

Tourmaline: The Kaleidoscopic Gemstone

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7.7 carat fancy blue-green Namibian tourmaline (set in 18k gold).
GORDON AATLO DESIGN

With their multitude of colors, gem tourmalines are among the most popular colored gemstones. Spectacular color-zoned tourmalines are valued as gems and crystal specimens, and some complexly zoned crystals contain nearly the entire spectrum of color variation found in the mineral world. The top-quality “neon” blue-to-green, copper-bearing tourmaline, the *Paraíba-type*, is one of the highest-priced colored gemstones, with values comparable to those of some diamonds. The wide variety and intensity of colors are related primarily to color-producing ions in the structure and to exposure to natural radiation. Gem tourmalines that form in magmatic, pegmatitic environments are most commonly elbaite and fluor-liddicoatite species, and the rarer gem tourmalines that develop in metamorphic rocks are generally dravite–uvite species.

KEYWORDS: tourmaline, gemstone, Paraíba-type, chromophores, gem deposits

TOURMALINE AS A GEMSTONE

Perhaps more than any other gemstone, tourmaline is renowned for its spectrum of colors, even within individual crystals (Fig. 1). In addition, tourmaline has the appropriate combination of beauty, durability, and rarity to make fine gemstones. Its moderate refractive index (~1.61–1.67; see also Hawthorne and Dirlam 2011 this issue) gives significant return of light, and its chemical complexity produces a wide range of appealing colors. Its relatively high hardness (7½ on the Mohs scale) makes it less likely to be scratched, and its lack of cleavage makes it unlikely to fracture during wear. Its growth as highly transparent material, mostly free of internal flaws, provides the gem-quality crystals required for cutting faceted stones (Fig. 1). These attributes make tourmaline well suited for fashioning, and it is available in sufficient quantities to support a commercial market. Gemmy crystals of tourmaline with sharp, undamaged morphology and rich colors are collected by mineral connoisseurs (Fig. 2), and cut stones are mounted into jewelry (Fig. 3). Clearly, tourmaline is one of the most important gem materials on the market today.

HISTORIC HIGHLIGHTS

Tourmaline gemstones have a distinguished and colorful history. At the beginning of the 18th century, Amsterdam lapidaries noticed that in mixed parcels of gem rough from Ceylon (now Sri Lanka), there were some gems characterized by relatively low density (~3.07 g/cm³), and they were given the name *turamalin*. These were thought to be a new type of gem, having gone unrecognized for some time, and

by 1717 they were referred to as *pierre de Ceylon* (King 2002). Nevertheless, the name *turamalin* was retained, and in the second half of the 18th century the spelling changed to *tourmalin*. In 1771 the term *tourmaline garnet* was coined, probably referring to *rubellite* (the pink to red gem variety of tourmaline). Until the early 18th century there were only small amounts of Ceylonese gem tourmaline on the market. In the late 18th century the discovery of rubellite deposits near Nerchinsk, Siberia, and the finds of Brazilian tourmalines, referred to as *smaragdus brasiliicus*, produced significant quantities of gem tourmaline (King 2002).

Long before it was recognized as a new gem, some magnificent red tourmaline gemstones had been mounted as jewels for Europe’s royalty. The great Czech crown of Saint Wenceslas, fashioned between 1346 and 1387, features a large, bright red “ruby” (39.5 × 36.5 × 14 mm) that is actually tourmaline (Hyršl and Neumanova 1999). The tourmaline in the Wenceslas crown is the oldest-known tourmaline gemstone, predating the coining of the word *tourmaline* by several hundred years. In 1925, Russian mineralogist Alexander Fersman identified a vivid pink, chicken’s egg-sized gem from the Kremlin’s Treasure Room as a Burmese tourmaline. It was traced to the reign of Emperor Rudolph II (1575–1612), and until Fersman’s work it was considered an oriental ruby (Glas 2002). At the turn of the last century, demand for tourmaline soared as it was popularized by one of its greatest enthusiasts, the Dowager



FIGURE 1 Broad spectral color range displayed by tourmaline. These cut stones weigh 3.71 to 16.21 ct. The round green stone at the top center is about 15 mm in diameter. FROM THE GIA COLLECTION; PHOTO BY ROBERT WELDON, REPRINTED WITH PERMISSION

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FIGURE 2 Specimen of polychrome elbaite crystals (28 cm tall), characteristic of gem tourmaline found in Pederneira, Minas Gerais, Brazil. SPECIMEN FROM DANIEL TRINCHILLO; PHOTO BY JAMES ELLIOTT



FIGURE 3 Pendant consisting of two Mozambique copper-bearing tourmalines (10.95 ct pink and 6.95 ct yellow) set in 18 k gold with diamonds. FROM THE BUZZ GRAY AND BERNADINE JOHNSON COLLECTION; PHOTO BY ROBERT WELDON



Empress Tz'u Hsi, who ruled China from 1860 to 1908. Her passion for carved pink tourmaline consequently led to its desirability among the Chinese royalty (e.g. Fisher 2008).

