

Editors

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DIAMOND

Artificially Irradiated Brown

The combination of irradiation and annealing is commonly used to enhance a diamond's color appearance. Although green, blue, yellow, and pink are the main colors created through this process, brown hues are occasionally introduced. The New York lab recently tested one diamond with treated brown color whose spectral features were helpful for identification.

This 1.04 ct round brilliant ($6.51 \times 6.53 \times 3.95$ mm) was color graded as Fancy Reddish brown (figure 1). The color was distributed evenly throughout the whole stone. It fluoresced weak-moderate yellow to long-wave UV radiation and very weak yellow to short-wave UV. Infrared spectroscopy revealed it was a type Ia diamond with very high concentrations of aggregated nitrogen and a weak hydrogen-related absorption at 3107 cm^{-1} . Also revealed in its infrared absorption spectrum were strong absorptions from optical centers H1a (1450 cm^{-1}) and H1b (4935 cm^{-1}) and a moderate absorption from H1c (5165 cm^{-1}). Weak absorptions at 1355 and 1358 cm^{-1} were also recorded.

UV-Vis-NIR absorption spectroscopy collected at liquid-nitrogen



Figure 1. This 1.04 ct diamond was color graded as Fancy Reddish brown and identified as artificially irradiated.

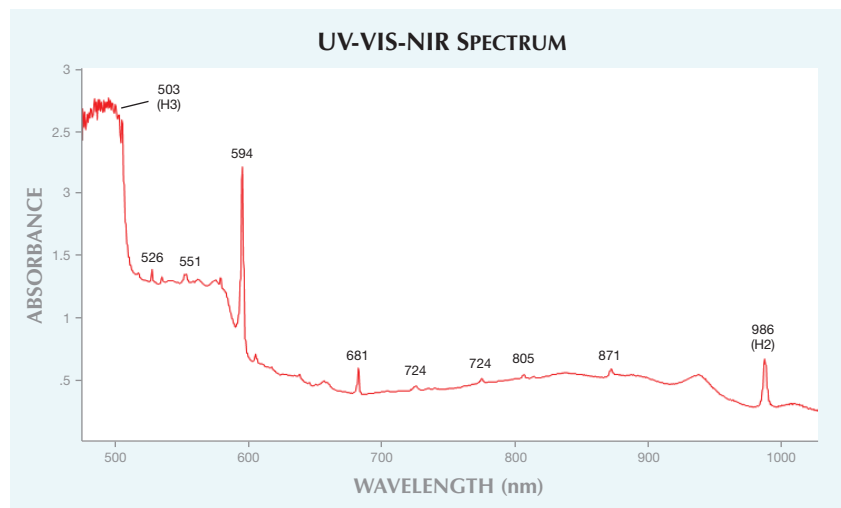
temperature yielded interesting features (figure 2). In addition to very

strong absorptions at 503 nm (H3 optical center), 594 nm, and 986 nm (H2), weak absorptions at 526, 534, 551, 578, 681, 724, 774, 805, and 871 nm were observed. Assignment for many of these weak peaks remains unclear. These features are not common in irradiated diamonds with more popular colorations.

The color of this diamond is obviously attributed to artificial irradiation. It is very likely that this diamond was heavily irradiated and then annealed at moderate temperatures. While the color looks natural, its spectral features are very distinct and easily separated from natural features.

Wuyi Wang

Figure 2. In the UV-Vis-NIR region, in addition to very strong absorptions at 503 nm (H3 optical center), 594 nm, and 986 nm (H2), nine weak absorptions were observed. The assignment for many of these weak peaks is not yet clear.



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

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Figure 3. This 2.34 ct Fancy yellow diamond contained a rare contact inclusion pair of diopside and pyrope.

