

A GEMOLOGICAL STUDY OF A COLLECTION OF CHAMELEON DIAMONDS

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Chameleon diamonds are among the rarest of gem diamonds. This article reports on a unique collection of 39 chameleon diamonds ranging from 0.29 to 1.93 ct, which exhibited temporary changes in color when heated to approximately 150°C and, for some, after prolonged storage in the dark (i.e., thermochromic and photochromic color changes, respectively). Most changed from “olive” green to brownish yellow or yellow, although some changed from light yellow to a more intense greenish yellow. The thermochromic and photochromic color change observed in the “olive” green chameleon diamonds is typical of “Classic” chameleons, whereas the solely thermochromic change shown by the light yellow group was the “Reverse” of that seen in Classic chameleon diamonds. The Classic and Reverse groups showed different spectroscopic and UV fluorescence characteristics, but all stones exhibited strong long-lasting phosphorescence after short-wave UV excitation. Hydrogen was identified in all samples by FTIR spectroscopy, and minor Ni-related emissions were detected by photoluminescence spectroscopy in most. Using this combination of reaction to UV radiation and spectroscopic properties, a gemologist can separate chameleon from other green diamonds without unnecessary exposure to heat.

The rarity of chameleon diamonds and their interest for the connoisseur are due to their unusual ability to change color temporarily when heated to about 150°C (“thermochromism”) or after prolonged storage in the dark (“photochromism”; see Fritsch et al., 1995). The stable color shown by chameleon diamonds is typically grayish yellowish green to grayish greenish yellow (“olive”), while the unstable hue is generally a more intense brownish or orangy yellow to yellow (figures 1 and 2). After heating, the color of a chameleon diamond quickly returns to its stable hue. The color change after storage in the dark is usually not as dramatic as that seen on heating. Some of these chameleons have a stable color reminiscent of “normal” green diamonds. While the green color of these diamonds is caused by exposure to radiation (either naturally or in the laboratory), the mechanism behind chameleon coloration is not yet well understood. Nevertheless,

chameleons are among the few green diamonds that can be conclusively identified as natural color, since this behavior cannot be created or enhanced in the laboratory.

Relatively little has been written about chameleon diamonds, and the precise definition of this behavior is not at all clear. For some members of the trade, a temporary photochromic color change must be present for a diamond to be referred to as “chameleon”; in contrast, many publications describe chameleon diamonds as having *either* a thermochromic (using rather low annealing temperatures) or photochromic temporary color change (Raal, 1969; *GIA Diamond Dictionary*, 1993; Fritsch et al., 1995).

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Figure 1. One of the more spectacular chameleon diamonds examined for this study was this 1.01 ct marquise diamond, shown at room temperature (left) and at approximately 150°C (right). Photo by T. Hainschwang.

Chameleon diamonds were first documented in 1943 (*GIA Diamond Dictionary*, 1993), and since then they have been described in several brief reports (see, e.g., Chabert and Reinitz, 2000). Extensive research on a single large chameleon diamond was published by E. Fritsch and colleagues (1995). Most recently, Shigley et al. (2004) reported additional data on chameleon diamonds, including the presence of Ni-related emissions detected by

photoluminescence spectroscopy. We believe the present article is the first extensive study of a large number of chameleon diamond samples; it is part of ongoing research by EGL USA on colored diamonds in collaboration with other gemological laboratories and universities worldwide. Some preliminary observations on this collection of chameleon diamonds were published by Deljanin (2004).

Figure 2. These images show typical color changes seen in chameleon diamonds of the Classic (top, 0.83 ct) and Reverse (bottom, 1.09 ct) types. The left images show the stable color, while the unstable color is on the right. Photos by T. Hainschwang.



MATERIALS AND METHODS

Thirty-nine chameleon diamonds were included in this study (as described in table 1 and illustrated in figure 3). Unfortunately, the geographic origins of these diamonds are unknown. The stones were purchased between 1987 and 2004: 40% were obtained in India, 30% in Antwerp, and 30% in Tel Aviv. All the diamonds were accompanied by grading reports from either GIA or EGL, which stated that, under certain circumstances, they exhibited a change in color.

The stable color of the chameleon diamonds was graded by the above laboratories, while the unstable color was described by two of the authors (TH and DS). Luminescence to ultraviolet radiation and phosphorescence were observed with a 4-watt UVP UVGL-25 Mineralight Lamp using 254 nm (short-wave) and 365 nm (long-wave) excitation. Observations between crossed polarizers were made with a gemological microscope using Leica optics at 10–60× magnification. Color distribution was studied with each stone immersed in methy-

lene iodide. The change in color was observed using a 6500 K daylight-equivalent light and a hot plate (range of 40–325°C); the temperature during the heating process was monitored using a thermocouple connected to a digital multimeter. The samples were also cooled in liquid nitrogen to monitor possible color changes induced by low temperature.

We recorded infrared spectra in the range of 6000–400 cm⁻¹ on a Nicolet Nexus 670 FTIR spectrometer, using a diffuse reflectance (DRIFTS) accessory as a beam condenser to facilitate the analysis of small faceted stones, with an accumulation of 100 scans at a resolution of 2–4 cm⁻¹. We recorded pho-

toluminescence spectra with the diamonds immersed in liquid nitrogen ($T \approx -196^\circ\text{C}$), using an Adamas Advantage SAS2000 system equipped with a 532 nm semiconductor laser and an Ocean Optics SD2000 spectrometer (resolution 1.5 nm) with a 2048-element linear silicon CCD-array detector. Vis-NIR spectra in the range of 400–1000 nm were collected with the SAS2000 system, using the same spectrometer and detector as described above, with a resolution of 1.5 nm and 60–250 sample scans. The measurements were performed using an integrating sphere at liquid nitrogen temperature. Also, to monitor changes due to heating, we recorded

TABLE 1. The 39 chameleon diamonds in this study and their changes in color.

Stone no./ Grading lab ^a	Weight and shape	Classic or Reverse group	Stable color	Unstable color ^a	Magnitude of color change
1.1/GIA	0.39 ct round	Classic	Fancy Dark grayish greenish yellow	Fancy Intense orangy yellow	Strong
1.2/GIA	0.64 ct marquise	Classic	Fancy Dark brownish greenish yellow	Fancy Deep brownish orangy yellow	Strong
1.3/GIA	0.43 ct marquise	Classic	Fancy Dark grayish yellowish green	Fancy Deep brownish orangy yellow	Strong
1.4/EGL	0.63 ct marquise	Classic	Fancy Deep green yellow	Fancy Deep brownish greenish yellow	Weak
1.5/GIA	1.60 ct pear	Classic	Fancy Dark yellowish brown	Fancy Deep brownish orangy yellow	Strong
1.6/GIA	0.46 ct pear	Classic	Fancy Dark grayish yellowish green	Fancy Intense orangy yellow	Strong
1.7/EGL	0.83 ct heart	Classic	Fancy Deep grayish yellowish green	Fancy Intense orangy yellow	Strong
1.8/GIA	1.75 ct cushion	Classic	Fancy Dark grayish yellowish green	Fancy greenish yellow	Weak
1.9/GIA	0.67 ct oval	Classic	Fancy Dark grayish yellowish green	Fancy Intense yellow	Strong
2.1/GIA	1.93 ct marquise	Classic	Fancy Deep brownish greenish yellow	Fancy Deep brownish orangy yellow	Strong
2.2/GIA	0.72 ct marquise	Classic	Fancy brownish greenish yellow	Fancy Deep orangy brown yellow	Strong
2.3/GIA	0.58 ct marquise	Classic	Fancy grayish greenish brown yellow	Fancy Deep brownish orangy yellow	Strong
2.4/GIA	0.81 ct heart	Classic	Fancy Deep brownish greenish yellow	Fancy Deep brownish orangy yellow	Strong
2.5/GIA	0.48 ct marquise	Classic	Fancy brownish yellow	Fancy Intense yellowish orange	Strong
2.6/GIA	0.29 ct marquise	Classic	Fancy brownish greenish yellow	Fancy Intense orangy yellow	Strong
2.7/GIA	0.57 ct heart	Classic	Fancy grayish greenish yellow	Fancy brownish yellow	Strong
2.8/EGL	0.46 ct round	Classic	Fancy Deep brownish greenish yellow	Fancy Deep brownish orangy yellow	Strong
2.9/EGL	0.52 ct round	Reverse	Fancy Light brownish yellow	Fancy greenish yellow	Moderate

