

Paraíba or Not? Cu-bearing Tourmaline with a Distinct Fe Concentration

Copper-bearing tourmaline, also known as Paraíba-type tourmaline (or paraiba tourmaline; LMHC 2012), is one of the most sought-after and appreciated coloured stones in the trade. This is mostly due to its vivid colour, which in the best cases is described as ‘neon’ or ‘electric’ blue. However, Cu-bearing tourmalines are found in many colours, ranging from saturated blue (sapphire-like colour) to vivid and light blue, greenish blue to bluish green, green, and even greenish yellow and purple. Known sources include Brazil (Paraíba and Rio Grande do Norte states), where this attractive variety of tourmaline was first discovered, Mozambique (Mavuco and Maraca in the Alto Ligonha pegmatite field) and Nigeria (Fritsch *et al.* 1990; Smith *et al.* 2001; Abduriyim *et al.* 2006; Laurs *et al.* 2008; and references therein).

Interestingly, Cu-free indicolite tourmaline with Fe²⁺ as a chromophore can sometimes show a greenish blue colour very similar to that of Paraíba-type tourmaline. This material is often marketed as Lagoon tourmaline and is known, for example, from Namibia and Afghanistan. The separation of non-Cu-bearing indicolite from Paraíba-type tourmaline is usually straightforward, based on chemical analysis, UV-Vis absorption spectroscopy or both (Merkel & Breeding 2009).

Here we describe an intermediate variety of tourmaline (Figure 26, centre—sample B), that was recently submitted to the Swiss Gemmological Institute SSEF (Krzemnicki 2021). This stone of impressive size and weight (61 ct) shows an attractive greenish blue colour

and exceptional clarity. Here we compare it to a similar Cu-bearing tourmaline from Nigeria (Figure 26, left—sample A) and a Cu-free indicolite from Namibia (Figure 26, right—sample C). Chemical variations among these three samples are best revealed by comparing the concentrations of their chromophores Cu and Fe (Table I), as measured by laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOF-MS) using SSEF’s GemTOF system (see Wang *et al.* 2016). The Paraíba-type tourmaline from Nigeria (sample A) is strongly dominated by Cu, resulting in a Cu/Fe ratio of 18, while the Cu concentration in the indicolite from Namibia (sample C) is near the detection limit of our instrument (0.08 ppm for Cu), resulting in a very low Cu/Fe ratio of 0.000025. By contrast, sample B contains both Fe and Cu, with an intermediate Cu/Fe ratio of 0.16.

Although very similar in their visual appearance, these three tourmaline samples can be separated by their UV-Vis-NIR absorption spectra (Figure 27). The colour of the Paraíba-type tourmaline (sample A) is primarily related to two broad Cu²⁺ absorption bands extending into the near-infrared range (centred at around 700 and 900 nm). The distinct predominance of the absorption band at 900 nm over the band at 700 nm is characteristic for any Cu-dominated (Paraíba-type) tourmaline. By contrast, the indicolite (sample C) is coloured by a single broad absorption band centred at around 720 nm due to Fe²⁺ (Merkel & Breeding 2009). The colour of the intermediate Fe-Cu tourmaline (sample B) is related to

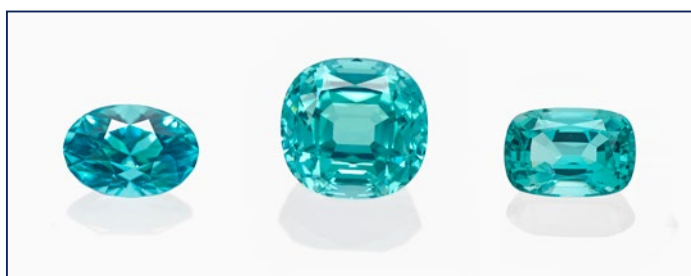


Figure 26: The three tourmalines of similar greenish blue colour examined for this study consist of (from left to right): a Cu-bearing Paraíba-type tourmaline from Nigeria (sample A, 19 ct) with a Cu/Fe ratio of 18; a tourmaline of intermediate composition (sample B, 61 ct) that is probably from Nigeria, with a Cu/Fe ratio of 0.16; and an Fe-bearing indicolite from Namibia (sample C, 23 ct) with a Cu/Fe ratio of 0.000025. Composite photo by M. S. Krzemnicki, © SSEF.

