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# GEM-QUALITY CUPRIAN-ELBAITE TOURMALINES FROM SÃO JOSÉ DA BATALHA, PARAÍBA, BRAZIL

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Unusually vivid tourmalines from the state of Paraíba, in northeastern Brazil, have attracted great interest since they first appeared on the international gem market in 1989. This article describes what is known of the locality at this time, but focuses on the most striking characteristic of these gem tourmalines: the unusual colors in which they occur. Quantitative chemical analyses revealed that these elbaite tourmalines contain surprisingly high concentrations of copper, up to 1.92 wt.% Cu (or 2.38 wt.% CuO). Their colors are due to  $\text{Cu}^{2+}$  or a combination of  $\text{Cu}^{2+}$ ,  $\text{Mn}^{3+}$ , and other causes. Some colors can be produced by heat treatment, but most also occur naturally.

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A new find of gem-quality elbaite tourmalines that occur in unusually bright shades of green and blue, among other colors, appeared on the international market in 1989. Some of the colors were so exceptional (figure 1) that they were described as "neon," "fluorescent," or "electric" in the trade (Reilley, 1990). A number of the hues, especially a slightly violetish "sapphire" blue, had seldom if ever been seen before in gem tourmaline (Koivula and Kammerling, 1989a). Prices for large, clean stones reached US\$1,000 or more per carat (Reilley, 1990; Federman, 1990); recently, they have begun to appear in fine jewelry (figure 2). It was subsequently revealed that some of the material has been heat treated (Koivula and Kammerling, 1990a), but it has not been clear whether certain colors are due only to such treatment or if they also occur naturally.

These exceptional gem tourmalines come from a small mine near the village of São José da Batalha, in the state of Paraíba, northeastern Brazil. They are commonly referred to (and will be so here) as "Paraíba tourmalines" (although more common varieties of gem tourmaline have been found elsewhere in the same state; W. Larson, pers. comm., 1990). This article reviews what is currently known about this locality and the tourmalines produced there, and reports the results of a comprehensive study into the cause of these unusual colors and the effect of heat treatment.

## LOCATION AND ACCESS

The mine is called Mina da Batalha (B. Cook, pers. comm., 1990). It is located on the upper flank of a hill known as Serra da Frade (figure 3), 4.5 km (2.7 mi.) northeast of the town of Salgadinho and very close to the village of São José da Batalha. As in most of the state of Paraíba, the area around the mine is a harsh dry scrubland, locally known as the *sertão*. The small local mining industry focuses primarily on industrial pegmatite minerals, especially tantalite. As of September 1990, access to the tourmaline deposit was restricted and required prior arrangements.



Figure 1. Paraiba tourmalines have generated major interest in the gem industry because many occur in unusual colors, some of which have never been seen before in this gem species. Some of the names used in the trade to describe these exceptional colors, illustrated here, are "neon," "electric," "turquoise," "sapphire," or "tanzanite" blue and "mint" green. These stones, which range from 0.39 to 1.47 ct, are courtesy of Gerhard Becker, Idar-Oberstein; photo by Robert Weldon.

## HISTORY

The story of the Paraiba tourmalines began in 1982, when Heitor Dimas Barbosa, who had once mined tourmaline in Minas Gerais, noticed brightly colored specks in samples of pegmatite ore shown to him by José Pereira, a local Paraiba *garimpeiro* (Koivula and Kammerling, 1990b). The two men searched numerous pegmatite deposits throughout this region for the next several months. Eventually, they located similar colored fragments (later identified as tourmaline) in the tailings of a small manganotantalite prospect on a hillock at the base of Serra da Frade. Over the next few years, Barbosa and a team of about 15 *garimpeiros* dug deep (up to 50 m) shafts and a number of galleries

into a decomposed granitic pegmatite. They operated under difficult climatic conditions (little water and high daytime temperatures), using only hand tools. During 1985–1987, their efforts produced tourmalines of various shades of green. Not until August 1987, however, did they encounter the distinctive "electric" and "sapphire" blue stones for which this deposit has become famous. Mr. Barbosa and his associates filed a joint claim on the mine in 1988 and formed the mining cooperative COGASBRA, which was registered by the National Department of Minerals (DNPM) on March 13, 1990. Currently, Mr. Barbosa holds exploration rights to the area that he has been mining, although the mining rights are in dispute.





Figure 2. The new Paraiba tourmalines are particularly attractive in fine jewelry, as indicated by this pin set with three Paraiba stones (total weight 2.13 ct). Created by the Gold Rush, Northridge, CA; photo by Shane McClure.

Figure 3. The Mina da Batalha workings can be seen here at the top of Serra da Frade, a hill composed of gently dipping beds of gray quartzite. Dumps of decomposed white rock mark entrances to the mine shafts that have been dug into the weathered pegmatite. Photo, taken August 1990, by Brian Cook.







Figure 4. White clay (altered feldspar) can be seen surrounding the main shaft of the tourmaline mine on Serra da Frade. The village of São José da Batalha appears in the background. Vertical shafts and horizontal tunnels have been dug into the weathered pegmatite in search of gem tourmaline. Photo, taken August 1990, by Brian Cook.

Figure 5. This 24.69-ct round brilliant cut is reportedly one of the largest faceted tourmalines to emerge to date from the new locality in the state of Paraíba. Courtesy of Kahlil Elawar Ltda.; photo © Harold & Erica Van Pelt.



## GEOLOGY AND OCCURRENCE

Gem tourmalines from São José da Batalha are found in a small, decomposed granitic pegmatite, in association with quartz, feldspar (altered to white clay), and lepidolite (figure 4). The pegmatite is a narrow dike cutting across the quartzite host rock. Tourmaline occurs mostly as crystal fragments that weigh less than a gram, although cut stones over 20 ct (4 grams) have been faceted (figure 5) and the authors have examined rough fragments as large as 10 grams. In rare instances, small crystals are recovered. The external features of these crystals often indicate that they have been broken in nature, and some are also severely etched (figure 6). Occasionally, tourmaline crystals have been found completely included in quartz matrix (as illustrated in Koivula and Kammerling, 1990a, p. 166).

Some crystals display a distinct, sometimes complex color zoning. Several contain a deep pink core, surrounded by a zone of "turquoise" blue and a thin pink rim; others have a blue center surrounded by violet, light blue, green, and gray areas. Other combinations have also been seen. Slices of these crystals are quite attractive (figure 7).

## MINING

The area continues to be mined primarily with hand tools. Dynamite is used only occasionally to break the surrounding host rock, which is considerably harder than the altered pegmatite. The miners have sunk vertical shafts into the decomposed pegmatite at various intervals; at different levels along these shafts, they have dug narrow horizontal tunnels (1.8 m high  $\times$  0.6 m wide) to follow the pegmatite dike. All of these underground workings have been excavated using candlelight as the sole source of illumination. Mining has been hampered by the lack of a proper ventilation system, and by the difficulty of hauling loose rock up and out of the mine. The conflict over mining rights has also led to periods when the operation had to be halted.

It is difficult to estimate how much gem material this mine has already produced, but the quantities available at the February 1990 Tucson gem show plus those stocks reported by other dealers (e.g., G. Becker, pers. comm., 1990) amount to at least 10,000 ct of rough and finished stones. There are indications that more is to be found at the mine (see, e.g., Koivula and Kammerling, 1990b), but, in the absence of careful geologic





Figure 6. This 13-mm high, 8.80-ct blue crystal of Paraíba tourmaline is a nice example of the small crystals found at the deposit. The rectangular, step-like surface features are attributed to etching. Stone courtesy of Brian Cook, *Nature's Geometry*; photo by Robert Weldon.

mapping and more systematic exploration, no estimate of the reserves can be provided at this time.

