COPPER AND TENORITE INCLUSIONS IN CUPRIAN-ELBAITE TOURMALINE FROM PARAÍBA, BRAZIL

By Franz Brandstätter and Gerhard Niedermayr

Inclusions of native copper and tenorite (CuO) were found in grayish green elbaite from São José da Batalha, Paraíba, Brazil. Native copper forms strongly dendritic platelets (about 100 µm long, 1 µm thick) oriented parallel to the c-axis of the host crystal in a trigonal arrangement. The much less abundant tenorite forms 20–30 µm platy grains. Electron microprobe analyses revealed that the tourmaline is cuprian elbaite (1 wt.% CuO), with significant contents of iron (2.7–3.1 wt.% FeO) and manganese (0.9–1.4 wt.% MnO). The CuO content of tourmaline around the native copper decreases toward these inclusions up to a factor of two. No such decrease in CuO was observed for the tenorite inclusions.

In 1989, unusually intense blue and green tourmalines appeared on the international market (figure 1). They reportedly came from a locality called Mina da Batalha, close to the village of São José da Batalha, in Paraíba State, Brazil (see, e.g., Koivula and Kammerling, 1989). Subsequent research revealed that the vivid yellowish green to blue-green colors of these tourmalines are mainly due to their copper (Cu) content (Fritsch et al., 1990; Rossman et al., 1991). Although the Cu concentration reported in these tourmalines (0.4–2.4 wt.% CuO) is among the highest ever analyzed in nominally Cu-free silicates, no information was available regarding the source of the Cu responsible for the unusual colors.

In September 1992, Mr. F. Janousek, a mineral collector from Vienna, showed us several pieces of tourmaline that he had selected in Brazil a couple of months previously from a lot of more than 100 similar-appearing tourmaline crystals and fragments. The miner from whom he purchased the material said that it came from Paraíba. All of the tourmalines contained numerous metallic yellow specks (similar to those seen on the table of the Paraíba tourmaline in figure 2). He gave us three representative pieces of this material and asked us to determine the nature of these unusual-appearing inclusions.

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Figure 1. The striking blues and greens of these elbaite tourmalines from Paraíba, Brazil, are caused by the presence of copper in their structure. Stones (largest, upper right, is 26.63 ct) courtesy of Michael Scott; photo © Harold & Erica Van Pelt.

PREVIOUS WORK

Bank et al. (1990) and Fritsch et al. (1990) provided brief comments on the regional geology and mining history of the Paraíba tourmalines, together with detailed reports about their mineralogical and gemological properties. Microprobe analyses proved the tourmalines to be elbaites, with MnO and CuO contents up to 3.0 and 2.4 wt.%, respectively. In these reports, no explanation was given for the source of the unusually high Cu content of these elbaites. Fritsch et al. (1990) mentioned typical inclusions for gem tourmalines: three-phase, liquid (in veils or "fingerprint" patterns), thin growth tubes parallel to the c-axis, and some doubly refractive crystals. Also mentioned and illustrated were "numerous yellowish specks" that local miners had assumed to be gold (see figure 11 on p. 197 of that article). X-ray fluorescence analyses cited by the authors revealed the presence of Mn, Fe, Cu, Zn, and Bi, as well as some S; this implies that these metallic inclusions could be composed of a sulfide with a certain Fe content. In a short item in the Fall 1992 issue of *Gems & Gemology*, Koivula et al. reported the appearance of such inclusions near the surface of a cut Paraíba tourmaline and suggested that they might be the product of epigenetic exsolution. They pointed to the fact that "microchemical testing with nitric acid, done on a crystal with exposed inclusions, indicated the presence of copper." Brandstätter and Niedermayr (1993) proved these inclusions to be native copper.

Henn and Bank (1990), Fritsch et al. (1990), and Rossman et al. (1991) investigated the origin of color in the cuprian elbaites. According to their findings, the incorporation of Cu^{2+} into the tourmaline structure is the main cause for the exceptional hues. Some modification of the elbaite colors to violet-blue and violet hues is ascribed to increasing absorption from Mn^{3+}.

