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Featuring:

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Pezzottaite, A New Gem

Red Beryl Update

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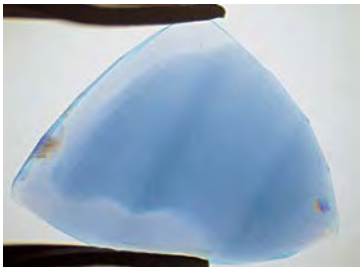

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DIAMONDS

A comparison of three historic blue diamonds. This summer's "Splendor of Diamonds" exhibition at the Smithsonian Institution in Washington, D.C., presented a unique opportunity for the public to view seven of the world's rarest diamonds (see, e.g., J. M. King and J. E. Shigley, "An important exhibition of seven rare gem diamonds," Summer 2003 *Gems & Gemology*, pp. 136–143). The closing of the exhibition brought another opportunity—for the contributors of this entry to compare the properties of three of the largest documented strongly colored blue diamonds. Two of these diamonds, the 45.52 ct Hope and the 30.62 ct Blue Heart, are part of the Smithsonian's permanent collection; the third, the 27.64 ct Heart of Eternity, was part of the special exhibit (figure 1). Arrangements were made to remove the Hope and the Blue Heart from their mountings and to allow the contributors one evening to examine and test them in conjunction with the Heart of Eternity prior to its being returned to its owner.

GIA has graded all three diamonds since the 1995 introduction of enhancements to its colored diamond color grading system (see J. M. King et al., "Color grading of colored diamonds in the GIA Gem Trade Laboratory," Winter 1994 *Gems & Gemology*, pp. 220–242). The Hope diamond was described as Fancy Deep grayish blue in an updated grading performed in 1996; the Blue Heart was graded Fancy Deep blue in 1997, and the Heart of Eternity was graded Fancy Vivid blue in 1999. Given the different color descriptions for each of these diamonds, this was a special chance to see how the color appearances related to the terms defined by the grading system.

In GIA's system, fancy-grade terminology is used to describe a range of the combined effect of tone (the lightness to darkness of a color) and saturation (the strength or purity of a color). For blue diamonds, for example, *Fancy Deep* describes those of medium to dark tone and moderate to strong saturation. *Fancy Vivid* describes those that are medium to dark in tone and strong to very strong in saturation. These fancy-grade ranges are further divided by color terms such as blue, blue-gray, or bluish gray to refine the location of the color appearance. "Cooler" colors, such as blue, appear more grayish or gray as they become darker in tone and/or weaker in saturation, and modifiers of *grayish* or *gray* are used in the color description to reflect this aspect. When the color space for blue diamonds was discussed by J. M. King et al. ("Characterizing natural-color type IIb blue diamonds," Winter 1998 *Gems & Gemology*, pp. 246–268), the authors noted that the range of saturation in which blue diamonds occur is relatively compressed. This means the appearance differences between color terms can be more subtle than similar terms for other colors.

From the report descriptions, one would expect these three diamonds to have similar tone (with small variations) and subtle differences in saturation. The Hope, which has been described as "steely" in appearance, is less saturated than the other two. The Heart of Eternity has the strongest color, with the Blue Heart falling between them. The Heart of Eternity's color is strong

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Figure 1. Shown here from left to right, the 30.62 ct Blue Heart, the 45.52 ct Hope, and the 27.64 ct Heart of Eternity are three of the largest strongly colored blue diamonds that have been documented gemologically. To encounter one such diamond is extremely rare, and to have an opportunity to observe all three together was a unique experience. Photo by Shane McClure.

enough for it to merit a different grade range (i.e., Fancy Vivid). Figure 2 shows the relationship of these three diamonds on a section of a tone/saturation grid.

This occasion also presented a chance to view the unique phosphorescence associated with some natural-color type IIb blue diamonds. Type IIb blue diamonds that phosphoresce do so almost solely in response to short-wave UV radiation and do not react to long-wave. King et al. (1998) noted that three-quarters of the blue diamonds that phosphoresced showed a very weak to weak reaction. The most common color was a chalky blue to green, with rare red or orangy red reactions. The Hope diamond's strong red phosphorescence to short-wave UV radiation has been described a number of times (and is illustrated in R. Crowningshield, "Grading the Hope diamond," *Gems & Gemology*, Summer 1989, p. 93), so it was interesting to note a similar reaction in the Heart of Eternity. When the UV source was turned off, both diamonds showed a similar intensity of phosphorescence; however, while the Hope's could be observed for more than a minute, the Heart of Eternity's faded rather quickly. In addition, the Hope's reaction was a slightly warmer red than that of the Heart of Eternity. The Blue Heart exhibited a more typical, very subtle white to

Figure 2. The three blue diamonds described here are placed on a portion of a tone/saturation grid to illustrate their relationship in color space. All are relatively similar in tone (lightness to darkness) but differ in saturation (the strength or purity of the color). The Hope is the least saturated, the Heart of Eternity is the most saturated, and the Blue Heart is between them in saturation and slightly lighter in tone.