^aDescriptions of the unstable colors for all of the diamonds were determined by the authors. Note that, presently, GIA only recognizes the Classic type (and not the Reverse type) as a chameleon diamond.

spectra at room temperature as well as with some stones heated to approximately 325°C; the higher temperature was used to assure that the diamond was in its unstable color state during the accumulation of the spectrum.

In addition to the 39 diamonds included in the chameleon collection, one additional chameleon diamond was analyzed (box A); the sample, referenced as TH-A1, was first described by Hainschwang (2001). An FTIR spectrum of a hydrogen-rich chameleon diamond, which was not part of the collection, called "TH-cham1," is included to compare the strength of color change with hydrogen content.

RESULTS

Color Description. Two different stable-color groups were observed in the chameleon diamonds (see figure 3, top):

1. Green with a gray, brown, or yellow color component ("olive"); or yellow with green, brown, or gray modifying colors. These are referred to hereafter as "Classic."
2. Light yellow with typically a greenish, grayish, or brownish component. These are referred to as "Reverse."

Stone no./ Grading Lab	Weight and shape	Classic or Reverse group	Stable color	Unstable color	Magnitude of color change
3.2/GIA	1.52 ct oval	Classic	Fancy grayish yellowish green	Fancy Deep brownish yellow	Strong
3.3/GIA	0.47 ct marquise	Classic	Fancy grayish yellowish green	Fancy brownish yellow	Strong
3.4/GIA	0.58 ct marquise	Classic	Fancy Deep brownish yellow	Fancy Deep brownish yellow	Strong
3.5/GIA	1.01 ct marquise	Classic	Fancy grayish yellowish green	Fancy Intense yellow	Strong
3.6/GIA	1.54 ct marquise	Classic	Fancy gray yellowish green	Fancy grayish yellow	Moderate to strong
3.7/GIA	0.41 ct round	Classic	Fancy Dark greenish gray	Fancy Intense yellow	Strong
3.8/GIA	0.29 ct round	Classic	Fancy Dark greenish gray	Fancy Deep brownish yellow	Strong
3.9/GIA	0.47 ct round	Classic	Fancy Dark grayish yellowish green	Fancy Intense yellow	Strong
3.10/GIA	0.47 ct round	Classic	Fancy grayish yellowish green	Fancy Intense yellow	Strong
3.11/GIA	0.51 ct round	Classic	Fancy gray greenish yellow	Fancy greenish yellow	Moderate
3.12/GIA	0.39 ct round	Classic	Fancy yellowish-yellowish green	Fancy orangy yellow	Strong
4.2/GIA	0.47 ct round	Classic	Fancy Light yellow	Fancy greenish yellow	Weak
4.3/EGL	0.57 ct round	Reverse	Light grayish greenish yellow	Fancy yellow-green	Moderate
4.4/GIA	0.56 ct round	Classic	Fancy Light grayish greenish yellow	Fancy brownish yellow	Weak
4.5/EGL	0.59 ct round	Reverse	Very Light yellow	Fancy Light greenish yellow	Moderate to strong
4.7/EGL	0.51 ct marquise	Reverse	Very Light grayish yellow	Fancy yellow-green	Strong
4.8/EGL	0.46 ct marquise	Reverse	Light grayish greenish yellow	Fancy Light yellow-green	Moderate to strong
4.9/EGL	0.58 ct marquise	Reverse	Light brownish yellow	Fancy greenish yellow	Moderate to strong
4.10/EGL	0.47 ct marquise	Reverse	Light yellow (U-V)	Fancy Light greenish yellow	Moderate
4.11/GIA	0.80 ct marquise	Classic	Fancy brownish greenish yellow	Fancy Intense orangy yellow	Strong
4.12/EGL	0.36 ct marquise	Reverse	Light yellow (U-V)	Fancy Light greenish yellow	Moderate



Figure 3. The collection of 39 chameleon diamonds (0.29 to 1.93 ct) is shown at room temperature (top) and when heated to 150°C (bottom). Photos by Julia Kagantsova, EGL.

The Classic group of chameleons (31 of the 39 diamonds) exhibited a distinct change in color when heated (figure 3, bottom). The unstable color varied from saturated brown-yellow to orange-yellow to yellow. The same change of color also was observed after prolonged storage in the dark for all except four stones, but it was not nearly as pronounced as the change induced by heating. Usually a couple of hours in darkness was sufficient to induce the color change. Cooling to liquid nitrogen temperature did not provoke a color change.

The Reverse group (8 of the 39 diamonds) differed from the first group in that heating induced only a weak-to-moderate change to a more saturated and greener color (again, see figure 3, bottom). Storage in the dark, even for days, did not provoke a change in color. As in the Classic chameleons, the color was not influenced by cooling to liquid nitrogen temperature (-196°C). We use the term *Reverse* for such chameleon diamonds, because their yellow-to-yellowish green color change is almost the opposite of the green-to-yellow change seen in typical chameleon diamonds.

The change in color due to heating began at approximately $100\text{--}120^{\circ}\text{C}$ in both groups. For the majority of the stones, the unstable color was most intense between 120 and 140°C . Although the diamonds were heated up to 300°C , no further changes in color were observed above about 140°C . At this temperature, a complete change in color could be induced within a few seconds.

Color Distribution. The color in most of the chameleon diamonds was evenly distributed; however, a few of the samples from the Classic group showed very slight patchy (irregular) color zoning. One diamond, also from the Classic group, exhibited very distinct yellow-brown banding (figure 4).

Anomalous Double Refraction. Between crossed polarizing filters, no characteristic pattern was seen. Some strain was observed in all samples, evident as interference colors of various intensity, and was mainly associated with inclusions. Deformation-related extinction patterns along octahedral slip planes (as typically seen in many brown to brownish

yellow-green diamonds) were observed in only a few samples, and were localized and very indistinct.

