

EDITORS

Thomas M. Moses | Shane F. McClure

Unusually Large CLINOHUMITE

Clinohumite, $(\text{Mg,Fe}^{2+})_9(\text{SiO}_4)_4(\text{F,OH})_2$, is a fairly rare collectors' stone with orangy yellow to brownish orange coloration. Faceted stones typically weigh <2 ct, but a few much larger stones have been cut (e.g., 36.56 ct, see L. Massi, "AIGS Bangkok inspects exceptional clinohumite from Tajikistan," *InColor*, Summer 2007, pp. 30–31). In the present report, we document the properties of an exceptionally large clinohumite weighing 84.23 ct ($32.6 \times 24.79 \times 17.77$ mm). For background information on the cutting of this stone, see Y. Zhukov, "Clinohumite—The mountain fire,"



Figure 1. This faceted clinohumite weighs an impressive 84.23 ct.

InColor, Spring 2011, pp. 48–51.

The stone was faceted into a pear brilliant and was brownish orange (figure 1). Internal features consisted of numerous two-phase inclusions (fig-

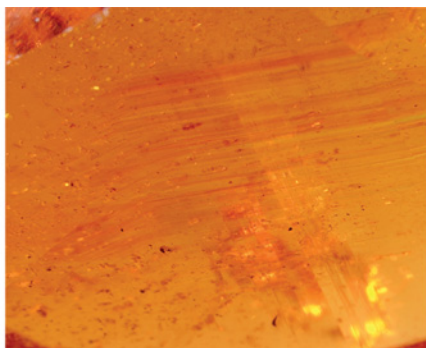
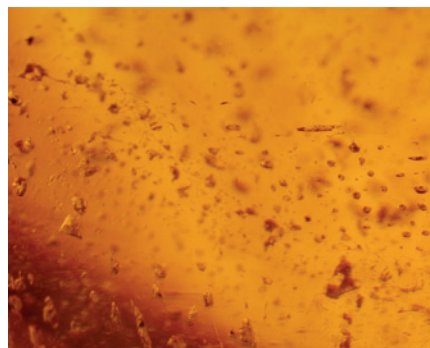
ure 2, left) and "fingerprints," as well as distinct angular brownish orange growth lines (figure 2, center), as documented previously in clinohumite (e.g., U. Henn et al., "Gem-quality clinohumite from Tajikistan and the Taymyr region, northern Siberia," *Journal of Gemmology*, Vol. 27, No. 6, 2001, pp. 335–339; and Winter 2004 GNI, pp. 337–338). Abundant twin planes were also seen with cross-polarized light (figure 2, right). The stone was inert to long-wave UV radiation, whereas short-wave UV produced moderate orange to strong chalky yellow fluorescence along the growth lines. Its Raman spectrum, along with gemological properties such as RI (1.635–1.670) and SG (3.21) values, confirmed that it was clinohumite. IR spectroscopy recorded typical absorptions for clinohumite, including a broad band centered at 3560 cm^{-1} due to OH stretching and additional bands at 4100 and 4510 cm^{-1} caused by MgOH units and Si-OH bonding,

Editors' note: All items were written by staff members of GIA laboratories.

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Figure 2. Microscopic observation of the clinohumite revealed two-phase (fluid-gas) inclusions, (left, magnified 35×), distinct angular brownish orange growth lines (center, 12×), and numerous twin planes (right, cross-polarized light, 75×).



respectively (R. L. Frost et al., "Near-infrared and mid-IR spectroscopy of selected humite minerals," *Vibrational Spectroscopy*, Vol. 44, 2007, pp. 154–161, <http://dx.doi.org/10.1016/j.vibspec.2006.11.002>). The FTIR and Raman spectra of this stone are available in the *G&G* Data Depository (gia.edu/gandg). Energy-dispersive X-ray fluorescence (EDXRF) spectroscopy detected major amounts of Mg, Fe, and Si, and traces of Ti and Mn, as expected for clinohumite.

There are two main localities that produce gem-quality clinohumite—the Pamir Mountains of Tajikistan and the Taymyr region of northern Siberia (Massi, 2007). Unfortunately, the geographic origin of the present clinohumite is unknown. It is the largest gem-quality clinohumite ever tested at GIA.

Kyaw Soe Moe and Wai Win

DIAMOND

Black Diamond, Colored by Strong Plastic Deformation

Black color in diamonds can have various natural or artificial causes, from inclusions (abundant graphite or pinpoints, or dense clouds) to heating or extremely strong irradiation. The New York laboratory recently examined a black diamond colored by another mechanism.

This round-cut diamond weighed

Figure 3. The black color of this 0.85 ct diamond is attributed to very strong plastic deformation.

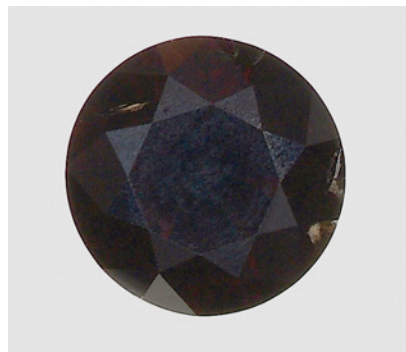


Figure 4. With magnification and very strong lighting, the diamond in figure 3 showed a dark brown color with banded linear distribution. Magnified 70x.

0.85 ct ($5.70 \times 5.78 \times 3.87$ mm) and was color graded as Fancy black (figure 3). Viewed with magnification and very strong fiber-optic illumination, it revealed fractures and mineral inclusions, as well as a dark brown color with banded linear distribution (figure 4). Strong plastic deformation and the related linear banding were also clearly revealed in the DiamondView. Its mid-infrared spectrum showed strong N-related absorption in the one-phonon region and a weak H-related feature at 3107 cm^{-1} . Also recorded were very strong absorptions from amber centers at ~ 4170 and 4070 cm^{-1} , with intensities of 2.0 and 1.1 cm^{-1} , respectively.

The vacancy cluster, a diamond lattice defect closely related to plastic deformation, usually absorbs visible light from $\sim 600\text{ nm}$ to lower wavelengths. When its concentration is very high, such as in this diamond, its absorption extends across the entire visible light region and blocks the vast majority of light. It is very rare to see a natural gem diamond with such strong plastic deformation that it causes a black appearance. This stone demonstrates yet another cause of natural black color in diamond.

Wuyi Wang

Coated Black Diamond

Gems & Gemology has reported on a number of interesting black diamonds in recent years (see the Spring 2007, Winter 2007, Fall 2008, and Summer



Figure 5. This 1.29 ct diamond proved to be coated to enhance its black color appearance.

