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COLORED STONES AND ORGANIC MATERIALS

Fura Gems' inaugural ruby sale. Fura Gems hosted its first sales event for rough Mozambican rubies in August and September 2021. The international gem mining and marketing company has assets in Colombia (emerald), Australia (sapphire), and Mozambique (ruby). After previous sales events for Colombian emeralds in the first months of 2021, the firm now offered its rubies to the trade for the first time.

Mozambican rubies have been available in the trade since 2009, and the region quickly became one of the most important sources for the red variety of corundum. Fura is only the third company to bring rubies to the trade in a formalized tender. During the first years after the deposit's discovery in 2009, gems were recovered by artisanal miners and traded locally.

In 2014, the first large-scale sale of Mozambican rubies by an organized mining group took place. During that tender, Gemfields offered nearly two million carats of rough ruby, and they have hosted 14 auctions since then. Mustang Resources hosted a rough ruby tender in 2017, which was not well received by the trade. Fura took over existing ruby mining permits and equipment in Mozambique from various companies, including Mustang Resources, acquiring the largest ruby mining license in the country.

Invited buyers were able to view Fura's rubies in Jaipur and Bangkok, locations that host the largest colored stone manufacturing industries in the world. Each company was able to view the stones over two days in a secured space. Precautions against COVID-19 included a limited number of attendees per day, which caused the entire event to last more than 24 days across the two locations. This allowed all potential buyers ample time to inspect the rough rubies.

Editors' note: Interested contributors should send information and illustrations to Stuart Overlin at soverlin@gia.edu or GIA, The Robert Mouawad Campus, 5345 Armada Drive, Carlsbad, CA 92008.

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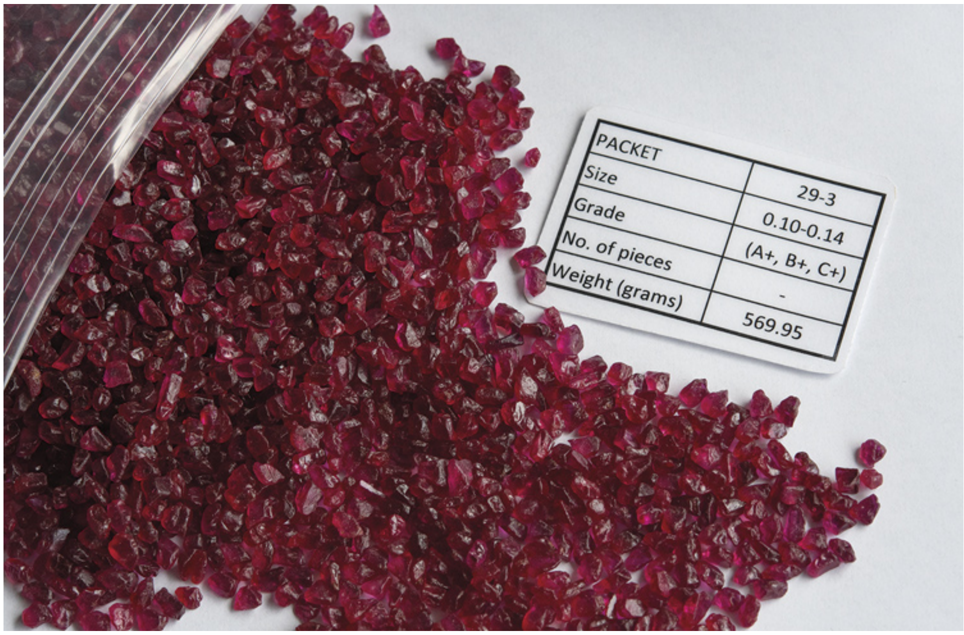
The rough gems were offered in pre-graded schedules, based on size and color. The grading system was designed with the gem cutting process in mind, especially aiming for the most commonly used calibrated sizes. Stones with similar hues are put in the same category, creating separate classes for stones with purer red color vs. those with a stronger orangy/purplish tint. Stones with lower saturation are separated from those with stronger saturation. Specific grades are designed to highlight those with lighter colors that would result in fancy sapphires such as pink and reddish orange.

All stones were offered as found in the mine and untreated. A significant percentage of Mozambican rubies can benefit from heat treatment to lighten the color, but this decision was left to the final buyer. While heat treating rubies might improve their appearance, it can also lower the value in the current market. This is especially true for larger stones.

Figure 1. Small lots made up of stones weighing more than 1 g often showed more color variety within a single grade. Photo by Wim Vertriest; courtesy of Fura Gems.



PACKET	29-3
Size	0.10-0.14
Grade	(A+, B+, C+)
No. of pieces	-
Weight (grams)	569.95

Figure 2. The majority of the stones offered were on the smaller side (below 0.5 g). These lots were highly desired by manufacturers for their intense colors and bulky appearance, which will result in smaller finished stones with a saturated bodycolor. Photo by Wim Vertriest; courtesy of Fura Gems.

The material showed a wide range of red tints, including strong orangy and purplish colors, but most goods still fell within the color range of ruby. Some stones had lighter saturation that could result in fancy sapphires, especially pinkish materials. This is in line with the regular production from Montepuez, Mozambique, that we have seen over the last decade. Rubies with a dark tone, sometimes referred to as "closed color," were rare at this tender. All the material showed some fluorescence under long-wave UV, a feature that is absent in certain types of classic Mozambican ruby.

Over 63 kg of rough ruby was offered (figures 1 and 2). The vast majority of the rough weighed under 0.5 g, but with a bulky shape that would result in a good yield. A few hundred stones weighed more than 0.5 g, and some exceptional pieces exceeded 2 g.

The rough rubies had the typical rounded crystal appearance of gems found in secondary deposits, as was confirmed by Fura, which mines the material from gravels that contain a higher concentration of rubies. This is in contrast with primary deposits, where gems are extracted directly from the host rock.

Evaluating rough rubies is a challenging affair. Before assigning a value to a parcel, buyers had to account for each stone's final shape and cutting style, weight, and potential improvement through treatment. They submitted closed bids via an online platform before the closing date. On closing day, Fura reviewed all the offers and, once accepted, notified the successful buyers.

The company reported that 35 of the 47 lots sold, including all high- to medium-grade lots. They also announced that the price per carat for goods in the calibrated sizes exceeded expectations. According to several ruby dealers, this category is in highest demand and the material was most attractive.

This auction comes at a time when the industry is struggling for rough stones, as many of the regular supply chains have been disrupted by the COVID-19 pandemic. The manufacturers have a clear hunger for rough rubies, though they also have limited financial reserves. Nevertheless, the addition of Fura as a Mozambican rough ruby supplier, along with Gemfields and the artisanal mining community, makes for an exciting change in the gem scene.

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Mabe cultivation in Mayotte. The Laboratoire Français de Gemmologie (LFG) received some mabe samples (figure 3) from Antoine Ganne of the Mayotte-based company Nuru Kombe for gemological characterization. According to the company, these samples were cultivated in *Pteria penguin* bivalves in a lagoon off the coast of Mayotte. This French territory is situated in the Indian Ocean between northwestern Madagascar and northeastern Mozambique, with one main island and several islets.

Mabe is the Japanese term designating an assembled cultured blister, traditionally from *Pteria penguin* but nowadays from other mollusks as well (CIBJO Pearl Commission, *The Pearl Book*, CIBJO, Milan, 2020, 79 pp.). Mabe is made of purpose-grown cultured blisters that have been cut from their shell. The original bead upon which they grew is removed, and the cavity is filled with various synthetic materials. It is then backed by a layer of shell, with the assemblage held together by an adhesive.

The studied samples ranged from light brown to brown (some of a "golden" color) with pronounced secondary colors such as blue, green, and red (again, see figure 3). Under the microscope, all samples presented the characteristic nacreous structures associated with overlapping layers of

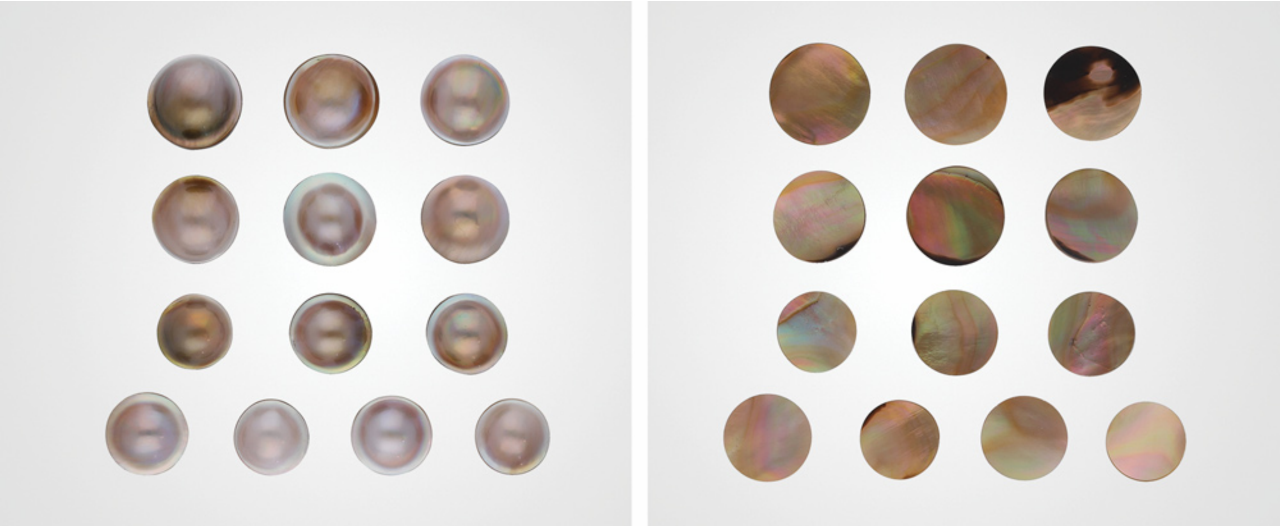


Figure 3. These assembled cultured blisters (mabe) showing a curved top (left) and flat bottom (right) were cultivated in Mayotte. The largest is 21 mm in diameter. Photos by LFG.

