Photoluminescence Features of Carbonado Diamonds

Wuyi Wang, Ren Lu, and Tom Moses
GIA Laboratory, New York

Carbonado is a natural polycrystalline diamond, usually with a gray-black color and a porous texture, that has been found only in alluvial deposits in Brazil, central Africa, and Russia. Unlike kimberlitic diamond, carbonado is opaque and does not contain typical mantle-derived mineral inclusions, and it has much smaller crystal sizes. Several models of carbonado genesis have been proposed, including metamorphism caused by a meteoric impact on the earth's crust during the Precambrian era, the transformation of organic sedimentary carbon into diamond in a cold subducted slab, and radiation-induced diamond formation from organic carbon (Robinson, 1978; Smith and Dawson, 1985; Kaminskii, 1987; Ozima et al., 1991; Shibata et al., 1993; Daulton and Ozima, 1996; Kamioka et al., 1996). However, its origin remains debatable (Heaney et al., 2005).

In recent years, some relatively large carbonados faceted for jewelry have been submitted to the GIA Laboratory for identification reports. These gemstones were nicely polished and suitable for detailed spectroscopic analysis. Here, we report on the photoluminescence features of three faceted carbonados collected at liquid nitrogen temperature and, based on our results, propose some constraints on the geologic conditions of their formation.

The sizes of these faceted carbonados varied from 8 to 24 ct (figure 1). They were opaque and consisted mainly of numerous micro-diamonds that formed a typical microporphyritic texture featuring void spaces of varying size. The fine-grained matrix exhibited either gray or orange to red colors under a gemological microscope (figure 2). Under the strong UV radiation of the DiamondView, they displayed regions with two different fluorescence colors: green, or orange to red. The sample with the gray matrix showed mainly green fluorescence, and the stone with the orange to red fine-grained matrix displayed strong red fluorescence (figure 3). In the sample that showed intermediate matrix features, the orange fluorescence was distributed mainly along the boundaries between diamond grains.

All three samples featured strong emission peaks from the NV centers. Emission from NV^- with ZPL at ~637 nm was much stronger in the orange to red fluorescence region than in the green fluorescence region. Moderately strong emissions from the H3 (N-V-N), 3H (interstitial), GR1 (vacancy), and H2 ($N\text{-}V\text{-}N^-$) defects were also detected. A weak 523.8 nm peak was observed in the sample with relatively strong GR1 emission. A very strong peak at 903.5 nm was observed in the sample with the orange to red fine-grained matrix. Other prominent features included emissions at 388.8, 470.2, 537.4, 546.1, 547.0, and 566.0 nm. The H3 and NV^- showed a clear shifting of emission peaks, with zero-

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phonon line (ZPL) positions at 503.4 to 503.6 and 637.2 to 637.5 nm, respectively. For this reason, the H3 and 3H emissions almost completely overlapped in spectra collected with 488 nm laser excitation, but they could be easily separated in the spectra collected with 325 nm laser excitation.

Peak broadening is a common feature for all the emission peaks, except for the one sharp peak at 546.1 nm. Instead of two separate peaks, the ZPL of GR1 occurred essentially as a broad band with the main peak at ~743 nm and a shoulder at ~740.5 nm. The peak width (full width at half maximum, or FWHM) of the NV centers in kimberlitic single-crystal diamonds was linearly correlated between the ZPLs at 575 and 637 nm. It increased gradually with increasing brown coloration caused by plastic deformation, but were all below 1.5 nm. In contrast, FWHM of NV centers in carbonados were much broader (2.5–4.5 nm) (figure 4), even though a linear relation was maintained. No H4 or N3 defects were detected in any of these samples. NV centers with similar broad peak widths have been reported in other carbonados (Kagi et al., 2007).

Since these carbonados were opaque, the regular absorption spectra in the infrared and UV-Vis regions could not be collected. However, the photoluminescence features observed in this study indicate that the samples contain a substantial amount of nitrogen impurity, but only a moderately aggregated form. The prevalence of NV centers and the H2 defect demonstrates the existence of a substantial amount of isolated nitrogen, which acts as an electron donor. The absence of the N3 and H4 defects indicates that the highly aggregated B-form nitrogen is likely absent in these carbonados. Significant radiation damage is another important feature of carbonados, as GR1 and 3H defects are induced by radiation exposure. Based on the stability and formation processes of these observed lattice defects, it is reasonable to believe that these photoluminescence features were introduced *after* the aggregation/formation of carbonado in a still-unknown geologic source. Due to their porous texture, carbonados are permeable to the infiltration of radioactive fluids. This irradiation produced defects such as vacancies (GR1) and interstitials (3H), and it also severely damaged the diamond lattice structure. The combination of vacancies with preexisting isolated nitrogen formed the NV centers, and with the A form of nitrogen induced the H3 and H2 defects.