COLOR AND OPTICAL PHENOMENA IN GEM TOURMALINE

The extensive range of colors in gem tourmaline, from colorless, through red, pink, yellow, orange, green, blue, and violet, to brown and black, generally reflects interactions at a structural level. Several mechanisms can cause color in tourmaline, the most common ones being crystal-field transitions (CFT), intervalence charge transfer interactions (IVCT), and color centers. The transition elements Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , Ti^{4+} , Cu^{2+} , and V^{3+} act as important color-causing agents, or chromophores, in tourmaline. Most transition element chromophores occupy the Y and Z edge-sharing octahedral sites (Hawthorne and Dirlam 2011), and they influence color and color intensity through both CFT and IVCT (TABLE 1). Trivalent chromium is also a strong chromophore in many tourmalines, but gem chromium tourmalines are relatively rare.

Naturally occurring colors can be produced or enhanced by natural irradiation (i.e. through the ionizing radiation of decaying isotopes such as ^{40}K , ^{238}U , and ^{232}Th) from minerals proximal to the tourmaline. For example, when tourmaline is associated with potassium feldspar or a U/Th-bearing accessory mineral (such as monazite or zircon), its color can be modified and intensified by radiation. In addition, irradiation can alter the color by creating color centers (e.g. Reinitz and Rossman 1988).

To achieve the best color when cutting a tourmaline gemstone, the pronounced dichroism of tourmaline must be taken into account. In general, the ϵ -ray of light traveling parallel to the **c** axis of the crystal, corresponding to the direction parallel to prism faces, is significantly absorbed compared to the ω -ray. The color of the gem rough typically appears darker and more saturated when observed parallel to the **c** axis. In dark brown crystals the effect can be so strong that the ϵ -ray is completely absorbed, and in the 19th century mineralogists used thin slabs of such crystals, cut parallel to the **c** axis, as a light polarizer (Anderson 1980). Dichroism in gem tourmaline is quite variable and may even make it challenging to identify.

TABLE 1 PARTIAL LIST OF TOURMALINE COLORS, VARIETIES, CAUSES OF COLOR, AND PROBABLE SPECIES^(a)

Color	Varietal name	Cause of color	Probable tourmaline species ^(b)
Colorless	Achroite	No or minor chromophores	Elbaite, "fluor-elbaite," fluor-liddicoatite, rossmanite
Pink and red	Rubellite	Mn^{3+} ^(c) , $\text{Mn}^{3+} + \text{Fe}$ ^(d) or Mn^{2+} - Mn^{3+} IVCT Natural radiation	Elbaite, "fluor-elbaite," fluor-liddicoatite, rossmanite
Yellow, yellow-green	Canary	Mn^{2+} ^(d) , Mn^{2+} - Ti^{4+} IVCT ^(d)	Elbaite, "fluor-elbaite," fluor-liddicoatite
Green	Verdelite	Fe^{2+} , Fe^{3+} ^(d) , Fe^{2+} - Ti^{4+} IVCT	Elbaite, "fluor-elbaite," fluor-liddicoatite
Green (deep)	"Chrome"	V^{3+} , Cr^{3+}	Dravite-uvite
Blue	Indicolite	Fe^{2+} , Fe^{2+} - Fe^{3+} IVCT	Elbaite, "fluor-elbaite," fluor-liddicoatite
Blue (neon)	"Paraíba-type"	Cu^{2+}	Elbaite, liddicoatitic tourmaline ^(e)
Brown	--	Fe^{2+} - Ti^{4+} IVCT	Dravite, elbaite, liddicoatitic tourmaline
Black	--	High concentrations of Fe^{2+} , Mn^{2+} , and/or Ti^{4+}	Schorl, elbaite, liddicoatitic tourmaline

^(a) Compiled after Zang and da Fonseca-Zang (2002), and from G. R. Rossman's spectroscopy website (<http://minerals.caltech.edu/FILES/Visible/tourmaline/Index.html>)

^(b) Species names are from the tourmaline classification of Henry et al. (2011). Those species that have not been currently accepted by IMA-CMNMC, but are likely to exist, are indicated by quotes.