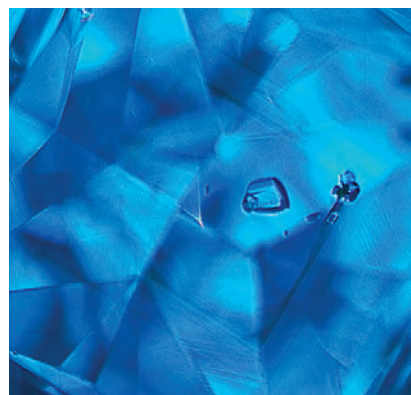
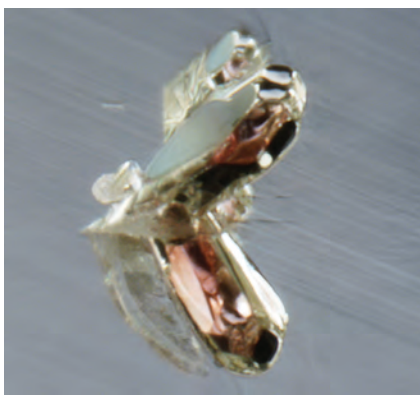


Figure 5. A few isolated prismatic, reddish pink pyrope crystals, the largest reaching the surface, were also visible through the pavilion (left, magnified 75 \times). The DiamondView image showed that the crystal inclusions formed in different growth zonations (right).

Diopside-Pyrope Contact Inclusion Pair

While isolated crystal inclusions are common in natural diamonds, it is rare to see two crystals in contact with one another. The New York laboratory recently examined a 2.34 ct Fancy yellow modified brilliant square (figure 3) that contained a pair of contact inclusions.

The inclusion pair showed red and green colors and a reflective interface in the face-up view (figure 4, left). When viewed through the pavilion, it clearly showed two inclusions: a small, green crystal atop a larger, reddish pink crystal (figure 4, right). Raman analysis identified the green

crystal as diopside and the reddish pink inclusion as pyrope. A few isolated prismatic, reddish pink pyrope crystals were also observed (figure 5, left). The DiamondView image revealed that the crystal inclusions formed in different growth zonations with different orientations (figure 5, right). This suggests the inclusions had a syngenetic origin, meaning they formed during the diamond's growth.

The host was a typical cape diamond with natural color. The diopside-pyrope mineral assemblage indicates the diamond formed in a peridotitic geological environment. Syngenetic inclusions, connecting or otherwise, are

useful in calculating the equilibrium pressure and temperature (EPT) of diamond formation. Such estimates can be found in the literature. The EPT for individual garnet-clinopyroxene inclusions is estimated at 5 GPa and 1138–1179°C (C.M. Appleyard et al., "A study of eclogitic diamonds and their inclusions from the Finsch kimberlite pipe, South Africa," *Lithos*, Vol. 77, 2004, pp. 317–332). The EPT for contact garnet-clinopyroxene inclusion pairs is estimated at 5 GPa and 1066–1072°C (see D. Phillips et al., "Mineral chemistry and thermobarometry of inclusions from De Beers pool diamonds, Kimberley, South Africa," *Lithos*, Vol. 77, 2004, pp. 155–179).

Still, the interpretation of these inclusions should be considered preliminary, since the EPT of solitary inclusions is subject to a changing geological environment during the prolonged growth period. Previous studies have also found that adjoining inclusions may represent the EPT of post-growth events, such as subsequent cooling of the earth's mantle or a temperature increase caused by kimberlite transportation, due to re-equilibration. Therefore, the diopside and pyrope inclusions in this sample may not represent the EPT at the time of diamond formation, though the aforementioned values fall within the diamond stability field.

Kyaw Soe Moe and Jason Darley

Figure 4. Red and green colors and a reflective interface were observed in the face-up view of the crystal inclusion (left, magnified 75 \times). Viewing the diamond through the pavilion revealed a small green crystal atop a larger reddish pink crystal (right, magnified 100 \times). The green crystal was identified as diopside and the reddish pink inclusion as pyrope.





Figure 6. This 15.01 ct cushion-cut diamond ($15.39 \times 12.84 \times 8.32$ mm) was color graded as Fancy Intense yellow. Its color was found to have been treated from the original Fancy Light yellow.

Treated Yellow with Unusual Spectroscopic Features

It is well known that some “off”-color diamonds can be irradiated by a high-energy electron or neutron beam and then annealed at moderate temperatures to introduce fancy yellow, orange, or even “champagne” colors by adding optical centers H3 and H4. This treatment was recognized as early as the 1950s (G. R. Crounshield, “Spectroscopic recognition of yellow bombarded diamonds and bib-

liography of diamond treatment,” Winter 1957-58 *G&G*, pp. 99–104). Along with gemological features such as color distribution, the occurrence of irradiation-related optical centers such as 595 nm absorption in the visible-light region and H1b and/or H1c in the infrared region is a very important indication of irradiation and annealing. Recently, we encountered a diamond with a treated yellow color that lacked these identifying features. Crounshield mentioned this type of treated yellow diamond, mainly in larger sizes.

