

Editors

Thomas Moses, Ilene Reinitz, and
Shane F. McClure
GIA Gem Trade Laboratory

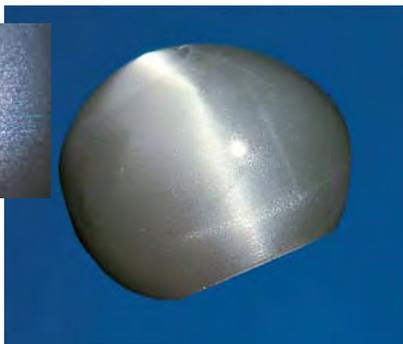
Contributing Editors

G. Robert Crowningshield
GIA Gem Trade Laboratory, East Coast
Karin Hurwit, Mary L. Johnson,
and Cheryl Y. Wentzell
GIA Gem Trade Laboratory, West Coast

An Unusual CAT'S-EYE CHRYSOBERYL

When the West Coast laboratory recently received a translucent gray chatoyant cabochon for identification from K & K International in Falls Church, Virginia (figure 1), the last thing we thought it could be was chrysoberyl, even though that was how it was represented by our client. Nothing about its appearance suggested chrysoberyl, not even the appearance of the inclusions. Gemological testing revealed a spot refractive index of 1.75, a specific gravity of 3.69 (measured hydrostatically), and no visible absorption spectrum or fluorescence. Although these properties could indicate chrysoberyl, they were

Figure 1. Although chatoyancy is common in chrysoberyl, this 7.29 ct cabochon is the first gray cat's-eye chrysoberyl seen in the laboratory. The color in this stone appears to be caused by dense concentrations of gray platelets, which are also the cause of the chatoyancy (inset, magnified 30×).



also consistent with several other gems. Nevertheless, the spectrum obtained with the Raman microspectrometer was a perfect match to our reference for chrysoberyl.

This is the first gray cat's-eye chrysoberyl we have seen in the laboratory. Microscopic examination of the 7.29 ct stone indicated that the inclusions were the probable cause of the gray color; they looked gray in transmitted light, while the host material appeared near-colorless. Chrysoberyl is seldom colorless, especially in gem quality. Instead of the long, fine needles or "silk" that are normally present in cat's-eye chrysoberyl, these gray inclusions formed a dense cloud of tiny, oriented reflective platelets. Light reflection from these platelets caused the chatoyancy. Even more unusual was the presence of a weak star oriented off-center toward one end of the stone (not completely visible in the photo). We have seen only a few star chrysoberyls in the lab. The last one we reported on was greenish brown and also had the star oriented off-center (Summer 1989 Lab Notes, p. 102).

SFM

DIAMOND

Blue and Pink, HPHT Annealed

As part of our ongoing research for means to identify HPHT-annealed diamonds, the East Coast laboratory recently analyzed 11 pink and four blue diamonds that had been subjected to this process (see, e.g., figure 2). These diamonds were submitted to the laboratory from Bellataire Diamonds, which is responsible for

marketing GE POL diamonds in the United States.

The diamonds weighed 0.75 to 14.93 ct. The pink diamonds showed a wide range of color saturation, from the equivalent of Faint to Fancy Deep; the blue diamonds ranged from the equivalent of Very Light to Fancy Intense. The clarity grades ranged from IF to VS₂ and from VVS₁ to VVS₂ for the pink and blue diamonds, respectively. The pink diamonds were type IIa, based on their mid-infrared spectra and their transparency to short-wave UV radiation. The blue diamonds were type IIb; that is, they showed both electrical semi-conductivity and characteristic boron features in the mid-infrared. According to Chuck Meyer, managing director of Bellataire Diamonds, the pink and blue diamonds represent a very small fraction of the overall GE POL production. Because of the rarity of the starting material that can generate these colors, he does not expect them to be readily available commercial items.

Gemologically, these HPHT-annealed diamonds show properties that are commonly observed in natural-color type IIa pink and type IIb blue diamonds, particularly the details of color zoning, and reactions to long-wave and short-wave UV. We would expect the same types of alteration of inclusions to occur as were previously reported for HPHT-annealed

Editor's note: The initials at the end of each item identify the editor(s) or contributing editor(s) who provided that item.

