

SOLUTION-GENERATED PINK COLOR SURROUNDING GROWTH TUBES AND CRACKS IN BLUE TO BLUE-GREEN COPPER-BEARING TOURMALINES FROM MOZAMBIQUE

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Several transparent, faceted, blue to blue-green copper-bearing tourmalines containing growth tubes and cracks surrounded by sleeves of pink color were examined for this report. On the basis of micro-observation, it is theorized that a radioactive solution was the probable cause of the pink color. The presence of the pink zones also supplied visual evidence that the host tourmalines had not been heat treated.

Over the past year, we examined nine blue to blue-green Cu-bearing tourmalines from Mozambique that contained surface-reaching growth tubes and cracks that were outlined or “sleeved” with obvious pink color zones (e.g., figure 1). These gems came from four different gem dealers over the course of the year.

The first gem, from Simon Watt, was a 14.12 ct blue heart-shaped mixed cut measuring $15.82 \times 13.68 \times 10.82$ mm that was purportedly from Mozambique. As shown in figure 2, this tourmaline contained a surface-reaching growth tube sleeved by a pink zone of moderate intensity.

Soon thereafter, Bill Vance and David Freeland Jr. sent us the 27.63 ct cushion mixed cut shown in figure 1. This gem, also said to be from Mozambique, measured $17.82 \times 17.13 \times 12.95$ mm. It contained a surface-reaching macroscopic growth tube under its table that was enveloped along its length by an intense zone of pink (almost red) color, which created a clear contrast against the blue bodycolor of its host.

The third and largest of the gems came into the GIA Laboratory for identification and origin determination. This tourmaline was a blue-green pear-shaped modified brilliant cut that weighed 33.26 ct and measured $24.34 \times 19.88 \times 12.89$ mm. It contained several thin surface-reaching growth

tubes that were all sleeved by narrow pink color zones. While these features were too small to be seen with the unaided eye, they were clearly evident with magnification. Chemical analysis by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) revealed that the country of origin for this gem was also Mozambique (for more on this technique, see Abduriyim et al., 2006).

The remaining six tourmalines, all pear shapes believed to originate from Mozambique, came from Mark H. Smith. They ranged from 1.07 to 2.66 ct, and were all light blue-green in color. Pink color zoning was associated with cracks extending from the pink-zoned growth tubes in these stones.

Although detailed gemological investigations have been performed relatively recently on Cu-bearing tourmalines from Mozambique (Abduriyim et al., 2006; Laurs et al., 2008), no inclusions of this nature were mentioned or illustrated in these published works. This suggests such inclusions—and their formation mechanism—are relatively rare in tourmaline.

Proposed Coloration Mechanism. It is well known and scientifically established that radiation can produce pink-to-red color in tourmaline (Nassau 1984), so it is logical to surmise that radiation is responsible for the pink color surrounding the surface-reaching growth tubes and related cracks in these blue to blue-green Cu-bearing tourmalines.

The most likely mechanism for the formation of the pink color in these tourmalines can be hypothesized from previous research by one of the authors (JIK) on smoky quartz and green diamond. The first of these articles (Koivula, 1986) described the coloration of smoky quartz crystals by naturally occurring radioactive hydrothermal fluids. The brown color was confined to a surface layer only a few millimeters thick; the color was darkest around surface features and surface-reaching cavities, as well as surrounding near-surface fluid inclusion chambers that were still intact, containing both liquid and gas phases. In fact, the presence of brown clouds of color surrounding these fluid inclusion chambers proved that the fluid they contained was radioactive at one time, since the “smoky”

See end of article for About the Authors and Acknowledgments.

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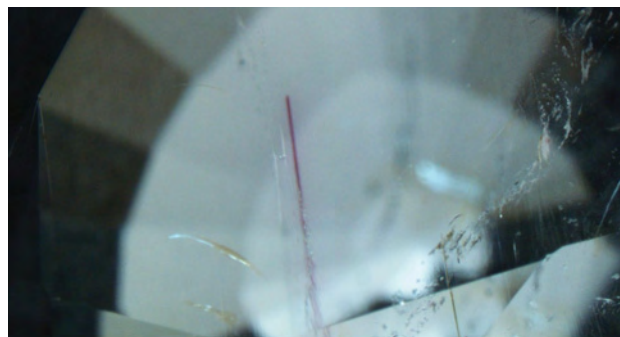
Figure 1. Of the Cu-bearing tourmalines examined for this report, this rich blue 27.63 ct gem contained the largest and most obvious rubellite-colored growth tube, which is clearly visible under the table facet. Photo by Robert Weldon.

color in quartz is the result of radiation (Nassau, 1984).

The second study (Koivula, 1988) documented a section of a natural diamond crystal with a negative-crystal cavity that was open to the surface through a thin neck. Trapped in the cavity was a small loose diamond crystal that was too large to escape through the neck. Brownish green radiation stains covered the inner walls of this cavity, its neck, and the surface of the trapped diamond crystal. However, no such stains were observed anywhere on the host diamond's outer surface.