MATERIALS AND METHODS

All analytic results mentioned here were obtained from Mr. Janousek's three tourmaline specimens, which he said were representative of the tourmaline lot he had seen in Brazil. All of the samples were grayish green: a 1-cm-long crystal fragment weighing 0.7 ct, a 0.9-ct cabochon, and a 1-cm-long terminated crystal that weighed 10 ct. The crystal showed the striated prism faces typical of tourmaline and the pyramid $\{10\bar{1}1\}$ only. At the irregular base of this crystal, white platy albite was intergrown with the gem host.

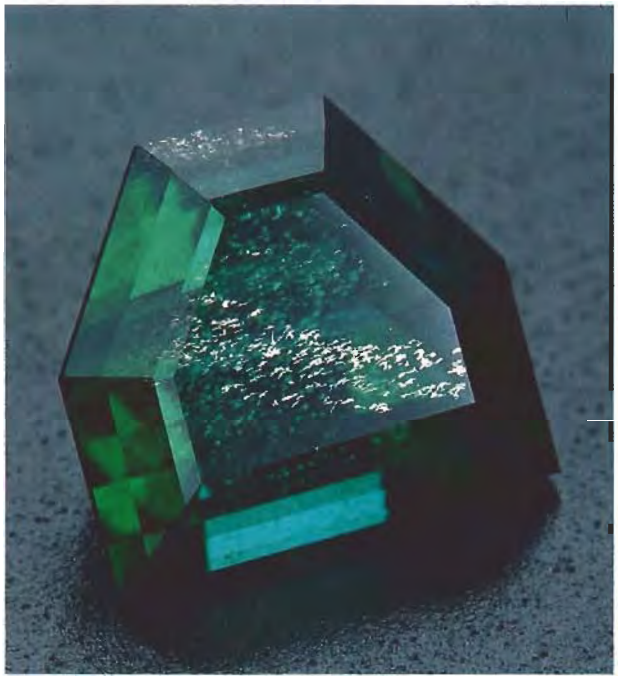

Figure 2. On this 2.41-ct faceted Paraíba tourmaline, the yellow platelets are seen near the surface, running across the table facet. Photo by Maha DeMaggio.

As a first step, the flattened crystal fragment was cut parallel to the c-axis and polished on one side. As a second step, the same crystal was cut perpendicular to the c-axis and a polished thin section was made.

Specific gravity was determined on all three specimens by the hydrostatic method; optical properties, using a standard gemological refractometer; and pleochroism, with a calcite dichroscope. Chemical composition was determined on two of these specimens (the cut crystal fragment and the cabochon). Qualitative chemical analysis and investigation of morphology and orientation of the inclusions on the polished tourmaline surface (cut parallel to the c-axis) were carried out on a JEOL JSM-6400 scanning electron microscope equipped with a KEVEX energy-dispersive system (SEM-EDS). Then five randomly located spots were selected on both specimens for quantitative chemical analysis with an ARL-SEMQ electron microprobe. To reduce sample decomposition, we analyzed the spots with a defocused beam (area 100 µm^2) at 15kV, 20nA. The analyses were corrected by standard procedures using natural and synthetic standards.

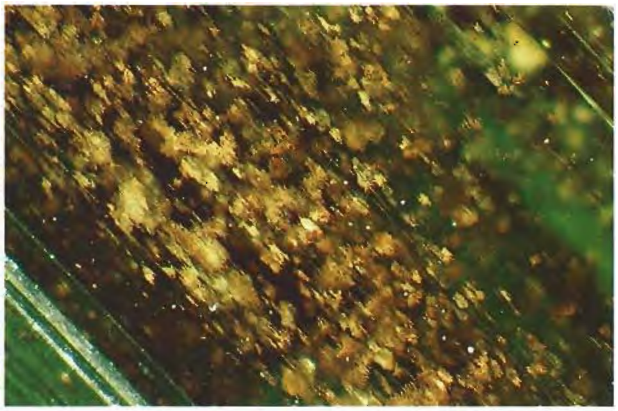

Figure 3. With magnification, numerous specks of a yellow metallic mineral were evident in the Paraíba tourmalines examined. Photo by Gerhard Niedermayr; field of view, 1.5 cm.