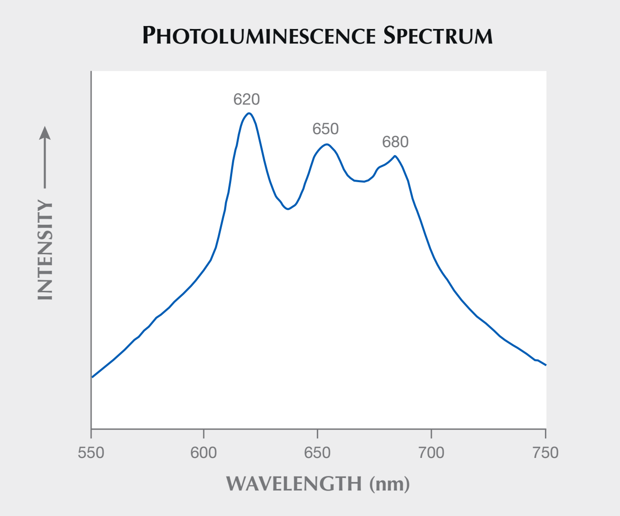
aragonite. The curved and flat sides looked very similar, suggesting they originated from the same mollusk species. The samples reacted purple to red under a long-wave UV lamp and remained inert under short-wave UV lamp excitation. Those with a more pronounced brown color exhibited a stronger intense luminescence. A similar luminescence reaction was observed in cultured pearls from *Pteria sterna* from Mexico (L. Kiefert et al., "Cultured pearls from the Gulf of California, Mexico," Spring 2004 *G&G*, pp. 26–38). This response is due to a type of porphyrin (a tetrapyrrole with a cyclic structure) that also plays an important role in the samples' coloration.

Raman analysis using a 514 nm laser revealed bands associated with aragonite along with a series of bands from 800 to 1600 cm^{-1} characteristic of porphyrins (S. Karampelas et al., "Raman spectroscopy of natural and cultured pearls and pearl producing mollusc shells," *Journal of Raman Spectroscopy*, Vol. 51, No. 9, 2020, pp. 1813–1821). Photoluminescence spectra obtained using a Raman spectrometer and the same laser excitation presented bands in the orange and red part of the electromagnetic spectrum at about 620, 650, and 680 nm (figure 4). The relative intensity of these bands can vary. Luminescence spectra using a xenon lamp with 365 nm excitation presented similar bands with additional bands at about 435, 465, and 525 nm. The latter bands are possibly linked to the nacre of the samples, while the triplet of bands at 620, 650, and 680 nm has been attributed to a uroporphyrin (Y. Iwahashi and S. Akamatsu, "Porphyrin pigment in black-lip pearls and its application to pearl identification," *Fisheries Science*, Vol. 60, No. 1, 1994, pp. 69–71).

The UV-Vis reflectance spectra of the samples featured a series of bands with various relative intensities at about 380, 400, 460, and 495 nm, along with a band at about 280 nm (figure 5). The latter band is linked to organic matter and the nacreous part of the samples, and the series is possibly linked to porphyrins (Kiefert et al., 2009).

All samples were inert under X-ray and EDXRF analysis, with an Mn content below the detection limit and Sr contents ranging from 3180 to 5280 ppm, indicating saltwater origin. X-ray microradiographs (figure 6) showed lighter tones at the rim, indicating a higher-density material such as calcium carbonate (usually aragonite) in the case of natural and cultured pearls, while the darker tones in the core indicated lower-density material such as organic matter and resin (S. Karampelas et al., "Real-time microradiography of pearls: A comparison between detectors," Winter 2017

Figure 4. Photoluminescence spectrum of a brown mabe sample from Mayotte using a Raman spectrometer under 514 nm laser excitation. Three bands appearing at the orange and red parts of the electromagnetic spectrum at about 620, 650, and 680 nm are linked with uroporphyrin.



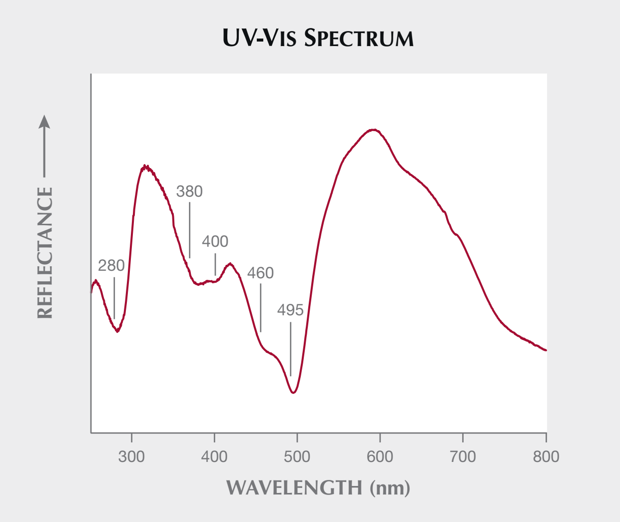


Figure 5. The UV-Vis spectrum of a brown mabe sample from Mayotte displays bands at about 380, 400, 460, and 495 nm that are linked to porphyrin, along with a band at about 280 nm that is linked to nacre and organic matter.

G&G, pp. 452–456). The samples, which could be called "mabe" or "assembled cultured blister" according to the current CIBJO standards, had a nacre thickness from 0.4 to 1 mm (again, see figure 6).

Mabe from Mayotte has only appeared recently in the market. The exact supply is still unknown, and other similar products are cultivated in other parts of the world, including Southeast Asia, Australia, and some Pacific island nations (P.C. Southgate and J.S. Lucas, *The Pearl Oyster*, 2008, Elsevier, Amsterdam). Nevertheless, this material could help develop the economy of Mayotte, where all the operations take place and jewelry pieces with a French touch are locally made.

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SYNTHETICS AND SIMULANTS

Honey brown and light yellow hydrogrossular: An uncommon jade imitation. Hydrogrossular or hydrogarnet is a translucent to opaque, water-bearing calcium aluminum silicate garnet that commonly shows microcrystalline texture. It has a range of colors: brown, colorless, green, gray, pink, and yellow. The most popular is the shade of green known in the trade as "Transvaal jade" or "African jade." Recently, the GIT-Gem Testing Laboratory (GIT-GTL) received two samples of hydrogrossular garnet for identification: the light yellow carved pendant (~70 ct, 36 × 21 mm) and the honey brown oval cabochon (8 ct, 15 × 12 mm) shown in figure 7. These are not typical colors used for jade imitations.

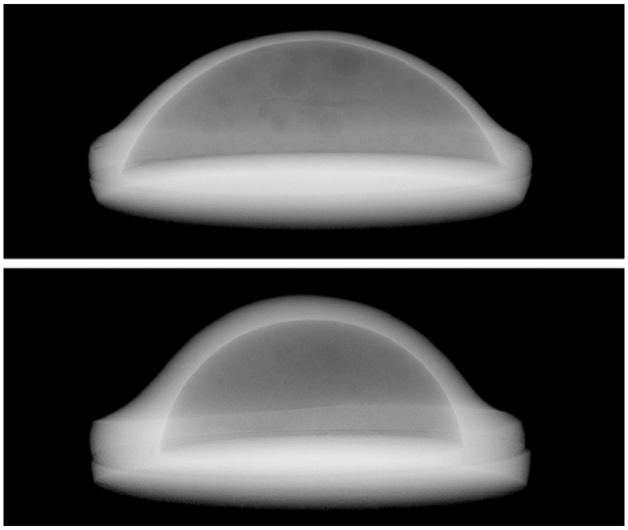

Figure 6. X-ray microradiographs of two mabe from Mayotte show a lighter rim due to higher-density material (calcium carbonate), while the darker tones at the core represent a lower-density material such as resin. The top sample (21 mm in diameter) has a nacre thickness of 0.4 mm. The bottom sample (13 mm in diameter) has a nacre thickness of 1 mm. Images by S. Leblan, LFG.

Standard gemological testing of the honey brown cabochon showed a specific gravity of ~3.66 and a refractive index of ~1.71, while those of the light yellow piece were

Figure 7. This light yellow carving (36 × 21 mm) and honey brown cabochon (15 × 12 mm) were identified as hydrogrossular. Photo by C. Kamemakanon; courtesy of Pachara Chonlakit.