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Figure 2. The laboratory recently examined several blue and pink diamonds that had been color enhanced by an HPHT process similar to that used to decolorize GE POL diamonds. These diamonds range from 0.75 to 3.59 ct.

near-colorless type IIa diamonds (T. Moses et al., "Observations on GE-processed diamonds," Fall 1999 *Gems & Gemology*, pp. 14–22), but these 15 diamonds did not show any diagnostic inclusions. Using a Raman unit, we obtained photoluminescence (PL) spectra on these HPHT-annealed pink and blue diamonds, which we compared to PL spectra for more than 100 natural-color pink and blue diamonds. It appears that some of the identification criteria proposed by D. Fisher and R. A. Spits ("Spectroscopic evidence of GE POL HPHT-treated natural type IIa diamonds," Spring 2000 *Gems & Gemology*, pp. 42–49) to differentiate D-to-Z range GE POL diamonds from natural type IIa diamonds may be applicable in the identification of the HPHT-annealed pink diamonds. We are using this spectroscopic method and other techniques to investigate possible identification criteria for both the pink and blue diamonds. *Matt Hall and TM*

With Flower-like Inclusions

Two rather different diamonds seen in the East Coast laboratory showed similarly shaped inclusion patterns reminiscent of flowers or stars. One, a 6.23 ct near-colorless partly rounded octahedron with a translucent, etched surface (and sparse brown radiation

stains) revealed the gray clouds shown in figure 3 (left) through two natural cleavage surfaces. The other, a 0.71 ct Fancy Deep brownish orange round brilliant, displayed its inclusions through the table (figure 3, right). The inclusion patterns in both diamonds showed six-fold symmetry, with at least two "rings" around the center part, one distinctly hexagonal.

In the 6.23 ct diamond, wide, petal-like gray clouds radiated from the center part of the inclusions; these clouds fluoresced yellow to

both long- and short-wave UV. The sample showed a strong line at 415 nm and a weak one at 563 nm in a desk-model spectroscope, and strong peaks in the mid-infrared at 3105, 3235, 4165, and 4494 cm^{-1} , which are related to hydrogen. These gemological properties and spectroscopic results were first described in 1993 (E. Fritsch and K. Scarratt, "Gemological properties of type Ia diamonds with an unusually high hydrogen content," *Journal of Gemmology*, Vol. 23, No. 8, pp. 451–460).

When the 0.71 ct round brilliant was viewed over diffused light, the saturated bodycolor showed some zoning, with concentrations of darker color around the edges of the star-like inclusions. The clouds themselves appeared to consist of pinpoints, and were rather narrow compared to the clouds in the other diamond. No part of this stone fluoresced to either wavelength of UV. The UV-visible spectrum showed rising absorption from about 500 nm toward the blue region, and the mid-infrared spectrum showed mostly type Ib with a small IaA component, and no absorptions due to hydrogen.

As discussed in a Spring 1999 Lab Note (pp. 42–43), such clouds in diamonds are actually phantoms, in which internal crystal planes of the diamond became outlined by minute

Figure 3. The gray "flower" in this 6.23 ct rough diamond (left, magnified 20 \times) is caused by concentrations of hydrogen. Concentrations of pinpoints produce a "star" shape in the 0.71 ct Fancy Deep brownish orange round brilliant on the right. In both cases, the morphology of the growing diamond crystal controlled the shape of the inclusions.



inclusions trapped during growth. Don't let the hexagonal appearance of the clouds fool you. As suggested in the earlier Lab Note, the clouds that form such a six-rayed star or flower still follow diamond's cubic crystal system: The inclusions are most likely trapped along the edges of a hex-octahedron, a common internal growth stage for diamond.

Wendi Mayerson and IR

An Historical Report

In the archives at GIA's Richard T. Liddicoat Library and Information Center, we found an early lab report (no. 294) that was personally signed by Robert Shipley Jr. on March 13, 1937. The item being tested was noted as a "green transparent brilliant in ladies [sic] 20 irid 80 plat ring." (The fee charged for determining the origin of color was \$10.) The comments on the report, shown in figure 4, note that the hardness is greater than 9 and was determined by using hardness points. The report also notes that the material was "Isotropic; shows strain spots of color localized beneath facet surfaces; breaks through surfaces at each spot." The item was set on an unexposed piece of AGFA film that, when developed, showed evidence of radiation, which resulted in the concluding remark: "Diamond: All tests known to this laboratory indicate color is due to alteration as result of exposure to bombardment by alpha particles, perhaps of radium."

Robert Shipley Sr. began providing laboratory services in Los Angeles under the auspices of the newly formed Gemological Institute of America in 1931. His son, Robert Shipley Jr., was the developer of a number of gemological instruments as well as a key staff member.