2010 Lab Notes sections and S. V. Titkov et al., "An investigation into the cause of color in natural black diamonds from Siberia," Fall 2003, pp. 200–209). This color, when natural, is typically caused by dark/intense mineral or cloud inclusions. It can also be induced by artificial irradiation or graphitization along fractures due to heating (naturally or in the laboratory).

Recently, the New York laboratory received a 1.29 ct black pear shape (figure 5) for color origin determination. Infrared absorption spectroscopy confirmed it was a type Ia diamond with hydrogen impurities. As expected, it was inert to both long- and short-wave UV radiation. However, microscopic examination revealed a distinctly lighter color along the facet junctions (figure 6), and these areas showed contrasting luminescence in the

Figure 6. In reflected light, the 1.29 ct diamond displays a distinctly lighter color along the facet junctions. Magnified 30x.



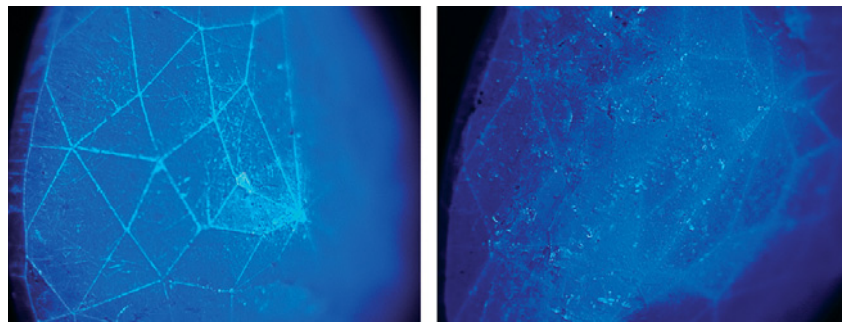


Figure 7. In the DiamondView, the coating on the black diamond was apparent from the different luminescence of the facet junctions, where it had apparently worn off (left). After cleaning with acetone and corundum powder (with client permission), the coating appeared smeared and the junctions were less distinct (right).

DiamondView (figure 7). The girdle also showed uneven concentrations of dark color, and there were scratches on the pavilion that were lighter than the black bodycolor; both of these could be easily observed with the microscope. Feathers within the diamond were dark colored due to black natural inclusions. It was obvious that this diamond, though rather dark, had been coated to further enhance its color.

This was our first encounter with a coated black diamond. Because of the coating, we did not issue a color grade. In this case, the black coating made the stone appear a deeper, more even black. Although coating a black diamond can improve its overall appearance or color distribution, in this case the treatment was detectable with a microscope.

Erica Emerson

Coated Diamond with Spectroscopic Features of a Natural-Color Pink

Coated diamonds are fairly commonly encountered, both in the trade and the grading lab. Most coatings consist of a thin film applied to one or more pavilion facets, often at or near the girdle edge, though sometimes the coating will completely cover the diamond's surface. Because of the value of natural-color pink diamonds, pink is a common choice for such coatings, which are intended to deepen a weak bodycolor or to mask an undesired one (e.g., Winter 2010 Lab Notes, pp. 299–300). This treatment can be identified through microscopic observation and UV-Vis spectroscopic features. In the case of pink-coated diamonds, the typical absorption band at ~520 nm (see A. H. Shen et al.,

"Serenity coated colored diamonds: Detection and durability," Spring 2007 *G&G*, pp. 16–34, <http://dx.doi.org/10.5741/GEMS.43.1.16>) is easily distinguished from the ~550 nm band in natural-color stones.

The 1.05 ct heart-shaped diamond in figure 8, recently submitted for color grading, initially received a grade of Fancy Light brown-pink. Its UV-Vis spectrum showed the broad ~550 nm absorption band (figure 9) typical of naturally colored pink diamonds. With magnification, however, a coating was clearly visible on the pavilion facets (figure 10). After the coating was removed by boiling the stone in acid, the color grade was revised to J (figure 8, right).

Because the normally diagnostic absorption band for a pink coating was shifted from 520 to 550 nm, spectroscopy alone would not have detected this coating. This reinforces the essential role of conventional observation in gem identification.

Sally Chan

Colorless Untreated Diamonds with High Levels of Strain

Diamonds form under enormous heat and pressure deep in the earth, and endure additional stresses during their journey to the surface. Such stresses can cause irregularities in their lattice structure, which can impart color to a diamond in a variety of ways. For example, brown color in type IIa diamonds is believed to be caused by vacancy clusters, and the depth of color generally corresponds to the degree of strain (D. Fisher et al., "The vacancy as a probe of the strain in type IIa diamonds," *Diamond and Related Materials*, Vol. 15, 2006, pp. 1636–1642, <http://dx.doi.org/10.1016/j.diamond.2006.01.020>; D. Fisher, "Brown diamonds and high pressure high temperature treatment," *Lithos*, Vol. 112S, 2009, pp. 619–624, <http://dx.doi.org/10.1016/j.lithos.2009.03.005>). Since high-pressure, high-temperature (HPHT) treatment can remove brown color from type IIa diamonds but has a minimal effect

Figure 8. This 1.05 ct diamond owed its apparent Fancy Light brown-pink color (left) to a coating. After the coating was removed by acid cleaning, the diamond was given a color grade of J (right).



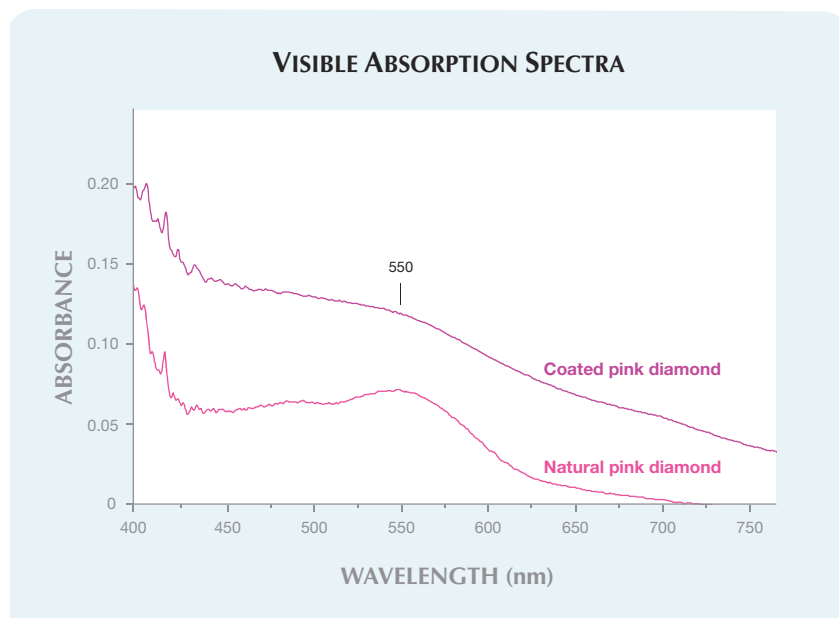


Figure 9. The coated diamond's absorption band at ~550 nm was very similar to that of a naturally colored pink diamond. Both spectra were collected at liquid-nitrogen temperature.

on strain, the presence of strain can be an important criterion for identifying HPHT-annealed stones.