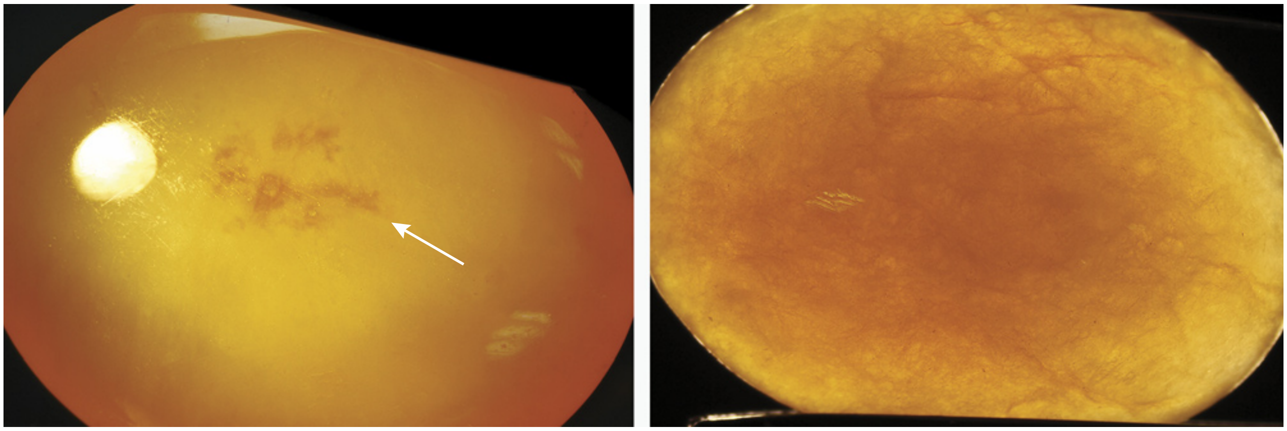

Figure 8. The microscopic observation of the honey brown hydrogrossular sample (left) revealed a fine-grained aggregate structure and color patches (white arrow), as compared with the coarse-grained aggregate structure of the brown jadeite sample (right). Oblique fiber-optic light. Photomicrographs by S. Promwongnan; field of view ~14 mm.

undeterminable due to the nature of the mounting and carving. Nonetheless, both stones exhibited weak red fluorescence to long-wave UV and were inert to short-wave UV radiation, and displayed massive fine-grained aggregate structures with a translucent glassy appearance (figure 8, left), which was quite different from the coarse-grained aggregate structure of jadeite (figure 8, right).

The identity was also confirmed by advanced testing. The Raman spectra of both samples showed dominant peaks at 374, 415, 548, 825, and 879 cm^{-1} and other smaller peaks at 246, 278, 508, 627, and 1005 cm^{-1} (figure 9) that matched perfectly with the spectrum of grossularite in the RRUFF reference database (R040065). Semi-quantitative chemical analyses of both stones revealed enriched contents of silica, calcium, and aluminum, which are closely consistent with grossularite, a calcium-aluminum garnet.

The infrared spectrum of the honey brown cabochon sample, measured in reflection mode between 580–1400 cm^{-1}, showed characteristic reflectance peaks at 616, 843, 866, and 954 cm^{-1} that are similar to the spectra of the hydrogrossular reference sample (figure 10) as well as green hydrogrossular (see Fall 2015 GNI, pp. 342–343). Note that the reflectance spectrum should be almost identical to the transmission spectrum of the sample, and the same features should be observed in both cases.

The infrared spectra of both samples, measured in transmission mode between 1000 and 5000 cm^{-1} and dis-

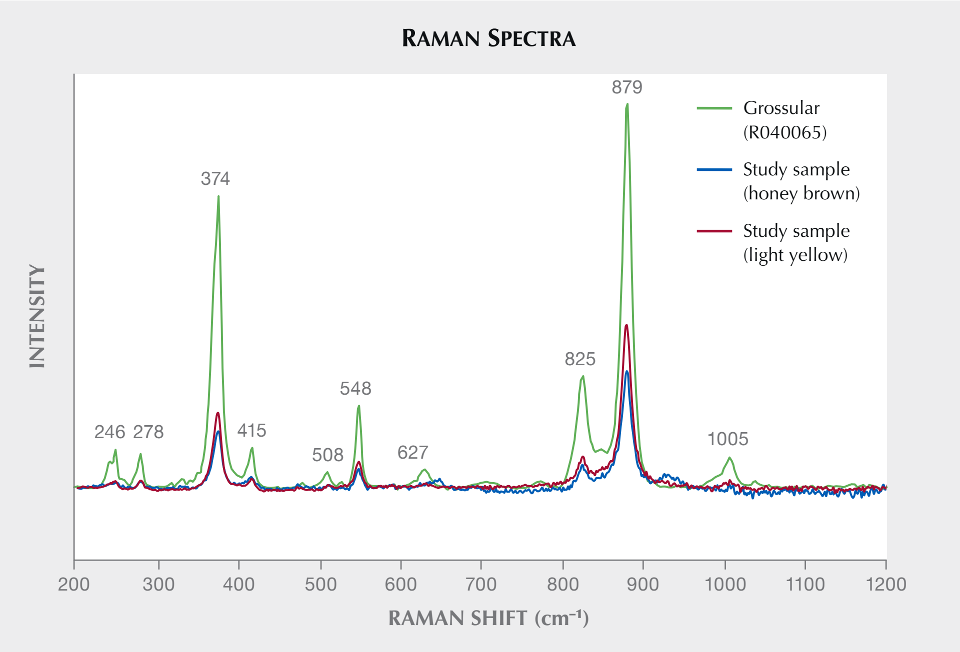

Figure 9. Raman spectra of the honey brown and light yellow samples (blue and red lines, respectively) as compared to the reference spectrum of grossularite from the RRUFF database (green).

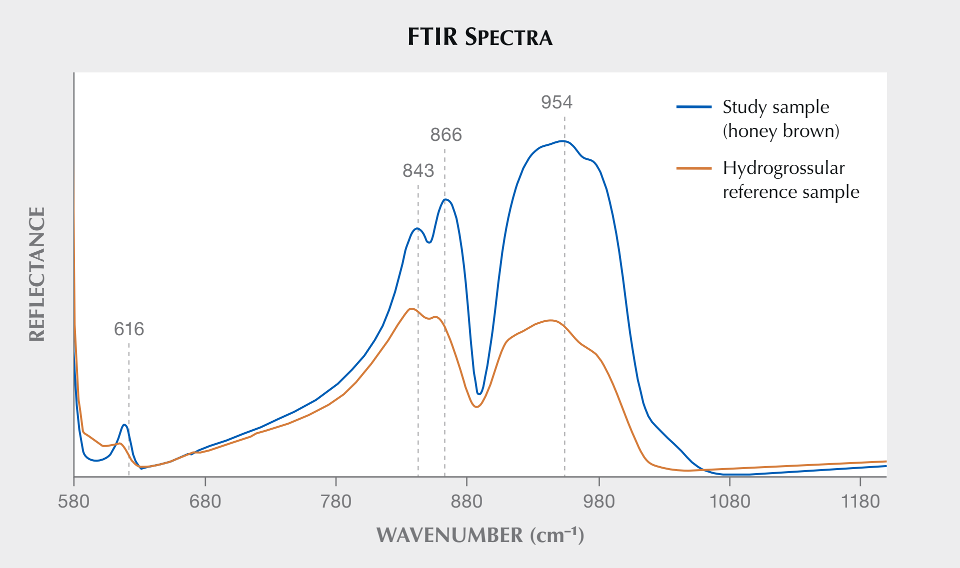

Figure 10. The infrared spectrum in reflection mode of the honey brown sample (blue line) exhibits characteristic reflectance peaks of hydrogrossular garnet at 616, 843, 866, and 954 cm^{-1}, as compared with the spectrum of the hydrogrossular reference sample (purple line). The spectrum of the light yellow sample was not measured due to the nature of the carving.

played in % transmittance, showed very strong broad absorption bands between ~3000–4000 cm^{-1} that are somewhat similar to the spectrum of our hydrogrossular reference sample (figure 11), and coincide with water-related absorption bands of hydrogrossular (>5 wt.% H_2O) centered at 3598 and 3662 cm^{-1} (see G.R. Rossman and R.D. Aines, "The hydrous components in garnets: Grossular-hydrogrossular," *American Mineralogist*, Vol. 76, No. 7-8, 1991, pp. 1153–1164). In comparison, our grossular (tsavorite and hessonite) samples reveal much narrower absorption bands between 3500–3700 cm^{-1} (figure 11). Thus, the presence of very strong broad (water-related) absorption bands has confirmed that both stones submitted for investigation were indeed hydrogrossular.

In summary, the gemological properties, Raman spectra, and chemical compositions of the light yellow and honey brown samples are consistent with those of grossular garnet. However, the infrared spectra showing characteristic transmission peaks of hydrogrossular at 616, 843, 866, and 954 cm^{-1} and very strong occurrence of structural water (i.e., significant OH replacing Si in tetrahedral sites) have confirmed that these two stones are indeed hydrogrossular rather than grossular garnet. It is worth noting that one of the materials commonly used to imitate jade is fine-grained aggregate hydrogrossular garnet, not single-crystal garnet.

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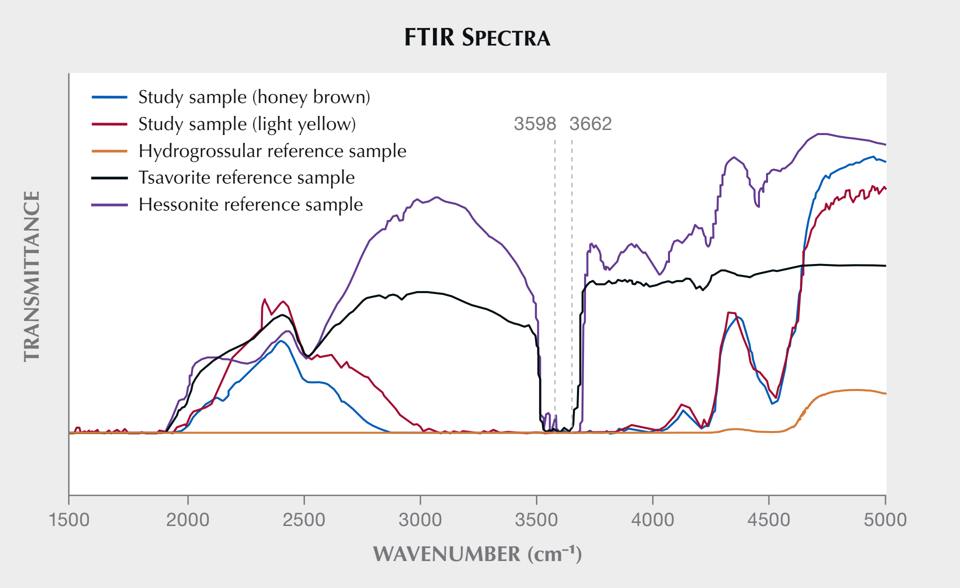

Figure 11. Infrared spectra by transmission mode of the honey brown and light yellow samples (blue and red lines, respectively) show very strong broad (water-related) absorption bands between ~3000–4000 cm^{-1} as compared with the spectra of a hydrogrossular reference sample (purple line) and grossular (tsavorite and hessonite) samples (green and black lines, respectively). The vertical dashed lines at 3598 and 3662 cm^{-1} mark water-related absorption bands of hydrogrossular (>5 wt.% H_2O) based on Rossman and Aines (1991).