Al Gilbertson

SYNTHETIC MOISSANITE: A Black Diamond Substitute

Several black round brilliants, ranging from 0.50 to over 20 ct were recently submitted to the East Coast laboratory

LABORATORY REPORT # 294

SENT BY R. Shipley Jr.

NATURE OF SPEC Green transparent brilliant in ladies 20 irid 80 plat ring

TESTS MADE:

Refractive Index _____ by _____

Specific Gravity _____ Wt. in H₂O _____ by _____

Pleochroism _____ by _____

Optic Character Isotropic by _____

Inclusions Isotropic; shows strain spots M

Hardness Spots of color localized beneath facet surfaces; breaks through surfaces at each spot. H.P. A

Additional Tests 9 cash spot H.P.

THE RESULTS OF THE ABOVE TESTS INDICATE THE SPECIMEN TO BE:

REMARKS: Diamond

All tests known to this laboratory indicate color is due to alteration as result of exposure to bombardment by alpha particles, perhaps of radium.

RECEIVED _____ TESTS BY _____ RETURNED _____ FEE _____

KEY: D. - Dichroscope; D.B. - Diamond Balance; E. - Endoscope; F. - Fluorescence; H.L. - Heavy Liquid; H.Pl. - Hardness Plates; H.Po. - Hardness Points; J.B. - Jolly Balance; L. - 10X Loupe; M. - Microscope; P. - Pocket Polaroscope; P.I. - Pearl Illuminator; R. - Refractometer; S. - Spectroscope.

Figure 4. This 1937 GIA laboratory report for a treated-color green diamond was signed by Robert Shipley Jr.

by a client who acquired them as synthetic black diamond, allegedly of Russian origin (see, e.g., figure 5). Examination with a fiber-optic light showed that the material was actually very dark bluish green, which is typical of diamonds that have been irradiated to "black." However, microscopic examination revealed strong doubling of numerous stringers and needles (figure 6), which proved that the stones were doubly refractive. These inclusions were reminiscent of those reported in near-colorless synthetic moissanite (see, e.g., K. Nassau et al., "Synthetic moissanite: A new diamond substitute," Winter 1997 *Gems & Gemology*, pp. 260-275). The specific gravity was measured hydrostatically as 3.20, which confirmed the identity

of these pieces as synthetic moissanite. Diamond imitations are frequently subjected to hardness testing in the trade, and one of these samples had several deep, eye-visible scratches on the table.

With the increased popularity of black diamonds in jewelry, this material could pose an identification challenge if small sizes were mounted. Although its homogeneous appearance—even under strong illumination, such as that from a fiber-optic light—is very different from that of natural-color black diamond, this would not rule out natural diamond treated by laboratory irradiation. The stringers and needles seemed to have some color associated with them; their appearance suggested that they



Figure 5. These round brilliants (the unmounted one weighs 10.30 ct) were represented as synthetic black diamond, but they were identified as very dark bluish green synthetic moissanite.



Figure 6. A strong light source showed this synthetic moissanite to be dark bluish green. With magnification, characteristic stringers and needles were visible as double images, proving the anisotropic nature of the material. Magnified 12 \times .

may have resulted from incomplete crystallization. Such inclusions, and the anisotropic nature of the material that they reveal, readily separate synthetic moissanite from diamond.

SFM and TM

RUBY

An Investigation of Fracture Fillers in Mong Hsu Rubies

As a common practice, the heat treatment of rubies and sapphires is at least several decades old. To improve their color and clarity, parcels of gems are heated in oxidizing or reducing environments to temperatures as high as 1,300°C to 1,900°C (T. Themelis, 1992, *The Heat Treatment of Ruby and Sapphire*, Gemlab Inc., Houston TX). Typically, the rough gems are covered with a "firecoat" material such as borax. (With regard to treatment in Thailand, Themelis [*op. cit.*, pp. 109–110] mentioned borax [hydrous sodium borate] as the most common additive to corundum during the heating process, although boric acid, oxidizing and reducing agents, ashes, topsoil or clay, buffalo dung, and banana leaves were also noted; "additive secrets" were carefully guarded by the treaters.) Using such a "firecoat" leads to a notable effect: Fractures and cavities in the heat-treated corundum become filled with a foreign substance.

