SPECTRAL DIFFERENTIATION BETWEEN COPPER AND IRON COLORANTS IN GEM TOURMALINES

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The authors used Vis-NIR spectral measurements combined with LA-ICP-MS data to investigate the usefulness of absorption spectra for differentiating between copper and iron as sources of greenish blue coloration in gem tourmaline. While both Cu^{2+} and Fe^{2+} produce absorption bands with maxima near 700 nm, Cu^{2+} also has a strong band with a maximum near 900–925 nm, where absorption due to Fe^{2+} is typically at a minimum. In addition, Vis-NIR spectroscopy successfully identified Cu in pink/purple and violet stones that could be candidates for heat treatment. For the blue, green, and violet Cu-bearing tourmalines of pale-to-moderate color intensity in this study, weight percent of CuO could be estimated from the absorbance at 900 nm. This relatively inexpensive identification method may prove to be a valuable screening tool for Cu-bearing tourmaline.

The availability of copper-bearing tourmaline from Mozambique (Abduriyim and Kitawaki, 2005; Laurs et al., 2008) has intensified the gemological interest that was first generated after discovery of cuprian tourmaline in Brazil's "Paraíba" State (Fritsch et al., 1990; Abduriyim et al., 2006, and references therein) and later in Nigeria (Smith et al., 2001; Abduriyim et al., 2006, and references therein). In 2007, the Laboratory Manual Harmonization Committee proposed that blue ("electric" blue, "neon" blue, violet-blue), bluish green to greenish blue, or green elbaite tourmaline of moderate-to-high saturation colored by traces of Cu and Mn be called "Paraíba" tourmaline, regardless of geographic origin.

Analytical procedures used to quantify Cu content include laser ablation–inductively coupled plasma–mass spectroscopy (LA-ICP-MS), electron-microprobe analysis, and energy-dispersive X-ray fluorescence (EDXRF; Fritsch et al., 1990; Abduriyim et al., 2006; Laurs et al., 2008). However, a simpler, less expensive supplementary procedure for evaluating Cu content is desirable in instances where cost or convenience is important. The visible–near infrared (Vis-NIR) spectroscopic instrumentation described in this article is easy to use, portable, and costs as little as $3,500. It can perform a measurement in one minute or less, on a rough or polished gem sample of any size.

Both iron as Fe^{2+} (Faye et al., 1968; Mattson and Rossman, 1987) and copper as Cu^{2+} (Fritsch et al., 1990; Laurs et al., 2008) can impart greenish blue coloration to gem tourmaline. The required absorption near 700 nm is associated with metal ions in distorted octahedral environments (Burns, 1993). Thus, whether coloration is due to Fe and/or Cu cannot reliably be distinguished by looking at a

Figure 1. These 26 faceted and preformed tourmalines (weights listed in table 1) were analyzed for this study. Left to right, top row: B1–B8; second row from top: G1–G8; second row from bottom: P1–P5; bottom row: P6, P7, V1, V2, and Y1. Photo by P. Merkel.

sample. In this study, we analyzed 26 gem tourmalines by Vis-NIR spectroscopy and LA-ICP-MS, and compared the two sets of data to investigate the potential for spectral differentiation between Cu and Fe as chromophores. An additional objective of this study was to determine whether the absorption near 900 nm could be used to estimate Cu content in tourmaline colored by this element.

MATERIALS AND METHODS

We studied 26 faceted and preformed tourmalines (figure 1). They are designated in table 1 according to the predominant color observed: blue and greenish blue (B), green and bluish green (G), pink (P), violet (V), and greenish yellow (Y). Most of the Cu-bearing tourmalines were from Mozambique, but we also included samples from Brazil and Nigeria. Most of the non-Cu-bearing tourmalines were from Afghanistan, Brazil, Mozambique, and Namibia. One "chrome" uvite, from Tanzania, was also included for comparison. The greenish yellow sample was added because Mozambique tourmalines of very similar color and with no spectral evidence of Cu^{2+} are being sold as copper-bearing (e.g., on eBay); it was included to illustrate that not all greenish yellow tourmalines from Mozambique derive their blue color component in the spectrum (i.e., absorption at 700 nm) from Cu^{2+}.