Reaction to UV Radiation. All samples exhibited characteristic long- and short-wave UV fluorescence. There were basically two types of responses:

1. *Classic group*: chalky white to chalky yellow to yellow, stronger to long-wave than to short-wave UV (figure 5)
2. *Reverse group*: chalky blue to blue to long-wave, and weaker chalky blue to yellow to short-wave UV (figure 6)

Most of the diamonds displayed moderate to strong luminescence to long-wave UV radiation, with a weak to moderate response to short-wave UV. The most interesting feature was that all stones exhibited persistent phosphorescence, more distinctly to short-wave than to long-wave UV. The phosphorescent color was yellow for all samples, but its strength and decay time varied considerably: Light yellow stones of the Reverse group that exhibited blue fluorescence had much weaker and shorter phosphorescence than the Classic-group diamonds that exhibited chalky white to yellow luminescence (again, see figures 5 and 6). Some of the diamonds of the Classic group emitted a faint, but still eye-vi-



Figure 4. This 1.93 ct chameleon diamond from the Classic group was the only sample that showed distinct color banding. Photo by T. Hainschwang.

ble, yellow glow over one hour later. In contrast, the phosphorescence of the Reverse group diamonds lasted just a few seconds to a few minutes. A Reverse-type diamond (TH-A1) analyzed prior to

BOX A: AN UNUSUAL REVERSE CHAMELEON DIAMOND

What is believed to be the first report of a “low-temperature” (i.e., below 200°C) thermochromic color change observed in a very high-nitrogen and high-hydrogen yellow diamond exhibiting Reverse chameleon behavior was published by Hainschwang (2001). The 1.09 ct marquise cut diamond, here referred to as TH-A1 (figure 2, bottom; figure 8, orange trace), exhibited a Vis-NIR spectrum with several hydrogen-related peaks—notably at 425, 440, 452, 462, 474, 545, and 563 nm—similar to the spectrum shown in figure 11 (green trace). The Reverse

chameleon diamonds included in the present article exhibit only a few of these absorptions, and they commonly show distinctly less IR-active hydrogen. Nevertheless, the color change shown by those diamonds is as strong, and in some stones stronger, than exhibited by sample TH-A1. An interesting characteristic of this diamond is that the luminescence and phosphorescence behavior change on heating (table A-1). Further research will be needed before the mechanism that produces these phenomena can be understood.

TABLE A-1. Variations in the emissions excited by UV radiation observed in sample TH-A1.

Luminescence	Long-wave UV		Short-wave UV	
	Room temperature	Hot (~200°C)	Room temperature	Hot (~200°C)
Fluorescence	Violetish blue	Zoned blue and yellow	Chalky bluish yellow	Blue with yellow zones
Phosphorescence	Weak yellow	Distinct blue	Distinct yellow	Weak blue

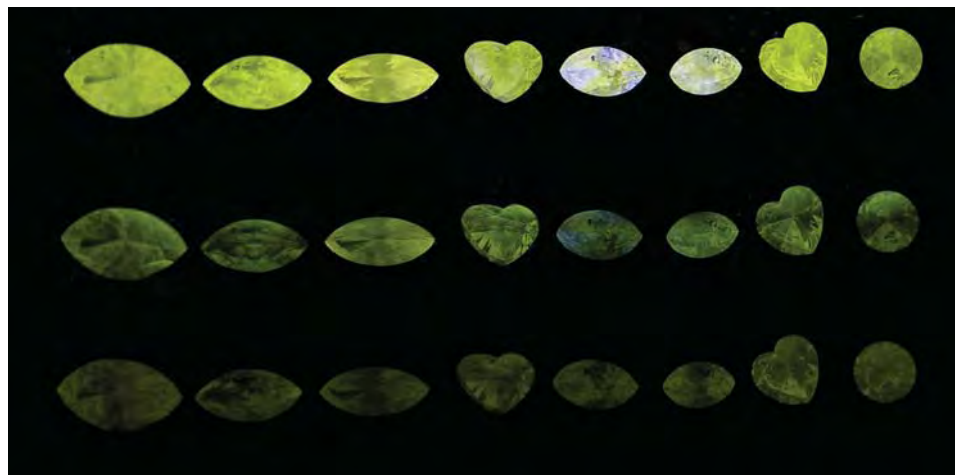


Figure 5. These samples (nos. 2.1–2.8, from left to right) demonstrate the appearance of Classic chameleon diamonds when exposed to long-wave UV (top row), short-wave UV (center row), and after the UV source was turned off (bottom row). Composite photo by T. Hainschwang.

this study exhibited a remarkable inversion of luminescence and phosphorescence behavior when heated (box A).

Infrared Spectroscopy. The infrared spectra also help distinguish the two groups of chameleon diamonds:

1. *Classic group:* low to moderate concentrations of nitrogen, mainly A aggregates (rarely A~B), and low-to-moderate hydrogen content (figure 7)
2. *Reverse group:* high to very high concentrations of nitrogen, mainly in the form of B aggregates (very rarely B<A), and low-to-high hydrogen content (figure 8)

Classic Group. The low-to-moderate nitrogen, type IaA chameleon spectra (Classic group) are characterized by hydrogen-related absorptions at 4496, 4167, 3235, 3186, 3181, 3160, 3143, 3138, 3107, 2786, and 1405 cm^{-1} (not all of these are visible in figure 7). A peak present in most Classic chameleons at 1434–1428 cm^{-1} (again, see figure 7) was relatively weak and broad (FWHM $\sim 25\text{--}35 \text{ cm}^{-1}$). This absorption was in no way related to the intensity of a platelet peak at 1358–1380 cm^{-1} , as described by Woods (1986; see figure 9). Most of the stones showed a weak type Ib character, which was visible as some hydrogen-related peaks such as the 3143 cm^{-1} line (Woods and Collins, 1983), a shoulder at 1135 cm^{-1} , and in a few stones as very weak sharp peaks at 1344 cm^{-1} .

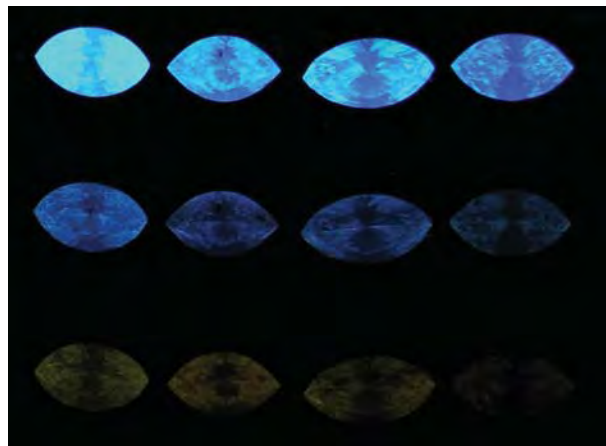
In addition to the hydrogen- and nitrogen-related features, the Classic chameleon diamonds exhibited absorptions at 1548–1544 cm^{-1} and 1590–1577 cm^{-1} , plus a weak peak at 1464 cm^{-1} .

Reverse Group. The high-nitrogen, mostly type IaB chameleon spectra (Reverse group) also exhibited

hydrogen-related features: sharp peaks at 4496, 4167, 3236, 3107, 3055, 2982, 2813 and 2786 cm^{-1} were observed (figure 8; peaks at 3055, 2982 and 2813 are too small to be seen at this scale). However, the Reverse chameleon diamonds lacked any features assigned to a type Ib character. The peak at 1430 cm^{-1} was found to be asymmetric and relatively strong and sharp (FWHM $\sim 8\text{--}9 \text{ cm}^{-1}$), and it could be directly correlated with the intensity of the platelet peak (figure 9) as documented by Woods (1986).