Such material has been noted

particularly in Mong Hsu rubies (A. Peretti et al., "Rubies from Mong Hsu," Spring 1995 *Gems & Gemology*, pp. 2–26; H. A. Hänni, "Short notes on some gemstone treatments," *Journal of the Gemmological Association of Hong Kong*, Vol. 20, pp. 44–52), and several hypotheses have been advanced as to how this material forms in the fractures. Two gemologists with substantial worldwide ruby-buying experience recently brought us some typical commercial Mong Hsu material from the market in Bangkok to learn more about these fracture-filling materials. We examined five pieces of heated rough, two of unheated rough, and two heated faceted rubies with a scanning electron microscope and an electron microprobe, to explore the composition and textures of the material(s) produced in the fractures.

The nature of the substance in fractures in heat-treated ruby is not well understood. It has been referred to both as a glass (e.g., K. Scarratt et al., "Glass filling in sapphire," *Journal of Gemmology*, Vol. 20, No. 4, 1986, pp. 203–207) and as a flux (e.g., Peretti *op. cit.*; J. L. Emmett, "Fluxes and the heat treatment of ruby and sapphire," Fall 1999 *Gems & Gemology*, pp. 90–92), but these two terms are neither synonyms nor antonyms. *Glass* refers to the state of the material (a

noncrystalline solid); *flux* refers to the ability of one substance to lower the melting point of another substance with which it is mixed.

We collected both back-scattered electron (BSE) images—which show the physical arrangement of the host ruby, the fracture, and the filling material—and EDX chemical information (assisted by Dr. Chi Ma, Caltech, Pasadena). We also analyzed two faceted samples by electron microprobe, to verify the EDX chemical analyses with the more accurate WDX technique and check for the presence of boron with a light-element detector. The presence of boron would be consistent with the reported use of borax in the heat-treatment process.

One unheated sample showed rough surfaces, with stepped crystal edges visible at high magnification. The freshly broken surface of one heated sample (figure 7, left) looked conchoidal under SEM examination at low magnification (figure 7, center); however, with higher magnification the fractured area was seen to consist of sharp-edged planes (figure 7, right). In contrast, exposed surfaces of these heat-treated rubies looked smooth-edged with magnification. This difference in texture shows that the ruby "molecules" have been rearranged at the gem's surface, similar to the etching and redeposition that gem crystals can undergo in pegmatites and hydrothermal environments.

Figure 8 (left) shows two ruby crystals that had been stuck together during heat treatment; in the region where the two rubies are joined together, the surfaces curve smoothly from one to the other (figure 8, center). A fine fringe of 40-micron-long sub-parallel ruby crystallites has grown on the smaller crystal in this sample (figure 8, right), which indicates redistribution of the corundum with the "firecoat" acting as a flux. We believe that these crystallites represent new growth for several reasons: They are too small and delicate to have survived mining in their undamaged state, and they are not quite parallel to one another, which indicates that they

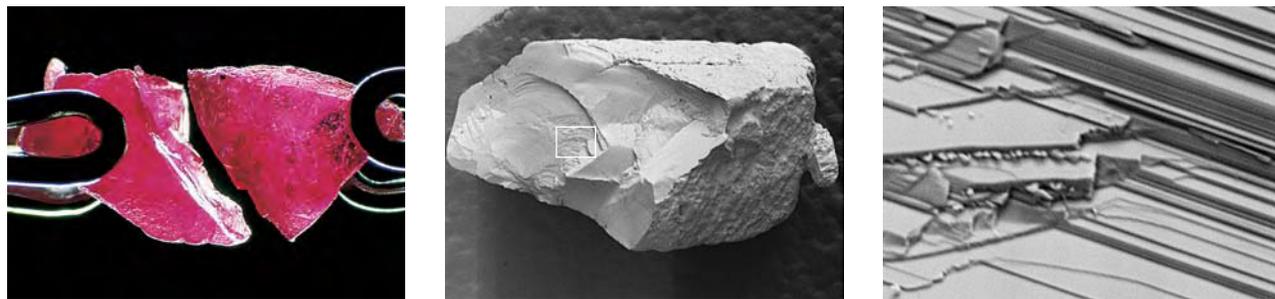


Figure 7. This 0.34 ct heat-treated Mong Hsu ruby was broken in two (left) and the fracture examined by SEM. At 19× magnification (center), the backscattered-electron SEM image showed conchoidal fracturing along the break. At higher magnification (1500×, right), sharp layers are seen along the broken surface.

probably grew fast rather than in equilibrium with their host crystal.