Table I: Fe and Cu contents of the three tourmalines in Figure 26, obtained by LA-ICP-TOF-MS.

Element	Sample A (Cu bearing)		Sample B (Fe-Cu bearing)		Sample C (Fe bearing)	
	Average (4)	Std. dev.	Average (4)	Std. dev.	Average (4)	Std. dev.
Fe (ppm)	113	15	4181	107	6194	444
Cu (ppm)	2037	69	670	12	0.16	0.04
Cu/Fe ratio	18		0.16		0.000025	

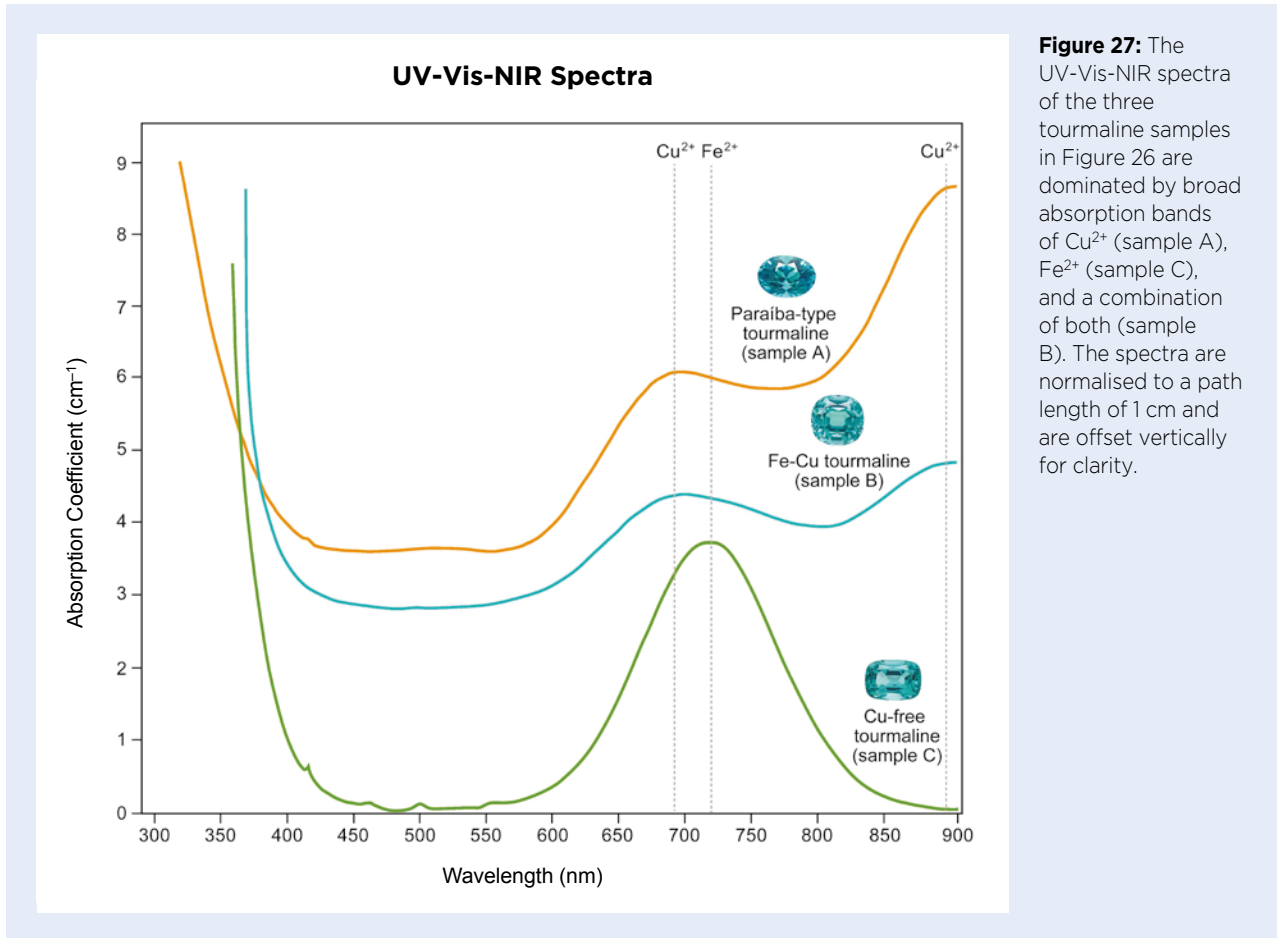


Figure 27: The UV-Vis-NIR spectra of the three tourmaline samples in Figure 26 are dominated by broad absorption bands of Cu^{2+} (sample A), Fe^{2+} (sample C), and a combination of both (sample B). The spectra are normalised to a path length of 1 cm and are offset vertically for clarity.

the absorption bands of both Cu^{2+} and Fe^{2+} . Because the bands at 700 and 900 nm have nearly equal intensity in this sample, it can be deduced that its colour is due to a combination of Cu and Fe.

Based on statistical processing of the trace-element data with a machine-learning algorithm (unsupervised non-linear t-SNE; Wang & Krzemnicki 2021), the origin of the intermediate Fe-Cu tourmaline (sample B) is in our opinion most likely Nigeria, although an independent confirmation of the mining site is still pending.

The recent appearance of greenish blue tourmaline with low Cu but distinctly higher Fe concentrations than typically found in Paraíba-type tourmaline (such as sample B) opens up interesting nomenclature considerations, similar to those long known for emerald and green beryl (related in that case to a gradual shift from Cr towards Fe). For the time being, given the relatively distinct concentration of Cu and the absorption spectrum with obvious Cu-related absorption bands, we feel that it is appropriate to call this particular stone ‘Paraíba-type tourmaline’ or ‘paraiba tourmaline’. However, this would not be the case for a stone (such as sample C here) that contains significantly less Cu or when Fe-related