The N-related absorptions in the one-phonon region were truncated in the Reverse chameleon spectra (see figure 8), so the strengths of the 1282 and 1175 cm^{-1} absorptions that indicate the relative amounts of A- and B-aggregates could not be compared. Consequently, to determine which aggre-

Figure 6. These samples (nos. 4.7–4.10, from left to right) demonstrate the appearance of Reverse chameleon diamonds when exposed to long-wave UV (top row), short-wave UV (center row), and after the UV was turned off (bottom row). Composite photo by T. Hainschwang.



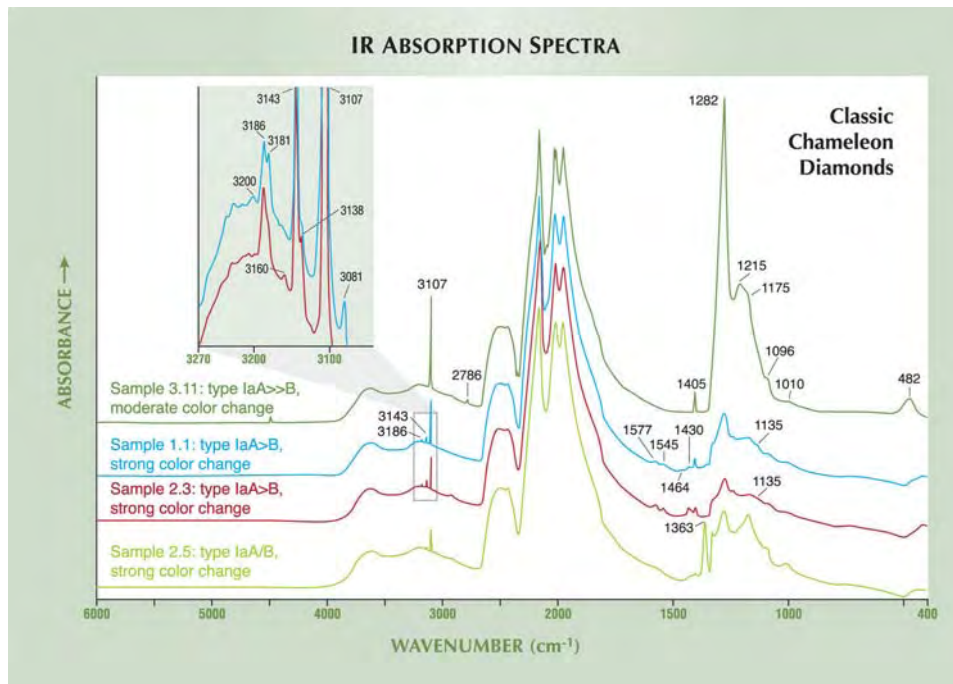


Figure 7. The infrared spectra of Classic chameleon diamonds show variable hydrogen and nitrogen contents. The spectrum of sample 2.5 is the exception, since strong B-aggregate absorption is very rare in such diamonds. The spectra show that the quantity of IR-active hydrogen does not correlate to the intensity of the color change. The hydrogen-related absorptions indicating a type Ib character are shown in the inset. The spectra have been shifted vertically for clarity.

gates were dominant, related peaks at 1010 cm^{-1} (B-aggregates) and 482 cm^{-1} (A-aggregates) were compared. In these stones, the 482 cm^{-1} peak was typically very weak or absent, whereas the 1010 cm^{-1} feature was always strong; it thus could be concluded that the Reverse chameleon diamonds are predominantly type IaB diamonds.

Several absorptions between 1577 and 1450

cm^{-1} were noted in spectra of certain Reverse group diamonds (i.e., at 1577, 1554, 1551, 1546, 1543, 1526, 1523, 1521, 1518, 1508, 1500, 1498, 1490, 1473, and 1450 cm^{-1}). None of the studied chameleon diamonds exhibited deformation-related amber center absorptions (i.e., with main features in the range of $4165\text{--}4065\text{ cm}^{-1}$; DuPreez, 1965 and Hainschwang, 2003).

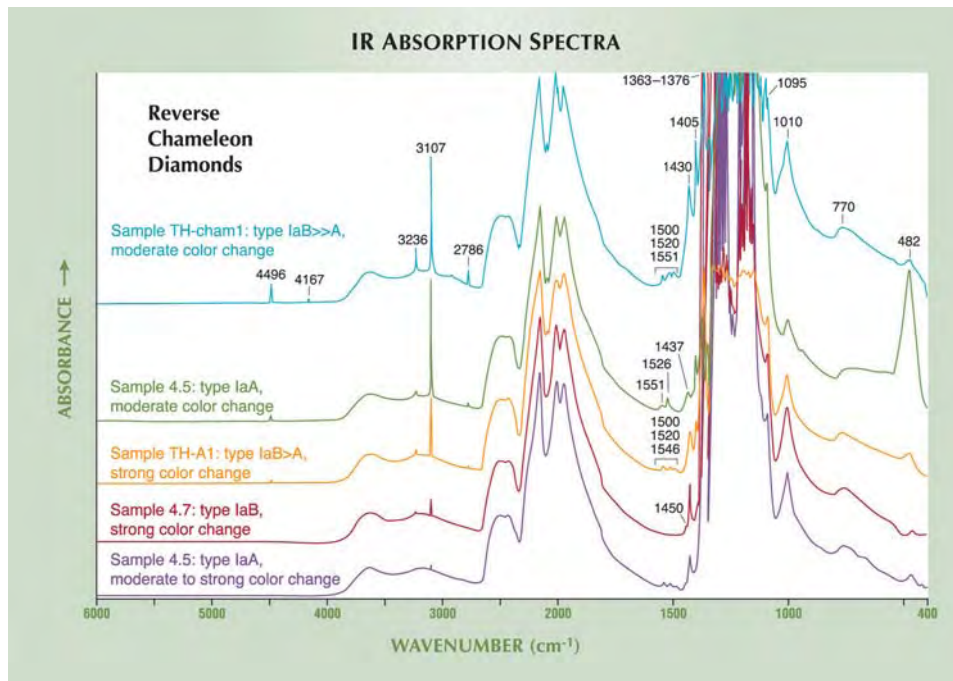


Figure 8. The infrared spectra of Reverse-chameleon diamonds show similar features, except for a more variable hydrogen content. The spectrum of sample 4.5 is the exception, since strong A-aggregate absorption is very rare in such diamonds. The spectra show that the quantity of IR-active hydrogen does not correlate to the intensity of the color change. The spectra have been shifted vertically for clarity.

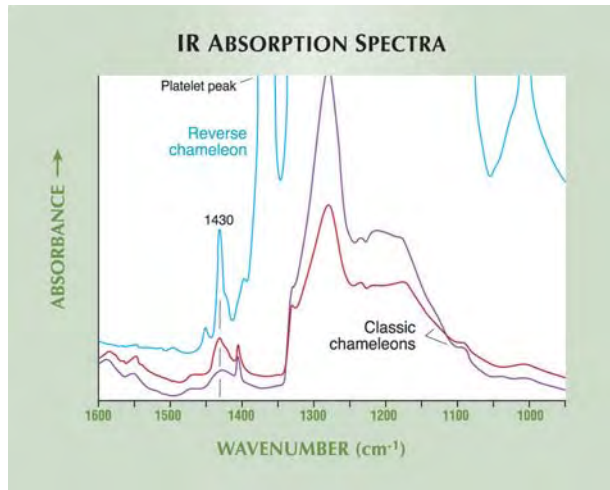


Figure 9. The 1430 cm^{-1} absorption is present in the IR spectra of both Classic and Reverse chameleon diamonds. However, the specific appearance of this absorption and absence of a platelet peak in the Classic chameleon diamonds indicates that the 1430 cm^{-1} peak in those diamonds has a different origin than the platelet-related 1430 cm^{-1} feature in the Reverse chameleons.