Another sample of heated rough showed that the “firecoat” material may form secondary veinlets branching off a fracture (figure 9) along parallel (parting) planes in the ruby. Where it reached the surface, the vein material appeared brighter in BSE images than the ruby around it, indicating that it had a higher mean atomic weight than the ruby. This brightness was relatively uniform (in all the samples where such material was observed), implying that the material was a homogeneous glass.

In reflected light, one faceted ruby showed broad fissures filled with foreign material (figure 10). These were easily seen with the SEM, as they appeared both brighter in the BSE images and softer than the surrounding corundum (deeper polishing lines are visible in figure 10). Note that the

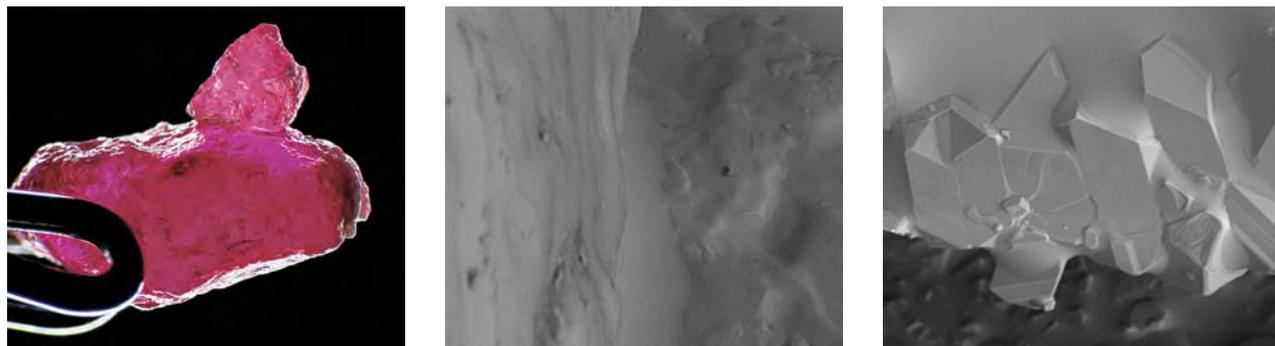
fissure in this ruby was not completely filled by the glass-like substance; a crack was still visible alongside the “glass.” A fissure in the second faceted ruby was quite thin and looked like a line of disconnected dots, even at high magnification, which prevented chemical analysis of fracture material in this sample.

SEM-EDX analysis revealed that the “glass” vein in one rough heated Mong Hsu ruby contained Na, Mg, Al, Si, P, Ca, and Ti, with phosphorus the largest peak after Al. Glass in a fissure in one of our faceted rubies contained the same elements, although with more Si than P. Electron microprobe analyses of five points in the filler in this sample revealed a relatively large amount of boron, up to 4.5 wt. % B_2O_3 , as well as P, Si, Al, and other oxides. This glass has an average composition of

$Na_{0.1}Mg_{0.2}B_{0.1}Al_{0.6}Si_{0.6}P_{0.2}O_3$. In 1995, Juan Cozar (“ICA laboratory alert update no. 56, 24 August 1995: Rubies with fissures and cavities filled with aluminum and sodium phosphate glass,” *South African Gemmologist*, Vol. 9, No. 3, pp. 16–17) provided SEM-EDX analyses of glass in heat-treated rubies that also contained major P, Al, Na, Si, and Ti, as well as minor Ca and Fe.

The “firecoat” used in the heat treatment is strongly indicated in the formation of this filler, as the commonly occurring mineral inclusions in ruby do not contain sufficient boron to produce this composition. However, neither borax nor inclusions of apatite can account for the large amount of phosphorus found here and by Cozar; this chemistry suggests that one or more additional components were added to the “firecoat.” In addition to

Figure 8. These two heated rubies (0.41 ct total) are attached to each other despite different crystallographic orientations (left—transmitted and reflected light; magnified 15×.) Center—This BSE image (magnified 750×) shows the surface curving smoothly where the two rubies are joined, demonstrating surface remobilization. Right—These 40-micron-high ruby crystals were growing on the free surface of the smaller ruby; they indicate recrystallization in the heat-treating environment (magnified 750×).