^(c) Commonly associated with ionizing radiation

^(d) G.R. Rossman, personal communication to B. Dutrow

^(e) Fluorine content not available



FIGURE 4 Faceted elbaite stones from Paraíba, Brazil (2.59–3.68 ct; the stone on the left is about 6 mm tall). These stones owe their intense, “neon” blue colors to the influence of Cu^{2+} in the tourmaline structure. In some cases, Cu^{2+} in combination with other cations modifies the resulting colors.
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Occasionally tourmaline crystals display chatoyancy. This light-scattering effect is caused by the interaction of light with bundles of parallel, microscopic, needle-like inclusions aligned along the *c* axis. Cabochons (rounded, convex, polished stones) are fashioned from these crystals to showcase their “cat’s-eye” appearance. The intensity of this phenomenon depends on the size and density of the tubes that cause this effect (Graziani et al. 1982).

In the absence of compositional data for tourmaline, gem miners and dealers use a series of color-based trade names that are common in the marketplace (TABLE 1). The classic varietal names are *rubellite* (rose, dark pink, to red), *verdelite* (yellow-green to green), *indicolite* (blue-green to blue), and *achroite* (colorless) (Zang and da Fonseca-Zang 2002). However, these trade names do not universally correlate with tourmaline species names. Tourmaline crystals with a given color can develop in several species, and some individual species can develop many colors. For example, elbaite and fluor-liddicoatite, which represent most of the tourmaline gemstones, can display a nearly complete color spectrum (see TABLE 1). Recently, additional color-based varietal names have come into popular use, such as *canary tourmaline* (yellow, Mn-rich elbaite from Zambia; Simmons et al. 2011) and *chrome tourmaline* (a vivid green tourmaline from Tanzania)—a perplexing name for a dravite-to-uvite tourmaline with significant vanadium content (Bank and Henn 1988). The intense blue-green tourmalines, termed *Paraíba-type*, are of special interest as gemstones (FIG. 4).

Paraíba-Type – The Most Precious Tourmaline

Copper-bearing tourmaline, in vivid blue-to-green and purple hues, is one of the most desirable colored gemstones in the world (FIG. 4). Following its discovery in the late 1980s in the Paraíba State of Brazil (e.g. Fritsch et al. 1990; Beurlen et al. 2011 and references therein), it became popular for its highly saturated “neon” colors, and prices escalated rapidly. Recent prices have reached ~US\$25,000/carot for exceptionally clean, intensely colored Brazilian stones. In the 1990s additional deposits were found in Paraíba State and in the neighboring Rio Grande do Norte State (Shigley et al. 2001), and more were discovered later in Nigeria (Milisenda and Henn 2001) and in the Alto Ligonha pegmatite district of Mozambique (Lauris et al. 2008 and references therein). Although the blue-to-green-to-purple colors of the Mozambique material are typically less saturated than those of the Brazilian stones, the lower price and greater availability have further enhanced this tourmaline’s popularity. Demand for gem laboratories to differentiate stones by locality has stimulated research into their provenance using the analysis of trace elements and isotopes (e.g. Abduriyim et al. 2006; Shabaga et al. 2010; Marschall and Jiang 2011 this issue).