Recently, the Carlsbad laboratory received two colorless type IIa diamonds for identification: a 0.90 ct E-color marquise and a 0.73 ct D-color round brilliant. Based on gemological and spectroscopic features, these diamonds were found to be natural and untreated. However, in the course of this determination, we also noticed that both showed an unusually high degree of "tatami" strain (figure 11) when viewed with cross-polarized

light. The strong strain patterns were more consistent with those seen in brown diamonds. Typically, type IIa colorless diamonds show a tatami pattern, but with a lower concentration of strain laminations.

In addition to visual assessment using crossed polarizers, an indirect but relatively reliable indicator of strain is the peak width of certain defects determined from photoluminescence (PL) spectra taken at liquid nitrogen temperature. The PL spectrum of the 0.90 ct diamond showed

both the neutral (575 nm) and negatively charged (637 nm) NV centers; the full width at half maximum (FWHM) for these centers was 0.89 and 1.56 nm, respectively. As with the observed strain, these values were much higher than is commonly seen in untreated colorless diamonds. A compilation of calculated FWHM values for 250 untreated diamonds in the D-E range showed that the NV⁰ center had an average width of 0.29 nm with a standard deviation of 0.07 nm; the highest value was 0.65 nm. For the NV⁻ center, the average width was 0.30 nm with a standard deviation of 0.10 nm; the maximum was 0.79 nm. These values are far lower than those for the 0.90 ct diamond.

It is unusual to find natural-color diamonds that endured such a high amount of stress during their history and yet remained colorless. One possible explanation is that the associated brown coloration was naturally annealed out during their geologic history.

Sally Eaton-Magaña

HPHT Treatment for Subtle Color Enhancement of Diamond

It is well known that HPHT annealing can remove brown coloration from natural type IIa diamonds, making them colorless to near-colorless. While a significant number of HPHT-

Figure 10. A pink coating on the diamond's pavilion facets was clearly visible with magnification (here, 40×).



Figure 11. These untreated natural type IIa diamonds (0.90 ct E color, left; 0.73 ct D color, right) experienced a high amount of stress, as evidenced by the extensive "tatami" strain seen in cross-polarized light. They are unusual since they do not show any of the brown color that typically correlates with such strain. (The apparent brown color in these images is an artifact of the lighting.)

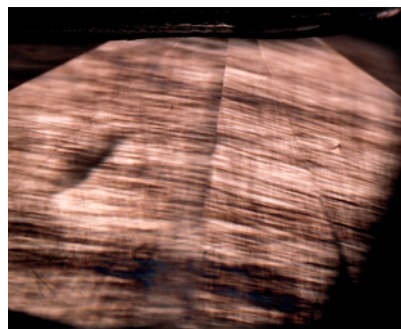




Figure 12. Shown here after HPHT treatment (E–F color, 1.74–2.57 ct), these type IIa diamonds originally had color grades of J–M. This demonstrates that HPHT annealing is being used to make subtle color improvements in such diamonds.

treated type IIa diamonds have been seen in gem laboratories over the past decade, little has been published on the characteristics of the starting materials. Recently, however, the New York laboratory had the opportunity to follow four diamonds through the HPHT treatment process.

When they were first received, three of the four round diamonds (1.8–2.6 ct) were color graded in the J–K range, with the fourth being M color. Photoluminescence spectroscopy confirmed that they were naturally colored. Infrared spectroscopy showed they were very pure type IIa; only one stone had an extremely weak hydrogen-related absorption, at 3107 cm^{-1} . When the diamonds reappeared in the lab very recently, their color ranged from E to F (figure 12). They also showed a 2–5% weight loss, consistent with the necessary repolishing after treatment. Their

photoluminescence spectra revealed the exact changes that were expected as a result of HPHT annealing.

Though the general impression of HPHT treatment in the trade is that it is used to turn obviously brown diamonds colorless, this experience suggests that such treatment may also be used to achieve more subtle improvements in diamond color.

Wuyi Wang

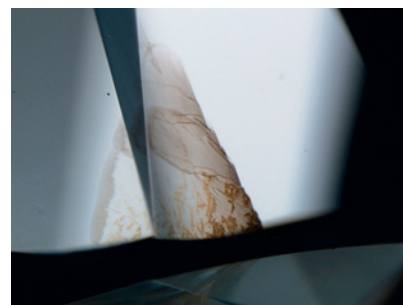
An Interesting Luminescent Cleavage in Diamond

Although diamond is the hardest natural substance, it still is susceptible to breakage along its cleavage directions. Often mistakenly described as a “fracture,” cleavage is one of the most common clarity characteristics in gem-quality diamonds, and generally is of little interest to gemologists. However,

the Carlsbad laboratory recently graded a type Ia colorless round brilliant with a remarkable cleavage-related feature. The cleavage showed prominent brown radiation staining, suggesting that radioactive fluids had been present in the post-growth environment (figure 13). When the diamond was viewed face-up in the microscope with darkfield illumination, the cleavage also exhibited pronounced green luminescence to visible light (figure 14, left); fiber-optic illumination made the green luminescence even more dramatic. Radiation stains are well documented in the gemological literature (e.g., J. I. Koivula, *The MicroWorld of Diamonds*, Gemworld International, Northbrook, Illinois, 2000).

Green luminescence in diamond is known to be produced by the H3 lattice defect (503.2 nm), which consists of two nitrogen atoms separated by a vacancy [N–V–N]⁰. When examined in the DiamondView, the stone showed clear green fluorescence along the cleavage (figure 14, right). Using this image as a map, we collected photoluminescence data from the cleavage area. In addition to the H3 defects, analysis also revealed high concentrations of the 3H interstitial defect (503.4 nm). An interstitial defect occurs when a carbon atom is displaced from its original lattice position, typically by radiation. Thus, the occurrence of 3H with the green luminescing H3 defects is consistent

Figure 13. The brown coloration confined to the cleavage area of this diamond resulted from the interaction of radioactive fluids in the post-growth environment. Magnified 20×.