Pink aventurine quartz with alurgite inclusions. "Strawberry quartz" is not a strictly defined term in gemology but generally recognized in the market as single-crystal quartz with numerous striped or flaky hematite inclusions, which cause a pink to red overall appearance (D.I. Belakovskiy, "New acquisitions of the Fersman Mineralogical Museum, Russian Academy of Sciences (1997–2001)," *New Data on Minerals*, Vol. 38, 2003, pp. 101–112). Strawberry quartzes, due to limited mine production and rough sizes, are usually cut into beads, cabochons, or faceted stones or used for small carvings, all very popular products in the Taiwanese market.

Recently, a bangle was submitted for identification service to the Taiwan Union Lab of Gem Research (TULAB) as strawberry quartz (figure 12). The bangle had a brownish pink color in appearance and had a number of orangy pink to orangy red flaky crystals visible under the microscope. It had a refractive index of 1.54 and a specific gravity of 2.60. The material was found to be crystal aggregates through a polariscope and showed aventurescence under penlight.

Figure 12. This bangle was submitted as "strawberry quartz" to TULAB. Photo by Shu-Hong Lin.

In order to identify this material and its inclusions, the bangle was analyzed with micro-Raman spectrometry and the RRUFF database. It was found that the material was actually polycrystalline quartz and the red flaky inclusions were muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) (figure 13). SEM-EDS analysis of the inclusions exposed to the surface further verified them as iron-bearing muscovite; however, EDXRF analysis revealed trace amounts of manganese in addition to iron. In other words, this bangle should be defined as brownish pink aventurine quartz with pink to red muscovite inclusions. In comparison to those strawberry quartz with hematite inclusions, the red muscovite showed slight differences under the microscope. Hematite inclusions in strawberry quartz are usually striped, hexagonal, or irregular flaky crystals with medium to very dark red color under the microscope (figure 14, left); however, the red muscovite inclusions in the sample were mostly rounded flaky crystals with medium light to medium orangy red color (figure 14, right).

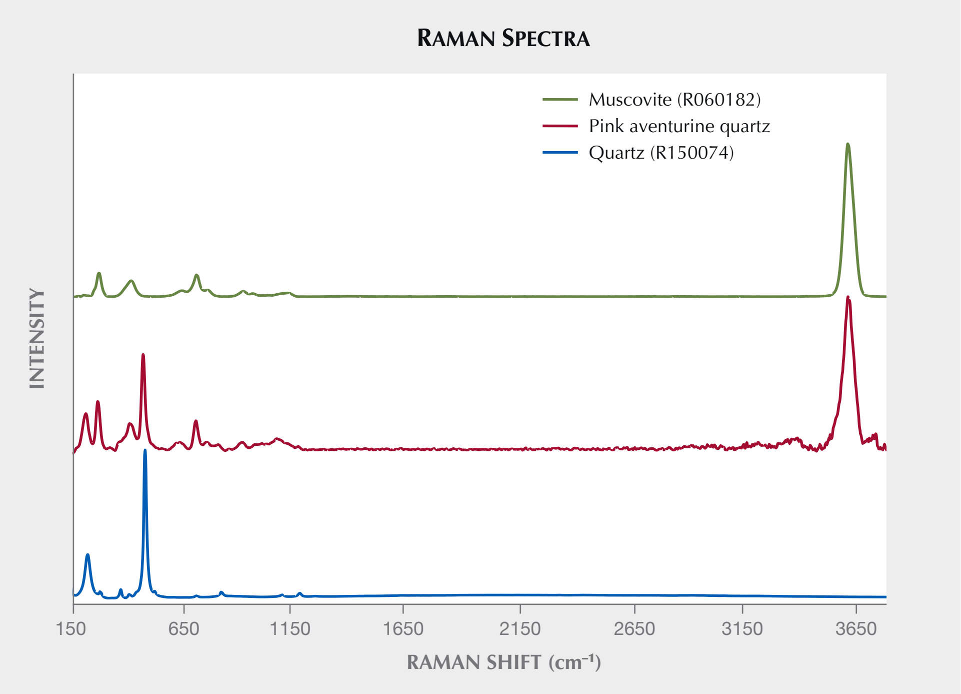

Figure 13. Raman spectra comparisons between the red inclusions and those of quartz and muscovite from the RRUFF database identified the bangle as aventurine quartz with orangy red muscovite inclusions. The stacked spectra are baseline-corrected and normalized.

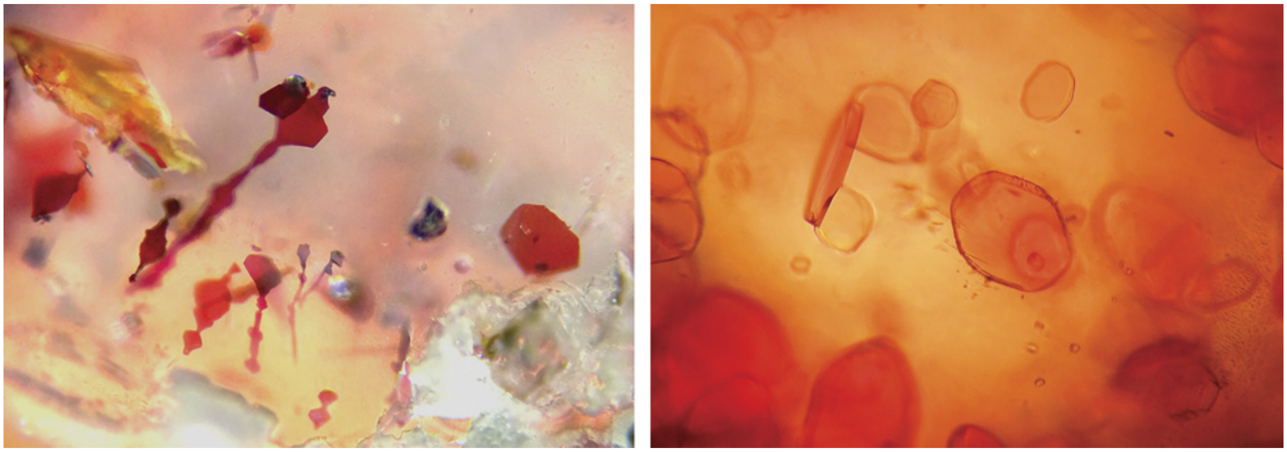

Figure 14. Microscopic images of the red striped and irregular flaky hematite in strawberry quartz (left) and the orangy red muscovite (alurgite) inclusions in the pink aventurine quartz sample (right). Photomicrograph by Shu-Hong Lin; field of view 1.26 mm.

Moreover, the visible light absorption spectra of the bangle were analyzed and compared to those of mica on the Mineral Spectroscopy Server of Caltech. The pink aventurine quartz presented absorption peaks at 445, 454, 515, and 548 nm (figure 15), consistent with the spectrum of alurgite (GRR727, Mineral Spectroscopy Server of Caltech), which is a reddish purple variety of muscovite.

Since "strawberry quartz" is not a strictly defined marketing name, consumers should notice that there are actually different types of quartz with various inclusions sold with the same trade name. As an atypical strawberry quartz material, pink aventurine quartz with alurgite can be distinguished with hematite-included strawberry quartz through the methods of polariscope, microscope, and micro-Raman spectroscopy.

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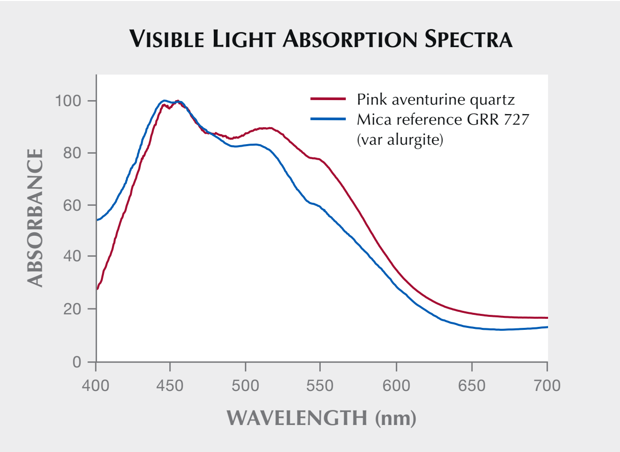
Figure 15. The visible light absorption spectrum of the pink aventurine quartz was compared to the reference spectrum of mica (Mineral Spectroscopy Server of Caltech); results revealed that the visible light absorption spectra were consistent with that of alurgite. The overlapped spectra are normalized.