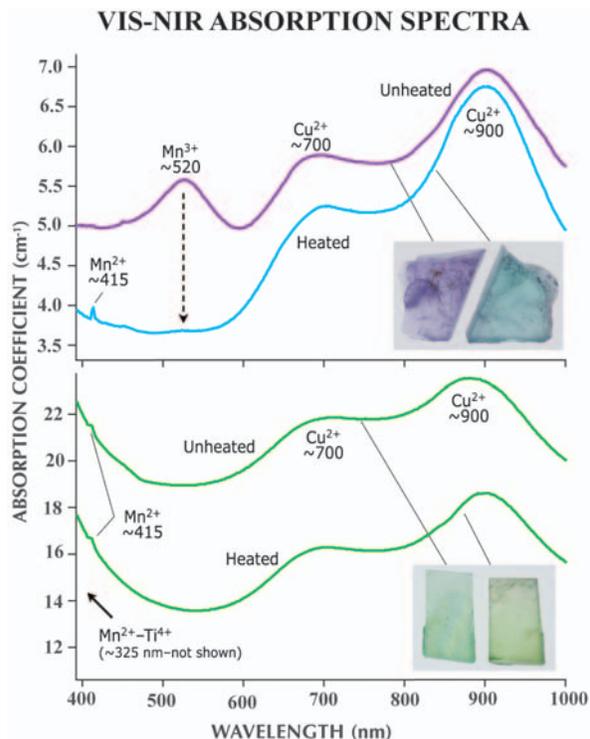


FIGURE 5 Visible light–near-infrared absorption spectra for two pairs of polished tourmaline slabs from Mozambique, before and after heating. (TOP) The dramatic change in color from violet to blue-green with heating results from the reduction of Mn^{3+} . (BOTTOM) Little change in color is observed when heating the yellowish green tourmaline due to strong Mn^{2+} - Ti^{4+} absorption. FIGURE FROM LAURIS ET AL. (2008), MODIFIED BY B. DUTROW; INSET PHOTOS BY C. D. MENGASON

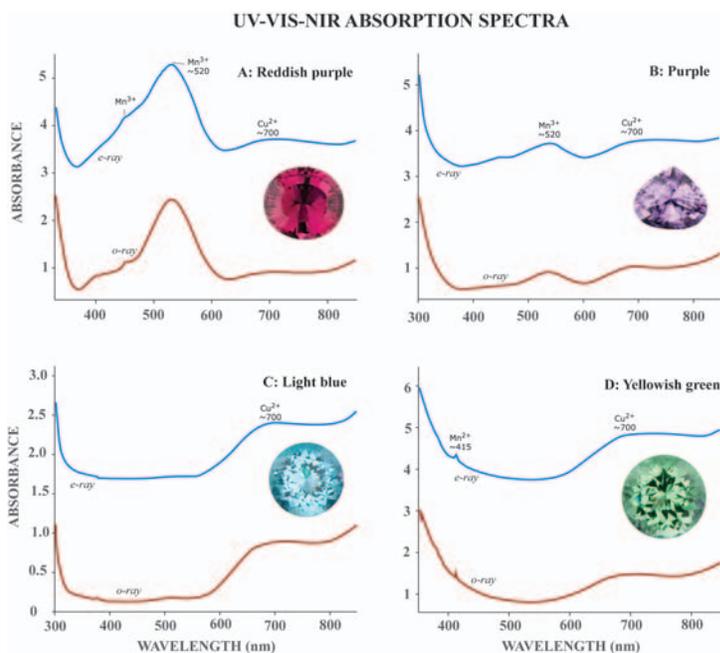


FIGURE 6 Ultraviolet–visible light–near-infrared absorption spectra for various colors of unheated Cu-bearing tourmaline from Mozambique. Two distinctive broad bands centered at ~700 and ~900 nm (the latter not shown in the spectra) are caused by Cu^{2+} ; some exhibit absorption between ~500 and ~550 nm due to Mn^{3+} . Weights of the inset stones are: (a) 12.90 ct, (b) 3.70 ct, (c) 1.46 ct, (d) 2.24 ct. FIGURE FROM LAURIS ET AL. (2008), MODIFIED BY B. DUTROW, INSET PHOTOS BY ROBERT WELDON

The coloration of Paraíba-type tourmaline is controlled mainly by a combination of the cationic concentrations and oxidation states of Cu, Mn, Fe, and Ti (Fritsch et al. 1990; Rossman et al. 1991; Laurs et al. 2008). In the absence of significant amounts of Fe and Ti, and when manganese occurs as Mn^{2+} , the tourmalines show an intense “neon” blue color due to strong Cu^{2+} absorptions centered at ~700 and 900 nm (Figs. 5, 6). Heat treatment of Cu- and Mn-bearing tourmaline reduces Mn^{3+} , which causes violet-pink coloration, to Mn^{2+} , which is a less intense chromophore in tourmaline (Fig. 5). Removal of the Mn^{3+} absorption at ~520 nm creates a transmission window from ~400 to 580 nm that yields the “neon” blue color (Fig. 4); heat treatment of a similar stone containing significant Ti and Fe produces a green coloration (e.g. Laurs et al. 2008). Paraíba-type tourmalines are typically elbaite species, but may also be fluor-liddicoatite (Karampelas and Klemm 2010).