Carbonado diamonds are geologically very old—2.6 to 3.8 billion years old, according to radiogenic lead isotopes analysis (Ozima and Tatsumoto, 1997; Sano et al., 2002). Just as in some kimberlitic diamonds, the mechanism by which isolated nitrogen escaped the nitrogen aggregation process over time remains a mystery, and it could hold a key to addressing the formation of carbonados.

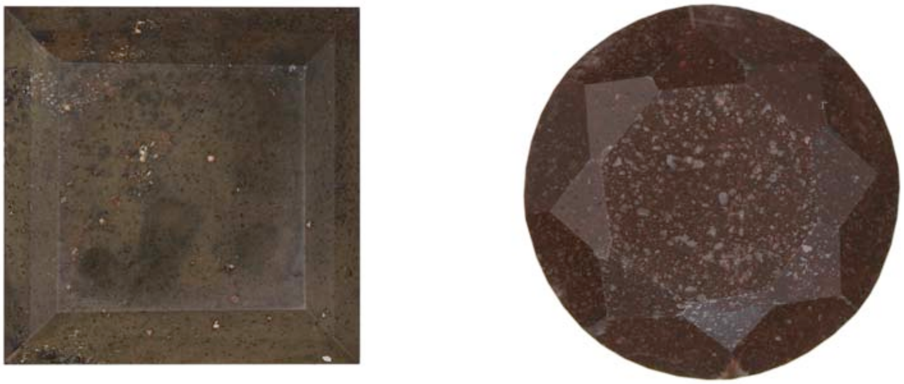

Figure 1. Several carbonados faceted as gemstones have been submitted to the GIA Laboratory for identification reports. The square cut on the left (15.8 x 15.8 x 12.2 mm) weighed approximately 24 ct, and was color graded as Fancy Dark brown. The round cut on the right (12.3 x 12.2 x 7.8 mm) weighed about 8 ct and received the same color grade.

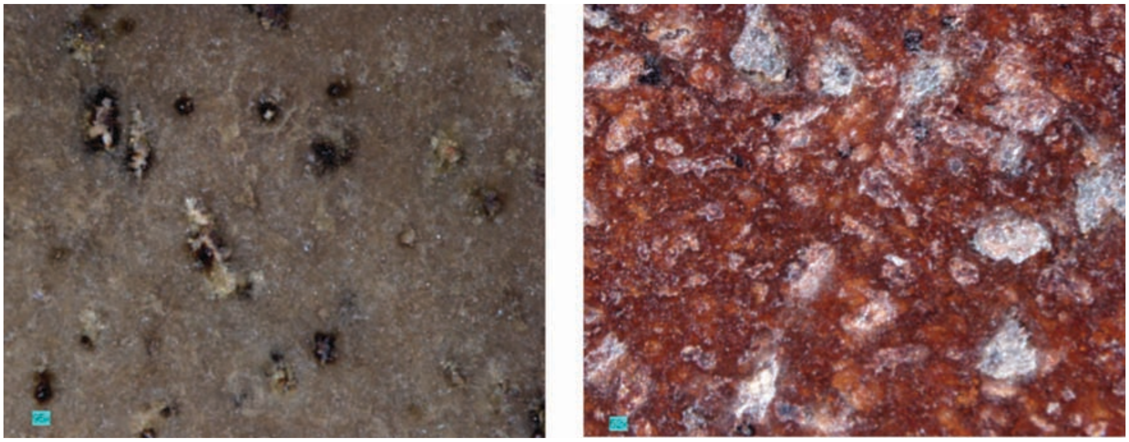

Figure 2. Carbonados consist of numerous micro-size diamonds with typical microporphyritic texture and different-size voids. Left image width: 1.2 mm. Right image width: 2.3 mm.