## MATERIALS AND METHODS

Over the course of this research project, we examined several hundred rough and faceted gem tourmalines that covered the entire range of colors available from the Paraíba deposit. From these, we selected 13 specimens of representative color for more detailed study. Indices of refraction were measured with a GIA Gem Instruments Duplex II refractometer and a filtered, near-monochromatic, Na-equivalent light source. Specific gravity was determined by the hydrostatic method. To confirm the identity of these specimens as elbaite tourmaline, we obtained X-ray diffraction data for five of them (samples R30, R50, R52, R66, and R67) using an automated Rigaku powder diffractometer operated at 35 kV and 15 mA.

Chemical analyses of all 13 specimens were obtained using a JEOL Model 733 electron micro-

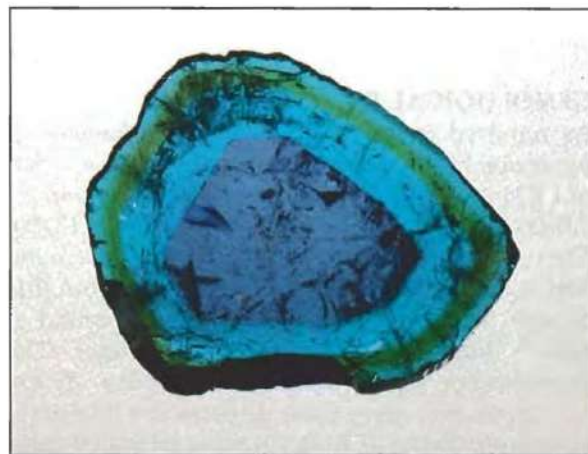


Figure 7. This 5.96-ct slice ( $15.20 \times 12.20 \times 3.28$  mm) of Paraíba tourmaline is representative of the somewhat complex color zoning that appears in some crystals. This color zoning reflects changes in chemical composition as the tourmaline crystallized. Courtesy of The Gold Rush, Northridge, CA; photo by Shane McClure.

probe (for operating conditions, see table 1; because two of the original samples virtually duplicated the color of other samples in the test group, only 11 are reported in the table). A Pyc-Unicam Model 8800 ultraviolet-visible spectrophotometer was used to record absorption spectra in the range of 250–850 nm for the same samples. We found it necessary to prepare crystallographically oriented pieces of some of these specimens to obtain quantitative absorption spectra that could be directly compared with their chemical composition. For this purpose, we selected three crystal fragments (R30, R50, and R52) and two faceted stones (R66 and R67) in the green to bluish purple color range on the basis of their color and color homogeneity. From each specimen, we cut a flat, parallel-windowed section in an orientation parallel to the optic axis (as determined either from striations on the prism faces of the crystal fragments—which are parallel to the optic axis—or, when there were no striations, by X-ray alignment photography). These five sections were subsequently ground to an appropriate known thickness (0.2 to 5 mm) and then polished using 1-micron-diameter alumina powder.

Quantitative absorption spectra in the 300–2000 nm range were recorded for these five specimens using a Cary Model 17I ultraviolet-visible/near-infrared spectrophotometer. The heating experiments were carried out in a Lindberg Model 51442 furnace.

## GEMOLOGICAL PROPERTIES

As reported in table 1, we recorded indices of refraction for the 13 specimens as  $\epsilon = 1.618$  to  $1.621 (\pm 0.001)$ , and  $\omega = 1.638$  to  $1.646 (\pm 0.001)$ . These values are typical of elbaite (Dietrich, 1985). Slightly lower values were reported by Bank et al. (1990) for material from this deposit. All of our specimens were also found to have a uniaxial negative optic character. The birefringence varied from 0.018 to 0.025. As expected for this gem, these elbaites are distinctly pleochroic (figure 8), with the most saturated color seen looking down the optic axis, that is, parallel to the direction of the omega refractive index (i.e., with the polarizer oriented perpendicular to the

optic axis; see Bloss, 1961, p. 147). The specific gravity of our samples ranged from 3.03 to  $3.12 (\pm 0.01)$ , which is slightly higher than for most elbaites (2.84–3.10; Dietrich, 1985).

The Paraíba tourmalines we examined were inert to both long- and short-wave ultraviolet radiation, as is commonly observed in other gem tourmalines. The inclusions are typical of those seen in all varieties of gem tourmalines (see, e.g., Gübelin and Koivula, 1986): three-phase inclusions (figure 9); liquid inclusions, sometimes in veils or "fingerprint" patterns; thin growth tubes parallel to the optic axis; and some doubly refractive crystal inclusions. Of particular interest are rare inclusions of tourmaline in tourmaline. Fig-

**TABLE 1.** Some gemological properties and electron microprobe analyses<sup>a</sup> of elbaite tourmalines from Paraíba, Brazil.

Property/ chemical component	R50	R378	R308	R362	R66
Property					
Color <sup>b</sup>	Yellowish green	Greenish gray	Purple-pink	Purple	Bluish purple ("tanzanite")
R.I.					
$\epsilon$	1.619	1.620	1.621	1.620	1.620
$\omega$	1.639	1.640	1.640	1.640	1.638
S.G. <sup>c</sup>	3.05	3.07	3.03	3.05	3.04
Pleochroism <sup>d</sup>					
$\epsilon$	Grayish green	Light gray	Light purplish pink	Light pink	Light, slightly grayish green
$\omega$	Medium yellowish green	Medium grayish green	Medium purplish pink	Medium purple	Medium bluish purple
Chemical Component (wt.%)					
Na <sub>2</sub> O	2.27	2.36	1.94	2.00	2.16
CaO	0.46	0.45	0.08	0.07	0.62
K <sub>2</sub> O	0.03	0.02	0.02	0.01	0.02
Li <sub>2</sub> O <sup>e</sup>	1.62	1.62	1.62	1.62	1.62
MgO	0.54	0.30	BDL	BDL	BDL
TiO <sub>2</sub>	0.10	0.07	BDL	BDL	BDL
V <sub>2</sub> O <sub>3</sub>	0.01	0.01	BDL	BDL	BDL
Cr <sub>2</sub> O <sub>3</sub>	BDL	BDL	BDL	BDL	BDL
MnO	1.47	2.99	0.53	0.52	1.32
FeO	0.22	0.12	BDL	0.01	BDL
ZnO	0.08	0.11	0.03	0.04	BDL
CuO	0.37	0.49	0.51	0.52	0.62
PbO	BDL	0.02	BDL	0.01	BDL
Bi <sub>2</sub> O <sub>3</sub>	0.39	0.06	BDL	0.02	0.15
Al <sub>2</sub> O <sub>3</sub>	39.04	38.73	42.37	42.14	39.66
B <sub>2</sub> O <sub>3</sub> <sup>e</sup>	10.94	10.94	10.94	10.94	10.94
SiO <sub>2</sub>	37.27	37.29	37.42	37.39	37.11
H <sub>2</sub> O <sup>e</sup>	3.13	3.13	3.13	3.13	3.13
Cl	0.01	BDL	BDL	BDL	BDL
Total	97.95	98.71	98.59	98.42	97.35