TREATMENTS AND SYNTHETICS

Gamma irradiation and heat treatment are techniques used to modify the color of many gem materials to make them more marketable (e.g. Nassau 1996). Pale-colored tourmaline is generally irradiated to add color; most commonly, near-colorless stones are transformed into vivid pink and red ones. Heat treatment is generally applied to dark tourmaline, with the heating conditions (peak temperature, time of heating and cooling, etc.) optimized on a case-by-case basis to achieve the desired color saturation and tone. Most commonly, dark blue or green material is heated to obtain lighter blue green or yellow green colors. Heat treatment of Paraíba-type tourmaline reduces the influence of the Mn^{3+} chromophore to create or enhance the intensity of the “neon” blue color (see above). The treatment temperature can range from 120°C to over 700°C, and a complete heating run can be less than 2 hours to over 48 hours. Details of the mechanisms involved in the color modifications in tourmaline during heat treatment are reported in Castañeda et al. (2006).

The synthesis of gemstones has an economic incentive. Most of the important gem minerals and their varieties [including sapphire (corundum), ruby (corundum), emerald (beryl), aquamarine (beryl), and diamond] have been successfully grown in laboratories as relatively large gem crystals using various techniques. However, gem tourmaline, common and widespread in pegmatites as large crystals, has not yet been synthesized (London 2011).

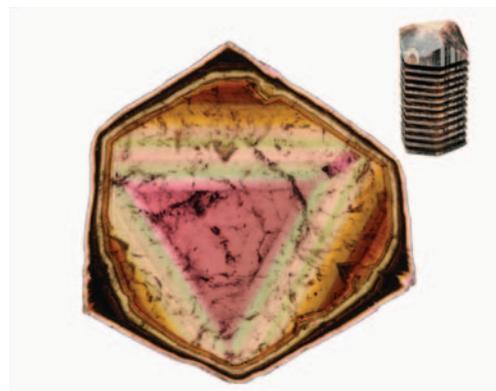


FIGURE 7 A slice of a large fluor-liddicoatite crystal (7 cm in diameter, viewed in plane-polarized light) from Anjanabonoina, Madagascar; the inset image shows the crystal cut into a series of slices perpendicular to the *c* axis. The zoning patterns, which likely are nonequilibrium features, reveal a complex growth history characterized by dramatically changing chemical environments. These chemical changes, combined with crystallographic effects, produced the color pattern observed. NATURAL HISTORY MUSEUM OF MILAN SPECIMEN; PHOTO BY ROBERTO APPIANI

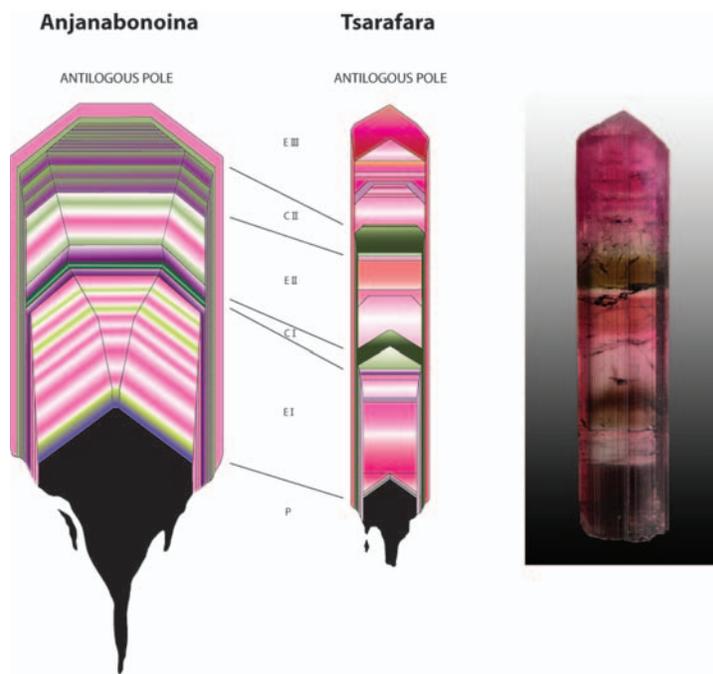


FIGURE 8 Comparison of the complex zoning patterns in fluor-liddicoatite crystals from Anjanabonoina and Tsarafara, Madagascar. Backlighting reveals the color zoning in the 8 cm long, gem-quality Tsarafara tourmaline (RIGHT). The lines join corresponding stages of crystal growth. From the bottom of the crystals to their termination, the following growth zones can be distinguished and interpreted in terms of chemical composition: P – primitive root, E1 – first evolved growth, C1 – first contaminated growth, EII – second evolved growth, CII – second contaminated growth, EIII – third evolved growth. GEM CRYSTAL FROM THE GERHARD WAGNER COLLECTION; PHOTO BY ROBERTO APPIANI