TREATMENTS

FTIR observation on sapphires treated with heat and pressure. Characteristics of sapphires heated with pressure have been discussed in several gemological publications in the past few years (e.g., M.S. Krzemnicki et al., "Sapphires heated with pressure – A research update," *InColor*, Vol. 42, 2019, pp. 86–90). As previously reported, heat with pressure treatment is commonly applied to Sri Lankan sapphires, in either untreated geuda or conventionally heated blue sapphires, to enhance the blue color. The material has been treated at high temperature (approximately 1200–1800°C) with an application of pressure at nearly 1 kbar, using the facilities at HB Laboratory Co., Ltd. (H. Choi et al., "Sri Lankan sapphire enhanced by heat with pressure," *The Journal of the Gemmological Association of Hong Kong*, Vol. 39, 2018, pp. 16–25).

Fourier-transform infrared (FTIR) spectroscopy is considered a useful tool in revealing heat treatment of corundum (e.g., C.P. Smith, "A contribution to understanding the infrared spectra of rubies from Mong Hsu, Myanmar," *Journal*

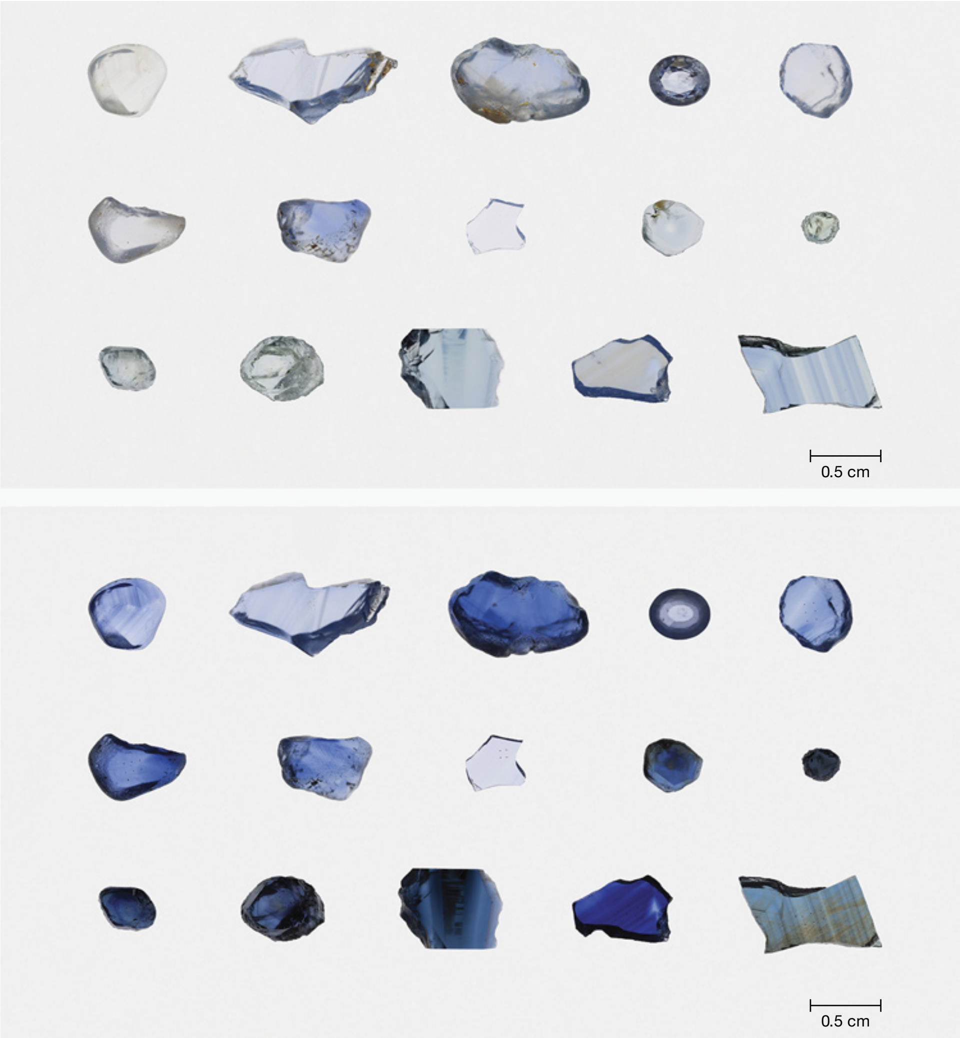


Figure 16. Color-calibrated photos of blue sapphires from different origins in the study before (top) and after (bottom) heat with pressure treatment. Photos by Sasithorn Engniwat.

of Gemmology, Vol. 24, 1995, pp. 321–335). Previous studies reported a great variability of FTIR spectra for sapphires heated with pressure, and FTIR spectra of this treated material generally showed a unique pattern of hydroxyl-related broad bands in the 2800–3500 cm^{-1} range, with the prominent position at around 3050 cm^{-1} (e.g., Krzemnicki et al., 2019). The origin of the resulting distinct IR broad bands has not been clearly determined. As discussed in Krzemnicki et al. (2019), broad bands centered at around 3050 cm^{-1} in sapphires heated with pressure share similar IR features observed in some acceptor-dominated corundum—heated or unheated natural materials, as well as laboratory-grown samples. (*Acceptors* refer to ions with the charge of –1 relative to the lattice, such as Mg^{2+} in corundum; see E.V. Dubinsky et al., "A quantitative description of the cause of color in corundum," Spring 2020 *G&G*, pp. 2–28.)

According to a previous study (M.D.T. Phan, "Internal characteristics, chemical compounds and spectroscopy of sapphire as single crystals," PhD dissertation, University of Johannes Gutenberg Mainz, 2015, https://d-nb.info/1075170532/34), iron (Fe^{3+}) content in corundum can affect the position of the 3310 cm^{-1} IR peak. In sapphires heated with pressure, the starting material is generally limited to Sri Lankan stones. Since blue sapphires from Sri Lanka typically contain relatively low Fe concentrations (A.C. Palke et al., "Geographic origin determination of blue sapphires," Winter 2019 *G&G*, pp. 536–579), the starting materials used in the study were expanded to various deposits, including Myanmar, Madagascar, Sri Lanka, Montana, Australia, Nigeria, Cambodia, and Thailand, to cover a wide range of Fe contents presented in natural corundum (figure 16). The 36 untreated and 8 conventionally heated blue sapphires were treated using heat with pressure under the conditions reported in Choi et al. (2018). Their FTIR spectra and chemical analysis using laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) were measured in the same analysis area to observe whether there was any change in FTIR spectra for different amounts of Fe. After heat with pressure treatment, the vast majority of treated sapphires in this study (>90%) showed essentially the same hydroxyl-related IR broad bands in the 2800–3500 cm^{-1} range with different prominent band posi-

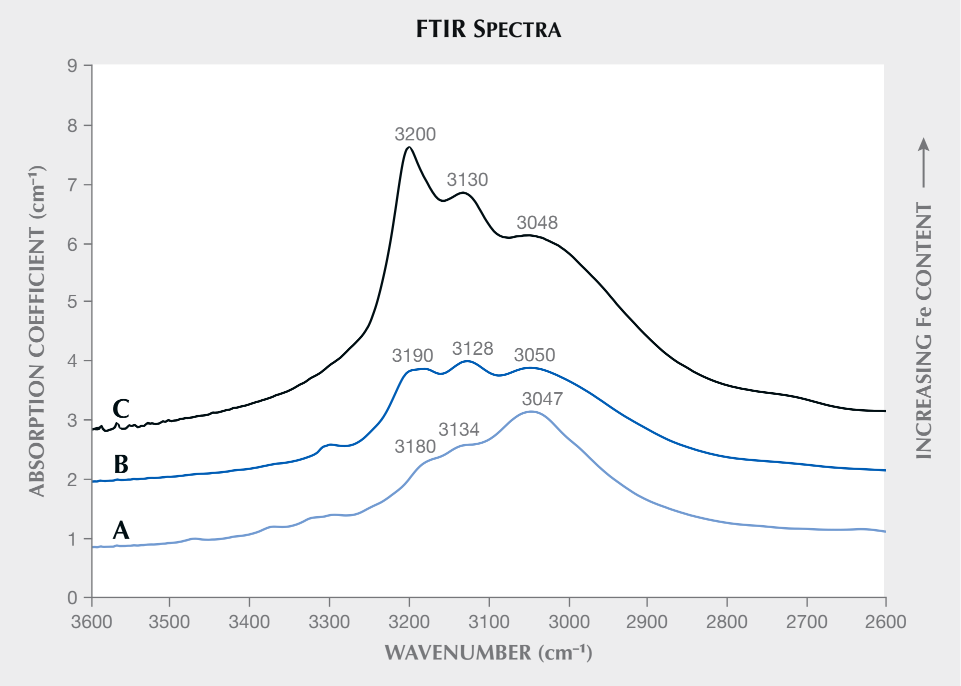


Figure 17. Comparison of representative non-polarized FTIR spectra from sapphires heated with pressure at different Fe concentrations: (A) 275 ± 25 ppma Fe, (B) 927 ± 48 ppma Fe, and (C) 2280 ± 163 ppma Fe. Spectra are offset vertically for clarity.

tions at around 3050, 3130, or 3200 cm⁻¹ (figure 17). The IR broad band centered at around 3050 cm⁻¹ with related bands at ~3130 and ~3200 cm⁻¹ (figure 17A) can be observed in sapphires heated with pressure that contained Fe <700 ppma (figure 18, circle), whereas IR broad bands with comparable band intensities at around 3050, 3130, and 3200 cm⁻¹ (figure 17B) can be found in treated sapphires with 550–1350 ppma Fe (figure 18, triangle). At relatively high Fe concentrations (>900 ppma) (figure 18, square), the FTIR spectra of sapphires heated with pressure displayed IR broad bands with a prominent band position at around 3200 cm⁻¹ (figure 17C). In the overlapped Fe range of the samples (500–700 ppma Fe and 900–1350 ppma Fe), different IR patterns could be obtained, possibly due to heterogeneity of the samples and different characteristics of analytical techniques—bulk analysis for FTIR and spot analysis for LA-ICP-MS.