Vis-NIR Spectroscopy. As was the case for standard gemological testing and FTIR spectroscopy, the two groups of chameleon diamonds also showed different absorption spectra in the visible to near-infrared range.

Figure 11. These Vis-NIR spectra compare the absorption features of a yellow-orange type Ib/aA diamond colored by the 480 nm band, a grayish yellow-green H-rich diamond, and a Classic chameleon diamond showing the 480 nm band and H-related features. The spectra have been shifted vertically for clarity.

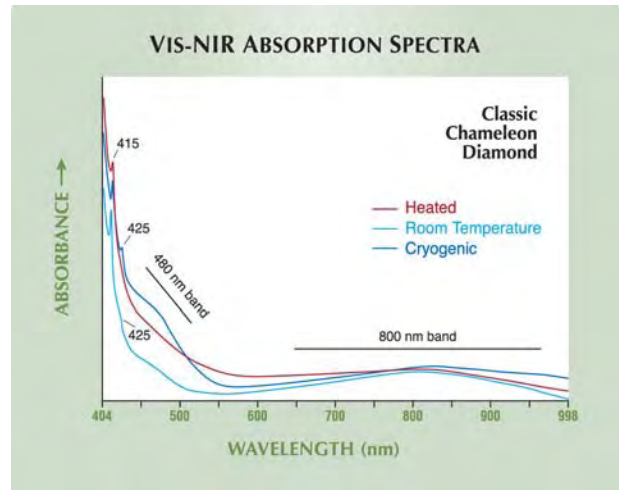
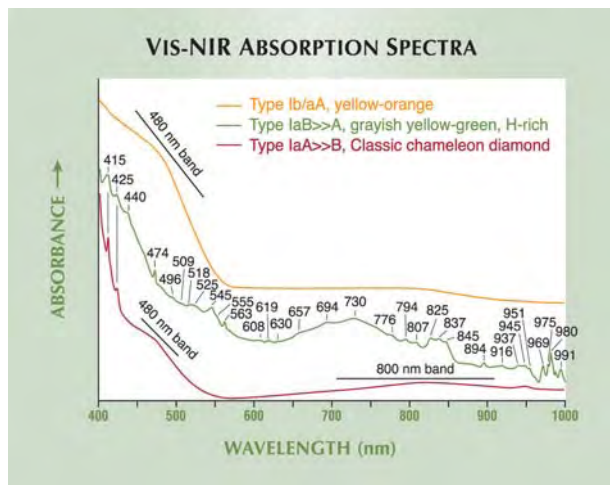
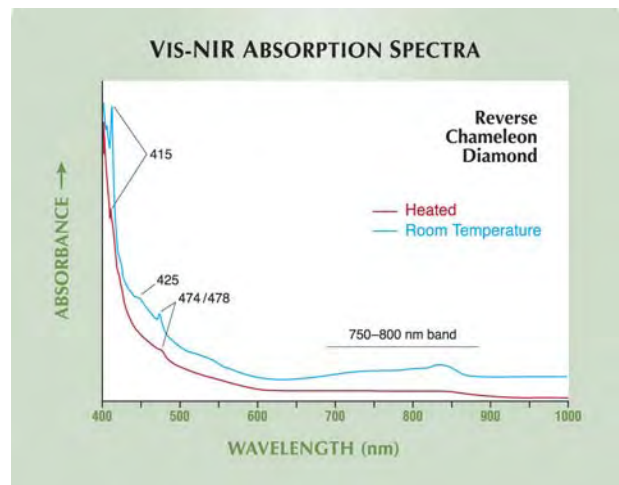


Figure 10. These Vis-NIR spectra were recorded for a Classic-group chameleon diamond at room temperature, when cooled with liquid nitrogen, and when heated. The characteristic 425 nm band and the broad features at 480 and 800 nm became less pronounced when the diamond was heated. The spectra have been shifted vertically for clarity.

Classic Group. Diamonds from this group showed absent or usually weak absorption at 415 nm (N3), weak absorption at 425 nm, a weak to distinct broad band at 480 nm, and a very broad band centered at 775–825 nm (figure 10).

Figure 12. These Vis-NIR spectra of a Reverse-group chameleon diamond were recorded at room temperature and when heated. Heating weakened the characteristic peaks between 415 and 478 nm and the broad band centered at 750–800 nm. The spectra have been shifted vertically for clarity.



Spectra taken at temperatures of 150–350°C (i.e., with a stone exhibiting its unstable color) revealed a weakening of all the above-mentioned absorption features. There was also a general decrease in transmittance in the blue and, particularly, green regions of the spectrum (again, see figure 10). This behavior was reported previously by Fritsch et al. (1995).

In addition to the hydrogen-related features recorded in the infrared spectra (e.g., at 3107 and 1405 cm^{-1}), evidence of hydrogen was found in the visible range as the 425 nm absorption, which always occurred together with the 480 nm band. The 480 nm band is known from type Ib/aA diamonds of orange to orangy yellow color (Field, 1992; Zaitsev, 2001, p. 296). In the experience of the authors, hydrogen-related bands are known mainly from the spectra of grayish green to grayish yellow diamonds. A comparison of these spectra with that of a Classic chameleon diamond can be seen in figure 11.

Reverse Group. Diamonds from this group showed strong N3 and N2 centers, with absorptions between 415 and 478 nm (“cape lines”) and a broad asymmetric band in the 650–900 nm region that was centered at 750–800 nm (figure 12). The differences between the spectra of heated and ambient-temperature stones were not always very distinct. All of the absorption features commonly weakened on heating (again, see figure 12).

Photoluminescence Spectroscopy. Again, two different groups of spectra were obtained, corresponding to the Classic and Reverse groups (figures 13 and 14). While the spectra differed considerably between the two groups, they also had some peaks in common, such as a strong emission at 701 nm. The Classic group exhibited a total of 44 PL emissions between 554 and 949 nm, versus 20 emissions for the Reverse group.

Classic Group. The broadband emission of the Classic group chameleon diamonds occurred mainly as one band centered at 630–650 nm; a weak band centered at 730 nm also was usually visible, which is caused by the vibronic structure of the 701 nm center (Iakoubovskii and Adriaenssens, 2001). The color of this luminescence induced by the 532 nm laser is equivalent to reddish orange or orangy red. In the experience of the authors, this broadband emission is similar to the one exhibited by type IaA/Ib orange to orangy yellow diamonds that exhibit the 480 nm band (figure 15), which is consistent with the comparison seen in figure 11.