<sup>a</sup>Electron microprobe analyses were performed on an automated, five-crystal JEOL 733 spectrometer operating at a beam accelerating potential of 15 kV, a current of 35 nA, and a spot size of between 10 and 25  $\mu\text{m}$ . K-alpha lines were analyzed for each element except Pb and Bi, for which M-alpha lines were used. Standards include: (Na)—Amelia albite, (Mg)—MgO, (Al, Si)—kyanite, (K)—microcline, (Ca)—anorthite, (Ti)—TiO<sub>2</sub>, (V)—pure element, (Cr)—Cr<sub>2</sub>O<sub>3</sub>, (Mn)—Mn-olivine, (Fe)—synthetic fayalite, (Cl)—sodalite, (Zn)—ZnO, (Cu)—pure element, (Pb)—galena or synthetic PbS, and (Bi)—pure element. Total iron is calculated as FeO; total manganese is calculated as MnO (even though it can be present as both Mn<sup>2+</sup> and Mn<sup>3+</sup>). Entries indicated by "BDL" were below the detection limits of the instrument (less than 0.01 wt% oxide). The data were corrected using the program CITZAF (Armstrong, 1988) employing the absorption correction of Armstrong (1982), the atomic number correction of Love et al. (1978), and the fluorescence correction of Reed (1965), as

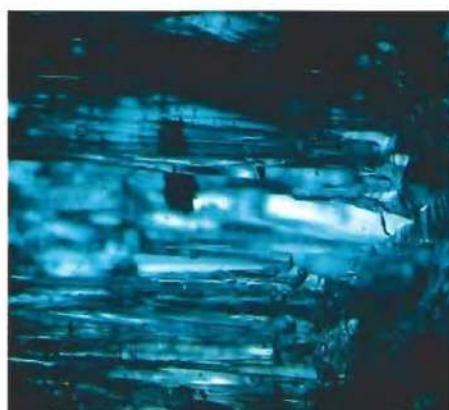
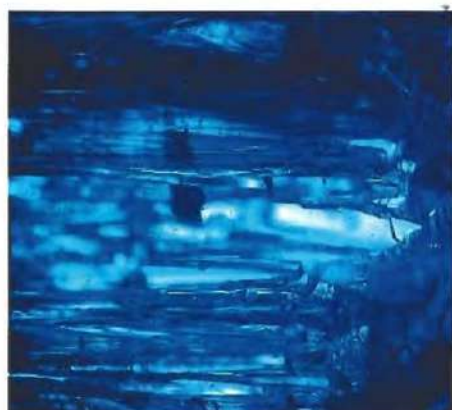


Figure 8. As with most elbaite tourmalines, the pleochroism in this "sapphire" blue Paraiba tourmaline is distinct: medium dark blue (left, polarizer perpendicular to the optic axis) and medium light greenish blue (right, polarizer parallel to the optic axis). Photomicrographs by John I. Koivula; magnified 6 $\times$ .

R52	R67	R305	R30	R319	R376
Blue	Violetish blue ("sapphire")	Bluish green ("mint")	Blue-green ("turquoise")	Bluish green	Green ("emerald")
1.619	1.618	1.620	1.621	1.620	1.620
1.639	1.638	1.640	1.646	1.640	1.640
3.11	3.06	3.09	3.12	3.12	3.11
Very light blue	Medium light greenish blue	Very light green	Medium bluish green	Light, slightly greenish blue	Medium bluish green
Medium light blue	Medium dark blue	Medium, slightly bluish green	Medium green-blue	Medium green	Medium green
2.26	2.35	2.32	2.49	2.47	2.51
0.55	0.47	0.19	0.05	0.24	0.30
0.02	0.02	0.02	0.02	0.02	0.04
1.62	1.62	1.62	1.62	1.62	1.62
BDL	BDL	0.18	BDL	0.95	0.06
0.01	0.01	0.07	0.06	0.11	0.02
BDL	BDL	0.01	0.01	0.01	BDL
BDL	BDL	BDL	BDL	BDL	BDL
2.30	2.55	1.32	1.48	0.85	2.16
BDL	BDL	0.15	0.07	0.34	0.04
0.01	0.01	0.11	0.25	0.08	0.52
0.72	0.74	1.08	1.76	2.37	2.38
0.01	0.02	0.01	0.01	0.02	0.01
0.11	0.08	0.83	0.01	0.03	0.05
38.95	38.47	38.99	38.58	39.35	38.31
10.94	10.94	10.94	10.94	10.94	10.94
36.97	37.06	36.75	36.53	36.83	36.89
3.13	3.13	3.13	3.13	3.13	3.13
BDL	0.01	BDL	0.01	BDL	BDL
97.60	97.48	97.92	97.01	99.36	98.98

modified by Armstrong (1988). Each specimen was analyzed at three different randomly selected locations; in this table, an average analysis is shown for each sample. Analyses were performed by Paul Carpenter.

<sup>a</sup>Color hue descriptions visually estimated. The "emerald" green specimen (R376) has been heat treated.

<sup>c</sup>Specific gravity values determined by the hydrostatic method.

<sup>d</sup>Pleochroic colors visually estimated using a calcite dichroscope.  $\epsilon$  = epsilon (color seen with light vibrating parallel to the optic axis).

$\omega$  = omega (color seen with light vibrating perpendicular to the optic axis).

<sup>e</sup>Values of Li<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O were calculated based on an assumed elbaite tourmaline stoichiometry.





Figure 9. For the most part, the inclusions observed thus far in Paraiba tourmalines—here, a three-phase inclusion—are typical of those seen in tourmalines from other localities. Photomicrograph by John I. Koivula; magnified 40 $\times$ .

ure 10 illustrates a needle of bright green tourmaline (identity confirmed by X-ray diffraction analysis) that cuts across a dark "sapphire" blue slice of Paraiba tourmaline. This specimen reportedly has not been heat treated (G. Becker, pers. comm., 1990).

Also, numerous yellowish specks—referred to as "gold" by some of the Brazilian miners—have been seen on a few crystals (see figure 11). Although microscopic examination revealed that these "specks" are pinkish yellow and have a metallic luster, X-ray fluorescence analysis of the specimen shown in figure 11 revealed the presence of Mn, Fe, Cu, Zn, and Bi, as well as some S. This implies that these inclusions could be composed of a sulfide, possibly iron containing, since the iron content of the stone for which the inclusions were analyzed is unusually high compared to other Paraiba tourmalines.

Because of their bright colors, Paraiba tourmalines could easily be mistaken for other gem materials, such as haüyne, lazulite (Bank and Henn, 1990), blue sapphire, tanzanite, or even emerald. However, these gem materials have very different gemological properties. Haüyne is isotropic with a lower R.I. and S.G. than tourmaline; lazulite has a similar R.I. and S.G. but a higher birefringence and is biaxial; sapphire and tanzanite have higher R.I.'s and S.G.'s, and in the case of sapphire there is usually a distinctive absorption spectrum, and emerald has a lower R.I. and S.G. and, again, a distinctive absorption spectrum. At

the February 1990 Tucson gem show, we saw a new production of apatites from Madagascar with colors similar to those of some Paraiba tourmalines, in particular, "turquoise" blue, bluish green, and light green (see also Bank and Henn, 1990; Koivula and Kammerling, 1990b). These two gem materials are easily separated on the basis of specific gravity or absorption spectrum.