This 15.01 ct cushion-cut diamond ($15.39 \times 12.84 \times 8.32$ mm) was color graded as Fancy Intense yellow (figure 6). Color was evenly distributed throughout the stone. It had a small black inclusion close to the edge in the table face. These measurements and internal features matched very well with a previously examined diamond in our database. Surprisingly, the earlier match was color graded as Fancy Light yellow. The significant difference in color appearance suggested that the diamond had been artificially treated after the initial examination.

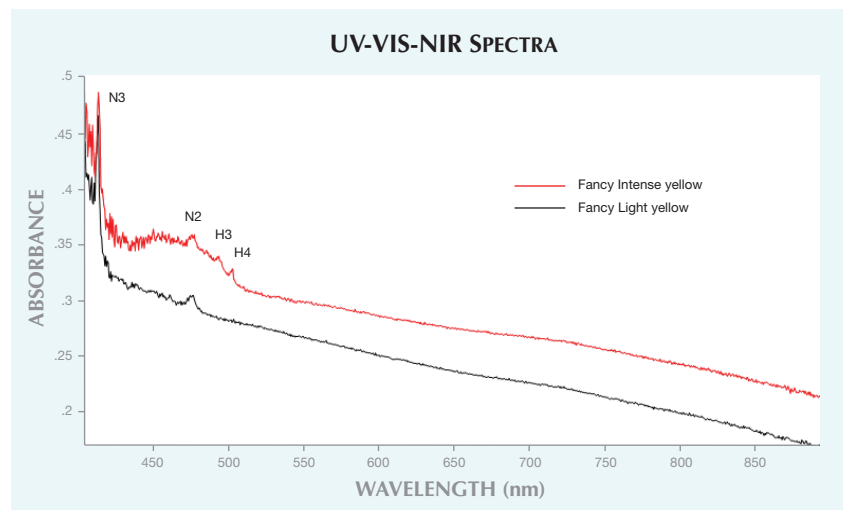
Infrared absorption spectroscopy showed virtually identical features in

both cases, such as very high concentrations of aggregated nitrogen and a very weak hydrogen-related absorption peak. In addition, weak absorptions at 1522 and 1546 cm^{-1} matched very well. Neither showed any irradiation- or treatment-related absorption features such as H1a, H1b, or H1c. The Fancy Light yellow diamond’s absorption spectra at liquid-nitrogen temperature simply showed a “cape” line with absorption peaks at 478 and 415 nm (N3) only. In contrast, absorptions of optical centers H3 (503 nm) and H4 (496 nm) with moderate concentrations were observed in the Fancy Intense yellow diamond (figure 7). No GR1 (741 nm) or 595 nm centers were observed in either instance. The occurrence of H3 and H4 was obviously responsible for the color change and must have been introduced after the initial examination.

Separating artificially irradiated from naturally irradiated diamonds is often a challenge. Improvements in this treatment technology, leaving no detectable 595 nm absorption in the visible region or H1b/H1c in the near-infrared region, could make the identification even more difficult.

Wuyi Wang

Figure 7. Absorption spectra collected at liquid-nitrogen temperature revealed that H3 and H4 centers were introduced in the Fancy Intense yellow diamond. No 595 nm center was detected, however.



Unusual Omphacite and Pyrope-Almandine Garnet Inclusion

Recently examined in the Carlsbad laboratory was a 2.03 ct Fancy yellow-green diamond containing an inclusion of omphacite, a grayish blue pyroxene, in contact with an orange garnet inclusion of the pyrope-almandine species (figure 8). Both were identified by optical and visual observations.