The chameleon diamonds of the Classic group (figure 13) were characterized mainly by usually strong emissions at 590 and 595 nm, sometimes a weak to strong peak at 701 nm with associated vibronic sidebands at 716 and 726 nm (Iakoubovskii and Adriaenssens, 2001), and several weaker but

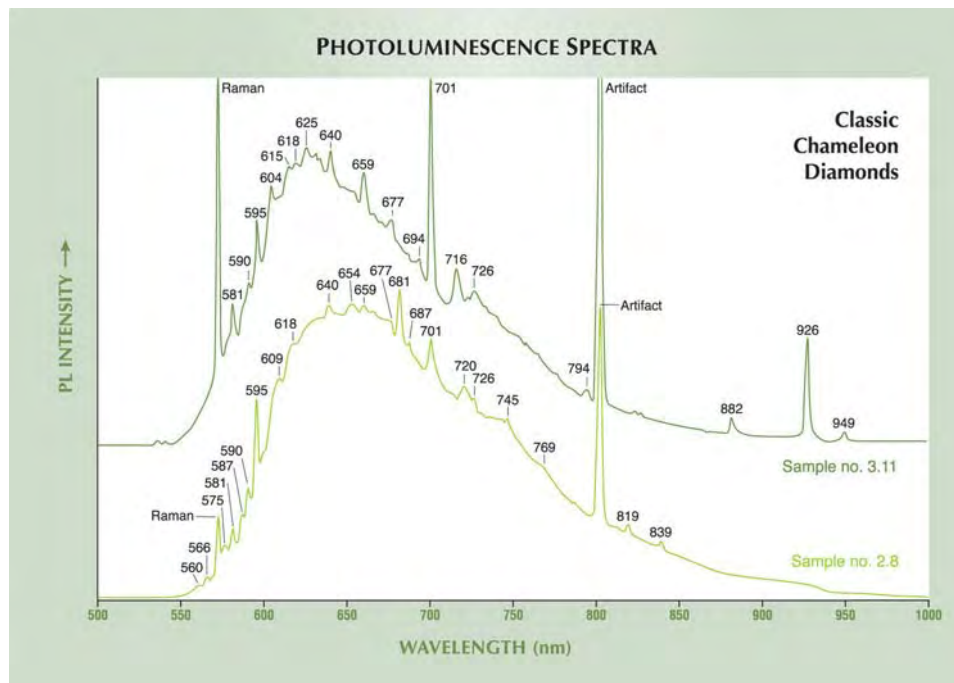


Figure 13. Typical PL spectra for Classic chameleon diamonds are shown here. The peaks in the NIR region between 700 and 950 nm are characteristic. The spectra have been shifted vertically for clarity.

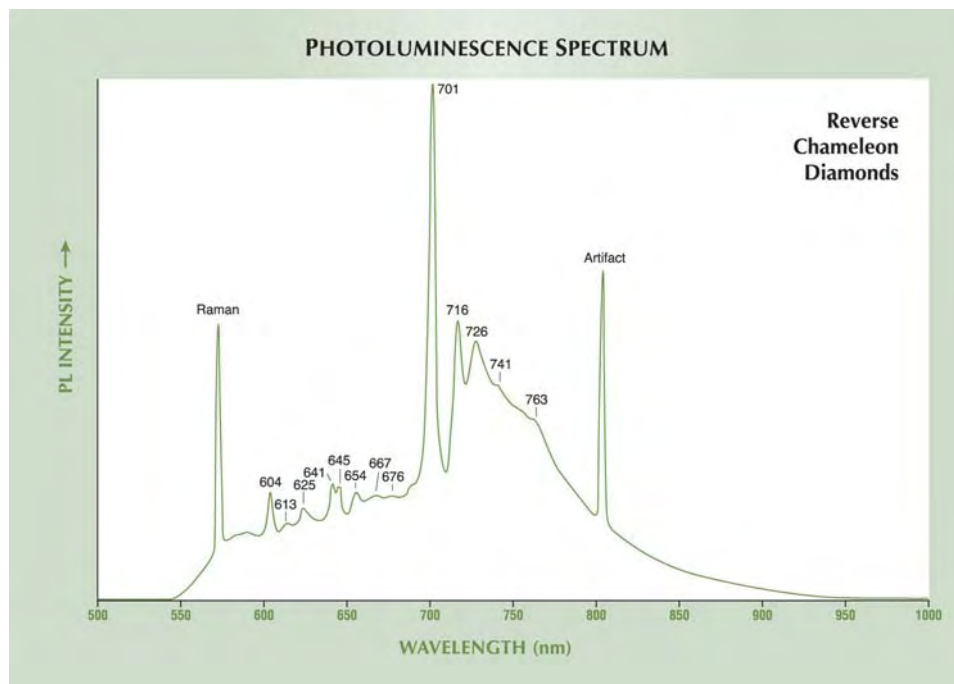


Figure 14. This PL spectrum is typical for a chameleon diamond of the Reverse group (sample 4.5) is shown here. Characteristic features include the peak at 604 nm, the dominant 701 nm center, the doublet at 641/645 nm, and the GR1 peak at 741 nm.

very characteristic peaks in the NIR region of the PL spectrum, at 769, 794, 800, 819, 839, 882, 926, and 949 nm.

Reverse Group. For the Reverse group, PL variations from stone to stone were minor (figure 14). These diamonds had luminescence spectra that basically consisted of one large, sloping plateau-like structure comprised of multiple bands between 580 and 800 nm. The luminescence excited by the 532 nm laser was equivalent to an orange yellow to orange emission.

The PL spectra of the Reverse group samples (figure 14) were characterized mainly by a peak at 604 nm, a doublet at 641 and 645 nm, and a strong to very strong emission at 701 nm with vibronic sidebands at 716 and 726 nm (Iakoubovskii and Adriaenssens, 2001). The PL peaks in the NIR region of the Classic samples were not present in the spectra of the Reverse chameleons, except for the 926 nm feature, which was detected in the spectra of two samples. Most of the Reverse group diamonds showed a very weak 741 nm GR1 peak and a weak feature at 763 nm.

DISCUSSION

Analysis of the Vis-NIR absorption spectra of the chameleon diamonds confirms that the transmission window between the two broad bands at 480 and 800 nm is responsible for the green color of the Classic group (Fritsch et al., 1995). On heating, the

480 nm absorption is slightly reduced and the 800 nm band practically disappears, which explains the change in color (Fritsch et al., 1995). The 800 nm band is very broad and ranges all the way from the red all the way to the yellow region. Therefore, there is a transmission window centered at about 560 nm, which is shifted toward the red and yellow regions on heating. The 480 nm band absorbs slightly in the blue and accentuates the transmission window at 560 nm in the green. Unfortunately, UV-Vis absorption spectroscopy at room and elevated temperatures did not record any features consistent with a change to a greener color in the Reverse group. Further work is needed to establish the cause of this color modification. The reduction of the bands centered at 750–800 nm would only explain a yellower color, but not a greener hue. A luminescence effect can be excluded, since no green transmission luminescence was observed in the Reverse chameleon diamonds, regardless of temperature.

The long-lasting phosphorescence is a very characteristic feature of chameleon diamonds. Conversely, the authors have noted a lack of phosphorescence in samples of yellow to “olive” hydrogen-containing diamonds with spectral properties similar to chameleons, but lacking any chameleon behavior.