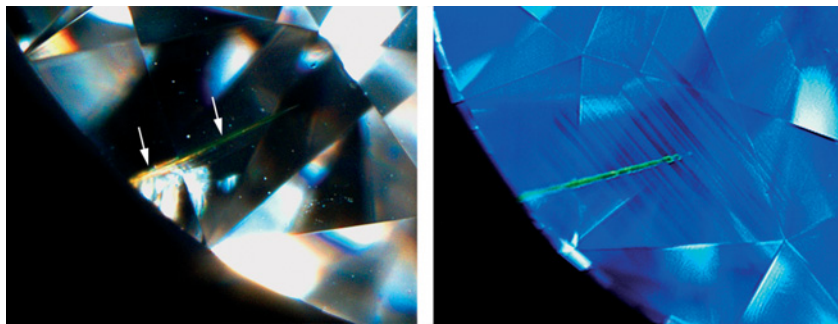


Figure 14. Darkfield illumination revealed green luminescence along the cleavage shown in figure 13 (left, see arrows; magnified 20x). In the DiamondView (right), green luminescence from the H3 defect was clearly visible. Magnified 30x.

with the microscopic evidence of radiation staining.

This is one of the more unusual examples of cleavage we have seen in the Carlsbad laboratory. The diamond's cleavage, radiation staining, and green luminescence all reveal important information about its history and indicate that radiation exposure occurred naturally.

Nathan Renfro and
Christopher M. Breeding

A Large HPHT-Annealed Pink Diamond

Unlike irradiation treatment, which usually adds additional color, annealing a natural diamond under HPHT

Figure 15. This 21.73 ct Light pink diamond proved to be HPHT annealed.



conditions can remove preexisting colors as well as create new ones. When a suitable type IIa brown diamond is HPHT annealed at temperatures appropriate for removing brown but not pink coloration, then the preexisting pink color can be enhanced. Such HPHT-treated type IIa pink diamonds have been available for more than 10 years (e.g., Fall 2000 Lab Notes, pp. 254–255).

The New York laboratory recently received the large pink diamond in figure 15 for identification. This marquise brilliant (28.15 × 15.41 × 7.71 mm) weighed 21.73 ct and was color graded Light pink. The color was distributed evenly throughout the stone with no detectable pink graining, and it showed typical blue fluorescence when examined in the DiamondView. The mid-IR spectrum showed type IIa features with no detectable hydrogen-related absorption at 3107 cm⁻¹. A weak band centered at ~550 nm was present in the UV-Vis absorption spectrum at liquid nitrogen temperature. This band is very common in naturally colored pink-to-red diamonds and can be made more visible by removing other unwanted colors. Photoluminescence spectra collected at liquid nitrogen temperature with varying laser excitations confirmed that this diamond was HPHT annealed.

HPHT annealing has become a very common type of diamond color treatment. With advances in processing techniques, a substantial number

of large diamonds can now be treated successfully, though these can still be identified by gem labs. This 21.73 ct pink diamond is one of the largest HPHT-treated pink diamonds identified in GIA's laboratories.

Wuyi Wang

SYNTHETIC DIAMOND

Gem-Quality CVD Synthetic Diamonds from Gemesis

In recent years, limited quantities of gem-quality synthetic diamonds produced by chemical vapor deposition (CVD) have reached the market. Most of these have come from Apollo Diamond Inc. (Boston, Massachusetts). We recently examined similar products introduced by Florida-based Gemesis Corp., better known for its HPHT-grown synthetic diamonds (J. E. Shigley et al., "Gemesis laboratory-created diamonds," Winter 2002 *GeG*, pp. 301–309). In November 2010, the company announced plans to market CVD-grown synthetics.

GIA examined 16 CVD synthetic diamonds (e.g., figure 16) that were faceted as round brilliants with the exception of one rectangular cut. They ranged from 0.24 to 0.90 ct, with an average weight of 0.46 ct. They were colorless (3 samples), near-colorless (11), and lightly colored (2). For the most part, clarity grades fell between IF and VVS, due to internal graining and a few pinpoint inclusions. Only four of the 16 samples had VS clarity.

Infrared absorption spectroscopy revealed that all of the CVD synthetic diamonds were type IIa. Unlike typical as-grown CVD products, no defect-related absorptions were recorded in either the mid- or near-infrared regions. Photoluminescence analysis of all samples showed moderately strong emission from the H3 optical center (zero-phonon line at 503.2 nm), moderately strong emissions from NV centers (575.0 and 637.0 nm), and moderate to strong emissions from the [Si-V]⁻ center (doublet at 736.6 and 736.9



Figure 16. These CVD synthetic diamonds were produced by Gemesis. The 0.39 ct round brilliant on the left was graded F color and VVS₂ clarity; the 0.83 ct sample on the right was graded I-VVS₂.

nm). In four samples, the [Si-V]⁻ concentrations were relatively high and could even be detected in the UV-Vis absorption spectra. A notable feature of these synthetic diamonds was their weak to moderate green fluorescence to short-wave UV radiation. Most were inert to long-wave UV radiation, with only five samples showing very weak green fluorescence. In the DiamondView, they exhibited strong green fluorescence and noticeable blue phosphorescence; characteristic growth striations also were easily seen.

Gemological and spectroscopic observations strongly suggested that these CVD synthetic diamonds were annealed after their growth, presumably to improve their color and transparency. This study confirms that the quality of CVD synthetic diamonds continues to improve. Nevertheless, gemological and spectroscopic features can clearly separate Gemesis CVD synthetics from natural diamonds.

Wuyi Wang and Thomas M. Moses

Treated Synthetic Diamonds with Pink Color Intensified by Fluorescence

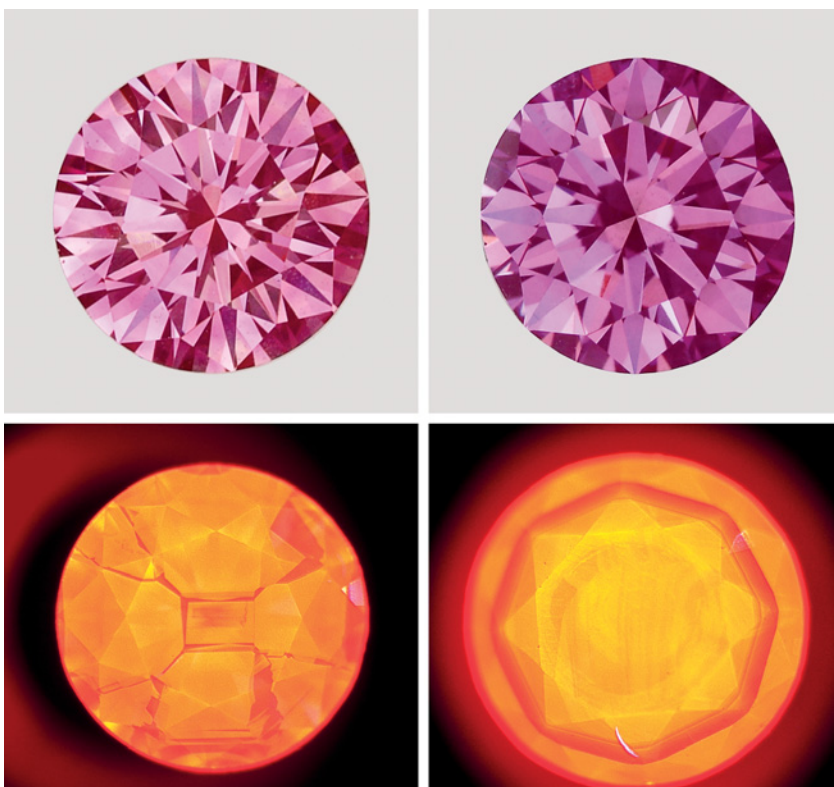
A combination of irradiation and HPHT annealing can create pink to red colors in both natural and synthetic diamonds. We have reported on a number of these treated stones over