#### X-RAY DIFFRACTION ANALYSIS

Measured lines in the X-ray diffraction patterns of the five tourmalines analyzed were determined to be closely related in both position and relative intensity to those from the pattern of a representative elbaite (1986 JCPDS Mineral Powder Diffraction File 26-964). Least-squares refinement of data for a Cu-rich specimen (R30) yielded unit-cell dimensions of  $a = 15.883 (\pm 0.004) \text{ \AA}$  and  $c = 7.111$

Figure 10. A needle of bright green tourmaline is readily seen as an inclusion in this slice of dark violetish blue tourmaline (R32) from Paraiba. The slice, 12.10  $\times$  6.60  $\times$  3.52 mm, is courtesy of Gerhard Becker; photo by Robert Weldon.





( $\pm 0.001$ ) Å. The five strongest lines in this pattern are 3.978(56)(220), 3.445(76)(012), 2.938(100)(122), 2.567(90)(051), and 2.029(54)(152), where these values represent the d-spacing (in Ångstroms), relative intensity, and Miller index (hkl) of each diffraction line. No significant differences were noted between the diffraction patterns of this specimen and those of the other four elbaite specimens. The *a* and *c* dimensions of the other four specimens were within 0.020 Å and 0.003 Å, respectively, of those for sample R30.

### CHEMICAL ANALYSIS

The electron microprobe analyses (again, see table 1) show that these tourmalines are typical elbaite and contain little Ti ( $\leq 0.11$  wt.% oxide), and Fe ( $\leq 0.34$  wt.% oxide), virtually no V or Cr ( $\leq 0.01$  wt.% oxide), and have Cu and Mn as major transition-element impurities. The highest concentration of copper measured in our samples was 2.38 wt.% CuO (or 1.92 wt.% Cu) for the "emerald" green cabochon (R376), and the largest concentration of manganese, 2.99 wt.% MnO, was found in the greenish gray crystal fragment (R378). Analyses performed at three random locations on each specimen with uniform coloration showed only very slight compositional variations.

As mentioned previously, however, some Paraíba tourmaline crystals exhibit distinct color zoning (again, see figure 7). Examination of such unusual crystals provides interesting information on the chemical environment that produced them. As shown in figure 12, the greatest differences in chemistry as one crosses boundaries between zones of various colors are for Cu and Mn. To a lesser extent, differences were also noted in the Fe and Ti contents.

It is interesting to note that small amounts of Bi, Pb, and Zn were detected in many specimens. These elements appear to have no influence on color, and have not often been reported in gem tourmalines (see Dietrich, 1985). Bank and Henn (1990) reported gold concentrations of 8.6 parts per million in this material; we did not attempt to confirm their finding.

Results of both the site-occupancy calculations based on charge-balance considerations and the microprobe analyses indicate that copper and manganese are present in the Y crystallographic site (using the site terminology for tourmaline of Deer et al., 1986).

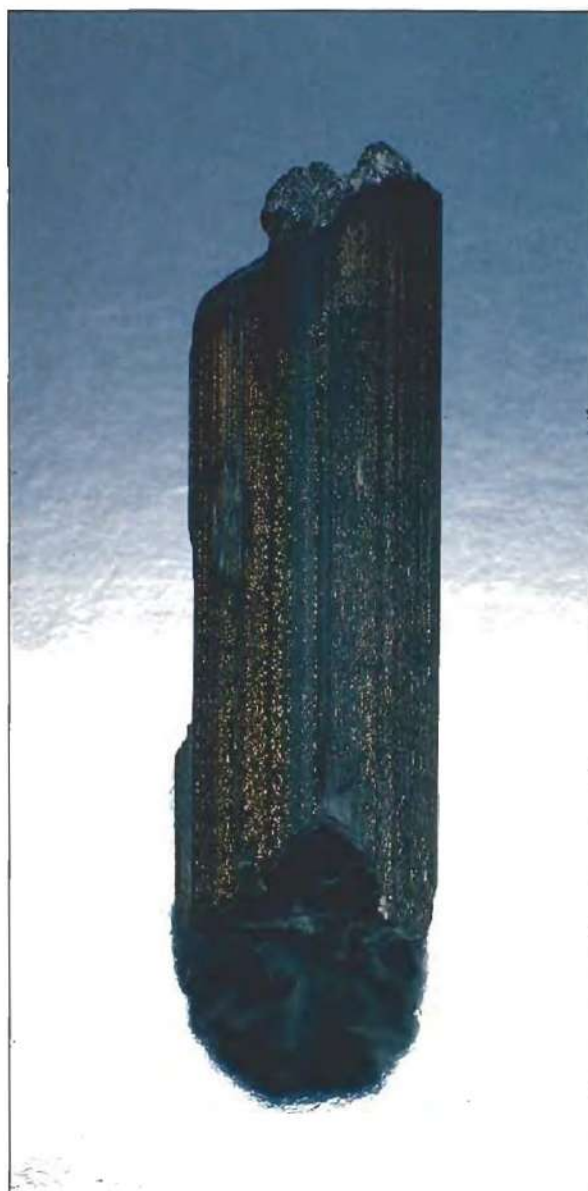


Figure 11. Numerous gold-colored specks near the surface of this Paraíba tourmaline crystal create an interesting optical effect. Stone courtesy of Beija Flor Gems; photo by Robert Weldon.

### COLOR

The cause of color in elbaite tourmaline has been extensively investigated. Most colors are due to small amounts of transition elements (Dietrich, 1985). In particular, blue to green hues have been attributed to various processes involving both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions (Mattson and Rossman, 1987).