For each sample, we determined specific gravity hydrostatically and measured refractive indices using a standard gemological refractometer. Vis-NIR spectra were collected with two different spectrometers. We analyzed most of the larger samples using a

Perkin-Elmer Lambda 950 spectrometer equipped with a 150 mm integrating reflectance sphere, in the range 350–1150 nm. The gem was held (~5° from normal) in the jaws of center-mount sampling module PELA-9038, and the beam was directed through the table and reflected back off the pavilion facets. Smaller samples (<1 cm) could not be reliably measured with this configuration, because they did not completely intercept the beam. They were instead measured using a StellarNet EPP2000-CXR CCD array spectrometer with an SL1 tungsten-krypton light source and a R400-7-VisNIR bifurcated fiber-optic reflectance probe, in the range 400–900 nm. These smaller gems were usually placed table-down on a white reflective standard. The small tip of the fiber-optic probe, providing both the analyzing beam and the collection of transmitted light, was placed near the culet and aimed toward the table. The beam reflected off the white standard back through the table to the probe. Intensity measurements with and without the gem in place allowed absorbance to be determined.

For both techniques, the approximate path of the analyzing beam consisted essentially of a dual traverse between the table and the culet. Both spectrometers provided absorbance vs. wavelength directly (uncorrected for path length). Spectral maxima of gems measured on both spectrometers were identical, and absorbance values were within ~10%. Some polarized absorption spectra were obtained using the Lambda 950 spectrometer in the transmission mode together with a calcite polarizer.

Trace- and major-element analyses of all samples were obtained at the GIA Laboratory in Carlsbad

TABLE 1. Properties and absorption data for the 26 tourmaline samples in this study.

Sample no.	Description	Locality	RI[a]	SG	MnO (wt.%)[b]	FeO (wt.%)[b]	CuO (wt.%)[b]	A/L (cm⁻¹) at 525 nm (Mn²⁺)	A/L (cm⁻¹) at 700 nm (Cu²⁺, Fe²⁺)	A/L (cm⁻¹) at 900 nm (Cu²⁺)	Estimated path length, L (cm)
B1	0.80 ct greenish blue	Brazil	1.619–1.641	3.09	**3.028**	0.028	**1.862**	0.249	3.029	2.686	0.70