The Reverse chameleons contain more nitrogen and hydrogen than the stones from the Classic group. There is a known correlation in diamond between the presence of hydrogen and relatively

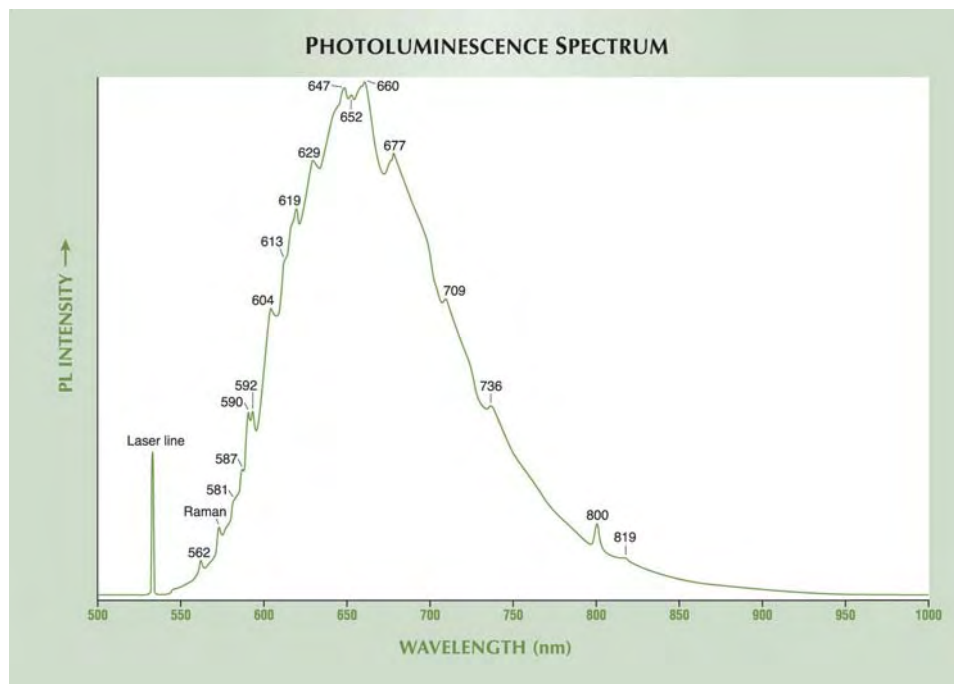


Figure 15. In this PL spectrum of a natural yellow-orange diamond colored by the 480 nm band, the broadband emission is very similar to the one observed in the Classic chameleon diamonds.

large amounts of nitrogen (Iakoubovskii and Adriaenssens, 2001; Rondeau et al., 2004); therefore, any H-rich diamond will be N-rich as well. As expected, Reverse chameleons show more distinct absorptions related to their hydrogen-rich character, in particular in the visible range, with bands of the “yellow-gray to violet to brown family,” for example, at 563 and 474 nm (Fritsch et al., 1991). Although no definite proof exists that these absorptions are due to a defect containing hydrogen, the authors can confirm that all these absorptions are exclusively present in hydrogen-rich diamonds and are therefore hydrogen-related. The absorption complex between approximately 600 and 900 nm, with apparent maxima in the range of 820–860 nm (not seen in Classic chameleons) is also probably H-related (see figure 11). Therefore, the change in color seen in the Reverse chameleon diamonds, mostly explained by the reduction in these bands at around 140°C and above, is clearly related to the presence of hydrogen. The exact atomic-scale nature of these defects is unknown at present.

In the infrared range, the C-H related absorptions in H-rich diamonds have been described by Fritsch et al. (1991), as well as by Woods and Collins (1983), and have been recently reviewed by DeWeerd et al. (2003) and Rondeau et al. (2004). In the chameleon diamonds studied here, no correlation was found between the strength of the color change and the amount of the IR-active hydrogen. On the contrary, yellow to “olive” diamonds with very high hydrogen content usually exhibit no chameleon behavior

(Hainschwang, 2004). “Olive” diamonds colored by plastic deformation do not show a chameleon behavior, either. However, such stones do clearly show different color distribution in the form of colored graining along octahedral slip planes (Hainschwang, 2003). The infrared spectra of such “olive” type IaA and Ib stones exhibit amber center absorptions (Du Preez, 1965), typically with the main feature being a double peak at 4165 and 4065 cm^{-1} (Hainschwang, 2003; Massi, 2003). Previous work has demonstrated that in strongly zoned Classic chameleons, the more intensely colored zones are richer in hydrogen; thus, at least the intensity of color appears to be hydrogen-related (F. Notari, pers. comm., 2004).

The presence of the 1495 cm^{-1} absorption seems to imply that Reverse chameleons have undergone irradiation and annealing (Zaitsev, 2001, p. 44) in nature, unlike the Classic ones. This natural irradiation is confirmed by the presence of a weak GR1 emission at 741 nm in the PL spectra of most Reverse chameleons.

The 1430 cm^{-1} absorptions seen in both groups appear to be different: In the Classic chameleons, the observed range of positions between 1434 and 1428 cm^{-1} , the band width of 25 to 35 cm^{-1} , and the missing correlation with the platelet peak indicate that this absorption is not the same as the 1430 cm^{-1} absorption described by Woods (1986). This is in fact the first report of this feature. In contrast, the sharp 1430 cm^{-1} absorption in the Reverse chameleons correlates well with the

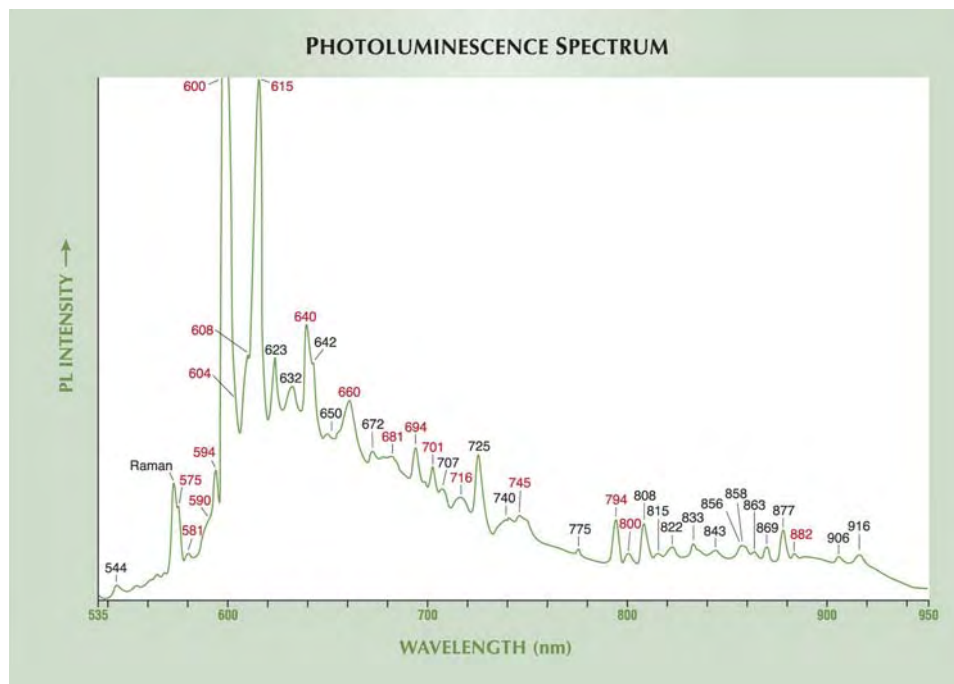


Figure 16. In this PL spectrum of a Ni-rich HPHT-treated synthetic diamond, the emissions in the NIR region are typical for Ni-related defects. There are many similarities to the features seen in Classic chameleon diamonds; identical peak positions are marked in red.

platelet peak and thus clearly points toward the feature published by Woods (1986).