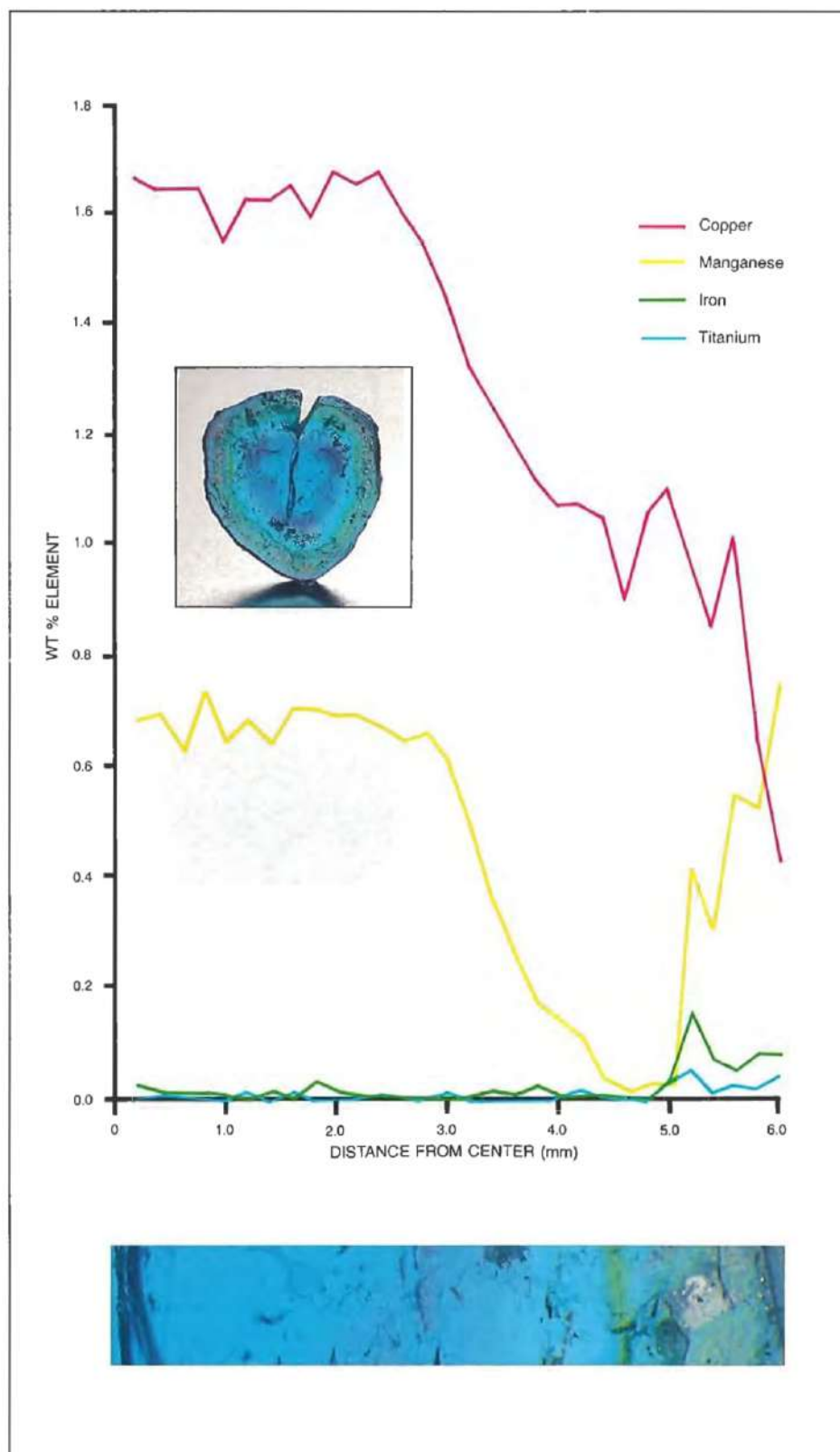


Figure 12. Changes in the chemical composition of the coloring agents—as determined by microprobe analyses taken at 30 points along a linear traverse (6 mm total distance) from the center to the edge of this Paraiba tourmaline crystal section (R363)—relate to the various color zones in the section. The copper concentration decreases from the center toward the edge. The manganese content decreases in a similar fashion, but reaches a low value at the narrow light blue and yellowish green zones (about 4.5 mm from the center), and then increases in the pink areas near the edge. Iron and titanium contents remain very low across most of the section, but show a slight increase near the edge. Note that the electron microprobe analyses were performed on an automated, five-crystal JEOL 733 spectrometer operating at a beam accelerating potential of 15kV, a current of 150 nA, a 5-second counting time, and a spot size of 30  $\mu\text{m}$ . K-alpha lines were analyzed for each element; standards include: (Ti)— $\text{TiO}_2$ , (Mn)—Mn-olivine, (Fe)—synthetic fayalite, (Cu)—pure element. Values are plotted for  $\text{TiO}_2$ , MnO, FeO, and CuO. Thirty analyses were performed at 200  $\mu\text{m}$  intervals along a linescan between the core and rim of this crystal. The data were corrected using the same procedure as described in table 1.



and to  $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$  charge transfer (Mattson, as cited in Dietrich, 1985, p. 129).  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$  have been identified as coloring agents in green dravite and uvite (Schmetzer and Bank, 1979), but never in elbaite.

Several earlier investigators have mentioned  $\text{Cu}^{2+}$  as a potential cause of color in blue and green elbaite on the basis of atomic emission spectrography. Warner (1935) observed that blue samples have a lower copper concentration than yellow-green ones, whereas Carobbi and Pieruccini (1946, 1947) found, on the contrary, greater amounts of copper in blue crystals. None of these authors, however, proved that this ion actually acts as a coloring agent in tourmaline. Staatz et al. (1955) mentioned the presence of trace amounts of copper in tourmaline (up to 0.0017 wt.%) but, again, did not relate it to color.  $\text{Cu}^{2+}$  was recently proposed as a possible coloring agent for the Paraíba material (Fritsch, as cited in Koivula and Kammerling, 1989b; and Bank et al., 1990), but this hypothesis was not proved at that time. Using ultraviolet-visible and near-infrared absorption spectroscopy, however, we can now demonstrate that copper is indeed partially responsible for the unusual coloration of these gem tourmalines.

Figure 13 illustrates the visible-range absorption spectra of nine Paraíba tourmalines that span the range of colors available. Several key features are evident in these spectral curves. First, there is an ultraviolet absorption "edge"—increasing absorption toward the U.V.—beginning at about 450 nm (most conspicuous in R376). Several of the spectra display a weak, sharp band at about 415 nm (especially notable in R67). Several others exhibit a broad band of varying intensity centered at about 515 nm (R308, R362). Finally, there is another broad absorption band beginning at about 600 nm and extending into the near-infrared (e.g., R376). The reader should note that element concentrations listed in table 1 as oxides cannot always be directly correlated with intensities of absorption features in a spectral curve (such as those in figure 13). Intensities of absorption features depend not only on the concentration of an element, but also on its valence state, position in the crystal structure, and—in the case of a charge-transfer mechanism—the proximity between the two ions involved in the crystal structure. It is possible that concentrations of coloring agents at much lower values than those shown in table 1 could still produce intense absorption features in the visible

spectrum, for example, through charge-transfer phenomena (for further information, see Fritsch and Rossman, 1987 and 1988).

We interpret the features shown in figure 13 as follows. The rise in absorption toward the ultraviolet starts at a higher wavelength and is more gradual in specimens that contain a larger amount of titanium, as listed in table 1. Because all specimens contain much more manganese than titanium, this absorption feature may be attributed to  $\text{Mn}^{2+} \rightarrow \text{Ti}^{4+}$  charge transfer (Rossman and Mattson, 1986). Still, other causes are possible.  $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$  charge transfer is known to occur in tourmaline between 400 and 500 nm (Mattson and Rossman, 1987; Taran and Lebedev, 1990). Also,  $\text{V}^{3+}$  or  $\text{Cr}^{3+}$ —at concentrations too low to be detected by electron microprobe—could cause a weak absorption in the same wavelength range. However, testing with a more sensitive instrument, an energy-dispersive X-ray fluorescence (EDXRF) spectrometer, did not detect either vanadium or chromium but easily detected the iron and titanium. Therefore, charge-transfer mechanisms involving  $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$  and  $\text{Mn}^{2+} \rightarrow \text{Ti}^{4+}$  are the more likely causes of the increase in absorption that starts at about 450 nm.

$\text{Mn}^{2+}$  is slowly transformed into  $\text{Mn}^{3+}$  by exposure to natural radiation such as that produced, for example, in a granitic pegmatite (Reinitz and Rossman, 1988). The darker blue to violet specimens from Paraíba (see figure 13) display a broad absorption band in the green that is centered around 515 nm and is attributed to  $\text{Mn}^{3+}$  (Manning, 1973). A weak, sharp absorption band at about 415 nm in the blue region, visible in the spectra of several specimens in figure 13, is attributed to  $\text{Mn}^{2+}$  (Rossman and Mattson, 1986; Reinitz and Rossman, 1988). More intense absorption attributed to  $\text{Mn}^{3+}$  in Paraíba tourmalines produces a shift toward more violetish colors ("sapphire" blue, violet) and even purplish pink. Note that the broad feature at 515 nm is responsible for the pink color of rubellite, which explains why "sapphire" blue and "tanzanite" bluish purple Paraíba tourmalines display a typical rubellite spectrum in the hand-held spectroscope (Kane, 1989; Hodgkinson, 1990). Their color is not that of rubellite, however, because the color of a gemstone (such as tourmaline) is primarily determined by broad absorption bands that are not always easily observable with a hand-held spectroscope.