RESULTS

Optical Properties. The gemological properties (refractive indices, birefringence, and specific gravity) of these three samples are consistent with those reported by Fritsch et al. (1990) for two—one yellowish green, the other greenish gray—Paraíba tourmalines of similar color. All three samples were grayish green color and with typical pleochroism (ε = yellowish green, ω = grayish green). Refractive indices were measured as follows: ε = 1.622–1.624, ω = 1.642–1.644, with a birefringence of 0.020; uniaxial negative. Specific gravity was 2.99.

Inclusions. When examined with magnification, all three specimens exhibited the standard suite of fluid, three-phase, and crystalline (e.g., tourmaline) inclusions typical for elbaite tourmalines. In addition, however, we noted platelets of a yellow material with a metallic luster (figure 3). In transmitted light, the yellow metallic inclusions turned out to be numerous minute, strongly skeletal, branching platelets on the average 100 µm long and only 1 µm thick (figure 4). They were reminiscent of the typical branching growth characteristic of native copper. With the microscope and reflected light (at a magnification of about 120×), we observed a few irregularly scattered grains that had a different reflectance behavior in the polished tourmaline sample that was cut parallel and perpendicular to the c-axis.

Chemical Analyses. As can be seen from table 1, there are some differences in the contents of CuO (1.01 and 1.02 wt.%) and FeO (2.71 and 3.10 wt.%)

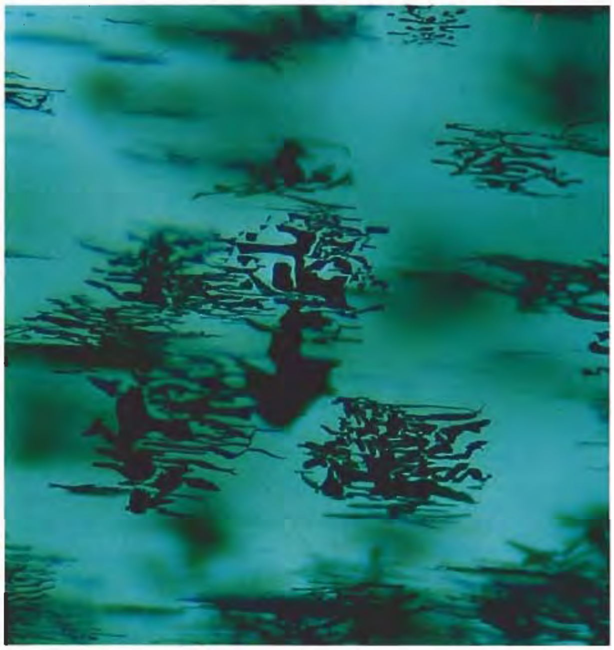

Figure 4. At higher magnification, the "gold"-colored specks reveal a dendritic form that is typical for native copper. Photo by Gerhard Niedermayr; field of view, 600 µm.

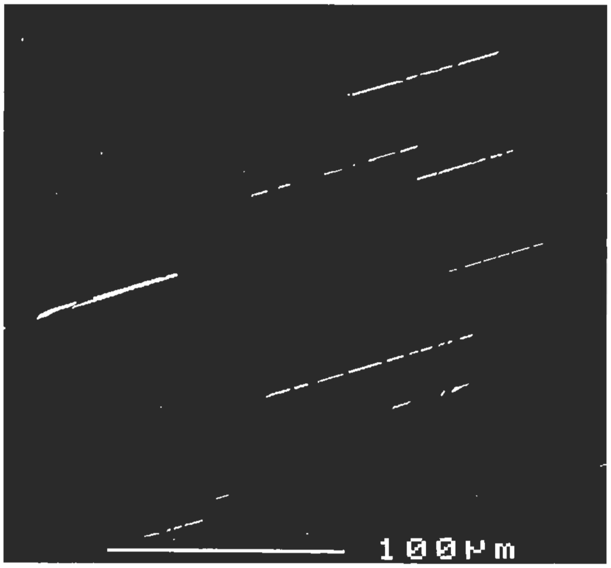

Figure 5. Note in this backscattered electron image of native copper (white) in cuprian elbaite (gray) from Paraíba that the copper inclusions are oriented parallel to the c-axis of the tourmaline. "Dashed lamellae" indicate the dendritic morphology of these platelets.

in the two specimens we analyzed as compared to the two specimens of similar color for which microprobe analyses were reported by Fritsch et al. (1990). Although the CuO content of our samples is within the total range (0.37–2.38 wt.%) for Paraíba elbaites of different colors given in that article, the FeO content is significantly higher (maximum FeO of 0.34 wt.%).