B2	4.02 ct greenish blue	Namibia	1.620–1.639	3.09	**1.454**	**2.972**	bdl	0.239	1.562	0.265	1.30
B3	1.44 ct greenish blue	Nigeria	1.619–1.638	3.06	**0.204**	bdl	**0.291**	0.113	1.440	2.307	0.75
B4	8.93 ct greenish blue	Afghanistan[c]	1.619–1.639	3.06	**0.331**	**0.126**	bdl	0.101	0.484	0.078	1.50
B5	5.67 ct blue	Brazil	1.620–1.639	3.08	**0.508**	**0.278**	bdl	0.119	1.477	0.255	1.30
B6	14.50 ct greenish blue	Mozambique	1.621–1.637	3.04	0.018	bdl	**0.076**	0.021	0.308	0.475	1.70
B7	7.50 ct greenish blue	Afghanistan	1.62–1.63	3.05	**0.264**	**0.571**	0.001	0.048	0.594	0.047	1.65
B8	36.33 ct greenish blue	Mozambique	1.62–1.64	3.05	0.016	bdl	0.025	0.020	0.182	0.286	2.80
G1	3.29 ct bluish green	Mozambique	1.620–1.640	3.09	**3.365**	0.018	**0.177**	0.051	0.717	1.087	1.15
G2	2.42 ct bluish green	Brazil	1.620–1.640	3.09	**0.978**	**1.706**	0.001	0.073	1.880	0.051	1.00
G3	8.81 ct green	Africa	1.622–1.642	3.09	**5.572**	**0.112**	**0.136**	0.106	0.669	0.775	1.60
G4	32.30 ct bluish green	Afghanistan	1.620–1.638	3.07	**1.272**	**1.012**	bdl	0.109	0.525	0.058	2.00
G5	14.21 ct green	Mozambique	1.620–1.639	3.07	**0.443**	**0.557**	bdl	0.107	0.423	0.061	2.05
G6	7.24 ct yellow-green	Mozambique	1.624–1.640	3.07	**0.714**	**1.134**	0.006	0.181	0.557	0.081	1.55
G7	46.16 ct bluish green	Mozambique	1.620–1.639	3.06	**0.258**	0.015	0.039	0.037	0.272	0.407	2.80
G8	1.64 ct green	Tanzania[d]	1.618–1.639	3.08	0.011	bdl	bdl	0.682	0.393	0.043	0.90
P1	6.68 ct pink	Brazil	1.620–1.639	3.05	**1.219**	**0.081**	bdl	0.612	0.135	0.207	1.30
P2	8.87 ct pink	Nigeria	1.620–1.640	3.06	**0.876**	bdl	0.002	0.933	0.284	0.491	1.50
P3	2.84 ct purple	Mozambique	1.620–1.640	3.05	**1.206**	bdl	**0.173**	1.038	0.622	1.314	1.05
P4	11.50 ct pink	Mozambique	1.620–1.639	3.04	**0.289**	bdl	0.042	0.488	0.282	0.398	1.70
P5	50.07 ct pink	Mozambique	1.62–1.64	3.06	**0.408**	0.038	0.028	0.346	0.321	0.398	2.20
P6	13.55 ct pinkish purple	Mozambique	1.620–1.640	3.06	**1.415**	bdl	**0.070**	0.336	0.309	0.470	1.90
P7	29.02 ct purplish pink	Mozambique	1.619–1.639	3.05	**2.234**	0.007	0.045	0.400	0.350	0.469	2.60
V1	5.05 ct violet	Mozambique	1.62–1.64	3.07	**2.402**	bdl	**0.478**	1.325	1.783	1.508	1.20
V2	14.28 ct violet	Mozambique	1.62–1.63	3.06	**1.056**	bdl	**0.209**	0.628	0.853	1.013	1.50
Y1	10.51 ct greenish yellow	Mozambique	1.625–1.640	3.07	**0.394**	**0.108**	bdl	0.272	0.330	0.082	1.80