Figure 3. While the cutting of each diamond is approached individually, a general difference in cutting philosophy is seen here in the profile view of the two heart-shaped diamonds. The Blue Heart (left) was cut in the early part of the 20th century and the Heart of Eternity (right) was cut in the 1990s. The two faceting approaches result in different face-up appearances. Photo by Shane McClure.

chalky blue reaction that also faded quickly. There is no known explanation for why two of these diamonds show such a dramatic reaction and the third does not.

The differences in cutting philosophy between the two heart-shaped diamonds also were intriguing (figure 3). Smithsonian records indicate that the Blue Heart was cut in the early part of the 20th century; we know that the Heart of Eternity was cut in the 1990s. Bearing in mind that each piece of rough is approached individually to achieve the best weight retention, color, clarity, and cut, there are still distinct differences in style between the two. The culet on the Blue Heart is near the center of the diamond, and is surrounded by radiating facets similar to how sapphires are cut. The edges between facets are sharp and well-defined, which often results in more brilliance in the face-up position (see again figure 1). The Heart of Eternity has a French culet (four pavilion mains) and a number of relatively large flat facets on the pavilion near the girdle. The angle between adjacent facets is rather shallow in a number of areas on the pavilion, making these facets appear less distinct. These cutting aspects help deepen and intensify the face-up color appearance of the Heart of Eternity.

These contributors also performed infrared spectroscopy on all three diamonds. The Hope has a large culet facet, and the infrared beam entered through the table and passed out the culet, for a path length of 12 mm through the diamond (assuming no internal reflections). The Blue Heart has a small culet that is subparallel to the table (11.9 mm in this dimension); thus, the infrared beam was aimed directly through these two facets. The Heart of Eternity does not have a culet facet, so the spectrum was taken across the width of the heart, with a beam path length of approximately 20 mm (again, assuming no internal reflections).

Mid-infrared spectra (8000–400 cm^{-1}) were obtained with a Bio-Rad Excalibur Fourier-transform infrared spectrometer using a KBr beam splitter and DTGS detector at 4 cm^{-1} resolution. The infrared spectrum of the Hope diamond is shown in figure 4. The absorption characteristics of the Blue Heart and the Heart of Eternity were essentially identical to that of the Hope diamond, but due to lower transmission of light through these samples the spectra were of lower quality.

There are two principal causes for the absorption features in this energy range: lattice vibrations of the diamond and electronic transitions due to substitution

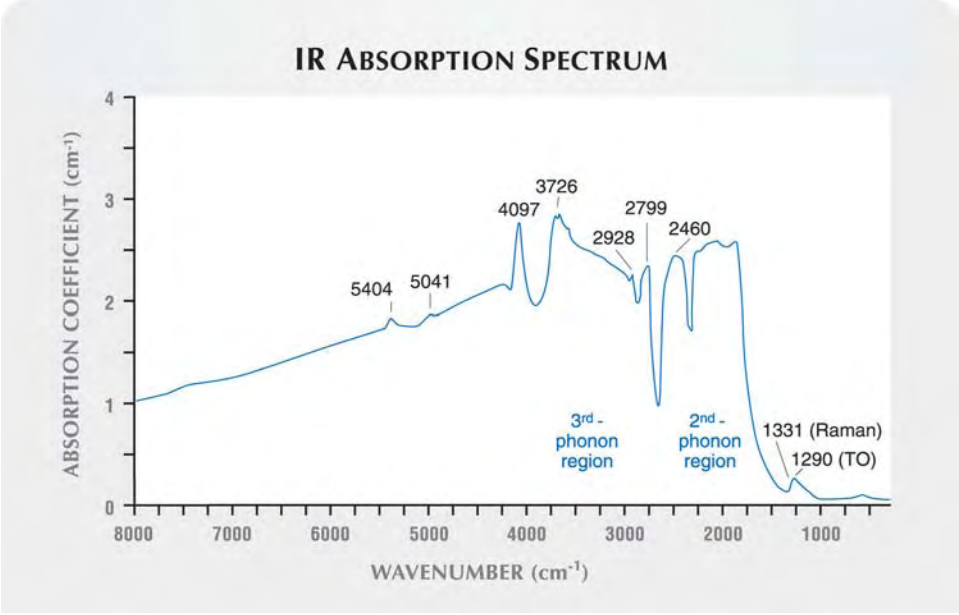

Figure 4. The infrared spectrum of the Hope diamond shows features that are consistent with boron-induced blue color and type IIb diamonds in general (see text). Note that portions of some bands in the 3800–1600 cm^{-1} region were actually off the scale of the spectrometer.