These two studies show that radioactive solutions can impart a post-growth shallow layer of color in gem materials. If they have surface-reaching features such as etch pits and cavities, channels, cracks, or growth tubes, then color-

Figure 2. Discovered in a 14.12 ct Cu-bearing tourmaline said to be from Mozambique, this pink-zoned growth tube was the first one of these inclusions examined for this report. Photomicrograph by J. I. Koivula; field of view 4.9 mm.



causing radioactive solutions can invade the crystal by capillarity, thereby imparting color to the inner surfaces of those features. If at some later point the outer surface of such a crystal is removed—either by natural causes such as etching or water abrasion, or through lapidary processes—then only the surfaces that have evaded removal (e.g., within growth tubes, etc.) will show the color imparted by the radioactive solutions. Since it is well known that exposure to radioactivity causes a pink-to-red color in tourmalines (see, e.g., Reinitz and Rossman, 1988), that is the probable explanation for the presence of the pink sleeves in these Cu-bearing tourmalines.

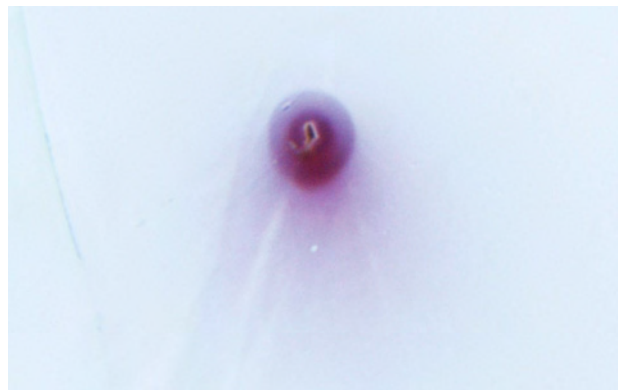
Micro-Examination. First, we used standard gemological techniques to confirm that the gems were tourmaline. Then we turned to energy-dispersive X-ray fluorescence (EDXRF) spectroscopy to determine that they were Cu-bearing, and we followed that with LA-ICP-MS chemical analysis on the four largest stones to confirm that their geographic origin was Mozambique.

The next step in the documentation process, and the purpose of this article, was to determine the nature of these unusual pink-sleeved growth tubes and cracks, and to document them photographically. This was accomplished using a gemological photomicroscope and various lighting techniques.

Like all growth tubes in tourmaline, these were oriented parallel to the optic axis (c-axis) of their hosts. In all instances where pink coloration was observed around a growth tube, that growth tube reached the surface of the host gem. Where the growth tubes were completely confined in the tourmaline, we did not see any associated pink color.

When looking down the length of a pink surface-reaching "needle" (figure 3), we observed bleeding of the pink

Figure 3. When viewed down the length of one of the pink "needles," the radiation-induced color can be seen to bleed out into the surrounding tourmaline host, becoming weaker until it gradually fades away. The diameter of the growth tube is 0.06 mm. Photomicrograph by J. I. Koivula.



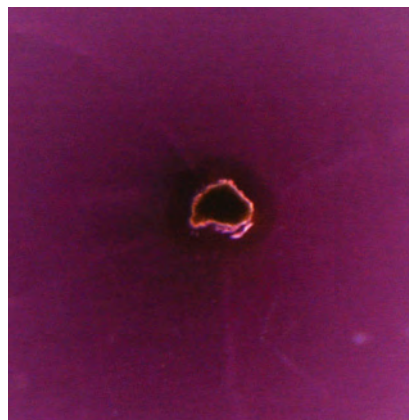


Figure 4. Viewed down the length of the growth tube, a dark red-to-pink zone can be observed immediately surrounding the tube, which itself is lined on the inner walls with a rusty-looking epigenetic coating (left). Wherever pink-zoned growth tubes reached the surface, their edges looked ragged, apparently due to the cutting process (right, reflected light). For a growth tube to show a pink sleeve of color, it must reach the surface of the host tourmaline. This tube is 0.07 mm in diameter at its broadest point. Photomicrographs by J. I. Koivula.

color into the surrounding tourmaline host, which became weaker until it gradually faded away. This is exactly what would be expected if a radioactive solution had entered by capillary action into open growth tubes on the surface of a tourmaline crystal. A thin zone of much darker pink-to-red color immediately surrounded all the colored tubes (figure 4, left), while a rusty-looking epigenetic coating lined the inner walls of the growth tubes. Exposure to the radioactive solutions could have taken place within the gem pockets that originally hosted the tourmalines, or within a specific part of the alluvial deposit after the tourmalines weathered from their host pegmatite. The radioactive solutions may have originated from interaction with radioactive minerals; such minerals are common in some Mozambique pegmatites (e.g., Dias and Wilson, 2000).

With magnification and surface-reflected light (figure 4, right), the edges of all the surface-reaching growth tubes looked ragged and rough. This is apparently due to damage

along the rims of the growth tubes that occurred during the faceting process.

As shown in figure 5, we observed a wide range in the diameters of the pink-colored growth tubes. Only the largest of these, such as that shown in figure 1, were visible without magnification.