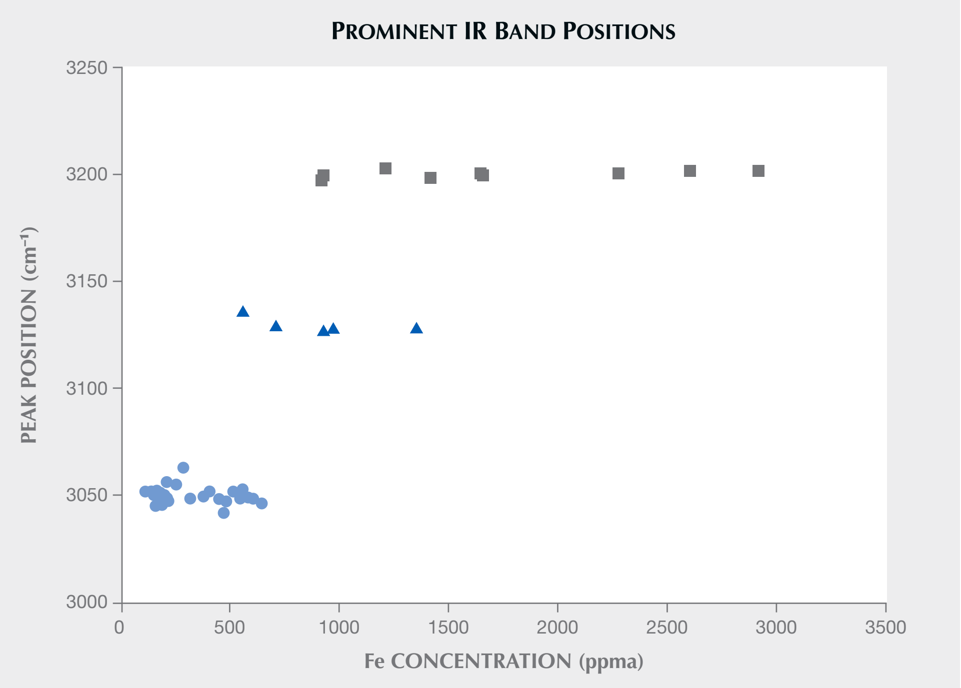


Figure 18. The relationship between which band of multiple IR absorption bands is prominent for sapphires heated with pressure and Fe concentrations analyzed by LA-ICP-MS of the treated materials. The circle (●), triangle (▲), and square (■) symbols correspond to FTIR patterns A, B, and C, respectively, from figure 17.

This study shows other possible FTIR spectra patterns that might be observed in sapphires heated with pressure, as well as prominent IR bands of the treated material that can shift position with different Fe concentrations.

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Heat treatment effects on the behavior of the 3161 cm^{-1} feature in low-iron metamorphic yellow sapphire. Heating is the most common treatment to improve the color and/or clarity of corundum. Untreated natural yellow sapphires from metamorphic deposits often have low color saturation; therefore, heat treatment is typically performed to intensify the yellow coloration. However, the chemical composition of the stones, the heating temperatures employed, the duration of the treatment process, as well as the composition of the furnace atmosphere—reducing or oxidizing—are also important factors that influence the color alteration (K. Nassau, "Heat treating ruby and sapphire: Technical aspects," Fall 1981 *G&G*, pp. 121–131; J.L. Emmett et al., "Treatments," in R.W. Hughes, Ed., *Ruby & Sapphire: A Gemologist's Guide*, 2017, pp. 197–247).

The identification of heat treatment in a yellow sapphire is challenging for gemologists. Apart from visible inclusion changes, Fourier-transform infrared (FTIR) absorption spectra are one of the few remaining clues to identify the treatment of low iron content metamorphic yellow sapphires. These sapphires as formed are acceptor dominated when $[Mg^{2+}] > [Ti^{4+}] + [Si^{4+}]$ with the charge compensation being accomplished totally or partially by hydrogen (H^+) (E.V. Dubinsky et al., "A quantitative description of the causes of color in corundum," Spring 2020 *G&G*, pp. 2–28). In corundum, H^+ forms a bond with oxygen creating OH^-. It is the OH^- that is responsible for the broad peak at 3161 cm^{-1} (and the series of peaks at 3161, 3242, and 3355 cm^{-1}) when associated with Mg^{2+} (C.P. Smith et al., "Infrared spectra of gem corundum," Fall 2006 *G&G*, pp. 92–93). However, the origin of the 3161 cm^{-1} peak is not well understood. The article by N. Fukatsu et al. ("Incorporation of hydrogen into magnesium-doped α-alumina," *Solid State Ionics*, Vol. 162, 2003, pp. 147–159) showed that when OH^- is incorporated into Mg^{2+}-doped synthetic sapphire, the 3161 cm^{-1} peak was not present but a broad band appeared in the 3000 cm^{-1} region. If the hydrogen is eliminated either in nature or in the laboratory, the trapped hole ($h^{\bullet}$) forms to provide charge compensation. The trapped hole pairs with Fe^{3+}, creating a trapped-hole-Fe^{3+} ($h^{\bullet}$-Fe^{3+}) pair, which is a very strong yellow chromophore in corundum. In this report, the authors aim to study the effects of heat treatment in changing the 3161 cm^{-1} feature and creating the yellow coloration.

Twelve yellow sapphires reportedly from Sri Lanka and Madagascar that initially displayed a weak to strong 3161 cm^{-1} peak or a 3161 cm^{-1} series in FTIR were selected for heat treatment in an oxidizing atmosphere (air) at 500°, 700°, 900°, and 1050°C for a fixed duration of six hours at each temperature. For a final step, some stones were heated at 1550°C in pure oxygen to assure the complete elimination of hydrogen. The samples were fabricated as optical wafers with at least two polished surfaces perpendicular and/or parallel to the c-axis. The samples possess a sufficiently large and clean area to get high-quality FTIR spectra. After each heat treatment step, FTIR spectra were collected at the same position for each sample by fixing it in an identical position in the sample holder.

Heat treatment can cause the H^+ to move to different sites by diffusion or at sufficiently high temperatures to diffuse completely out of the sample. The diffusion coefficient of hydrogen in corundum is exponentially dependent on temperature. After heat treatments at 500°C and 700°C, the intensities of 3161 cm^{-1} peaks and the color appearance of the stones were essentially unaltered. Thus, there is little outward diffusion for a sample of this size. However, heating at 900°C and above for six hours in air will begin to diffuse the hydrogen out of the lattice. As the hydrogen begins to diffuse out, trapped holes form and pair with Fe^{3+} to maintain charge compensation, increasing the yellow coloration.

At the same time, the amplitude of the 3161 cm^{-1} feature will decrease proportionally. The test at 1550°C for six hours was conducted in pure oxygen to eliminate any possibility of the water vapor in air contributing hydrogen. With this last step, the outward diffusion of all the hydrogen in the stone was complete, eliminating OH^- peaks in FTIR spectra and maximizing the yellow trapped-hole coloration.

Figure 19 shows these heating processes as applied to stones from Sri Lanka with a strong 3161 cm^{-1} feature and to some of the stones from Madagascar with a weak 3161 cm^{-1} feature. As expected, both types exhibited a similar diffusion reduction in the initial hydrogen content with temperature and time. The coloration of some of the Madagascar stones was zoned, with areas colored by the $h^{\bullet}$-Fe^{3+} pair, by $h^{\bullet}$-Fe^{3+} plus Fe^{3+}, and some by Fe^{3+} only, depending on the distributions of Fe^{3+} and $h^{\bullet}$-Fe^{3+} in the stone. Usually, the zones in which $h^{\bullet}$-Fe^{3+} is dominant will increase yellow coloration with high-temperature heat treatment by removing the hydrogen, whereas the areas with Fe^{3+} alone are rarely strongly zoned.

Interestingly, a characteristic peak at 3161 cm^{-1} in certain Sri Lankan samples could be occasionally transformed to the broadband series in 3000 cm^{-1} region with a broad band at 2625 cm^{-1} when heated at 900°C and above in air, as presented in figure 20. Previously, the 3000 cm^{-1} broad band series has been reported as indicative of heat treatment observed in Punsiri-type heated blue sapphires (G. DuToit et al., "Beryllium treated blue sapphires: Continuing market observations and update including the emergence of larger size stones," *GIA Research News*, 2009, https://www.gia.edu/gia-news-research-nr62609) and could be observed in unheated high-Fe yellow sapphires from