Although omphacite and garnet sometimes occur as solitary crystals in diamonds that form in an eclogitic environment, the color contrast between these two inclusions in contact offers a more striking scene. Other bimineralline inclusions in diamond have been previously reported, such as chromium pyrope and pyroxene (e.g., E.J. Gübelin and J.I. Koivula, *Photoatlases of Inclusions in Gemstones*, ABC Edition, Zurich, 1986, p. 95), but this



Figure 8. Contact inclusions of grayish blue omphacite and orange pyrope-almandine garnet confirmed the eclogitic origin of this 2.03 ct Fancy yellow-green diamond. Also observed was graphite along the interface between the inclusions and diamond host. Image width: 1.22 mm.

is the first example of an omphacite and pyrope-almandine contact inclusion seen in the Carlsbad laboratory. We also observed graphitization between the contact inclusion and the diamond host, and around one other solitary omphacite crystal.

Examined under polarized light, the diamond showed low-order dark gray strain around both the bi-mineralic inclusion and the solitary omphacite crystal with the graphitized interface, as in figure 9. However, other solitary omphacite inclusions in the diamond that did not show graphitization displayed high-order colored strain halos. While we do not

Figure 9. Examined in polarized light, the area around the omphacite/pyrope-almandine contact inclusion displayed low-order strain. Image width: 1.22 mm.



Figure 10. In this $9.96 \times 9.56 \times 7.32$ mm polymer-beryl assemblage (left), an inclusion-free region with increasing thickness from the girdle to the culet was easily visible under darkfield illumination at $20\times$ magnification (right).

know the exact cause of the high- and low-order strain variation, it could be related to graphitization, since the inclusions with graphite along their interface seemed to show less strain.

This contact inclusion is a noteworthy example of how microscopic observations can provide clues to geologic origin while also raising unanswered questions, such as the potential relationship between graphitization and the degree of strain.

Troy Ardon and Tara Allen

Polymer-BERYL Assemblage

Recently, two transparent green octagonal step-cut samples (see figure 10, left) were submitted to the New York laboratory for emerald origin reports. Initial gemological testing revealed some characteristics typical of natural, clarity-enhanced emeralds with a fracture-filling polymer. The refractive indices measured 1.570–1.578 and 1.572–1.580 on the table facets, and infrared spectra collected through both girdles showed features typical of natural beryl, as well as polymer-related features in the $3100\text{--}2800\text{ cm}^{-1}$ region. Microscopic examination revealed jagged and irregular two-phase inclusions through the table and crown.

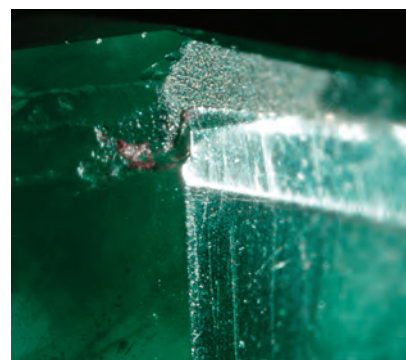
Still, some unusual features raised suspicion about the nature of the treatment. The samples had a hydrostatic SG of 2.43 and 2.37, unusually low for emerald (which usually measures around 2.7). No chromium-related lines were observed with the



handheld spectroscope. Furthermore, both displayed strong, even whitish blue fluorescence under long-wave UV light, with a similar but weaker reaction under short-wave UV. The fluorescence appeared to originate in the pavilion and reflect through the stone.

Closer microscopic examination revealed that the natural two-phase inclusions were present only in the crown and in a confined, domed region extending into the pavilion (figure 10, right). The pavilion showed no inclusions within several millimeters of the surface, which was heavily scratched and yielded easily to a pointer probe. The unknown layer on the pavilion tapered toward the girdle, where a boundary between the pavilion and crown material was visible (figure 11). Under immersion in isopropyl alcohol, the beryl portion ap-

Figure 11. The polymer base thinned from the culet to the girdle, where a border separated it from the natural beryl top. Reflected light; magnified $50\times$.



peared to have little or no green color, while the outer layer on the pavilion showed distinct green coloration. We determined that the beryl portion lacked sufficient color to be considered emerald.

To confirm the identity of the top and the base, we turned to Raman spectroscopy. Raman spectra taken from the table facets of each stone were consistent with beryl, while spectra from the pavilion corresponded with the polymer (figure 12). Notably, none of the spectral features from the table and pavilion overlapped, clearly demonstrating that the top and base were composed of different materials. We concluded that these specimens consisted of a natural beryl top and "core," with a thick, faceted polymer layer on the pavilion. Because a large portion of each sample was composed of polymer, we considered this case analogous to the case of heavily treated, lead glass-filled rubies, which receive

a conclusion of "manufactured product". Identification reports with this conclusion were issued for the two green assemblages, with an additional description of them as a "manufactured product consisting of colored polymer and beryl."