ZONED GEM CRYSTALS

Tourmaline crystals are sensitive to physicochemical changes in their growth environment and are effective recorders of this information (van Hinsberg et al. 2011 this issue). Such crystals are typically zoned—some with extraordinary color zoning with dramatically variable colors (Figs. 7, 8). In gem-bearing pegmatites, the “roots” (the most primitive portions) of the tourmaline crystals are typically black and are generally schorl or foitite (Fig. 8). The black root is commonly overgrown by gem tourmaline that may show compositional variations involving several changes in chromophore elements (Figs. 2, 7, 8). Such chemical variations can result in *simple zoning*, typically from nearly black Fe-Mg-rich elbaite to green-to-blue Fe-bearing elbaite to pink Mn-rich or Mn-poor elbaite to pale pink rossmanite. In many cases, a “reverse” geochemical trend is shown at the latest stages by a green overgrowth, producing “watermelon” color zonation (pink core, colorless-to-white midsection, and green rim) in sections cut perpendicular to the *c* axis.

Complexly zoned crystals can be spectacular. They are typically characterized by oscillatory and sector color zones that reflect interactions between the surface energies of distinct faces and the dynamic local chemical environment, such that different chromophoric cations are incorporated into chemical zones within the tourmaline (Fig. 7; e.g. Lussier and Hawthorne 2011). The large, beautifully color-zoned crystals of fluor-liddicoatite from Madagascar are particularly illustrative of this style of zoning (Figs. 7, 8; Dirlam et al. 2002). Although they show a relatively drab, dark color on the outside (Fig. 7, INSET), when they are cut perpendicular to the *c* axis a myriad of geometric patterns appear, including triangular zones and three-rayed

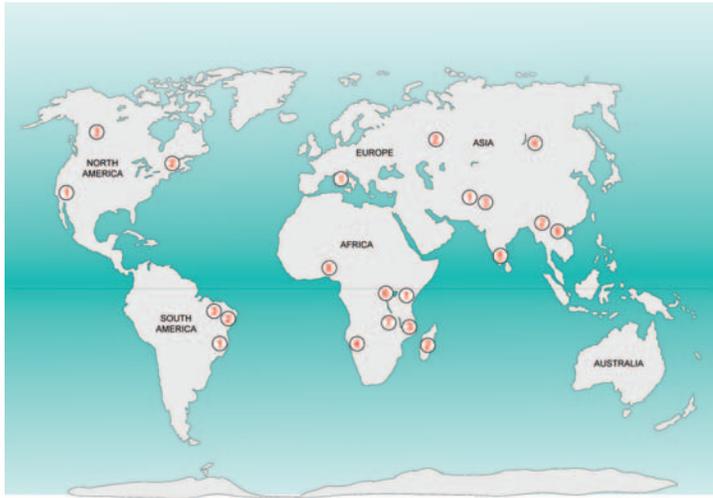


FIGURE 9 Major world gem tourmaline-producing localities. □ Historic gem production; ▼ limited gem production; ▼ significant gem production; ◆ exceptional gem production. FROM SHIGLEY ET AL. (2010) AND REFERENCES THEREIN

“stars” surrounded by oscillating color zones (FIG. 7; e.g. Dirlam et al. 2002; Rustemeyer 2003). Chemical sector zoning is shown by the central triangle (representing the pedion face) and the surrounding triangular zones and the star (representing pyramidal faces). In some rare cases, relatively thin and elongated gem crystals are sufficiently transparent to display this dramatic color variation (when backlit) without being sliced (FIG. 8).

GEM TOURMALINE LOCALITIES, GEOLOGIC ENVIRONMENTS, AND INCLUSIONS

Gem tourmalines have been found in a variety of locations throughout the world (FIG. 9). One of the most notable tourmaline discoveries took place in April 1978 at the Jonas mine, Conselheiro Pena, Minas Gerais, Brazil (SOUTH AMERICAN LOCALITY 1 IN FIG. 9; Cornejo and Bartorelli 2010). These intense deep red crystals include the Rocket (a prism 107 cm tall; see FIG. 4 in Hawthorne and Dirlam 2011) and the Tarugo (a cluster 82 cm long and weighing 74 kg, corresponding to 375,000 ct). Giant prismatic crystals, up to ~1 m in length and 35 cm in diameter, have been found in Madagascar, primarily as polychrome crystals that provide colorful sliced material.

