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Generation history of carbonado inferred from photoluminescence spectra, cathodoluminescence imaging, and carbon-isotopic composition

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ABSTRACT

Carbonado diamonds from the Central African Republic were investigated using spectroscopic observations and C-isotopic analysis. Based on photoluminescence (PL) spectra, carbonado samples were classified into two groups: Group-A, which exhibits an intense PL band at 504 nm; and Group-B, which exhibits PL bands at 504, 575, and 638 nm at room temperature. PL spectra measured at 120 K gave well-resolved side-band structures of 504 nm bands. Consequently, the 504 nm band of Group-A can be assigned to the 3H center attributable to self interstitials in diamond, whereas the 504 nm band from Group-B can be assigned to the H3 center attributable to a vacancy (□) trapped at nearest-neighbor substitutional nitrogen (N) pairs. The PL band at 575 nm, which is attributable to neutral N-□ pairs, is known to increase its width with increasing residual stress in diamond aggregates. The average FWHM of the 575 nm band and the standard deviations were 3.80 and 0.54 nm for Group-A carbonado, and 2.80 and 0.38 nm for Group-B carbonado. These values suggest that Group-A carbonado samples have higher residual stress than the Group-B samples. The presence of an H3 center and the lower residual stress in Group-B carbonado both suggest that they originated from higher temperatures compared to Group-A. Radiation halos were observed in cathodoluminescence (CL) images of both Group-A and Group-B samples. The CL halos are traces of radiation damage from radioactive nuclides. The texture of the haloes suggests that the radiation damage was a secondary event after formation of the carbonado diamonds. The average C-isotopic composition of Group-A is –23.6 ± 0.52‰ in $\delta^{13}C_{PDB}$ and that of Group-B is –26.3 ± 0.65‰. Group-A carbonado was enriched systematically in ^{13}C compared with Group-B carbonado. Isotopic fractionation might occur as a result of the different thermal history of carbonado.

Keywords: Carbonado, cathodoluminescence, photoluminescence, carbon isotope, diamond, radiation damage

INTRODUCTION

Carbonado is a polycrystalline diamond aggregate characterized by a ^{13}C-depleted isotopic composition, a lack of mantle-derived mineral inclusions (Trueb and Butterman 1969; Trueb and de Wys 1969, 1971; Vinogradov et al. 1966), and fluencies from radioactive nuclides that are suggested from both the significant radiation damage and fissiogenic noble gasses. Mineralogical and geological information on carbonado has revealed a crustal assemblage of mineral inclusions, highly reduced phases such as Fe, Ti, Si, SiC, etc. of primary origin (De et al. 1998), and a lack of association with kimberlitic magma. Rare-earth-element (REE) abundance patterns of carbonado from the Central Africa Republic (CAR) closely resemble those of kimberlite (Cullers and Graf 1984; Akagi and Masuda 1988; Kagi et al. 1994) whereas carbonado from Brazil exhibited REE patterns that differ greatly from those of kimberlite (Shibata et al. 1993; Kamioka et al. 1996). Recently, an attempt was made to duplicate the carbonado microstructure by sintering diamond powders without a catalyst at high pressure and high temperature (De et al. 2004). Based on those observations, several independent assumptions on the genesis of carbonado have been proposed, including metamorphism caused by a large impact on the Earth's crust in the Precambrian era (e.g., Smith and Dawson 1985); transformation of organic sedimentary carbon into diamond in a cold subducted slab (e.g., Robinson 1978), and others. Most of these models consider crustal carbon as the starting material of carbonado diamonds, suggesting that the ^{13}C-depleted isotopic compositions of carbonado strongly constrain the models proposed so far for the origin of carbonado. Radiation-induced diamond formation from organic carbon has also been proposed as a possible origin of carbonado (Kaminskii 1987), and the subsequent detection of spontaneous fission products in noble gases supported this hypothesis (Ozima et al. 1991). Furthermore, photoluminescence (PL) spectra of carbonado were observed that enabled the temperatures experienced by carbonado to be estimated (Kagi et al. 1994). In a previous paper, we investigated approximately fifty carbonado samples from CAR and found that their PL spectra fell mostly into two groups, named A and B by us, although an intermediate PL feature was also found.

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Group-A carbonado transformed to Group-B at 400 °C. These two carbonado groups exhibited different behavior during an oxidation reaction (Kagi et al. 1994). These differences suggest that the two groups of CAR carbonado samples had different thermal histories following diamond crystallization. Recently, De et al. (2001) reported a systematic correlation between C-isotopic composition and the color of cathodoluminescence (CL) in CAR carbonados. According to their study, the diamonds exhibiting green-colored CL were depleted in ^{13}C compared with those exhibiting orange CL. The close link between the spectroscopic properties and isotopic compositions may provide a clue to the origin of carbonado.