*Emily V. Dubinsky and
Donna Beaton*

Bicolored SPINEL

The Bangkok laboratory occasionally sees bicolored stones submitted for identification, but a blue and red sample weighing 14.60 ct and measuring $22.06 \times 12.39 \times 6.29$ mm (figure 13) recently caught our attention. Standard gemological testing gave an RI of 1.718 and a hydrostatic SG of 3.60, confirming the stone was a spinel. The red portion fluoresced a medium red in long-wave ultraviolet light and was inert in short-wave UV, whereas the blue region was inert in both long-



Figure 13. This 14.60 ct gem was identified as a bicolored spinel. Its blue and red zones were caused by the presence of iron and chromium, respectively.

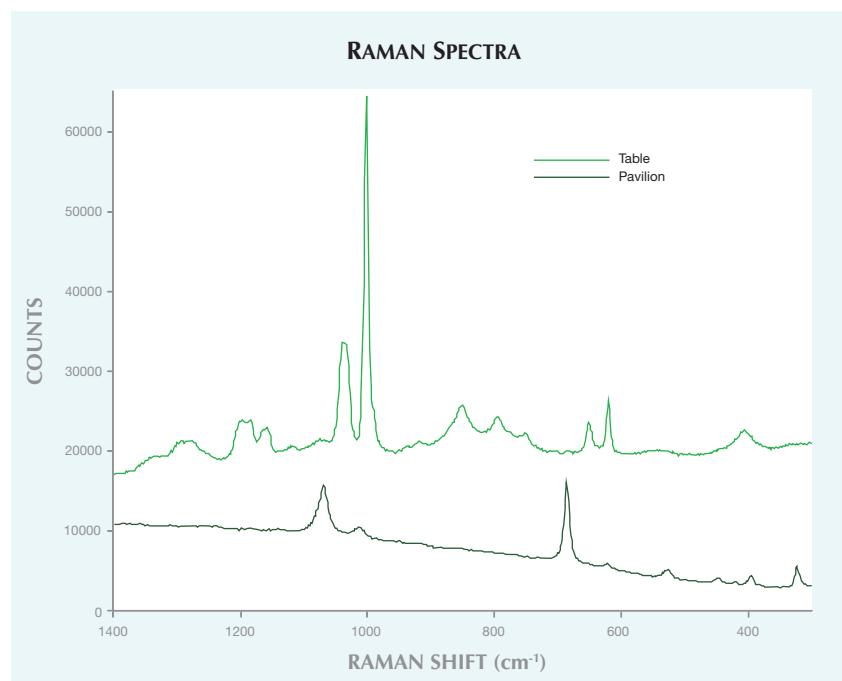
and short-wave. Microscopic examination of the inclusions revealed small octahedral crystals and growth tubes. Investigation of the photoluminescence using Raman spectroscopy at liquid-nitrogen temperature indicated that the stone had not been heated to alter its color.

Because of the unusual color zoning, we took advantage of the opportunity to collect the UV-visible spectrum on both the blue and red areas of the stone. As expected, the blue area exhibited a prominent feature at 458 nm and a broad absorption in the 550–680 nm region, caused by the presence of iron. The red area had strong absorption bands at 387 and 540 nm, indicating chromium.

While spinels are routinely submitted to the Bangkok laboratory for identification, a search of our databases found this was the first bicolored spinel.

Garry DuToit

Figure 12. Raman spectra collected from the table facet of both samples were consistent with beryl, whereas spectra from the pavilion facets were consistent with a polymer. Raman spectroscopy was performed with 514 nm excitation laser. The spectrum of the pavilion is offset 10,000 counts for clarity.