[a] RI values of preforms were measured to the hundredths.
[b] Average of two LA-ICP-MS analyses; bold type indicates gems with moderate-to-high levels (>0.05 wt.% oxides) of Mn, Fe, and Cu. Abbreviation: bdl = below detection limit.
[c] Likely but uncertain origin.
[d] Uvite, containing ~7.80 wt.% Mg, 2:1 Ca:Na, 0.21 wt.% V, and 0.01 wt.% Cr.

using a Thermo X Series II ICP-MS with a New Wave UP-213 laser ablation sampling system. We analyzed two random locations on the girdle of each gem, and processed the data using boron as an internal standard.

To investigate the effects of heating on the Vis-NIR spectra of Cu-bearing tourmalines, we measured the absorption spectra of 10 additional preforms (2–12 g; spectrally indicated to contain Cu) that were initially various shades of violet or brownish violet both before and after heating for one hour at ~600°C (and for three samples, after being heated again to ~700°C for one hour). Although heating for one hour at 550°C is usually sufficient to fully remove the pink color component, traces of Mn³⁺ absorption have remained in some stones under this condition. The intention in this study was to investigate whether somewhat

VIS-NIR ABSORPTION SPECTRA

Greenish Blue and Bluish Green Tourmaline

— B3 1.44 ct Cu-bearing, Nigeria
— B5 5.67 ct Fe-bearing, Brazil
— B7 7.50 ct Fe-bearing, Afghanistan
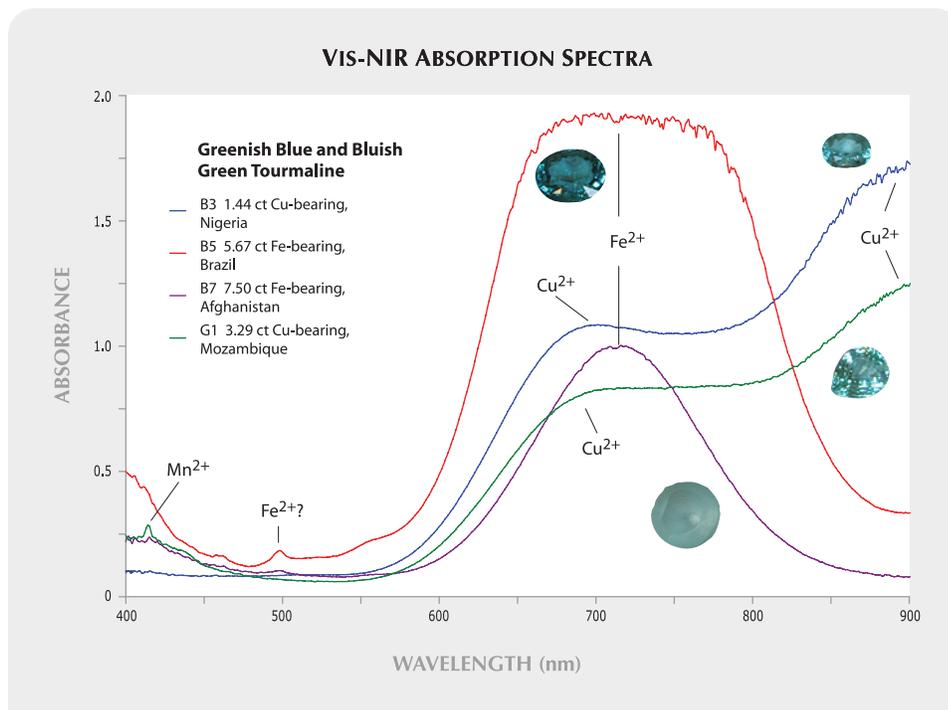— G1 3.29 ct Cu-bearing, Mozambique

Figure 2. Vis-NIR absorption spectra (collected with the EPP2000 spectrometer) are shown for selected greenish blue (B3, B5, and B7) and bluish green (G1) tourmalines colored by Fe^{2+} or Cu^{2+}.

higher temperatures would alter the Cu^{2+} absorption. We placed the samples in a Pyrex beaker containing alumina powder, and then raised and lowered the temperature at a rate of about 50°C/hour to minimize thermal shock.

RESULTS AND DISCUSSION

Chemical and spectral data for the 26 tourmalines are compiled in table 1. The RI, SG, and absorbance values (per centimeter of path length; A/L) at 525, 700, and 900 nm are given along with the average concentrations of MnO, FeO, and CuO determined by LA-ICP-MS. (MnO data are included because Mn^{3+} can produce a red-magenta color component and Mn^{2+} can produce a yellow component in tourmaline.) Most samples have significant levels of either Cu or Fe, but not both. Data are also included for one green tourmaline that is colored primarily by vanadium (sample G8). As determined from an analysis of the LA-ICP-MS data (see *G&G* Data Depository at www.gia.edu/gandg), most of the tourmalines were identified as elbaite, whereas B4, G6, and Y1 were found to be liddicoatite, and G8 to be uvite.

Vis-NIR Spectroscopy. As illustrated by the spectra in figures 2 and 3, both Cu^{2+}- and Fe^{2+}-bearing samples have absorption maxima in the vicinity of 700 nm. It is this component of the absorption by traces of Fe^{2+} or Cu^{2+} that produces greenish blue color in gem tourmaline (Faye et al., 1968; Smith, 1978; Mattson and Rossman, 1987; Rossman et al., 1991). Due to the similarity of the ~700 nm bands produced by the two metal ions, color induced by Cu^{2+} and Fe^{2+} cannot reliably be distinguished either visually or by visible-range absorption spectra. However, as further illustrated by the Vis-NIR absorption spectra in figures 2 and 3, the samples containing substantial Cu^{2+} (see table 1) have an additional absorption peak in the neighborhood of 900 nm, similar to what has been observed in earlier studies (see figure 5 in Bank et al., 1990; figure 14 in Fritsch et al., 1990; and Laurs et al., 2008). Additionally, as also seen in prior investigations (Faye et al., 1968; Mattson and Rossman, 1987), Fe^{2+} has an absorption *minimum* near 900 nm (along with additional absorption in the region of ~1000–1200 nm).