Gem tourmalines are found in a number of geologic settings. Most gem tourmalines form in granitic pegmatites where they are concentrated in miarolitic cavities. Such miarolitic pegmatites are typically emplaced in the continental crust at moderate to shallow depth, in a pressure range of 1–3 kilobars (0.1–0.3 MPa). The ages of these gem tourmaline-bearing pegmatites are variable. Many of the largest such pegmatitic fields, including those in Brazil, Namibia, Mozambique, and Madagascar, are about 500–550 million years old and formed during the latest stages of the tectonometamorphic Pan-African event involving the Gondwana supercontinent. However, some gem tourmaline-bearing pegmatites formed more recently. The famous tourmaline-bearing pegmatites of southern California, USA, formed about 100 million years ago (Snee and Foord 1991), and those on Elba Island, Italy, formed about 6.2 million years ago (Dini et al. 2002). Metamorphic rocks can host unusual deposits of gem-quality tourmaline, such as the well-known “chrome” tourmaline from Tanzania (Simonet 2006). Because they are highly resistant to mechanical and chemical weathering (van Hinsberg et al. 2011), gem tourmalines can accumulate in eluvial and alluvial deposits, such as those found in Madagascar (Dirlam et al. 2002).

Inclusions in tourmaline reflect the environment of its formation and, in rare cases, provide a fingerprint for specific deposits (Koivula 1994 and references therein). For example, native copper inclusions are indicative of gemstones from Paraíba, Brazil (Fritsch et al. 1990). Other mineral inclusions in tourmaline include albite, muscovite, lepidolite, fluorapatite, monazite, pyrite, pyrochlore-group minerals, quartz, zircon, and, more rarely, minerals such as hydroxylherderite, manganotantalite, and topaz (Koivula 1994). Most of these mineral inclusions are consistent with a pegmatitic paragenesis. However, the inclusions found in tourmaline are more commonly in the form of trapped fluids. These fluid inclusions manifest themselves as negative crystals (fluid-filled voids shaped like the host crystal), fine randomly arranged capillary-like tubes, partially healed fractures, and sometimes growth tubes. Fluid inclusions in tourmaline, generally single-phase gas or two-phase aqueous liquid-plus-gas inclusions, represent fluid

Continent	Country	Locality	Significance
North America	(1) California, USA	Mesa Grande district	□
		Pala district	▼
		Ramona district	□
		Warner Springs	▼
(2) Maine, USA	Oxford County	▼	
(3) Northwest Territories, Canada	O’Grady Lake	□	
South America	(1) Minas Gerais, Brazil	Araçuaí district	◆
		Conselheiro Pena district	◆
		Malacacheta district	▼
		São José de Safira district	◆
	(2) Paraíba, Brazil	São José da Batalha area	▼
(3) Rio Grande do Norte, Brazil	Parelhas area	▼	
Africa	(1) Kenya	Mangare and elsewhere	▼
	(2) Madagascar	Antsirabe-Betafo area	▼
		Fianarantsoa area	▼
		Tsitondroina area	▼
	(3) Mozambique	Nampula Province	◆
		Zambézia Province	▼
	(4) Namibia	Karibib area	▼
	(5) Nigeria	Nassarawa Province	◆
		Oyo Province	◆
	(6) Tanzania	Arusha area	▼
		Morogoro area	▼
		Tanga area	▼
	(7) Zambia	Kabwe district	□
Lundazi district		▼	
Europe	(1) Italy	Elba Island	□
	(1) Russia	Mursinka	□
Asia	(1) Afghanistan	Nuristan Province	◆
		Kunar Province	◆
	(2) Myanmar	Shan State	▼
		Mandalay State	▼
	(3) Pakistan	Gilgit-Baltistan	▼
		Azad Kashmir	▼
	(4) Russia	Transbaikalia	▼
	(5) Sri Lanka	Various	□
(6) Vietnam	Yen Bai Province	▼	

trapped during some stage(s) of tourmaline development, and they can be used to establish the pressure–temperature–fluid evolution of the system (e.g. van Hinsberg et al. 2011).