In our previous study, the PL spectra were measured at room temperature and those spectra were not well-resolved. Furthermore, the wavelength range also was limited. In the present study, measurements were undertaken at low temperature to resolve the fine structures in PL spectra and the measured range was extended. We can therefore make accurate spectroscopic assignments of the PL spectra and discuss the relationship between the C-isotopic composition and spectral properties of carbonado. Monochromatized CL images were also obtained to investigate the two-dimensional distribution of luminescence in carbonado.

SAMPLES AND EXPERIMENTAL METHODS

Samples

Carbonado samples studied here were taken from alluvial deposits in the Central African Republic; the average grain size was between 5 and 10 mm. REE abundances, thermal analysis, and PL spectra at room temperature for some samples studied here have been published previously (Kagi et al. 1994). Six carbonado samples (J8-0089, O22-007, O22-001, O22-012, O23-002, S7-0023) from that suite of samples were selected for the present study. Each stone was crushed to fragments several hundreds micrometers in diameter before analysis. Large fragments with diameters of several millimeters were polished for CL imaging. It should be noted that the polishing procedure can increase the temperature considerably and change the PL spectra, as described later, so cooling liquid was applied to the specimen.

Photoluminescence spectra

PL spectra were measured on fresh, unpolished surfaces of crushed carbonado fragments. PL spectra were obtained at 300 and 120 K with a Raman microprobe consisting of a 30 cm single polychromator (250is; Chromex, Inc.), equipped with an optical microscope (BX60, Olympus Optical Systems, Inc.), Ar$^+$ laser (5500 A, Ion laser technology, Inc.), a CCD camera with 1024 × 256 pixels (DU420-OE; Andor Technology), and a super notch filter (HIPF-514.5-1.0; Kaiser Optical Systems, Inc.) installed at the Laboratory for Earthquake Chemistry, University of Tokyo. The spectral resolution of the present system is approximately 0.04 nm. Detailed instrumental descriptions have been published elsewhere (Kawakami et al. 2003). Excitation light of the Ar$^+$ gas laser was a 488 nm line. Its power was 3 mW at the sample surface. The beam size of the incident light was approximately 2 µm for measurements at room temperature. PL spectra at 120K were obtained with a 5 µm diameter laser beam using a cryogenic cell (Linkam Scientific Instruments Ltd.) and a 20× objective lens. We also observed PL images under an optical microscope equipped with the notch filter that removed the intense Rayleigh scattering from the incident laser.

Cathodoluminescence image

CL images were obtained using a scanning electron microscope (SX-40A; Topcon Corp.) fitted with a SPEX 1/3 m grating monochromator installed at the National Institute for Material Science, Ibaraki, Japan. The electron beam diameter was 2 µm and the beam current was 8–10 nA. An accelerating voltage of 20 kV produced the most efficient CL from 2 µm below the sample surface (Piccirillo et al. 2004). The sample was held at 110 K on a liquid-nitrogen-cooled cold stage. Luminescence emitted from the sample was focused using an elliptical mirror to an entrance slit of a monochromator with a 300 grid/mm grating and was detected using a photomultiplier tube (R1104; Hamamatsu Photonics K.K.). Monochromatized CL emission images appearing on the monitor of the microscope were photographed. The spectral resolution was approximately 20 nm in wavelength.

In preparing CL samples, special caution was taken to avoid increasing the sample temperature because luminescence features are changed easily by annealing. However, all polished specimens prepared in this study underwent heating that changed the PL spectra before and after treatment. It is safe to say that the CL images obtained in this study and presumably in other studies were obtained from artificially annealed sample surfaces.

Carbon-isotopic composition

A fragment of crushed carbonado weighing ca. 0.2 to 0.8 mg was burned in pure oxygen in the presence of CuO powder at 1000 °C in a sealed glass quartz tube for half a day to produce CO_2 for analysis. Before combustion, quartz tubes were heated at 1000 °C in air to remove potential organic contaminants. Generated gas was purified cryogenically with a liquid nitrogen trap where all incondensable gases were pumped away and a subsequent trap consisting of an electric heater and liquid nitrogen at –100 °C trapped frozen water. Gas pressure in the vacuum line during purification was monitored using an electronic manometer. The isotopic ratio of C of the purified CO_2 gas was determined on a mass spectrometer (SIRA10; VG) installed at Tokyo University of Agriculture and Technology. Results are given in the standard δ^{13}C notation relative to the PDB standard. Overall precision of the present method, including preparation and analysis, is about ±0.2‰.

RESULTS

Photoluminescence spectra

Figure 1 shows PL spectra of the carbonado samples measured at room temperature. Three PL lines were observed at 504 nm (2.46 eV), 575 nm (2.16 eV), and 638 nm (1.95 eV) for the suite of samples. According to our previous classification, samples O22-007, O23-002, and S7-0023, which exhibit an intense PL line at 504 nm, are Group-A, whereas samples J8-0089, O22-001, and O22-012, which exhibit PL lines at 575 nm and 638 nm, are Group-B. A 2 µm diameter laser beam, much smaller than the sample size, was used in this study. For that reason, we confirmed that each stone showed uniform PL behavior. PL images observed under an optical microscope revealed that Group-A carbonado emitted light green PL and Group-B emitted orange PL.