Along with manganese, copper is the major

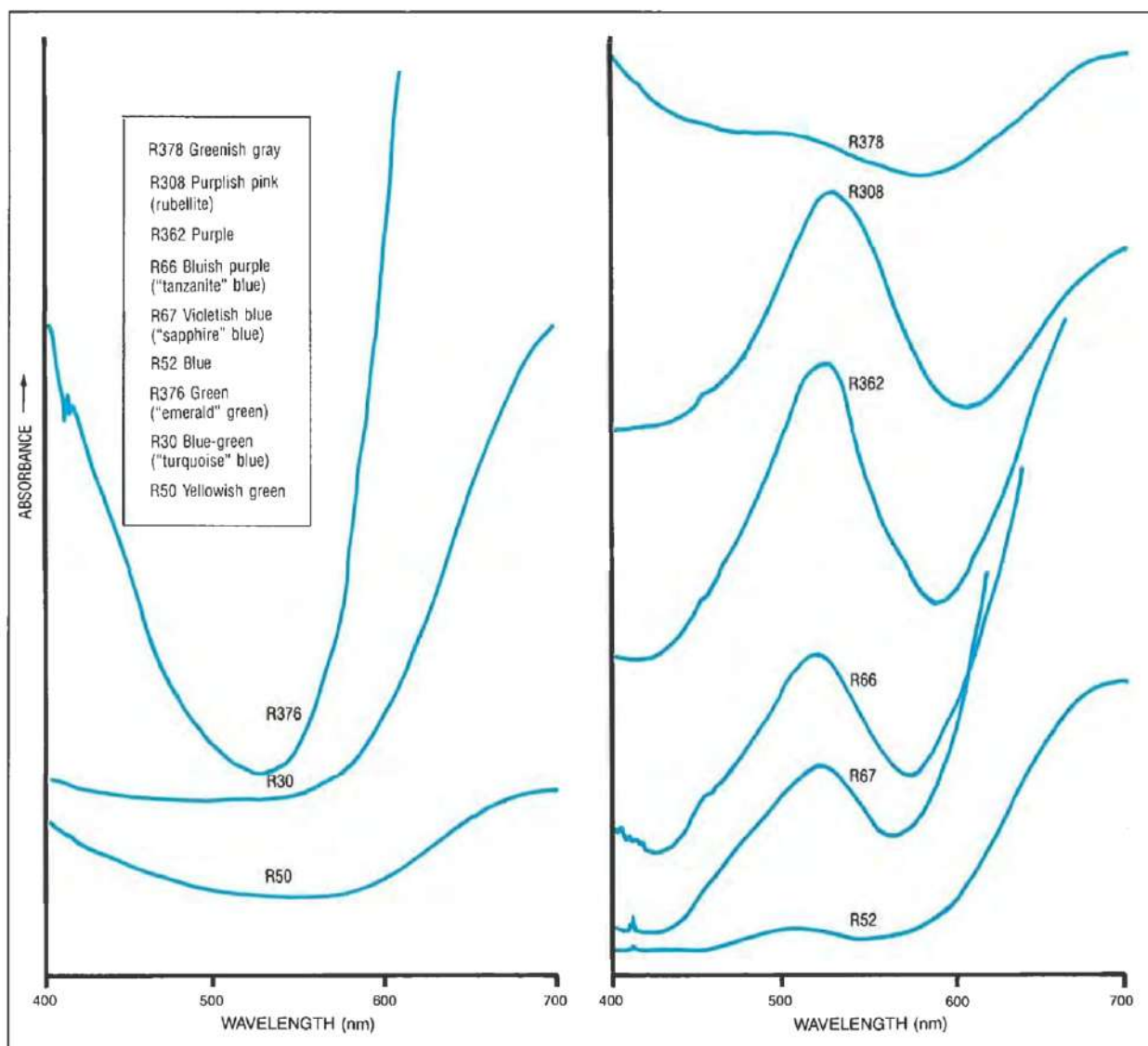


Figure 13. These visible-range absorption spectra for nine Paraíba tourmalines of various colors were recorded using nonpolarized light for samples that varied in size, shape, and optical orientation relative to the position of the incident light. Therefore, the vertical scale is in arbitrary units. However, for a given spectral curve, the intensities of absorption bands relative to one another are meaningful and characteristic of that particular color. The three spectra on the left (R50, R30, R376) illustrate absorption at the red end of the spectrum (above 600nm) due to increasing amounts of  $\text{Cu}^{2+}$ . The six spectra on the right (R52, R67, R66, R362, R308, and R378) show the broad absorption band centered at about 515 nm that is due to  $\text{Mn}^{3+}$  (in addition to the absorption from  $\text{Cu}^{2+}$ ). In several spectra of this latter group, a weak, sharp band is visible at 415 nm; this is due to  $\text{Mn}^{2+}$ . Note that specimen R376 is known to have been heated.

coloring agent for these Paraíba tourmalines. When it is the dominant coloring agent, it is responsible for the spectacular "turquoise" blue hue (see figures 1, 13, and 14). We interpret the broad absorption band above 600 nm (for example, the unpolarized spectra of R30 and R376 in figure 13), which actually is the edge of the pair of bands at approximately 695 and 920 nm, as arising from

absorption by  $\text{Cu}^{2+}$ . As can be seen in figure 14, the maxima of these two broad bands are located at about 690 and 900 nm in the  $E \perp c$  direction.\* They are shifted slightly in the  $E \parallel c$  direction, and are

\* "E" stands for the electric vector, which is in the direction of light vibration, and perpendicular to the direction of light propagation. For example,  $E \perp c$  is what one would see looking down the optic axis.



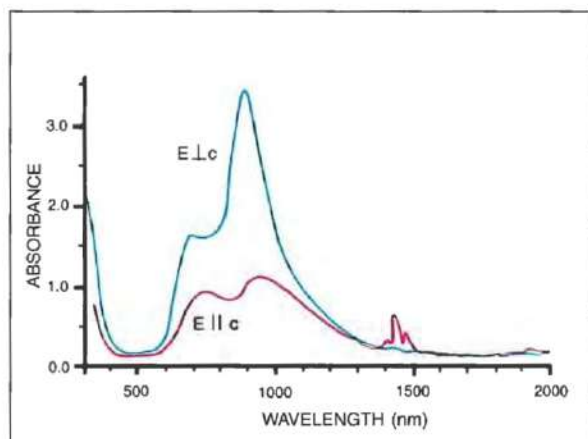


Figure 14. These polarized optical absorption spectra for a "turquoise" blue Paraíba tourmaline (R30) illustrate the absorption features due to  $\text{Cu}^{2+}$ . The spectra were recorded with light vibrating parallel ( $E \parallel c$ ), and then perpendicular ( $E \perp c$ ), to the optic axis of the tourmaline. Typically, gem spectra are recorded on a U.V.-visible spectrophotometer with the stone in a random optical orientation, because it is often difficult or impossible to position a cut stone in the instrument precisely. This leads to the spectra one normally sees published (e.g., figure 13). However, spectral features are most accurately recorded from parallel polished pieces of known optical orientation and using a polarizing filter, as was done for the spectra reproduced here.

located at about 740 and 940 nm. The intensities of these broad bands depend on the direction of polarization, especially for the  $E \perp c$  band (in contrast to the results reported by Bank et al., 1990). In an unpolarized spectrum, the two pairs of bands merge, and appear at about 695 and 920 nm (and for simplicity, are designated as such in the rest of this text). Also seen in the spectra in figure 14 are a series of sharp bands in the near infrared between 1400 and 1500 nm, which are visible in all tourmalines. These bands, strongly polarized in the  $E \parallel c$  direction, arise from the first overtones of O-H stretching vibrations (Wickersheim and Buchanan, 1959 and 1968; Gebert and Zeman, 1965).