SEM analysis of the dendritic platelets proved that they are indeed native copper. The SEM investigations of one specimen revealed that the platelets are oriented parallel to the c-axis of the tourmaline (figure 5). In the thin section cut perpendicular to the c-axis, the arrangement of the copper platelets revealed the trigonal symmetry of tourmaline (figure 6). In addition, we subsequently identified (by SEM-EDS, confirmed by microprobe) the grains seen at high magnification as tenorite (CuO). As seen on the scanning electron micrograph, the tenorite grains (figure 7) commonly form subhedral platy crystals measuring 20–30 µm. In contrast to the copper platelets, the tenorite inclusions apparently do not show an oriented intergrowth with the host crystal.

Electron microprobe traverses perpendicular to the copper platelets and to the c-axis of the host tourmaline (figure 8) indicated that the CuO content of the tourmaline examined decreases—from 1.2 wt.% (maximum) to about 0.6 wt.% (minimum content)—in the direction toward the inclusions. We did not observe a corresponding variation in the CuO content of the tourmaline around tenorite inclusions.

TABLE 1. Electron microprobe analyses (in wt.%) of four elbaite tourmalines from Paraiba, Brazil.[a]

	Sample No.[b]			
Oxide	1a	1b	2	3
SiO_2	36.6	36.8	37.27	37.29
TiO_2	0.17	0.14	0.10	0.07
B_2O_3	n.d.	n.d.	10.94	10.94
Al_2O_3	40.2	38.2	39.04	38.73
Cr_2O_3	< 0.02	< 0.02	< 0.02	< 0.02
FeO	2.71	3.10	0.22	0.12
MnO	1.42	0.92	1.47	2.99
CuO	1.01	1.02	0.37	0.49
MgO	0.49	0.52	0.54	0.30
CaO	0.25	0.34	0.46	0.45
Li_2O	n.d.	n.d.	1.62	1.62
Na_2O	2.22	2.29	2.27	2.36
K_2O	0.03	0.04	0.03	0.02
H_2O	n.d.	n.d.	3.13	3.13

[a] *For description of equipment and analytical technique, see the "Materials and Methods" section.*

[b] *Samples 1a and 1b are the average of five single analyses on two of the grayish green tourmalines examined for this article. Sample 2 is a yellowish green elbaite (GIA no. R50) and sample 3 is a greenish gray elbaite (GIA no. R378), as reported in Fritsch et al. (1990). Total Fe and Mn are given as FeO and MnO, respectively. Li_2O, B_2O_3, and H_2O were not determined (n.d.) for samples 1a and 1b, and were calculated on an assumed stoichiometry for samples 2 and 3.*

DISCUSSION AND CONCLUSION

The existence of inclusions of native copper and tenorite, together with the determination of a high Cu content, in some Paraíba tourmalines indicates that these elbaites formed under unusual conditions for a granitic pegmatite environment.

Because to date there have been no comprehensive reports on the local geology, one can only speculate about the origin of the Cu enrichment. For example, pegmatitic fluids could have been enriched in Cu as a result of the interaction with pre-existing Cu-bearing mineralization or by the accumulation of Cu in an earlier magmatic stage of the pegmatite's evolution. Typically, however, granitic rocks have very little Cu, and Cu is not known generally to accumulate in pegmatitic melts (see, e.g., Wedepohl, 1974).

Irrespective of the process that caused the Cu enrichment, from our observations it seems most likely that the native copper (and tenorite?) inclusions were formed in an early stage of cooling after crystallization of the tourmalines had begun. The assumption of syngenetic precipitation of native copper during growth of these tourmalines does not agree with the observation of unoriented, scattered copper platelets in triangular arrangement (again, see figure 6). It is also possible, however, to interpret the tenorite inclusions as remnants of pre-existing Cu mineralization. This hypothesis is supported by our findings that—in contrast to the chemical changes observed in conjunction with the inclusions of native copper—there was no systematic change in the CuO content of the host tourmaline in relation to the tenorite inclusions. However, we cannot exclude with certainty the possibility that because of the small size of the tenorite inclusions, any chemical change around them is below the detection limit of the microprobe.