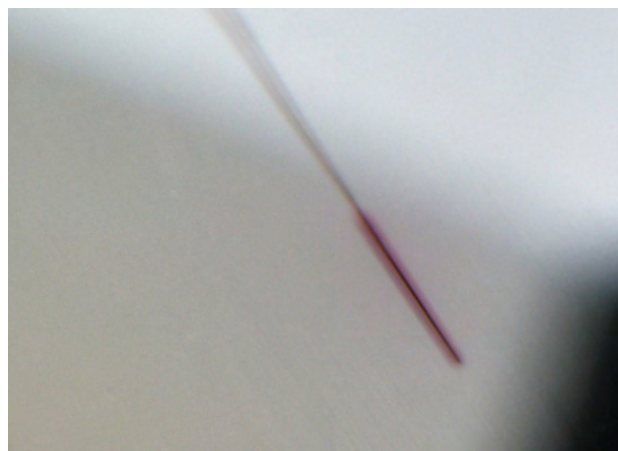
We also noticed that when epigenetic matter completely blocked a growth tube, the color-inducing radioactive solution only penetrated to the point of blockage, so the coloration stopped there as well. As a result, some growth tubes had partial sleeves of pink color (figure 6).

During this examination, we also saw pink color zoning associated with cracks extending from or between the pink-zoned growth tubes, as well as from some surface-reaching cracks (figure 7, left). Just as we observed with the growth tubes, higher magnification and immersion clearly showed that the pink coloration emanated from the inner walls of these cracks and gradually dissipated into the host tourmaline (figure 7, right).

Figure 5. Pink-colored growth tubes in Cu-bearing tourmalines have a wide range of diameters; only the largest will be clearly visible without magnification. Photomicrograph by J. I. Koivula; field of view 2.9 mm.



Figure 6. As shown here, if epigenetic matter blocks a growth tube, then the color-inducing radioactive solution can only penetrate to the point of blockage, effectively stopping the pink coloration. Photomicrograph by J. I. Koivula; field of view 2.2 mm.



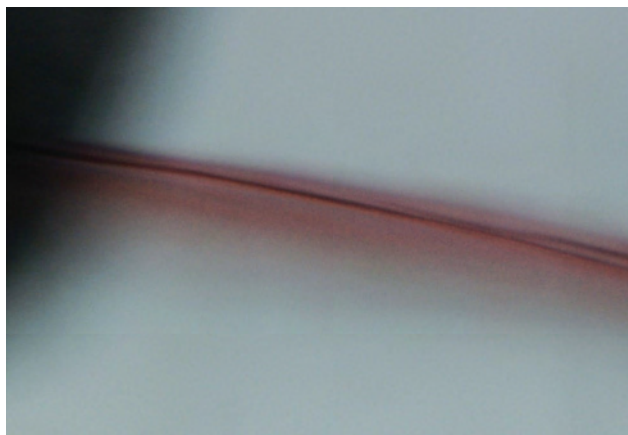


Figure 7. The inner walls of any fissures or cracks that reached the surface (or surface-reaching growth tubes) in these Mozambique tourmalines were also colored pink to red by natural irradiation (left; field of view 2.9 mm). At higher magnification, the penetration of the pink-to-red color into the surrounding tourmaline is clearly visible (right; field of view 0.8 mm). Photomicrographs by J. I. Koivula.

Abduriyim et al. (2006) indicated that heat treatment at around 500°C is used to produce a desirable “neon” blue color in Cu-bearing tourmaline. This article also stated that purplish pink and pink colors faded when exposed to temperatures between 400 and 500°C. And in their 2008 report, Laurs et al. indicated that a temperature of 530°C was used to drive off pink-to-purple color and produce vivid blues and greens. The fading of radiation-caused pink-to-red color in tourmaline through heat treatment is well documented in the literature (Nassau, 1984). The temperatures mentioned in such fading experiments range from 260°C to 400°C, with no red or pink color possible at all above 750°C. Together with Dr. Emmanuel Fritsch of the University of Nantes, one of the authors (JIK) did a number of fading experiments on a variety of gem materials in the early 1990s using both heat and light. In these experiments, the color faded completely between 450°C and 500°C for all the pink-to-red tourmalines tested.

In view of this, we believe that the blue to blue-green

bodycolor shown by these Cu-bearing tourmalines must be of natural origin and not the result of heat treatment. If these gems had been heat treated, then the pink zones surrounding the growth tubes would have faded, and would not show such an intensity of color.

Conclusion. To the authors’ knowledge, the coloration of tourmaline surrounding surface-reaching growth tubes and cracks by invading radioactive solutions is not mentioned anywhere else in the literature. The fact that all of the examples described in this report came from Mozambique suggests that this type of inclusion feature may be characteristic of that locality, although granitic pegmatites worldwide are known to host radioactive solutions. The presence of the pink zones surrounding surface-reaching growth tubes in these otherwise blue to blue-green gems also provides clear proof that the host tourmalines were not heat treated, since the temperature required to artificially produce such colors in Cu-bearing tourmalines would fade the pink color.

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