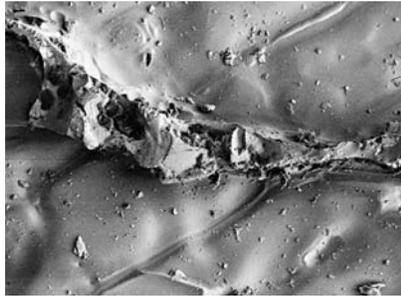
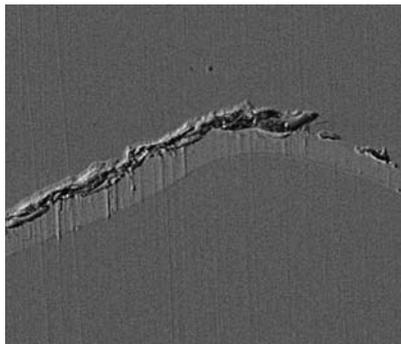


Figure 9. This 2.34 ct heated rough ruby appeared to be held together by a layer of “firecoat.” Additional veinlets spread out from the main vein along parting planes. The relative brightness of this material indicates that it has a higher mean atomic weight than the ruby. BSE magnified 150 \times .

some of the materials Themelis mentioned, high-technology materials such as BPSG (boron phospho-silicate glass), useful to the semi-conductor industry for its low flowing point of 700° to 1000°C, could yield the composition we found.

The texture and chemistry of all the fillers we observed was consistent with glass formed from chemicals

Figure 10. The large glass-filled fissures crossing the table of this 1.09 ct heated Mong Hsu ruby appear brighter than the surrounding ruby in this BSE SEM image. The deeper polishing lines indicate that the filler is softer than the ruby. Notice the gap along one side of the “glass.” Magnified 600 \times .



used to coat the rubies during the heat-treatment process. At this time, if this material is visible with a standard gemological microscope, the GIA Gem Trade Laboratory refers to it with the following comment: “Foreign material is present in some surface reaching fractures.” If large filled cavities are present on the stone, we state instead, “Foreign material is present in some surface cavities.” We plan to continue to investigate heat-treated Mong Hsu rubies to explore additional questions regarding this glassy material.

MLJ and SFM

TOURMALINE Rough from Paraíba

Wilford Schuch of King Prestor John Corp., New York, submitted the bright violet and blue rough stone shown in figure 11 to the East Coast lab this summer. The client was seeking confirmation that this 19.49 ct stone, which he had purchased in Brazil, was tourmaline from Paraíba. Although he was offered smaller pieces of other rough, up to 5 ct, only this piece showed the “electric” colors that took the gem trade by storm 10 years ago.

The refractive indices of 1.630–1.659 (taken on a flat portion of the crystal), along with the uniaxial character and S.G. (measured hydrostatically) of 3.09, identified the rough as tourmaline, although these refractive indices are at the high end of the range. The overall morphology was equant, but there were striations parallel to the c-axis, a common feature in tourmaline. The stone showed pleochroism in deep violet-blue and a lighter blue-green. It was inert to both long- and short-wave UV. Microscopic examination revealed a large fracture, small reflective crystalline inclusions, and two-phase inclusions, some arranged in a “fingerprint.” The hand spectroscope showed broad absorption in the green and red areas of the spectrum.

UV-visible spectroscopy confirmed these broad bands, with strong absorption above 600 nm; a wide, moderately strong peak centered at 500 nm; and



Figure 11. All physical, chemical, and spectroscopic properties pointed to Paraíba, Brazil, as the source of this 19.49 ct bright violet and blue tourmaline.

a weak absorption at 414 nm. EDXRF qualitative chemical analysis, under conditions sensitive for transition metals and heavier elements, revealed Cu, Mn, Ca, Ti, K, Bi, and Ga.

This combination of properties is comparable to those described for tourmaline from Paraíba (E. Fritsch et al., “Gem-quality cuprian-elbaite tourmalines from São José da Batalha, Paraíba, Brazil,” Fall 1990 *Gems & Gemology*, pp. 189–205), especially the violetish blue sample from that study. However, both refractive indices were significantly higher, and the birefringence was slightly higher, than the values reported previously. Our client received an identification report with the conclusion “tourmaline,” and a separate research letter stating that the 19.49 ct rough showed properties consistent with this locality. To the best of our knowledge, the Paraíba region is the only source of gem-quality copper-bearing tourmalines. IR

PHOTO CREDITS

Maha Tannous photographed figures 1, 5, and 11. Elizabeth Schrader took figure 2. Vincent Cracco provided figure 3. Shane McClure photographed the figure 1 inset and figure 6. Mary Johnson provided figures 7 and 8 (center and right for both) 9, and 10. John Koivula was the photographer for figures 7 and 8 (both left).