Figure 6. In this thin section of Paraíba tourmaline cut perpendicular to the c-axis, the arrangement of copper inclusions clearly reveals the trigonal symmetry of the host crystal. Photo by Gerhard Niedermayr; field of view, 600 µm.

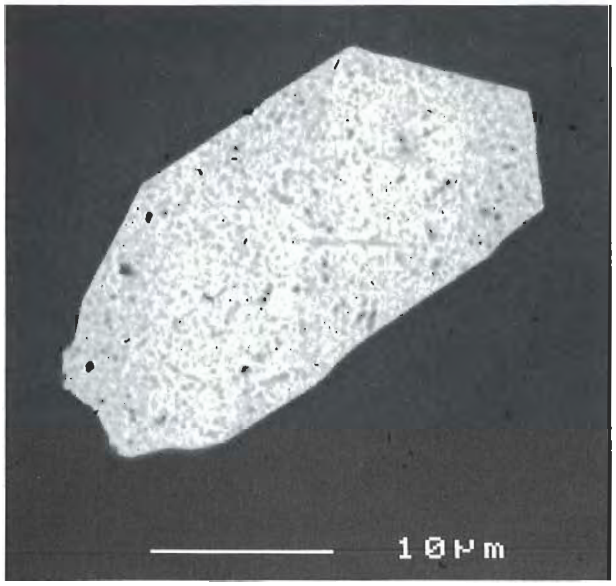

Figure 7. Subhedral tenorite (light gray) can be seen in this backscattered electron image of cuprian elbaite (dark gray) from Paraíba, Brazil.

The trigonal arrangement of the copper platelets indicates exsolution from the cuprian tourmaline. This had been suggested earlier by Koivula et al. (1992), who interpreted these inclusions as epigenetic exsolution, but did not explicitly state that they might actually be copper platelets. Similar types of growth features have been observed in ruby and sapphire: rutile needles and silk, formed by exsolution, that exhibit an epitaxial relationship to the host corundum. Gübelin and Koivula (1986) described diskettes of copper formed by solid-solution exsolution in labradorite feldspar ("sunstone") from Oregon. A more extensive investigation of this interesting material has since been made by Johnston et al. (1991).

In a compilation of native-element inclusions in minerals, Koivula (1991) mentioned copper inclusions in analcime, apophyllite, datolite, labradorite, natrolite, orthoclase, prehnite, quartz, calcite, and gypsum. To our knowledge, none of

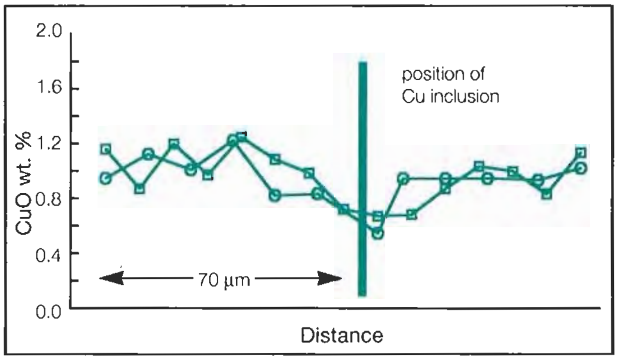

Figure 8. From this plot of CuO content in a Paraíba tourmaline (two electron microprobe traverses) as it relates to distance from native copper inclusions, it is evident that the CuO content of the host tourmaline decreases as the beam gets closer to the inclusions.

these mineral species contains Cu in its crystal lattice. Thus, for the minerals Koivula described, it is most likely that native copper precipitated syngenetically on earlier faces of the growing crystals of these minerals. The Paraíba tourmalines differ in that Cu^{2+} is incorporated into the tourmaline structure to a certain extent (e.g., Rossman et al., 1991). As described earlier, the copper platelets are aligned parallel to c but are otherwise scattered throughout the host crystal in an irregular manner. Therefore, we assume that these platelets are more likely a product of epigenetic exsolution than of epitactic overgrowth.

In any case, tourmaline must be added to the list of silicates where inclusions of native copper have been detected.

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