absorption features dominate the Cu^{2+} bands.

In an ongoing study, we are currently focusing on this nomenclature issue with the aim of better defining to what extent an Fe-Cu-bearing tourmaline should be referred to using the Paraíba name and at what point it should be properly called an indicolite tourmaline with low traces of Cu.

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PEARLS

Art Nouveau Pendant with a Large Blister Pearl

Natural pearls are, and always have been, a rarity. Particularly fine natural pearls are highly treasured and attain top prices at auctions. Sometimes natural pearls are attached to a shell, requiring them to be cut out and reworked slightly on the shell side. These are known as blister pearls (CIBJO 2021), and are usually not as highly valued as round natural pearls, but they are still rare (Zhou *et al.* 2017).

Similar in appearance to blister pearls are cultured blisters. These half-pearls are cultivated on the inside

surface of a mollusc's shell. A small nucleus, usually made from mother-of-pearl, is attached to the shell and left to accumulate nacre over a period of usually about two or three years. Cultured blisters have a lower value than natural blister pearls, similar to the price difference between cultured and natural spherical pearls (Hänni 2012 and references therein).

Recently, a goldsmith submitted a pendant mounted with a pearl to the DDI Foundation German Diamond Institute for testing (Figure 28a). It contained delicate



Figure 28: (a) This pendant featuring an oval-shaped blister pearl (17 mm wide) was submitted for testing. (b) A side view of the pendant shows the delicate Art Nouveau gold artwork and how a portion of the pearl's rim is covered by the mounting. (c) The open back of the pendant reveals concentric rings that follow the outline of the pearl. Photos by T. Jordi and L. Kiefert.