Other common chromophores such as Mn^{2+}, Mn^{3+}, Fe^{3+}, and charge-transfer transitions also do not appear to produce strong absorptions in the vicinity of 900 nm (Mattson and Rossman, 1987; Reinitz and Rossman, 1988). Thus, absorption near 900 nm provides a potentially useful property to distinguish coloration by Cu and Fe and to estimate copper content. The spectral comparisons in figures 3 and 4 illustrate that the 900 nm absorption also can be used to assess the presence of significant Cu^{2+} in tourmalines of other hues, such as green and vio-
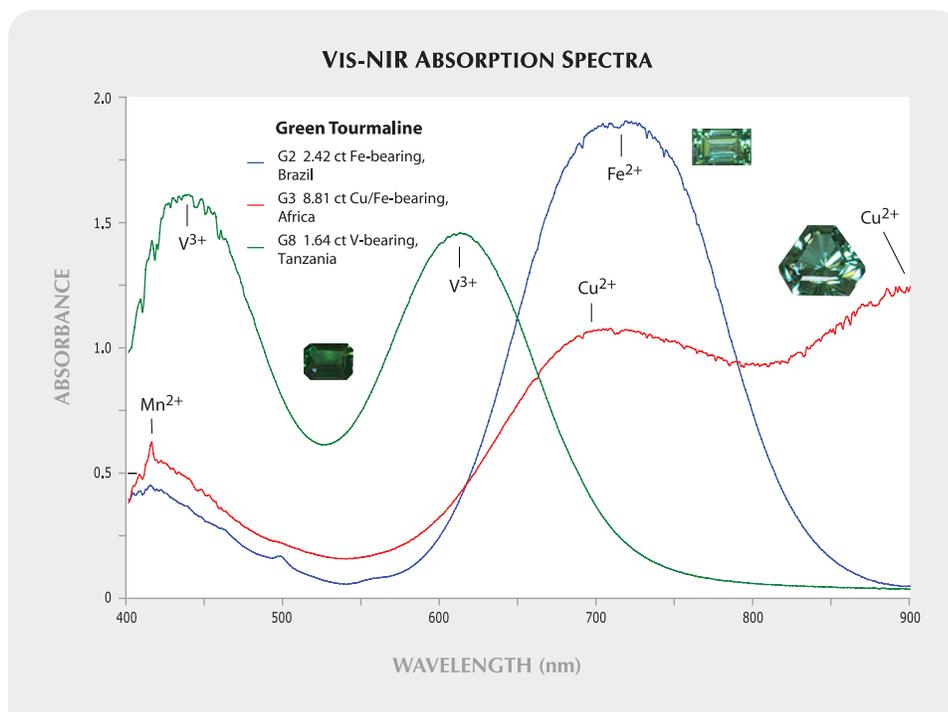
VIS-NIR ABSORPTION SPECTRA

Green Tourmaline
— G2 2.42 ct Fe-bearing, Brazil
— G3 8.81 ct Cu/Fe-bearing, Africa
— G8 1.64 ct V-bearing, Tanzania

Figure 3. These Vis-NIR absorption spectra (collected with the EPP2000 spectrometer) are from green tourmalines colored primarily by Cu^{2+} (G3), Fe^{2+} (G2, G3), or V^{3+} (G8).

let, which contain additional colorants. The green coloration of G2 and G3 in figure 3 may arise in part from Mn^{2+} contributions to blue absorption (which includes the narrow band at ~415 nm; Rossman and Mattson, 1986) combined with the red absorption by Fe^{2+} and/or Cu^{2+} near 700 nm. Substantial Mn^{3+} absorption at ~510–530 nm contributes to the color of the pink and violet samples in figure 4. The spectrum of V^{3+}-colored green uvite sample G8 (see footnote d in table 1 and Schmetzer et al., 2007) is also included in figure 3 for comparison.