the past few years (see, e.g., Lab Notes: Winter 2005, pp. 341–343; Spring 2010, pp. 51–52 and 52–54; and Winter 2010, pp. 300–301). Two more examples recently submitted (on sepa-

rate occasions) to the New York laboratory showed an unusual fluorescence effect.

The two round brilliants (0.47 and 0.63 ct; figure 17) were color graded Fancy Vivid purplish pink and Fancy Deep purple-pink, respectively. Their mid-IR spectra indicated they were type Ib, with a very low concentration of isolated nitrogen. However, they did not display the “tatami” strain pattern expected for such diamonds, so we tested them using the DiamondView. The 0.47 ct round brilliant showed the cuboctahedral pattern typical of HPHT synthetic growth, while the 0.63 ct sample had a CVD growth pattern; both displayed strong orange luminescence (figure 17, bottom). Microscopic examination revealed strong color zoning along growth sectors in the 0.47 ct synthetic, but this effect was very subtle in the 0.63 ct sample

Figure 17. These treated-color synthetic diamonds (0.47 and 0.63 ct) have an evenly distributed face-up color. Their DiamondView images (bottom) display the patterns typical of HPHT (left) and CVD growth (right).



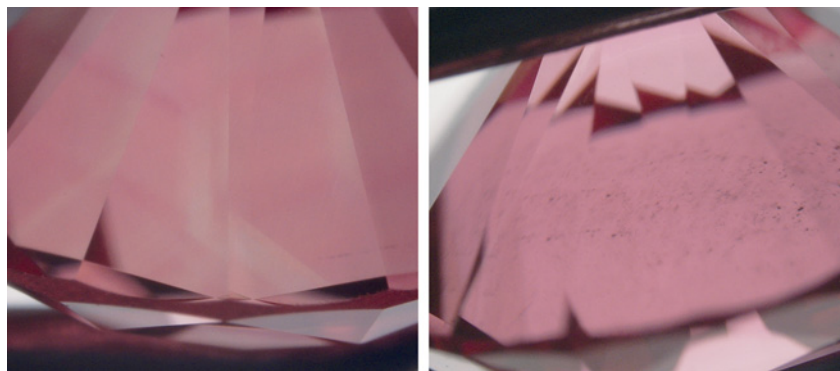


Figure 18. In diffused light, the 0.47 ct pink synthetic diamond displayed strong, uneven color zoning along growth sectors (left, magnified 45×). The 0.63 ct sample only showed subtle color zoning (right, 35×).

(figure 18). The former had only a VVS₁-grade feather in the lower girdle facet, while the latter contained graphitized feathers and tiny black particles (possibly graphite).

The diamonds' UV-Vis-NIR absorption spectra were collected at liquid-nitrogen temperature with broadband illumination (Avantes AvaLight-HAL-S) and a CCD detector (Ocean Optics HR-4000). This light source has significant emission in the visible-light region (>400 nm) but very little in the UV region. The 575 nm feature (zero-phonon line of NV⁰) appeared as a negative peak (figure 19), caused by fluorescence. Strong fluorescence was also present in the ~650–825 nm region from the NV⁻ center (637 nm). In addition, a sharp peak at 595 nm was recorded in the absorption spectra, and this peak, together with the strong NV features at 575 and 637 nm, were also detected in low-temperature photoluminescence spectra. These features suggest that both pink synthetic diamonds had undergone post-growth treatments, such as irradiation and annealing. These treatments caused the vacancies to migrate and combine with preexisting isolated nitrogen atoms, forming the NV centers that produce the strong purplish pink color.

The absorption spectra of most pink diamonds that are naturally colored by NV centers show a transmission window in the red region with a

smooth, gentle slope (indicated by the blue dotted line in figure 19). These samples had a more pronounced window (represented by the shaded region) due to the emission from NV⁻ centers. Fluorescence from the NV⁻ center, activated by visible light, strongly enhances pink to red color in diamond. This phenomenon is not as obvious in natural-color pink diamonds that are colored by

NV centers, due to their much lower concentrations.

Kyaw Soe Moe

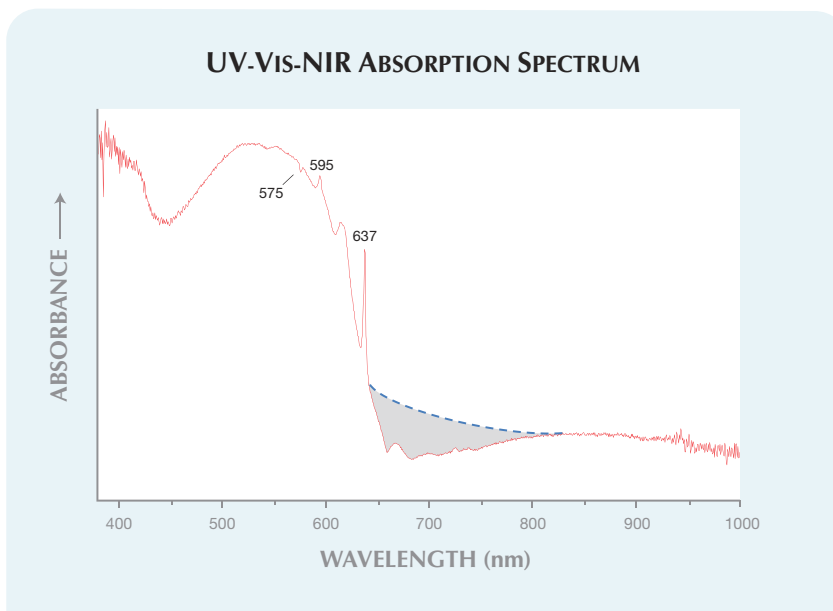
PEARL

Cultured Pearls from *Pteria Sterna* With Plastic Bead Nuclei

It is generally agreed that freshwater mother-of-pearl shell nuclei produce the best results for both saltwater and freshwater beaded cultured pearls. Occasionally, other materials such as saltwater shell, ceramic, plastic, or wax have been used, but these are not common due to high rejection and mortality rates (P. C. Southgate and J. S. Lucas, Eds., *The Pearl Oyster*, Elsevier, Amsterdam, 2008).