Figure 15 shows that the broad bands at about 695 and 920 nm in both polarization directions correlate in intensity with the copper concentrations determined in these same specimens by microprobe analysis. This is the first proof ever published that these absorption bands are actually

caused by  $\text{Cu}^{2+}$ . In addition, this is the first documented evidence of  $\text{Cu}^{2+}$  acting as a coloring agent in tourmaline (for more details, see Rossman et al., 1990).

It is interesting to note, as a confirmation of the conclusion drawn above, that synthetic Na-Cu tourmaline spherulites hydrothermally grown by Taylor and Terrell (1967) also have a green to blue color. Very recently, Taran and Lebedev (1990) presented polarized absorption spectra of synthetic Na-Al tourmalines doped with copper; these spectra show the same absorption features (at approximately 695 nm and 920 nm) that we obtained on the natural tourmalines investigated here.

Figure 15. This graph shows the direct correlation in samples R30, R50, R52, R66, and R67 between copper concentration (obtained by microprobe analysis) and the intensity of the absorption bands between 690 and 940 nm in the near infrared that are due to  $\text{Cu}^{2+}$ . Intensity values were measured for the two broad bands that are present in the polarized spectra, in each polarization direction (see figure 14). Solid circles = 900-nm band; open circles = 690-nm band; solid triangles = 940-nm band; open triangles = 740-nm band. The fact that the groups of symbols for these four bands nearly fall along straight lines is proof that copper is the cause of these bands, and is a principal coloring agent of these Paraíba tourmalines.

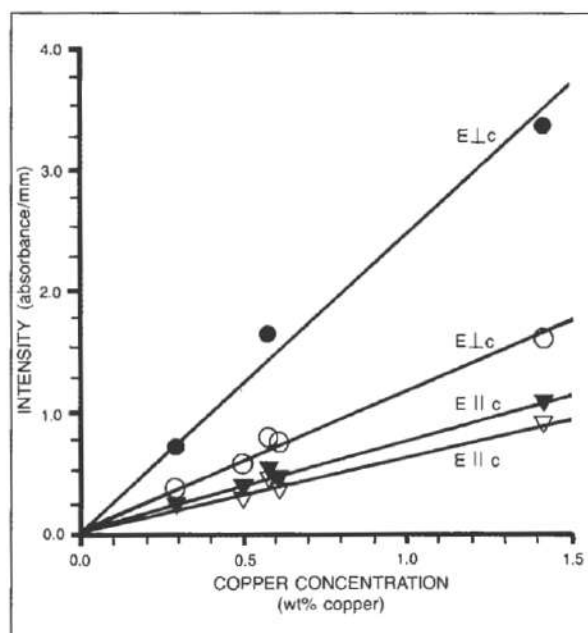




Figure 16. This 5.33-ct "emerald" green mixed-cut cabochon of Paraiba tourmaline (sample R376) is representative of one of the most attractive colors of this material. Photo by Robert Weldon.

The green color in Paraiba tourmalines is due to both an intense absorption edge toward the ultraviolet and strong  $\text{Cu}^{2+}$  absorptions, without any  $\text{Mn}^{3+}$  being present. An example of "emerald"

green tourmaline from Paraiba is illustrated in figure 16.

None of the absorption features related to  $\text{Cu}^{2+}$  can be clearly identified with a hand-held spectroscope. Furthermore, classical gemological testing methods cannot be used to demonstrate that a tourmaline indeed contains copper.

#### HEAT TREATMENT

As mentioned above, some tourmalines from this mine have been heat treated. Identification of a heat-treated stone is confounded by the fact that some colors that occur naturally can also be produced by heat treatment. We subjected five polished sections and 12 rough crystal fragments of Paraiba tourmalines, representing the typical range of color found at this locality, to heat treatment to document the color-change behavior.

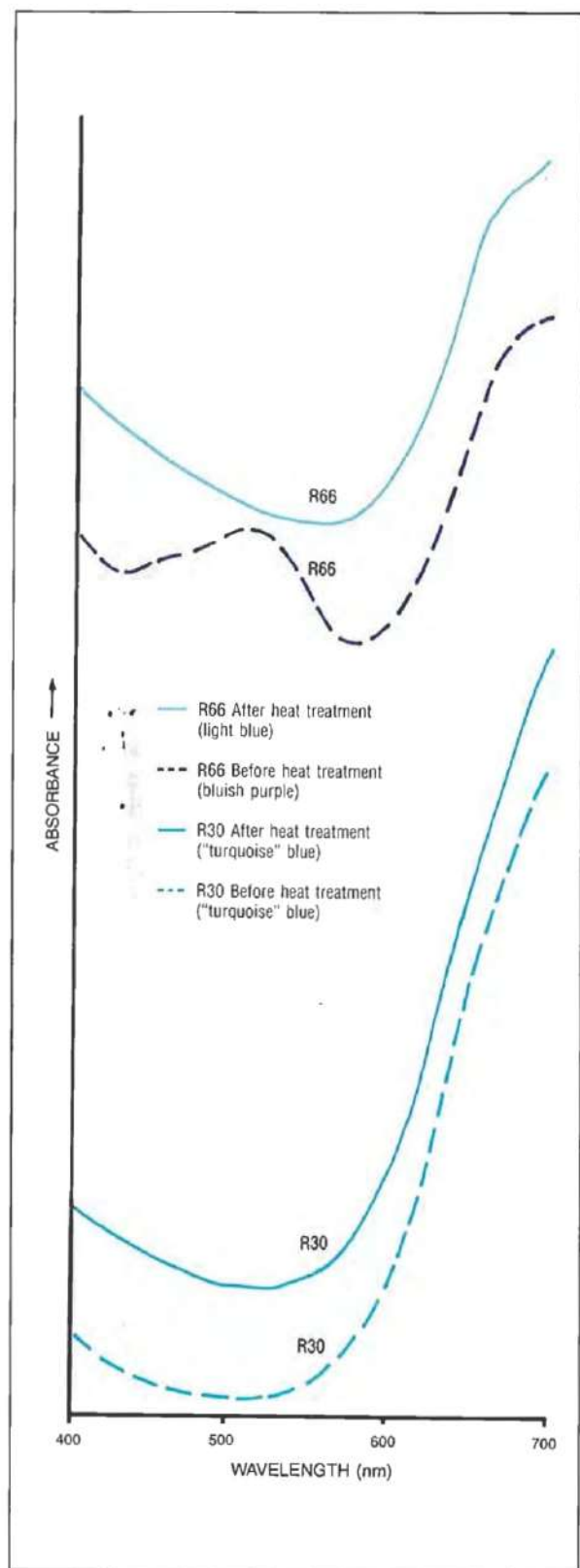
First, a sand bath was preheated to  $600^{\circ}\text{C}$  in order to burn out any water or impurities that might influence the results of the heating experiments. The samples were then buried in the sand at room temperature, and the temperature was raised to  $550^{\circ}\text{C}$  over a period of 2.5 hours. This temperature was held for four hours. The samples were then allowed to cool in the unpowered furnace at its natural cooling rate of approximately  $50^{\circ}\text{C}$  an hour. Our results are consistent with those previously published by G. Becker (as cited in Koivula and Kammerling, 1990a).