Without exception, the samples in our study with moderate-to-strong absorption features near 900 nm had substantial levels of Cu. In contrast, those with substantial absorbance near 700 nm and low absorbance near 900 nm had significant levels of Fe and minimal Cu (again, see table 1). Absorption spectra of all the samples of this study, as well as complete LA-ICP-MS data, are available in the *G&G* Data Depository.

Blue, greenish blue, and green tourmalines with substantial absorbance at 900 nm but greater absorbance at 700 nm may be colored by a combination of Fe^{2+} and Cu^{2+}, because for gems colored by Cu^{2+} alone (e.g., G1 and B3 in figure 2) there is usually *greater* absorbance at 900 nm than at 700 nm. G3 was the only sample examined that had moderate levels of both iron (0.112 wt.% FeO) and copper (0.136 wt.% CuO); as with the other Cu-bearing

gems, the strong absorption near 900 nm shows the presence of copper (figure 3). The relative absorbances at 700 and 900 nm suggest that most of the absorption near 700 nm in G3 is also due to copper. The lack of absorption near 520 nm and the sharp band near 415 nm implies that the Mn in G3 is in the form of Mn^{2+}. This African gem was reportedly from Namibia, but it could be of Nigerian origin; to our knowledge, Cu has not been reported in Namibian tourmaline.

The absorbance features near 900 nm for P5 and P6 in figure 4 are consistent with their Cu contents. The absorbance value for P5 is substantial despite its low Cu content due to the relatively long analyzing path length for this large gem. This result and similar behavior for B8, G7, and P7 illustrate that CuO levels as low as ~0.03 wt.% can readily be detected spectrally in large stones. In contrast, the behavior in figure 4 of P1, which contains some Fe but no Cu, exemplifies a situation where caution must be exercised in spectrally assessing the presence of Cu. Relatively weak absorptions near 700 and 900 nm in pink or red tourmaline such as P1 may be related to Mn^{3+} rather than Cu^{2+}. A low-intensity Mn^{3+} band has been observed previously near 700 nm (Manning, 1973; Reinitz and Rossman, 1988), and a weak Mn^{3+} band has also been reported in the region of ~900–1025 nm in thin-layer synthetic elbaite with

VIS-NIR ABSORPTION SPECTRA

Figure 4. Vis-NIR absorption spectra (collected by the Lambda 950 spectrometer) are shown for pink (P1 and P5) and pinkish purple (P6) tourmalines from Brazil and Mozambique. Samples P5 and P6 contain substantial amounts of Cu.
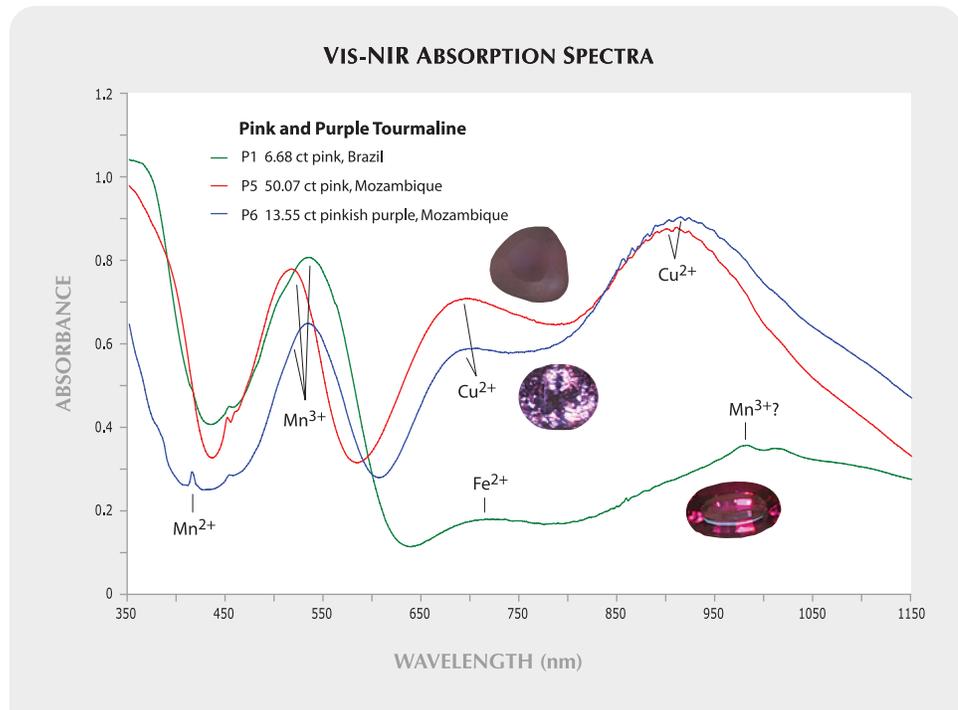
Mn as the only colorant (see figure 7 in Taran et al., 1993). Fe^{2+} probably contributes to the absorptions near 700 and 1050 nm (Faye et al., 1968; Mattson and Rossman, 1987) in P1, but the weak absorption near 900 nm may be due to Mn^{3+}. The small bumps at ~970 and 1000 nm are due to OH vibrational overtones (Rossman et al., 1991).

