methods used in figures 14 and 15 are not very effective at separating the Mozambique blue-green elbaite from the Nigerian tourmalines, but they are effective in separating tourmalines from the two African localities from those found in Brazil. In addition, our samples from the three Brazilian mines fell into discrete or partially overlapping fields. The chemical data also showed that, in general, the more intense blue-green and "emerald" green colors correlated to higher Cu and Mn contents.

However, a number of trace elements such as Mg, Ga, Pb, and Bi were present at different levels in the Mozambique blue-green elbaite compared to what was detected in blue-green stones from Nigeria. A ternary diagram of Mg-Zn-Pb (figure 16)

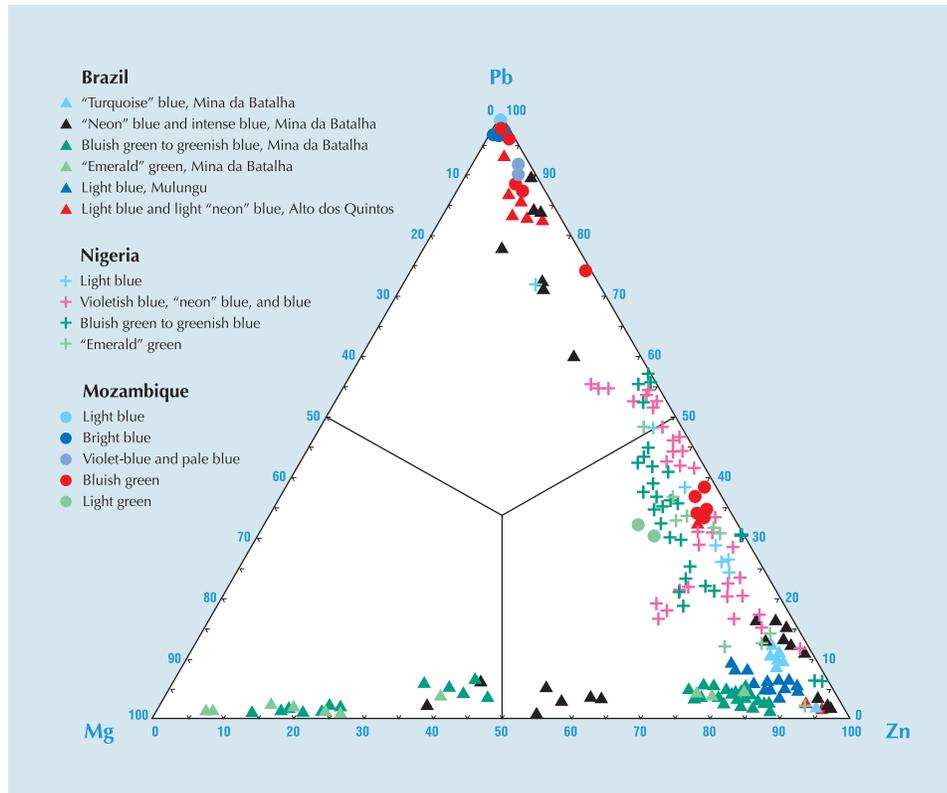


Figure 16. This Mg-Zn-Pb ternary diagram indicates that the Nigerian specimens are typically Pb-Zn dominant, the Brazilian samples are Mg-Zn dominant, and the Mozambique tourmalines are Pb dominant with some transitional Pb-Zn compositions.

provides a convenient way to help differentiate some Cu-bearing tourmaline from these three countries. The Nigerian specimens occupy the Pb-Zn-dominant fields, while most of the Brazilian tourmalines fall into the Mg-Zn region, and most of the Mozambique samples are Pb dominant (with some intermediate Pb-Zn compositions). There is a clear separation in the tourmaline samples from two of the Brazilian mining areas (Mina da Batalha and Mulungu), and in the samples from Nigeria, and Mozambique. However, some Alto dos Quintos specimens overlap the Nigerian and other Brazilian stones. Most importantly, whereas the low Cu- and high Mn-bearing (violet-blue, pale blue, and light green) Mozambique samples cannot be separated conclusively from the Brazilian materials with figures 14 and 15, this ternary diagram clearly distinguishes these localities.