Recently, we received two yellowish brown samples (both ~8 mm in diameter; e.g., figure 20) for identification. Microradiography revealed centrally positioned beads that were noticeably more transparent to X-rays than typical freshwater shell nuclei. The beads appeared to have distinct

Figure 19. In this UV-Vis-NIR absorption spectrum (here, of the 0.47 ct sample), the unusual shaded region represents the strong emission of NV⁻ centers, which contribute to the pink bodycolor. In most natural-color pink diamonds, this region normally shows the absorption indicated by the blue dotted line.



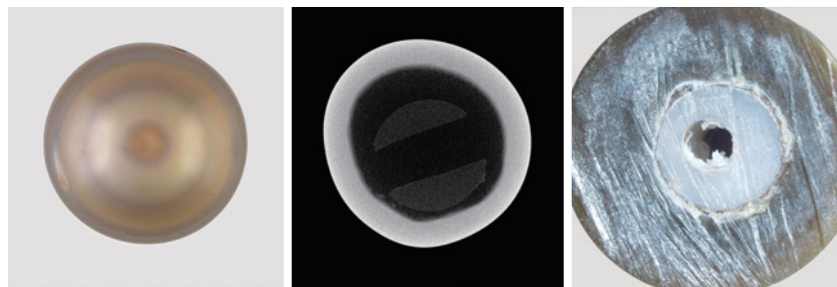


Figure 20. This cultured pearl from *Pteria sterna* (left, ~8 mm in diameter) proved to have a plastic bead. X-ray computed microtomography of a similar sample (center) showed the presence of a near-X-ray-transparent bead as well as a drill hole. When the first sample was sawn in half (right), a white plastic bead was revealed inside.

uniform edges and drill holes, although the cultured pearls themselves were not drilled. One had a slight exterior depression apparently corresponding to one end of the drill hole.

Further gemological testing (UV fluorescence, UV-Vis reflectance spectroscopy, and EDXRF analysis) indicated that these samples were from the saltwater mollusk *Pteria sterna*, a species native to the Sea of Cortez in Mexico. Although we have occasionally seen cultured pearls with near-X-ray-transparent beads, and reported on some of them in the Lab Notes section (e.g., Summer 1988, pp. 114–115; Spring 1994, p. 45), we decided to acquire the samples from the client in order to investigate further and identify the material that was used.

One of the two samples was examined using X-ray computed microtomography to obtain more detailed images of its internal structure (figure 20, center). The resulting images confirmed, with more detail, a distinct uniform bead outline and drill hole. The second sample was cut in half for visual observation and Raman spectroscopic analysis. The exposed bead was semitranslucent, white, with a plastic-like appearance (figure 20, right), and was easily scratched using a metal probe. Raman spectroscopy showed a dominant peak at 997 cm^{-1} , which corresponded to predominantly aromatic functional groups of possible polystyrene materials.

This is the first time we have reported on plastic beads used in *Pteria*

sterna mollusks. Whether this atypical bead material is becoming more prevalent is unknown.

[Note: Though we have used the term *cultured pearl* in this note for simplicity, we recognize that in this instance the usage may not be in agreement with recognized definitions, e.g., the CIBJO *Pearl Book*.]

Chunhui Zhou and Akira Hyatt

Large Conch Pearl

Pearls from the Queen conch, *Strombus gigas*, have long been collectors' items, prized for their unique and attractive color and surface structure. Conch pearls come in a range of colors from white to yellow to brown, but the most desirable is pink.

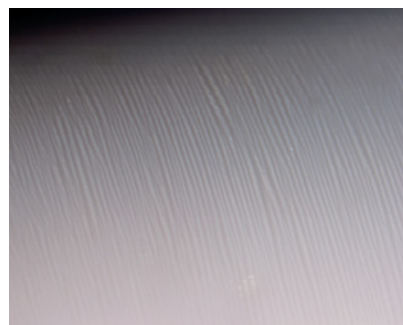
Recently, a large conch pearl mounted in a pendant (figure 21) was submitted to the New York laboratory for identification. The baroque-shaped light pink to white specimen measured $35.20 \times 21.65 \times 16.33\text{ mm}$, weighed approximately 100 ct, and showed a very fine flame structure (figure 22). X-radiography revealed an unusually large number of layered natural growth structures, which corresponded to the contours of the pearl's surface.

Raman and UV-Vis reflectance spectra were collected from both the light pink and white regions of the pearl. Raman spectroscopy of the pink area with 514 nm excitation showed two small peaks at 1520 and 1130 cm^{-1} , which are characteristic of the pigments responsible for pink color in

Figure 21. The very large conch pearl in the pendant weighs approximately 100 ct. By comparison, most conch pearls (left, 8.04 ct, $13.53 \times 10.65 \times 7.95\text{ mm}$) are much smaller, as are South Sea (second from right, 13.00 mm) and akoya cultured pearls (right, 6.75 mm).



Figure 22. The large conch pearl in figure 21 displayed a very fine flame structure. Magnified 100 \times .



conch pearls. These peaks were barely visible in the spectrum of the white area. The UV-Vis reflectance spectrum of the pink area also showed stronger absorption between 480 and 560 nm than did that of the white area; this absorption in the green region of the spectrum is responsible for the pink color. All of these results suggested that the pink color was natural and not the result of treatment.

Though most conch pearls are small (see E. Fritsch and E. B. Misiorowski, "The history and gemology of Queen conch 'pearls,'" *Winter 1987 G&G*, pp. 208–221), large ones have been reported. The 2005 "Allure of Pearls" exhibit at the Smithsonian Museum of Natural History (www.mnh.si.edu/exhibits/Pearls/index2.htm) featured two loose pink conch pearls belonging to collector Susan Hendrickson that weighed 17.70 and 22.40 ct, as well as the Queen Mary Brooch set with two pink conch pearls weighing 24.90 and 28.10 ct. We reported on another large conch pearl in 2008 (125.26 ct; Spring 2008 Lab Notes, p. 72); though that baroque specimen was somewhat larger than this pearl, the bodycolor was a mix of pink, orange, and white. Most conch pearls are far smaller (again, see figure 21), making this specimen a true rarity, in both size and quality.