Estimation of Cu^{2+} Abundance. The above examples illustrate the use of spectroscopy for qualitative assessment of the presence of Cu. However, spectral measurements can also provide quantitative *estimates* of Cu levels. Figure 5 illustrates that for most of the Cu-bearing tourmalines studied, there is a reasonably linear relationship between the absorbance at 900 nm divided by the path length in centimeters (A_{900}/L) and the copper content (wt.% CuO).

The ±50% error bars for the A_{900}/L values in figure 5 represent the estimated uncertainty due to several factors. The first factor is the variation in the extinction coefficient (a measure of the absorbing strength of a colorant) of Cu^{2+} with crystallographic direction. Polarized absorption measurements have shown that the extinction coefficient of Cu^{2+} near 900 nm is reduced by about three-fold for the extraordinary ray (i.e., $E \parallel c$) relative to the ordinary ray ($E \perp c$; Rossman et al., 1991). There is also a slight shift in the absorption maximum between the ordinary and extraordinary rays. Therefore, the precise absorbance at 900 nm that is produced by a given concentration of Cu^{2+} will be somewhat

Figure 5. In this diagram, the absorbance at 900 nm divided by path length in centimeters (A_{900}/L) is plotted against Cu content. Data are shown only for tourmaline samples with low-to-moderate absorbance (≤1.7), since they were least affected by surface reflections. The A_{900}/L values include error bars for a ±50% estimated uncertainty.

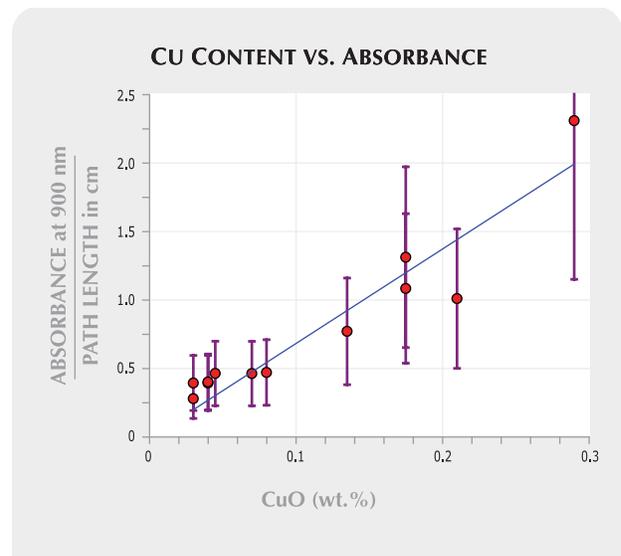**CU CONTENT VS. ABSORBANCE**

Figure 6. The blue-to-green color of tourmaline may be caused by absorption mainly due to copper (e.g., the three stones on the left, 3.86–11.69 ct) or to iron (the three on the right, 2.86–6.89 ct). Such material may be spectrally differentiated to identify whether it should be classed as Paraíba-type tourmaline. Courtesy of the Gladnick Collection and Palagems.com; photo by Robert Weldon.