CONCLUSIONS

In addition to its scientific value as a recorder of the geologic environments during its formation, tourmaline is a fascinating and beautiful gemstone known for its full spectrum of colors. Its attractive and complex color zoning and its occurrence as sharp prismatic crystals make it highly sought-after by mineral connoisseurs and gem aficionados. Particularly notable are large (up to 1 m long) crystals of elbaite, intricately zoned crystals of liddicoatitic tourmaline, and vivid blue-to-green Paraíba-type elbaite. Tourmaline’s remarkable variety of colors and its availability as large, gem-quality crystals are directly related to its most common mode of formation, within miarolitic cavities in moderately to highly differentiated granitic

pegmatites. The most important commercial deposits—all pegmatitic—are located in Brazil, Mozambique, Nigeria, and Afghanistan. Demand for this attractive gemstone will continue to drive mining and will likely result in additional discoveries that will yield magnificent crystals and deepen our knowledge of the dynamic Earth processes leading to its formation.

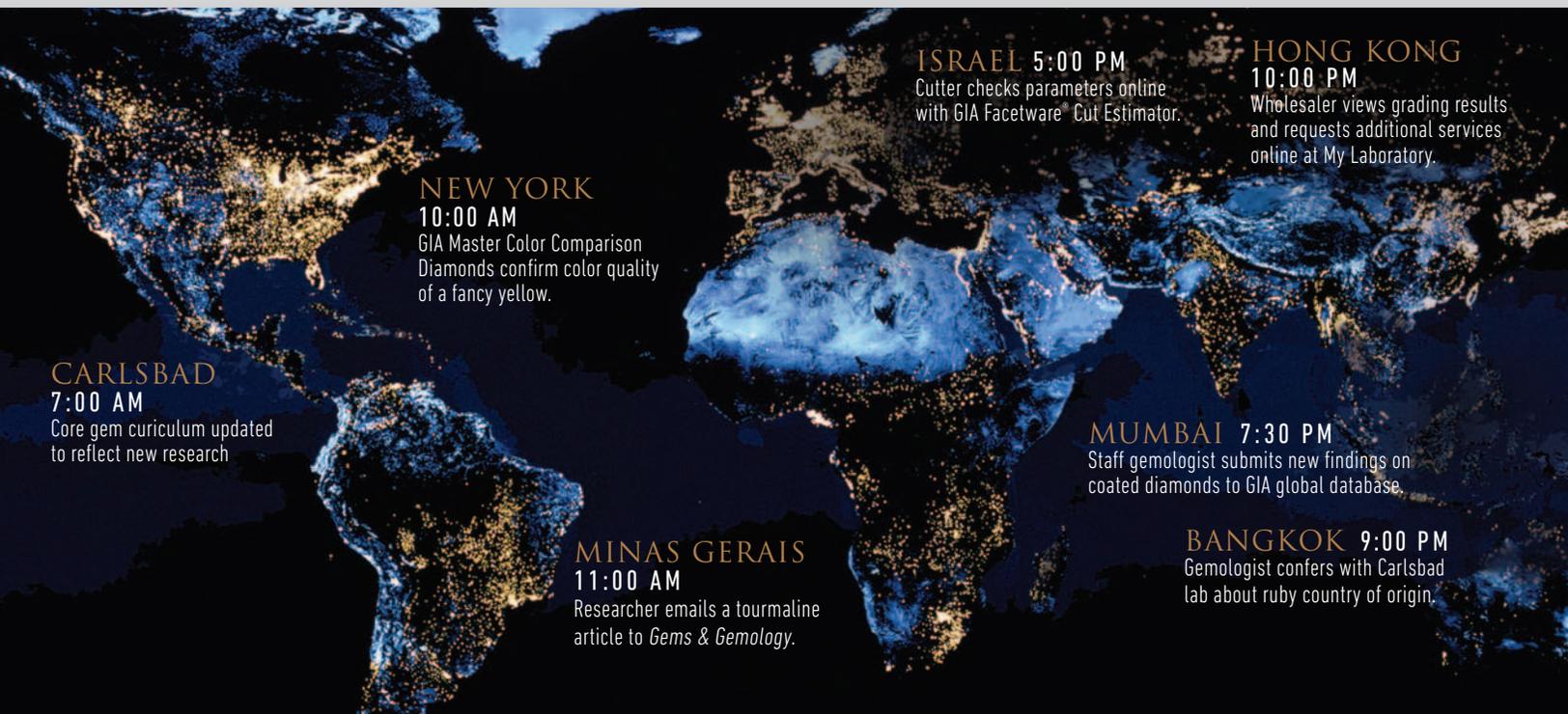
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ISRAEL 5:00 PM
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