JaeWon Chang and Akira Hyatt

SAPPHIRE

Natural and Synthetic Green Sapphires with Similar Color but Remarkably Different Chromophores

Recently, two green gems were submitted to the New York laboratory. One stone (12.80 × 10.90 × 8.75 mm; figure 23, left), mounted in a ring with numerous transparent near-colorless stones, was easily identified as a natural sapphire by its inclusions and trace-element content measured by LA-ICP-MS. The other gem (2.07 ct; 7.77 × 6.09 × 4.93 mm) had no readily apparent inclusions (figure 23, center). Careful examination of the latter gem in immersion revealed faint curved color banding,

indicative of a melt-grown synthetic. LA-ICP-MS analysis confirmed that it was synthetic sapphire, as cobalt was the only trace element detected (average 25 ppm). Previous reports on cobalt-doped melt-grown synthetic sapphires were published in Spring 1996 Lab Notes (p. 51), Spring 2001 Gem News International (pp. 75–77), and Spring 2008 Lab Notes (pp. 72–73).

Sapphires—whether natural or synthetic—with such a distinct green coloration are rarely seen in the lab, and it is quite interesting that two very different compositions produced such a similar coloration. UV-Vis-NIR spectroscopy of the natural sapphire showed an absorption spectrum typical of corundum with a high iron content: strong lines at 450, 388, and 377 nm from Fe³⁺, and broad bands at 580 and 700 nm due to Fe²⁺-Ti⁴⁺ intervalence charge transfer (figure 24). In addition, the 1050–1075 nm band (due to Fe³⁺) was surprisingly strong. It is well known that a high content of Fe³⁺ induces a yellow coloration in sapphire, and even small concentrations of Fe²⁺-Ti⁴⁺ pairs contribute a blue color component. The resulting green color of this sapphire, which had an average Fe content of 1155 ppm, is quite consistent with its composition.

Polarized UV-Vis-NIR spectra of

the synthetic sapphire showed only two broad bands centered at 450 and 660 nm, which have been attributed to Co³⁺ substituting for octahedral Al³⁺ (e.g., R. Müller and Hs. H. Günthard, "Spectroscopic study of the reduction of nickel and cobalt ions in sapphire," *Journal of Chemical Physics*, Vol. 44, No. 1, 1966, pp. 365–373, <http://dx.doi.org/10.1063/1.1726471>). The two band positions were virtually identical for the ordinary and extraordinary rays, but the intensity of the 660 nm band was greater for the ordinary ray. Furthermore, a weak sharp line at approximately 691 nm was visible in the ordinary ray spectrum. A transmission window near 500 nm in the spectra of both samples is largely responsible for their similar green coloration.

Color coordinate calculations using the spectra reported in Müller and Günthard (1966) for 2-mm-thick wafers gave L*a*b* coordinates of 81/51/20 and 86/–34/36 for the ordinary ray and extraordinary ray, respectively (again, see figure 23). These correspond to a coloration that is remarkably similar to the synthetic sapphire reported here, supporting our conclusion that its color is due to Co³⁺.

Emily V. Dubinsky

Figure 23. The 12.80-mm-long sapphire on the left was identified as natural, with its color due to a high iron content. The 2.07 ct gem on the right is a cobalt-bearing synthetic sapphire. For comparison, color coordinates (far right) were calculated for optical spectra reported in Müller and Günthard (1966) for Verneuil synthetic sapphire containing Co³⁺ (ordinary ray, top; extraordinary ray, bottom).



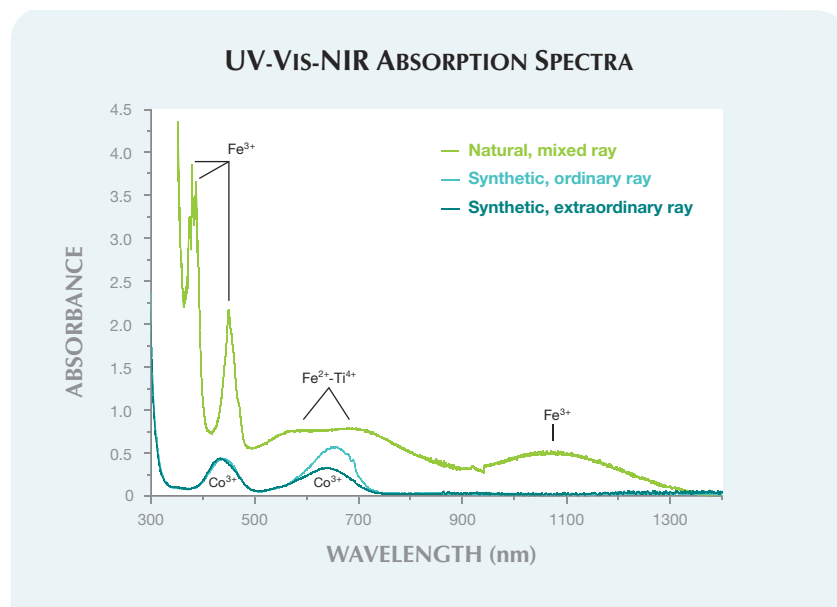
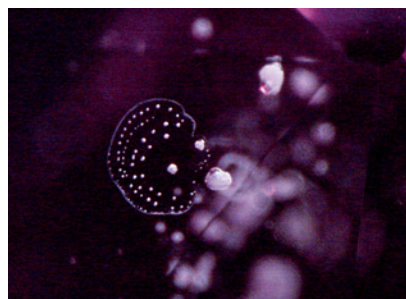


Figure 24. In these UV-Vis-NIR spectra, the natural green sapphire shows strong Fe-related features that are absent from the synthetic sample, which has bands attributed to Co^{3+} . The approximate path lengths of the beam are 9 mm for the natural stone and 5 mm for the synthetic sample.

Unusual Be-Diffused Pink Sapphire . . . A Cautionary Note

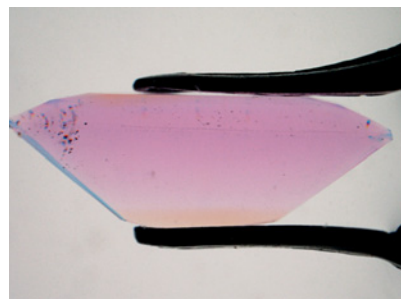
The Carlsbad laboratory recently examined a 1.40 ct pink sapphire with unusual orange color zones that was submitted for a sapphire report. Initial microscopic observation revealed numerous thermally altered light-colored crystals, some of which were surrounded by discoid “fingerprints” (fig-

Figure 25. The altered appearance of these crystals, which are probably zircon, is consistent with the high-temperature heat treatment necessary for Be diffusion of the host sapphire. Magnified 70 \times .



ure 25), an inclusion scene consistent with high-temperature heat treatment. Immersion revealed a planar orange zone near the culet and a shallow orange zone parallel to the table facet (figure 26). Orange color zones in heat-treated pink sapphires may be indicative of beryllium-diffusion treatment. However, when the stone was tested by laser-ablation inductively coupled plasma-mass spectrometry

Figure 26. The orange color zones along the culet and table of this pink sapphire, as seen immersed in methylene iodide, were caused by Be-diffusion treatment. Magnified 10 \times .