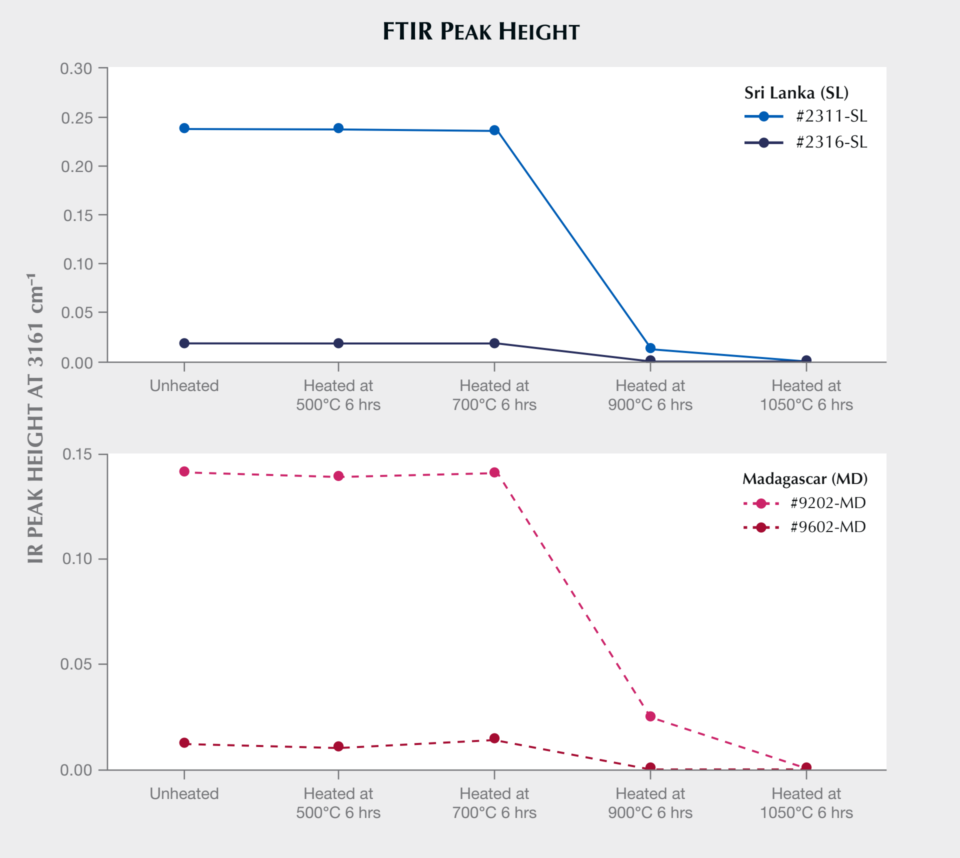

Figure 19. Plot of FTIR peak height at 3161 cm^{-1} of representative yellow sapphires from Sri Lanka (above) and Madagascar (bottom), before and after heating at different temperatures between 500° and 1050°C for six hours.

basalt-hosted deposits, such as Thailand and Australia (Fall 2016 GNI, pp. 325–327). However, the 3000 cm^{-1} broad band series could also be found in heat-treated Sri Lanka yellow sapphires, as seen from this study.

In summary, heat treatment was carried out in an oxidizing atmosphere to increase the trapped-hole color centers and deepen the yellow coloration. Sri Lankan samples colored mainly by the h$^{\bullet}$-Fe^{3+} pair can produce stronger yellow coloration by heat treatment, but only at high temperatures (900°C and above). The heating temperature at 900°C starts to change the 3161 cm^{-1} peak/series in FTIR and the color appearance in metamorphic yellow sapphires. It may well be that heating for a much longer time at 900°C would more completely diffuse out the hydrogen. The amplitude of the 3161 cm^{-1} peak is insignificantly altered when heated at low temperature (below 700°C) but

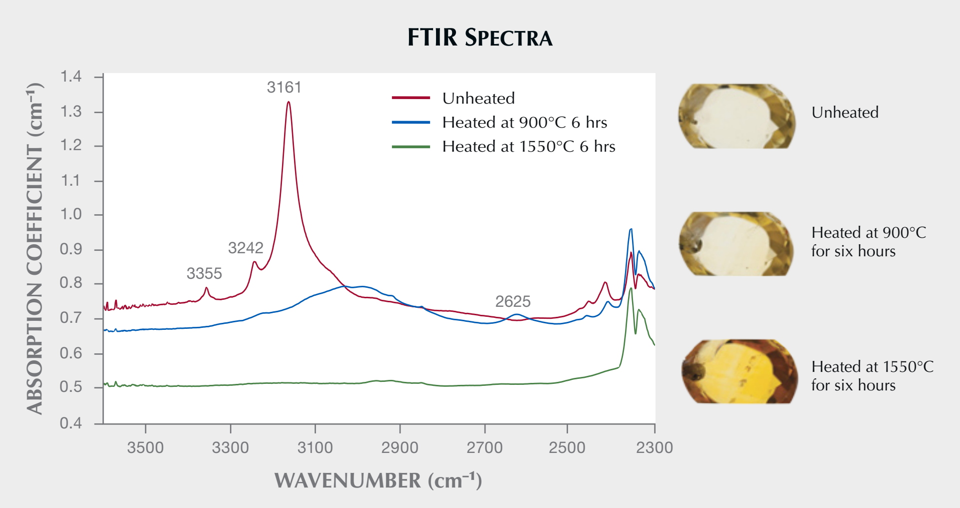

Figure 20. Sri Lankan sample no. 2801 showing a 3161 cm^{-1} series (red) in FTIR with initially light yellow color, then altered to 3000 cm^{-1} broad band series (blue) with a bit stronger yellow zone after heating at 900°C for six hours. Finally, the broad bands disappeared (green) and a much stronger yellow coloration was generated at 1550°C, thickness 3.748 mm, 190 ± 41 ppma Fe.

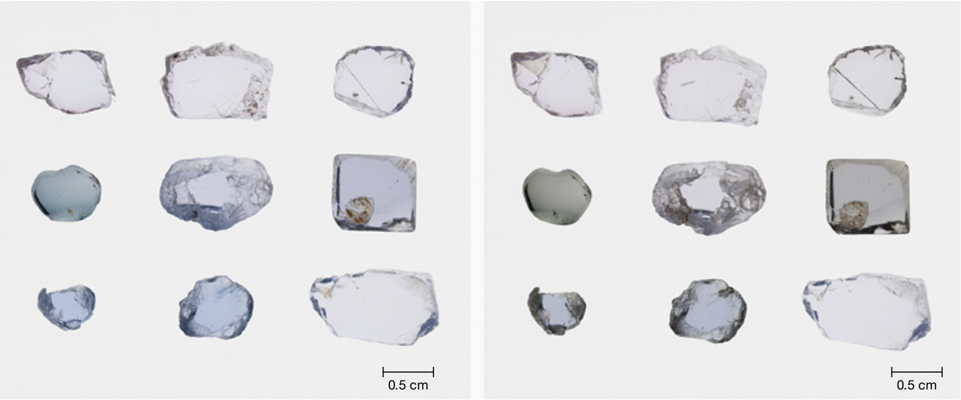

Figure 21. Color-calibrated photos of blue to violet spinels before heating (left) and after heating at 1000°C for four hours (right). There are three groups of spinel samples in this study: violet (top row), iron-dominated blue (middle row), and cobalt-dominated blue (bottom row). Photos by Sasithorn Engniwat.

can be greatly reduced when heated at 900°C and above, and sometimes converted to the 3000 cm^{-1} broadband series, and then it disappears at much higher heating temperature. Although the 3000 cm^{-1} broadband series might not be indicative of heat treatment in basalt-related yellow sapphires, it is able to indicate heat treatment in Sri Lankan yellow sapphires. Careful consideration should be exercised when using FTIR to identify heat treatment in corundum.

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Spectroscopic characteristics of low-temperature heated blue to violet spinel. Although spinel is rarely treated, there have been some heated spinels available in the trade. The effect of heat treatment on pink to red spinel has been previously reported (e.g., S. Saeseaw et al., "Distinguishing heated spinels from unheated natural spinels and from synthetic spinels," 2009, *GIA Research News*, https://www.gia.edu/gia-news-research-NR32209A; A. Peretti et al., "Heat-treatment of spinel," in *World of Magnificent Spinels: Provenance and Identification*, GRS Gemresearch Swisslab, 2015, pp. 269–278). Chromium-bearing spinel with pink to red color generally becomes darker after heat treatment, and the clarity of spinel containing particulate clouds can be significantly enhanced by heating between approximately 950° and 1150°C (S. Saeseaw et al., 2009).

In addition to the most popular pink to red spinel, another important and desirable variety is blue spinel, especially with a vibrant cobalt blue color. The dominant chromophores in blue to violet spinel includes Fe^{2+} and Fe^{3+} at both tetrahedrally (T) and octahedrally (M) coordinated sites of spinel structure as well as Co^{2+} at the T site (G.B. Andreozzi et al., "Color mechanism in spinel: A multi-analytical investigation of natural crystals with a wide range of coloration," *Physics and Chemistry of Minerals*, Vol. 46, 2019, pp. 343–360; V. D'Ippolito et al., "Color mechanism in spinel: Cobalt and iron interplay for the blue color," *Physics and Chemistry of Minerals*, Vol. 42, 2015, pp. 431–439). Previous works have revealed the application of cobalt diffusion treatment to enhance blue color in spinel (e.g., S. Saeseaw et al. "GIA lab reports on a new cobalt diffusion treatment of natural spinel," *GIA Research News*, 2015, https://www.gia.edu/gia-news-research/cobalt-diffusion-natural-spinel-report). A study on the heat treatment of blue spinel without external chemical diffusion is lacking in the literature, to our knowledge.