#### NOMENCLATURE OF "PARAÍBA" TOURMALINE

The Association of Gemmological Laboratories (AGL) in Japan currently specifies that a blue-to-green tourmaline showing the characteristic "neon" color due to copper can only be called "Paraíba" as a trade name on an identification report when the stone is confirmed to be from Brazil. AGL allows the "Paraíba" name to be used for tourmalines from Rio Grande do Norte (Mulungu and Alto dos Quintos), since separating them from Mina da Batalha stones is difficult, and material imported into Japan is a mixture of tourmalines from both states. This policy is consistent with that advocated by most gem dealers who are handling the Brazilian "Paraíba" tourmaline. However, as supported by the research reported in this article, Cu-bearing tourmalines from Brazil, Nigeria, and Mozambique are difficult to distinguish from one another by standard gemological testing methods. Therefore, AGL and the Laboratory Manual Harmonization Committee (LMHC) decided to reconsider the nomenclature for "Paraíba" tourmaline. The LMHC consists of representatives from the AGTA-Gemmological Testing Center (U.S.), CIS-GEM (Italy), GAAJ Laboratory (Japan), GIA Laboratory (USA), GIT-Gem Testing Laboratory (Thailand), Gübelin Gem Lab (Switzerland), and SSEF Swiss Gemmological Institute (Switzerland). At the LMHC's October 2005 meeting in Lucerne, and at the February 2006 Gemstone Industry & Laboratory Conference in Tucson, the LMHC group agreed to define "Paraíba" tourmaline as a blue ("neon" blue,



Figure 17. Surrounded by diamonds, the center stone in this ring is a 10.91 ct oval-cut Paraíba tourmaline that was faceted in 2003 from a crystal found during the original discovery of this tourmaline in the late 1980s at Mina da Batalha. The intense "neon" blue color of this unheated stone is representative of the finest tourmaline from this mine. Courtesy of a private collector, in collaboration with Brian Cook and Butch Vallee (*The Crystal Image*, Laguna Beach, California) and Mona Lee Nesseth, *Custom and Estate Jewels*, Laguna Beach; photo © Harold & Erica Van Pelt.

or violet), bluish green to greenish blue, or green elbaite tourmaline containing Cu and Mn, similar to the material that was originally mined in Paraíba, Brazil; any "Paraíba" tourmaline, regardless of its geographic origin, shall be described with the following wording on a gem identification report:

- Species: Elbaite
- Variety: Paraíba tourmaline
- Comment: The name "Paraíba tourmaline" is derived from the locality where it was first mined in Brazil.
- Origin: Origin determination is optional

This policy is consistent with current CIBJO practice, which defines "Paraíba" tourmaline as having a "green to blue color caused by copper," but no definition is made according to locality. Thus, CIBJO also considers "Paraíba" tourmaline to be a general variety or trade name.

At present, AGL will fall into step with the recommendation of the LMHC group, and will disclose a new nomenclature for "Paraíba" tourmaline later this year.

## CONCLUSION

Since the initial discovery of magnificent brightly colored tourmaline at Mina da Batalha in Brazil's Paraíba State (figure 17), Cu-bearing elbaite has also been mined from Brazil's Rio Grande do Norte State (Mulungu and Alto dos Quintos), as well as in Nigeria and Mozambique. Overlap in the gemological properties and chemical compositions of tourmaline from these localities makes it difficult to distinguish their geographic origins with the testing techniques available in most gemological laboratories.

The common presence of yellowish brown needle-like growth tubes in the Nigerian tourmalines is suggestive of their origin. Also, native copper was most commonly seen in the Nigerian and a few Brazilian tourmalines, but thus far it has not been documented in stones from Mozambique.

This study has shown that chemical fingerprinting by the LA-ICP-MS technique is useful for distinguishing Cu-bearing tourmaline from the various localities.

Geochemical plots of CuO+MnO versus Ga+Pb, CuO+MnO versus Pb/Be, and Mg-Zn-Pb reveal that quantitative data for these elements may permit a reliable distinction of Brazilian stones from their counterparts mined in Nigeria and Mozambique. The Nigerian tourmalines contained larger amounts of the trace elements Ga, Ge, and Pb, whereas Brazilian tourmalines were enriched in Mg, Zn, and Sb. The Mozambique samples showed high contents of Be, Sc, Ga, and Pb, and Bi, but a lack of Mg.

Although the major laboratories have agreed to use *Paraíba tourmaline* as a trade name for blue ("neon" blue, or violet), bluish green to greenish blue, or green Cu- and Mn-bearing elbaite, some labs may wish to provide the additional service of establishing the precise country of origin. On the basis of the research completed to date, such a distinction usually requires quantitative chemical analysis. As further discoveries are made in other parts of the world, additional research will be needed to reconfirm the criteria or establish new ones.

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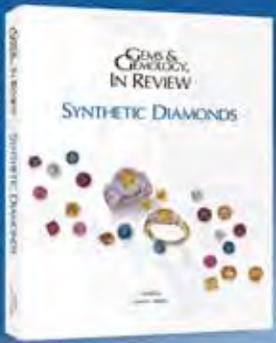
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