The Classic chameleon category shows two absorptions (at 1590–1577 and 1548–1544 cm^{-1}) that may correspond to those reported at 1580 and 1544 cm^{-1} by Collins and Mohammed (1982) in natural brown diamonds. Interestingly, the somewhat broad 1434–1428 cm^{-1} feature was only present together with the 1548–1544 cm^{-1} and 1590–1577 cm^{-1} absorptions; none of them occurred as isolated features. Even though these absorptions were found only in the Classic chameleon diamonds, which were richer in hydrogen, a direct correlation between them and the hydrogen content could not be established with certainty. Nevertheless, our observations indicate that these absorptions may tentatively be assigned to a hydrogen-related defect. The features at 1546, 1543, 1518, and 1500 cm^{-1} seen in the Reverse chameleons have been described by Iakoubovskii and Adriaenssens (2001) and Hainschwang (2004) in hydrogen-rich diamonds. The absorptions at 1577 and 1546 cm^{-1} seem to be the same as those seen in the Classic chameleons.

Emissions at 581 and 596 nm detectable by PL spectroscopy have been reported previously, for diamonds with yellow luminescence (Zaitsev, 2001, pp. 212, 216) to long-wave UV. They are absent in Reverse chameleons, which primarily luminesce blue to long-wave UV. The vibronic structure of the 701 nm center (with its sidebands at 716 and 726 nm) was identified by Iakoubovskii and Adriaenssens (2001) as probably nickel-related. The 794 nm emis-

sion seen in the PL spectra of many Classic chameleon diamonds is interpreted as a nickel-nitrogen defect that has been documented in synthetic and certain natural diamonds (Lawson and Kanda, 1993). A distinct doublet at 883 and 884 nm found in synthetic diamonds grown by the temperature-gradient method with a Ni catalyst was assigned to a nickel defect (Lawson and Kanda, 1993); in certain samples, a single peak at 882 nm was found instead (figure 16). The peak observed in the Classic chameleon diamonds at 882 nm can most probably be assigned to the same or a similar Ni-related defect.

The 926 nm PL peak in the Classic (and rarely also the Reverse) chameleon diamonds has been recorded by one of us (TH) in some hydrogen-rich violet-blue-gray and “straw” yellow diamonds, as well as in one HPHT-treated yellow diamond that was originally olive-brown. In this diamond, the 926 nm peak (absent before treatment) was created during the HPHT process (2000°C at 65 kbar for 10 minutes). Interestingly, it was produced together with a vibronic system, yielding peaks at 701, 716, and 726 nm (Hainschwang et al., 2005). The tentative assignment of the 701 nm center to a Ni-related defect by Iakoubovskii and Adriaenssens (2001) leads to the possible attribution of these apparently related features to a nickel-nitrogen defect. This is due to the fact that a defect created by the annealing of a “normal” type Ia diamond most probably involves nitrogen. Assuming that this is a nickel defect as proposed by the above authors, its creation by annealing indicates a nickel-

nitrogen complex for the defects at 701 and 926 nm.

Most of the other sharp bands in the PL spectra of Classic chameleon diamonds also have been observed in natural brown diamonds (Smith et al., 2000; Zaitsev, 2001; Hainschwang, 2003), and the ones seen in the Reverse chameleons are seen in hydrogen-rich diamonds from the Argyle mine (Iakoubovskii and Adriaenssens, 2001). The defects responsible for most of these emissions are unknown. Many of the PL emissions shown by Classic chameleons are reminiscent of those seen in synthetic diamonds grown with a Ni catalyst; such stones characteristically show multiple emissions in the NIR range (figure 16).

The presence of Ni in the Classic and the Reverse chameleons as indicated by PL spectroscopy was recently confirmed by one of us (TH) using EDXRF chemical analysis: two Reverse and two Classic chameleons were analyzed and all of them exhibited rather distinct Ni peaks.

The observation of a color change solely induced by relatively low heat in the Reverse chameleons indicates that a thermochromic color change can be caused by a hydrogen-related defect. The photochromic color change induced by storage in the dark is unique to the Classic chameleon diamonds. Three factors may be involved in the combined thermochromic and photochromic chameleon behavior of the Classic group: the implied weak type Ib character, a specific (although unknown) hydrogen-related defect, and possibly the presence of Ni.

The Classic and Reverse groups are related to some degree and do have significant properties in common. However, the fact that the Reverse group lacks a photochromic color change and exhibits only a weak-to-distinct thermochromic color change raises the question as to whether such solely thermochromic diamonds should be called chameleon diamonds, or whether this name should be reserved for diamonds exhibiting both thermochromic and photochromic color change. Presently, the GIA Gem Laboratory only recognizes diamonds in the latter, "Classic" group as chameleons.

CONCLUSIONS

This study has differentiated two sample groups from a collection of 39 chameleon diamonds: those showing only thermochromic color change and those that exhibit both thermochromic and photochromic behavior. Each group exhibited distinctive hue changes. We propose the term *Classic* for

those that show the green-to-yellow behavior with heating or after prolonged storage in the dark; this color change is commonly associated with chameleon diamonds. Those that lack a photochromic color change—that is, they become slightly greener and more saturated only when heated—are here called *Reverse* chameleons.

The presence of the 480 nm band and hydrogen-related features such as the 425 nm absorption suggests that Classic chameleon diamonds fall between very hydrogen-rich diamonds and type IaA/Ib diamonds that exhibit the 480 nm absorption band (figure 11). This is also strongly indicated by the fact that some truly hydrogen-rich diamonds such as the Reverse chameleons exhibit this "low temperature" (i.e., below 200°C) thermochromic color change. This is further confirmed by comparison of the PL spectra of Classic chameleons and those of type Ib/aA orange diamonds that exhibit the 480 nm band (again, see figures 13 and 15). Hydrogen-rich diamonds very frequently exhibit PL spectra reminiscent of those of the Reverse chameleons (Hainschwang, 2001; Iakoubovskii and Adriaenssens, 2001). The influence and role of single nitrogen and the 480 nm band in the color change of the Classic chameleon diamonds will be the subject of future research by the authors.

We have shown that the easiest way to identify chameleon diamonds is by heating them to moderate temperature and observing the change in color. However, this study proved that the Classic chameleon diamonds also could be identified by a combination of their spectroscopic properties and their reaction to UV radiation. This is preferable to heating, to avoid modifying the color of green diamonds that are not chameleons; their radiation-caused coloration is rather sensitive to heat and in some cases absorptions in the visible range are known to be modified at temperatures as low as 275°C (see, e.g., Collins et al., 1988). All of the chameleon diamonds exhibited yellow phosphorescence after exposure to short-wave UV. The absence of this yellow afterglow in any hydrogen-containing yellow to "olive" diamond indicates that no chameleon effect will be present. Also, in the experience of the authors, stones that lack traces of hydrogen in their IR spectra and stones that show amber-center absorption were never found to exhibit this unusual change in color (see e.g., Hainschwang, 2003). The Reverse chameleon diamonds cannot always be identified without heating, but since yellow diamonds are not permanently modified by

simple heating at relatively low temperature, the heating test is not problematic for such samples.

The presence of hydrogen and nickel in these diamonds has been demonstrated by various spectroscopic methods; emissions assigned to Ni impurities were identified particularly in the Classic group by PL spectroscopy.

At present, we can only speculate about the cause of the color change in Classic chameleon diamonds.

The results presented here point toward a defect involving hydrogen combined with the 480nm band, which is related to isolated single nitrogen atoms. This combination seems to cause the thermochromic and photochromic change in color; whether Ni plays a role in this color change remains to be seen. In the diamonds exhibiting only a thermochromic color change, such as the Reverse chameleons, the defects appear to be solely hydrogen-related.

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