To understand the change of chromophores in blue to violet spinel caused by heat treatment, this preliminary study involved exploratory heat treatment of samples from various localities: Madagascar, Myanmar, Tanzania, and Vietnam. The samples were separated into three groups: violet, iron-dominated blue, and cobalt-dominated blue spinel (figure 21, left). UV-Vis-NIR spectrum of representatives in each group show relatively similar absorption spectra (figure 22), consisting of a strong UV-edge absorption at approximately below 330 nm; multiple absorption bands between 350 and 1100 nm of Fe^{2+}, Fe^{3+} at T and M sites; and multiple bands between 500 and 670 nm of Co^{2+} at the T site (Andreozzi et al., 2019; D'Ippolito et al., 2015). With a very similar absorption pattern between violet and blue iron-dominated spinels, the difference in color appearance is associated with different intensity of absorption bands which is more intense in iron-dominated blue spinel due to higher Fe concentrations (Andreozzi et al., 2019). The spinel samples were heated at 600°, 700°, 800°, 900°, and 1000°C in air and held for four hours at each heating temperature. Progressively heating from 600° to 1000°C showed that violet color changed little in this temperature range, whereas blue spinel became more grayish after heating at approximately 800°–900°C (figure 21, right). Heat treatment could affect the color appearance of iron-dominated blue spinel colored much more than cobalt-dominated blue spinel. After heat treatment (figure 23), the spectra displayed generally broader absorption bands, with less prominent bands below 650 nm and more prominent bands at around 920 nm. The broadening of the chromium emission peak in photoluminescence spectroscopy (PL) is an effective criterion for detecting heat treatment in spinel (e.g., Saeseaw et al., 2009; Peretti

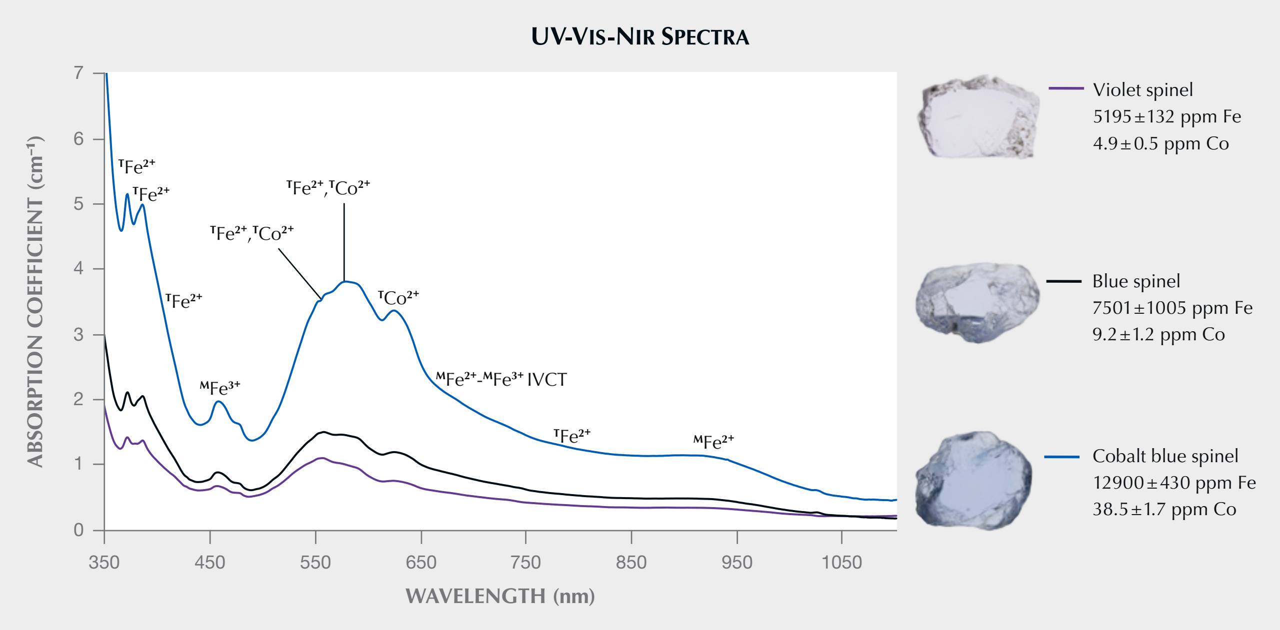

Figure 22. Representative UV-Vis-NIR spectra of unheated spinels for the three color groups. They have relatively similar absorption spectra with different intensities and some band positions, depending on Fe and Co contents. A series of Fe absorption bands in the spectrum consists of Fe^{2+} at T site ($^{T}Fe^{2+}$) bands at approximately 371, 385, 400, 558, 580, and 780 nm; Fe^{2+} at M site ($^{M}Fe^{2+}$) band at around 920 nm; Fe^{3+} at M site ($^{M}Fe^{3+}$) band at 457 nm; $^{M}Fe^{2+}$-$^{M}Fe^{3+}$ intervalence charge transfer (IVCT) band at about 655 nm; and Co^{2+} at T site ($^{T}Co^{2+}$) bands at approximately 558, 580, and 625 nm (Andreozzi et al., 2019; D'Ippolito et al., 2015). Fe and Co concentrations reported in the figure were analyzed by LA-ICP-MS.

et al., 2015). PL spectra of the treated samples in this study were also analyzed and showed that the Cr emission peak of the material broadened after heating at 800°–900°C. The change in color and spectroscopic data after heat treatment resulted from a direct spinel transforming to a partially inverse spinel (R. Widmer et al., "Effects of heat treatment on red gemstone spinel: Single-crystal X-ray, Raman, and photoluminescence study," *Physics and Chemistry of Minerals*, Vol. 42, 2015, pp. 251–260) as well as the changes of valence and site distribution of Fe chromophores in the spinel structure. The less desirable blue color of the treated spinel in this preliminary study, regardless of any improvement in clarity, suggests that the heat treatment of the blue to violet spinels was likely unintentional. In addition, as demand for gray colored spinels has increased in the trade over

Figure 23. UV-Vis-NIR spectra comparisons of cobalt blue (top), blue and violet spinels (bottom) in figure 22, before heating (solid line) and after heating at 1000°C for four hours (dashed line). Broader absorption bands, with less prominent bands below 650 nm and more prominent bands at around 920 nm, were observed.

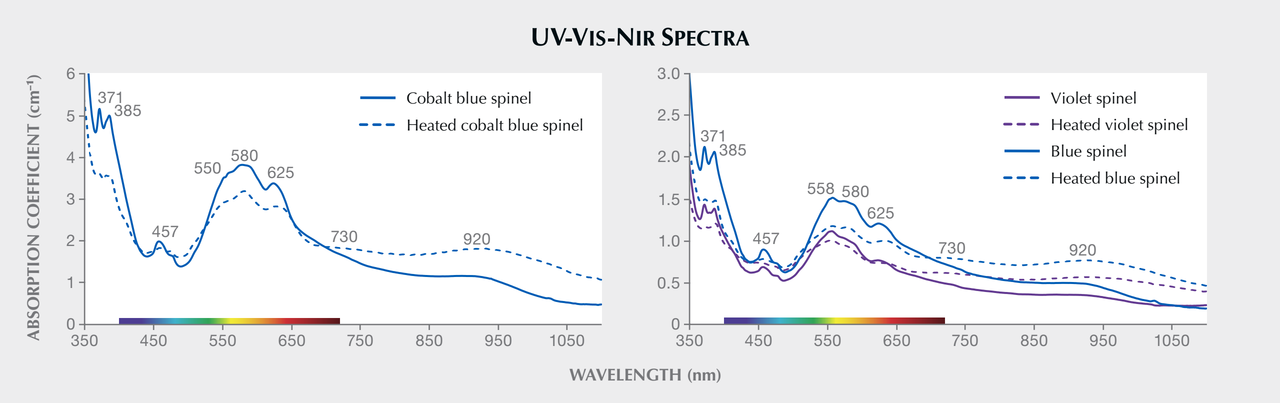

Figure 24. The GIA Library & Museum Facebook page stimulates spirited discussion among gemologists, bibliophiles, and gem enthusiasts. Photo composite by Robert Weldon/GIA.

the past few years (Spring 2019 GNI, p.130), some concerns about heat treatment in gray spinels should be raised.

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ANNOUNCEMENTS

GIA Library and Museum Facebook group. Dedicated to the beauty and fascination of gemological books and mineral exhibits, the Richard T. Liddicoat Gemological Library & Information Center and the GIA Museum launched a Facebook group on August 2, 2021.

The group has attracted over 600 bibliophiles, museum curators, gemological enthusiasts, students, researchers, and experts worldwide. It aims to provide greater digital access to our library and museum and stimulate enthusiastic discussion of the many themes covered in our collection of books, periodicals, and exhibits (figure 24). These subjects include gemology, geology, mineralogy, jewelry manufacturing, design, jewelry history, localities, and the gem industry.

Features include library-curated video segments and book reviews, commentary on rare bookplates or covers, and short interviews with notable library patrons. The Facebook group also highlights specific rare books from the library's digital collection on the Internet Archive (https://archive.org/details/gialibrary). A growing proportion of the library's notable rare books and manuscripts are digitized and offered to the public—free of charge. Over 700 books have been digitized, and the project is ongoing. The museum provides unique glimpses and the stories behind some of the amazing gems and minerals from GIA's collection.

To become a member of this group, please visit https://www.facebook.com/groups/gialibraryandmuseum

James Shigley receives Robert M. Shipley Award. Dr. James E. Shigley (figure 25), GIA's distinguished research fellow, has received the American Gem Society's Robert M. Shipley Award for his significant contribution to the science of gemology. The prestigious award was announced at the AGS Conclave in Dallas on September 13. Dr. Shigley was unable to attend the ceremony but was honored at GIA's Carlsbad campus by president Susan Jacques, research colleagues, and family, where he was presented with a plaque and pin acknowledging his decades of commitment to gem research.

During his almost 40-year career with the Institute, Shigley has authored or coauthored more than 85 *Gems & Gemology* articles, edited the *G&G In Review* book series, and been the face of GIA's research mission, lecturing extensively on gems and gem identification. He is also the recipient of the 2017 AGS Lifetime Achievement Award.

Figure 25. Dr. James Shigley is the 2021 recipient of the American Gem Society's Shipley Award. Photo by Kevin Schumacher.