SYNTHETIC DIAMOND

Silicon-Vacancy Defect in HPHT-Grown Type IIb Synthetic

The [Si-V] optical center, which has zero-phonon lines at 736.6 and 736.9 nm and is active in absorption and luminescence, is common in CVD synthetic diamonds. Very few natural



Figure 14. The [Si-V]⁻ center was confirmed in these two HPHT-grown type IIb synthetic diamonds. The 0.51 ct round brilliant on the left was color graded as Fancy Light blue, and the 0.79 ct sample on the right had Fancy Deep blue color.

diamonds contain this defect, and it has long been considered an important identification feature of CVD synthetic diamonds. The New York lab recently tested two type IIb HPHT synthetic diamonds that showed moderately intense emission of this defect.

One was a 0.51 ct round brilliant (5.19 × 51.6 × 3.07 mm), color graded as Fancy Light blue. The other was a 0.79 ct round brilliant (5.99 × 6.05 ×

3.54 mm) with Fancy Deep blue color (figure 14). Absorption spectra in the mid-infrared region showed moderate boron-related absorption in the Fancy Light blue synthetic and very strong boron-related absorption in the Fancy Deep blue sample. Fluorescence images recorded with the DiamondView showed both octahedral and cubic growth sectors, typical patterns for HPHT synthetics (figure 15). Strong blue phosphorescence

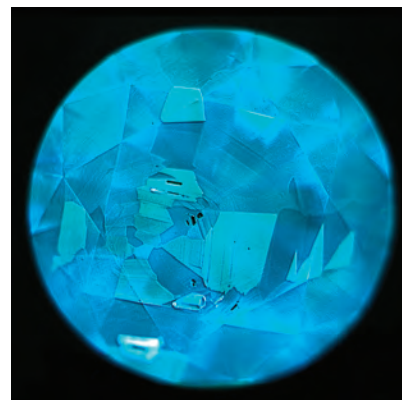


Figure 15. The fluorescence image of the 0.79 ct sample showed the typical growth pattern of an HPHT synthetic diamond. Strong blue phosphorescence was also observed.

was also observed. But the most notable feature found in these two synthetic diamonds was the [Si-V]⁻ defect. Weak but distinct emissions at 736.6 and 736.9 nm were recorded in both with 633 nm laser excitation at liquid-nitrogen temperature (figure 16).

The [Si-V]⁻ defect reported earlier in an HPHT-grown synthetic diamond (also type IIb; see Winter 2010 Lab Notes, p. 302) was believed to be a very unusual feature. The discovery of two additional occurrences suggests that this defect may be more common in HPHT synthetic diamonds than previously expected. It is not fully understood why the feature has not been observed in type IIa HPHT synthetics. Because this optical center is a common feature of CVD synthetic diamonds, documenting it in HPHT-grown synthetics underscores the importance of testing with multiple technologies.

Wuyi Wang and Kyaw Soe Moe

Figure 16. Weak but distinct emissions at 736.6 and 736.9 nm were recorded in both HPHT synthetics with 633 nm laser excitation at liquid-nitrogen temperature. These emissions are attributed to the [Si-V]⁻ center, which is common in CVD synthetic diamonds.

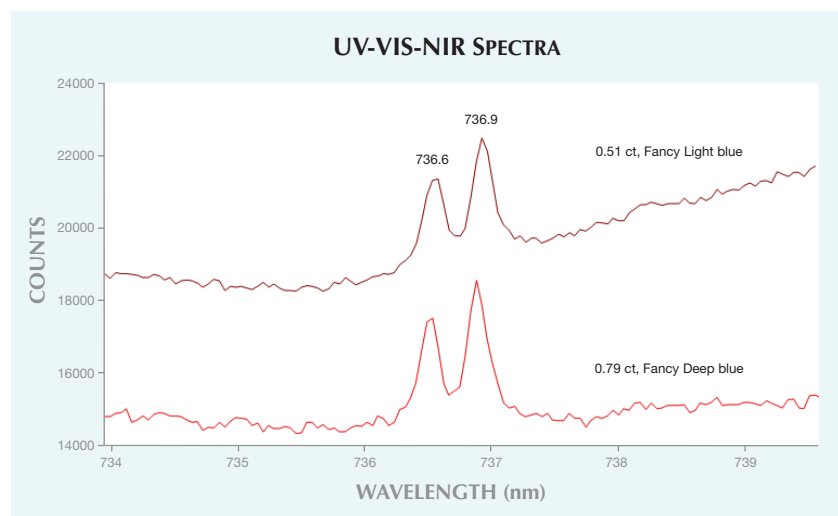


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