The most noticeable effect of this heat-treat-



Figure 17. These pairs of Paraiba tourmaline fragments show the effect of heat treatment on this material. Originally, both specimens in each pair were the same color (with the range of colors chosen to represent those typical of this locality); the lower specimens were subsequently heat treated to illustrate the color change produced. As described in the text, heat treatment results in blue to green for virtually all colors of starting material. Photo by Robert Weldon.





ment procedure was that all samples turned green or "turquoise" blue (figure 17). This can be related to the disappearance of the broad,  $Mn^{3+}$ -related band at about 515 nm (figure 18). Thus, bluish purple material becomes light blue with heating. During heat treatment,  $Mn^{3+}$ , which produces a pink coloration, is reduced to  $Mn^{2+}$ , which gives rise to no significant color. The sharp  $Mn^{2+}$  band at 415 nm appears during heating, but it is so weak that it is not visible in the spectra in figure 18. Such behavior is well known in rubellite tourmaline (see Reinitz and Rossman, 1988, and references therein).

Contrary to the report of Bank et al. (1990), we found that the  $Cu^{2+}$  absorptions were not changed by heat treatment. We conclude, therefore, that heat-treated Paraiba tourmalines exhibit colors attributed to  $Cu^{2+}$  and possibly to  $Mn^{2+} \rightarrow Ti^{4+}$  and  $Fe^{2+} \rightarrow Ti^{4+}$  charge transfer. These colors include "turquoise" blue and several shades of green. This also implies that colors having an  $Mn^{3+}$  component in their absorption spectra (violetish blue to purple to pink) are very unlikely to be the result of heat treatment.

Since the heat treatment of Paraiba tourmalines appears to be prevalent (Koivula and Kammerling, 1990a), it is worth noting that some of the colors produced by heat treatment also occur naturally, that is, in tourmalines that have not been heat treated. For example, some color-zoned tourmaline slices show green to blue areas colored by  $Cu^{2+}$  alone next to pinkish areas colored by  $Mn^{3+}$  (see figures 7 and 12). These slices could not have been heat treated; otherwise, they would have lost their pink coloration due to the reduction

Figure 18. These visible-range absorption spectra were recorded for representative Paraiba tourmaline specimens R66 and R30 before and after heat treatment (at 550°C for four hours in an open atmosphere). Neither stone had been treated prior to coming into our possession (G. Becker, pers. comm., 1989). Heat treatment has not affected the  $Cu^{2+}$  absorption above 690 nm in either stone. Therefore, the blue-green ("turquoise") color of specimen R30, which is due to  $Cu^{2+}$  alone, remains unchanged after heating. In specimen R66, however, heat treatment has removed the broad band centered at about 515 nm because  $Mn^{3+}$  has been reduced to  $Mn^{2+}$  (which causes little or no light absorption). Consequently, the color of this material has changed from bluish purple to light blue.

### COMMENTS ON COLOR "BRIGHTNESS"

Such descriptive terms as *neon*, *fluorescent* (which is actually very misleading), and *electric* have been used in the trade to describe some of the blues and greens in which the Paraíba tourmalines occur. It has been speculated that the "brightness" that makes these tourmalines so desirable can be attributed to three principal factors (K. Hurwit, pers. comm., 1990): a more attractive hue, a lighter tone, and a higher saturation than those green-to-blue tourmalines from other localities that are commonly seen on the gem market. The first factor, the hue, is a judgment on which the trade seems to agree (see, for example, Federman, 1990). The second aspect—a lighter than average tone—is due to the fact that, for faceted stones in the common size range, only a small portion of the visible light going through the stone is actually absorbed, thus leading to a less-dark color as compared to common green to blue tourmalines which absorb more light for the same size range. The third factor—higher saturation than average—may be related to the nature of the absorption spectrum. Three situations can be distinguished. In the Paraíba tourmalines, copper produces a very abrupt increase in absorption around 600 nm in those stones with the highest copper concentration; that results in a "purer," more saturated color that is nonetheless light in tone (since only a small portion of the light passing through the stone is actually absorbed). The presence of the 515-nm band, due to a small amount of  $Mn^{3+}$ , reduces the saturation slightly in the "sapphire" blue and "tanzanite" violet stones. Finally, the presence of more intense  $Mn^{3+}$  features (the 515-nm band), only slightly less intense than the  $Cu^{2+}$  features, results in a very desaturated grayish appearance in some stones because there is nearly equal absorption across the entire visible spectrum.

of  $Mn^{3+}$  to  $Mn^{2+}$ . Thus, the "turquoise" blue areas in these color-zoned crystals, although colored by  $Cu^{2+}$  only, are not the result of heat treatment. The same could be said of the green needle in the dark blue slab illustrated in figure 10. To our knowledge, however, the "emerald" green color has been seen only in heat-treated tourmalines from Paraíba.

### CONCLUSION

Copper concentrations recorded for elbaite tourmalines from São José da Batalha (0.37–2.38 wt.% CuO) are so high that they are significantly above the range of copper content documented so far in natural elbaite (see Staatz et al., 1955; Dietrich, 1985; and analytical data gathered by the authors). Therefore, a copper content of more than 0.1 wt.% CuO can at this time be considered proof that the elbaite under investigation comes from this deposit.

This is the first time that  $Cu^{2+}$  has been shown to be a coloring agent in tourmaline. Alone, it causes a "turquoise" blue color. If  $Mn^{2+} \rightarrow Ti^{4+}$  or  $Fe^{2+} \rightarrow Ti^{4+}$  charge-transfer mechanisms are also present, the color shifts to various shades of green. Additional absorption by  $Mn^{3+}$  causes violetish, purplish, or pinkish hues to appear and reduces saturation.

During heat treatment,  $Mn^{3+}$  is reduced to  $Mn^{2+}$  (but  $Cu^{2+}$  is unaffected). Thus, the "rubellite" component of the color is removed, and heat-treated Paraíba tourmalines are green or "turquoise" blue.

We believe that the copper concentration found in the Paraíba tourmalines is among the highest reported in silicate minerals that do not contain copper as a major constituent (as compared to, e.g. chrysocolla or diopside). This raises the question of why copper occurs in these gem-quality tourmalines, since this element is not often concentrated in silicate minerals.

Copper concentration in a granitic pegmatite environment is also quite unusual. In the absence of additional information on the mineralogy and chemistry of this pegmatite, one can hypothesize that tourmaline must have provided the most favorable crystallographic site for copper incorporation during crystallization of the pegmatite minerals.

Standard gemological testing alone cannot provide evidence of the presence of copper or the use of heat treatment in Paraíba tourmalines. However, advanced analytical techniques, such as ultraviolet-visible absorption or X-ray fluorescence spectroscopy, can help identify the presence of copper (and hence this locality of origin). U.V.-visible spectroscopy can also reveal the presence or absence of  $Mn^{3+}$  absorption bands to evaluate the likelihood of heat treatment.



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