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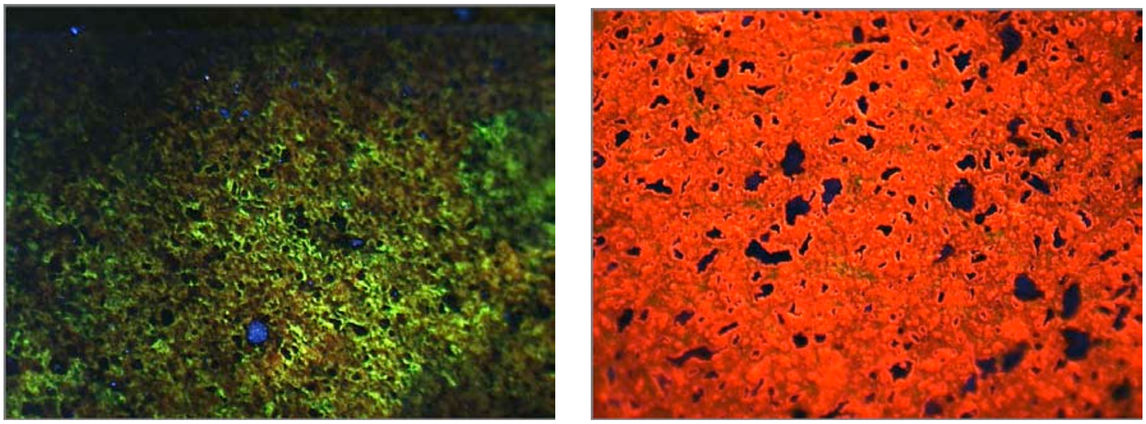

Figure 3. Under the strong UV radiation of the DiamondView, the carbonado samples displayed regions of either green or orange to red fluorescence. The square-cut sample in figure 1, which has a gray matrix, is dominated by green fluorescence arising mainly from the 3H defect. The round-cut sample in figure 1, which had an orange to red fine-grained matrix, displayed strong red fluorescence arising from the NV centers.

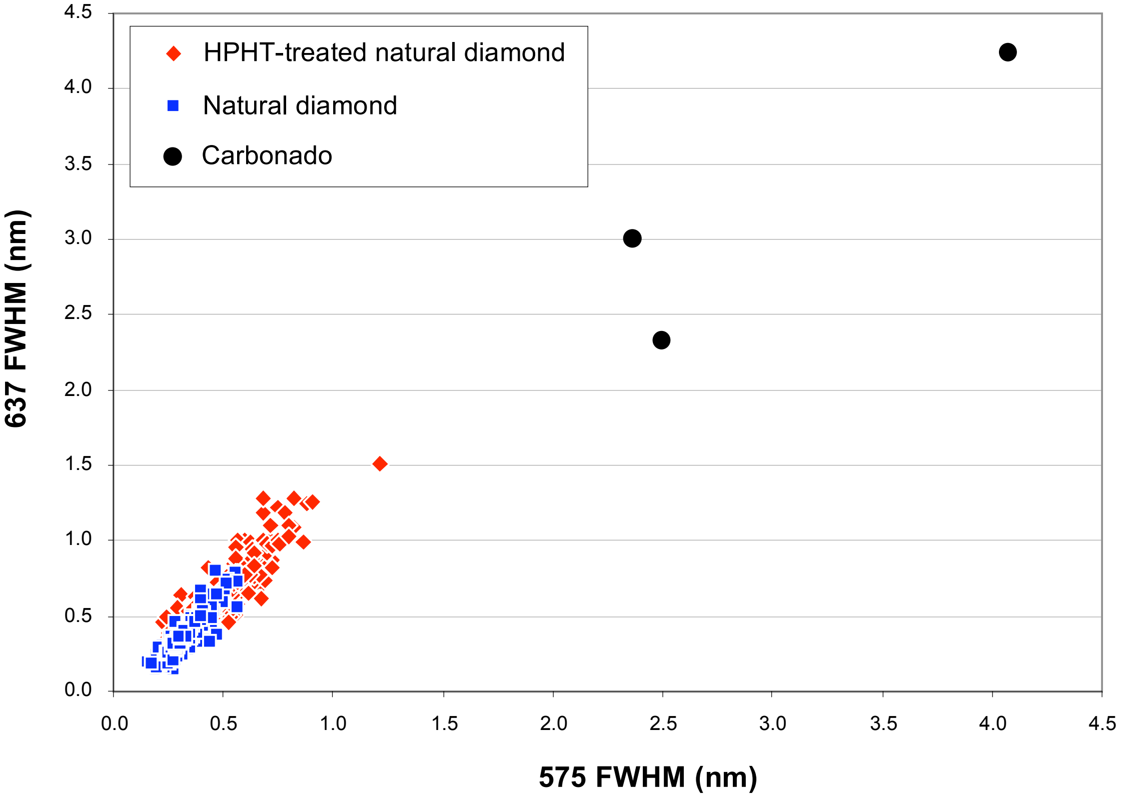

Figure 4. The emission peaks from the NV centers in carbonados are much broader than those observed in the photoluminescence spectra of kimberlitic single-crystal diamonds.

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