(LA-ICP-MS) in the girdle area (as is GIA's standard practice, to avoid placing an ablation spot in an area that could affect the stone's appearance), no Be was detected. This was not surprising because there was no orange color near the girdle.

The orientation of the orange zoning in this sapphire was perpendicular to the c-axis. This is a common orientation for natural orange zones in pad-paradscha sapphire that are caused by trapped hole defects induced by an excess of natural magnesium (J. L. Emmett et al., “Beryllium diffusion of ruby and sapphire,” Summer 2003 *G&G*, pp. 84–135). To rule out such orange zoning from naturally incorporated trapped hole centers, it was necessary to check for the presence of Be directly in one of the orange color zones. After obtaining permission from the client, LA-ICP-MS measurements revealed more than 35 ppma Be in an orange area, which is enough to impart significant orange color in a pink sapphire.

It was obvious from the shape and orientation of the color zones that the stone was beryllium-diffusion treated as a tabular preform or piece of rough that had sufficient sacrificial material to allow all traces of Be to be removed from the girdle area during cutting. It is difficult to say whether this was a deliberate attempt to defeat the standard practice of testing for beryllium in the girdle. Nevertheless, careful gemological observation in immersion and an understanding of color modification in corundum prevented this Be-diffused sapphire from being misidentified as a standard heated sapphire.

Nathan Renfro and Amy Cooper

Unusually High Beryllium in Three Blue Sapphires

Trace amounts of natural beryllium are sometimes detected in untreated sapphires, such as those from Madagascar. Typically, natural concentrations range from <1 ppma to about 4–5 ppma Be. Higher concentrations (>15 ppma) are usually associated with beryllium diffusion treatment.



Figure 27. This 3.21 ct sapphire contained relatively high levels of naturally occurring beryllium.

In addition, naturally occurring beryllium in corundum is often present with traces (usually <1 ppma) of niobium, tantalum, light rare-earth elements, and thorium (see A. Shen et al., "From the GIA Laboratory: Beryllium in corundum: The consequences for blue sapphire," *GIA Insider*, Vol. 9, No. 2, Jan. 26, 2007).

During routine testing, three blue sapphires recently submitted for identification were found to contain relatively high levels of beryllium. The three consisted of one ring-mounted stone and two loose sapphires weigh-

Figure 28. Higher concentrations of Be in this blue sapphire (values in ppma are shown next to each spot) were often associated with the presence of milky clouds. Magnified ~75×.

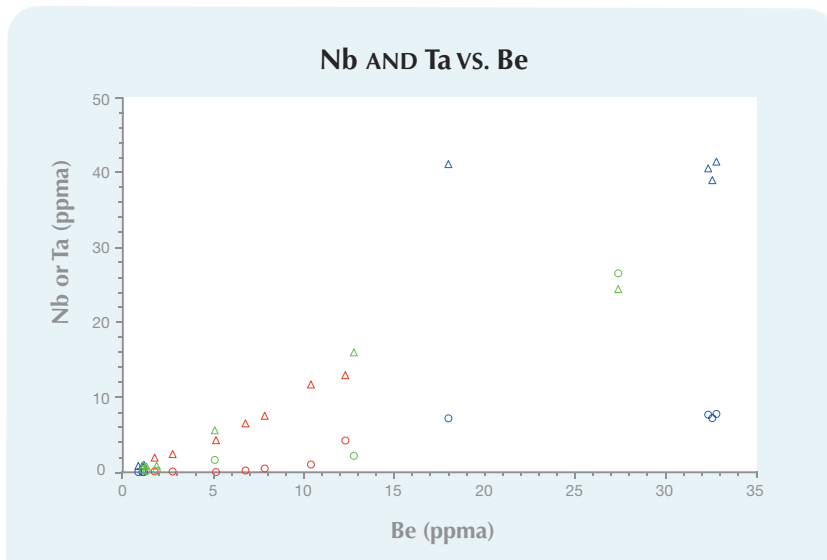
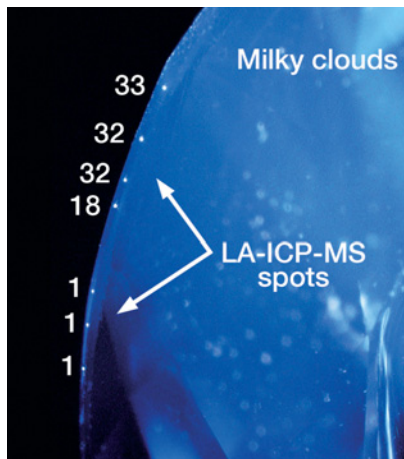


Figure 29. The concentrations of niobium (Nb, circles) and tantalum (Ta, triangles) showed an overall positive correlation to Be levels in the three sapphires (red = 3.17 ct, blue = 3.21 ct, and green = mounted sapphire). To convert to units of ppmw, the ppma values are multiplied by 0.44 for Be, 4.56 for Nb, and 8.87 for Ta.

ing 3.17 and 3.21 ct (e.g., figure 27). Two of the samples showed microscopic evidence of heating, while the other sapphire (3.17 ct) had inclusion features that proved it was unheated. The 3.21 ct stone showed a chalky blue reaction to short-wave UV radiation (consistent with its low iron content) and strong blue bands when viewed in immersion, while the other two sapphires were inert to long- and short-wave UV radiation due to their relatively high iron contents. All three stones contained milky clouds.

Trace-element analysis of all three sapphires with LA-ICP-MS showed a wide range of Be concentrations, from virtually absent up to 33 ppma (figure 28). The concentrations of Be were, in general, positively correlated to various transition metals and light rare-earth elements, including niobium, tantalum, tungsten, lanthanum, cerium, hafnium, and thorium (e.g., figure 29). Higher concentrations of all these elements, including Be, were often associated with the clouds, as documented previously in Be-bearing untreated sapphires. Magnesium also showed a positive correlation with Be, but with large

variations. Titanium showed both positive and negative correlation with Be, possibly due to Ti concentration variations in the blue zones.

The amount of Be in these sapphires is similar to or higher than that recorded in some Be-diffused stones. Their properties suggest that they came from at least two different deposits or deposit types, but their specific origins could not be determined. This is another example showing that thorough gemological and chemical analysis is necessary to identify beryllium-diffusion treatment.

Ren Lu and Andy H. Shen

PHOTO CREDITS

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