of boron into the diamond structure. The lattice vibrations appear from 4000 to 1200 cm^{-1}, and consist of the transverse optic (TO) mode, the Raman-active mode, and bands in the second- and third-phonon regions (King et al., 1998). The broad absorbance that results from substitution of small amounts of boron for carbon in the diamond structure starts roughly at 3000 cm^{-1} and extends into the near-infrared and red region in the visible spectrum; it is the cause of the blue color (see S.D. Smith and W. Taylor, "Optical phonon effects in the infra-red spectrum of acceptor centres in semiconducting diamond," *Proceedings of the Physical Society, London*, Vol. 79, 1962, pp. 1142–1153; I. G. Austin and R. Wolfe, "Electrical and optical properties of a semiconducting diamond," *Proceedings of the Physical Society*, Vol. 69B, No. 3, 2003, pp. 329–338). As reported by Smith and Taylor (1962), the other absorption features seen in figure 4 are due to boron-related electronic transitions (2928, 2799, and 2460 cm^{-1}) and the combination modes of the boron transitions and lattice vibrations (5404, 5041, 4097, and 3726 cm^{-1}). The spectra of all three blue diamonds lacked any detectable nitrogen bands in the 1400–1000 cm^{-1} region, consistent with the definition of type II diamonds.

To our knowledge, this is the first mid-infrared spectrum obtained on the Hope diamond; it shows features consistent with the presence of boron as the cause of the blue coloration and its categorization as a type IIb diamond.

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A natural yellow diamond with nickel-related optical centers. A Fancy Light yellow 2.95 ct round brilliant diamond was recently submitted to the SSEF Swiss Gemmological Institute for color authenticity determination (figure 5). In the course of standard testing, we noticed the presence in its UV-visible spectrum of clear nickel-related optical centers, which are usually encountered in flux-grown synthetic diamond. Further spectroscopic analysis, as described below, in combination with the growth patterns, proved that this Ni-containing diamond was natural and not a synthetic. Although the presence of nickel in natural diamonds has been previously documented (C. J. Noble et al., "Electron paramagnetic resonance investigations of nickel defects in natural diamonds," *Journal of Physics: Condensed Matter*, Vol. 10, 1998, pp. 11781–11793), we are not aware of any previous mention of this in the gemological literature.

Microscopic observation of this diamond revealed several small black-to-brown inclusions of unknown origin. Numerous swirl-like patterns were visible with darkfield illumination, and were more distinct when crossed polarizers were used. With long-wave UV radiation, the stone showed a strong "lemon" yellow reaction, which was mostly even except for a few weaker zones close to the culet. The short-wave UV reaction was similar in color though weaker in intensity. No magnetic test was performed.

The infrared spectrum showed a strong platelet-related peak (higher than the two-phonon zone) and a large and saturated absorption band between 1300 and 1050 cm^{-1}. These features are typical for type Ia diamonds that contain significant concentrations of nitrogen. Several characteristic peaks in both the one- and three-phonon zones indicated that the diamond also contained a moderate concentration of hydrogen. This is consistent with its yellow UV fluorescence. If we consider both the presence of a well-defined 1010 cm^{-1} peak and the absence of the 484 cm^{-1} peak, it is reasonable to assume that the majority of nitrogen was present as B aggregates.

The UV-Vis absorption spectrum, recorded at approximately –120°C, showed a strong N3 center, with an absorption coefficient of 2.0 cm^{-1} at 415.2 nm. A series of weak peaks (343.6, 347.3, 360.3, 363.5, and 366.9 nm) were recorded that so far have been described only in synthetic diamonds (J. E. Field, *The Properties of Natural and Synthetic Diamond*, Academic Press, London, 1992). Also present was another series of weak peaks (467.9, 473.0, 477.5, and 546.7 nm) that have been previously attributed to nickel- and nitrogen-related absorptions in annealed type Ib synthetic diamonds (J. E. Shigley et al., "The gemological properties of Russian gem-quality synthetic yellow diamonds," Winter 1993 *Gems & Gemology*, pp. 228–248). In addition, a weak peak was recorded at 793.3

Figure 5. This 2.95 ct Fancy Light yellow natural diamond was found to contain Ni-related absorption features in the UV-visible region that have previously been associated only with synthetic diamonds. Photo by M. Krzemnicki, © SSEF.