dependent on the arbitrary orientation of the axes of the gem relative to the direction of the analyzing beam. Second, there is some uncertainty as to the exact path length traveled by the beam in these measurements, due to the complex geometry of the cut gemstones and the potential effects of inclusions. Third, the absorbance at 900 nm reflects the average bulk concentration of Cu^{2+}, while LA-ICP-MS is a spot analysis and only measures the surface composition. Last, the recorded absorbances are influenced by surface reflections, which may be particularly significant for darker gems. The straight-line fit of the data in figure 5 excludes the highest-absorbance (>1.7) Cu-bearing tourmalines, for which surface reflections greatly limit the maximum absorbances measurable by the techniques of this study. The correlation represented by the line in figure 5 is remarkably good ($r^2 = 0.88$) considering the sources of variability. The slope of 6.86/cm translates to a CuO content of ~0.15 wt.% per unit of absorbance/cm at 900 nm.

Estimation of Fe^{2+} Abundance. Estimating Fe^{2+} content from absorbance near 700 or 1100 nm is more problematic. Cu^{2+} absorption can interfere near 700 nm, and absorptions due to OH stretching vibrational overtones can begin to interfere at wavelengths >950 nm (i.e., sample P1 in figure 4; see also the *G&G* Data Depository). Like that of Cu^{2+}, the Fe^{2+} absorption depends on orientation. However, the major additional sources of uncertainty in the estimation of iron content are the presence of Fe^{3+} and the nonlinear relationship between iron concen-

tration and Fe^{2+} absorbance (Smith, 1978; Mattson and Rossman, 1987).

Effects of Heat Treatment on Vis-NIR Spectra. Heat treatment is commonly applied to Cu-bearing tourmaline to create or enhance blue/green coloration (Fritsch et al., 1990; Abduriyim et al., 2006; Laurs et al., 2008). While our heating experiments on 10 violet or brownish violet samples removed some absorption features (particularly the Mn^{3+} band near 520 nm) to produce blue or green hues, none of the heated samples showed significant changes in the positions or intensities of the Cu^{2+} absorption bands at ~700 and ~900 nm. Therefore, Vis-NIR spectroscopy can be used to evaluate the Cu^{2+} content of tourmaline samples that have been heat treated.

CONCLUSIONS

Spectral measurements can provide information on the causes of color in gemstones, whereas chemical analyses only indicate which elements are present. In this study, Vis-NIR spectroscopy coupled with LA-ICP-MS analyses demonstrated that absorption spectra can be useful in assessing the contribution of Cu^{2+} to the greenish blue color component in gem tourmaline. Both Fe^{2+} and Cu^{2+} produce absorption bands with maxima near 700 nm, but only Cu^{2+} has a strong maximum near ~900 nm, where the absorption due to Fe^{2+} is typically at a minimum. All the samples in our study with a moderate-high absorption feature near 900 nm contained substantial Cu. In contrast, samples with a substantial absorption

band near 700 nm, but low absorbance near 900 nm, had significant levels of Fe and little or no Cu. Spectral analysis cannot replace more quantitative procedures such as LA-ICP-MS or even EDXRF. Based on this study, however, absorption measurements in the region of 900–925 nm appear to be a relatively quick and simple means for assessing the presence of Cu in gem tourmaline, the key criterion for designation of a stone as "Paraíba" or "Paraíba-type" (e.g., figure 6). Furthermore, in blue, green, and violet gems of pale-to-moderate color intensity, it was possible to estimate wt.% CuO within ~50% accuracy. Spectral measurements may also aid in selecting off-color Cu-bearing tourmalines that are suitable candidates for heat treatment.

We have shown that simple CCD array spectrometers with fiber-optic reflectance probes offer a relatively portable and inexpensive method to screen rough or faceted gem tourmalines (even small samples) for Cu. Most common Vis-NIR spectrometers in gemological laboratories are not well suited to measure Cu^{2+} concentrations because they are configured to measure transmittance of light through a sample, and therefore are useful for performing reasonably quantitative measurements only on parallel-polished slabs or on faceted gemstones with fairly large parallel facets. Nevertheless, fiber-optic probe attachments or small integrating sphere accessories may be compatible with some more-traditional spectrometers.

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