Figure 2 shows PL spectra of carbonado obtained at 120 K. Observing the PL spectra at low temperature reveals the fine structure of the spectra that results from the vibronic transition relating to phonon interaction. For example, the Group-A sample exhibits PL with a zero phonon line at 504 nm and its phonon side bands at higher wavelength (Fig. 2a). The Group-B sample also shows weak PL at 504 nm (Fig. 2b), but displays a different side-band structure from that of Group-A as shown by the inset of Figure 2b shows Group-B carbonado. This side-band structure observed for Group-B carbonado is assigned to the H3 center of diamond (Davies 1977; Zaitsev 2001). It is difficult to distinguish 3H and H3 centers at room temperature because the positions of most intense zero phonon lines of these two centers differ by only 0.2 nm (Zaitsev 2001). The most prominent difference in the PL spectra between 3H and H3 lies in the relative intensity of the zero phonon line at 504 nm (purely electronic transition) and the adjacent phonon side bands. The 3H center exhibits a very strong zero phonon line and the remarkably weak side bands at 520 and 535 nm. On the other hand, the H3 center exhibits the zero phonon line at 504 nm and the phonon side bands with moderate intensities at 510 and 520 nm (Collins 1999; Steeds et al. 1999b; Zaitsev 2001). Another difference is

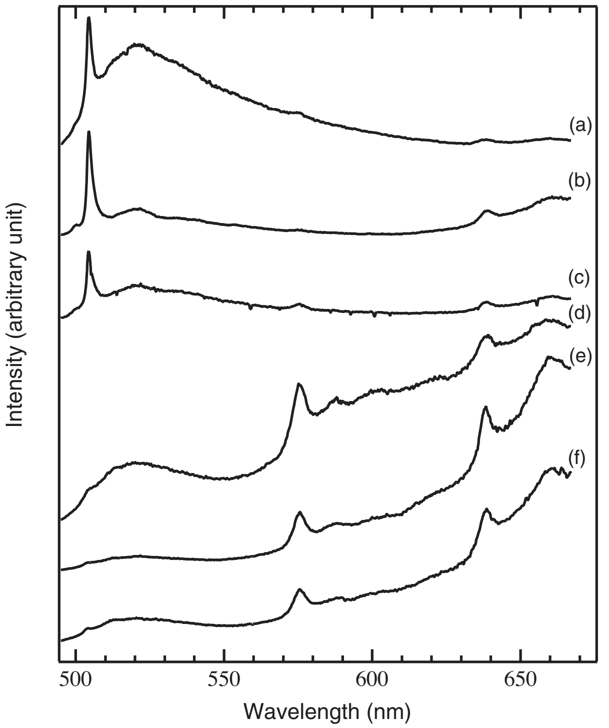

FIGURE 1. Photoluminescence (PL) spectra of carbonado observed at room temperature. (**a**) OCT23.002 (Group-A), (**b**) OCT22.007 (Group-A), (**c**) SEP7.0023 (Group-A), (**d**) JAN8.0089 (Group-B), (**e**) OCT22.012 (Group-B), (**f**) OCT22.001 (Group-B).

that the intensity of the zero phonon line for H3 is extremely weak at room temperature (see Fig. 2b). By observing the fine structure, including side bands at low temperature (see Figs. 2a and 2b), we attribute the 504 nm band of Group-A carbonado to the 3H center and that of Group-B to the H3 center. Detailed descriptions and implications of these color centers are described in a subsequent section.

Carbon-isotopic compositions

The C-isotopic compositions were determined on the three Group-A and three Group-B stones and the results are listed in Table 1. We measured isotopic compositions on more than one fragment of each stone; standard deviations for each sample are also listed in Table 1. The average C-isotopic compositions and their standard deviation are –23.6 ± 0.5‰ for Group-A carbonado and –26.3 ± 0.7‰ for Group-B carbonado. It is unambiguous that Group-A shows a higher $\delta^{13}C$ value than Group-B. Carbon-isotopic compositions of CAR carbonado have been reported previously by several groups. According to Kamioka et al. (1994), the C-isotopic compositions of six CAR samples ranged from –29.7 to –24.4‰. Shelkov et al. (1997) reported C-isotopic compositions of Ubangui carbonado ranging from –28.1 to –25.2‰, with an exceptional sample having $\delta^{13}C = -5.8‰$. Most recently, De et al. (2001) reported ion-microprobe analyses on CAR carbonado

TABLE 1. Chemical composition and carbon isotope composition of Central African carbonado samples

Sample	Group	C (%)	H (%)	$\delta^{13}C$ (‰)
S7-0023	A	94.5	0.67	–22.6(1)
O23-002	A	95.4	0.63	–24.1(1)
O22-007	A	92.0	0.73	–23.7(2)
O22-001	B	98.3	0.63	–25.8(3)
O22-012	B	96.5	0.65	–27.6(3)
J8-0089	B	90.7	0.83	–26.5(1)

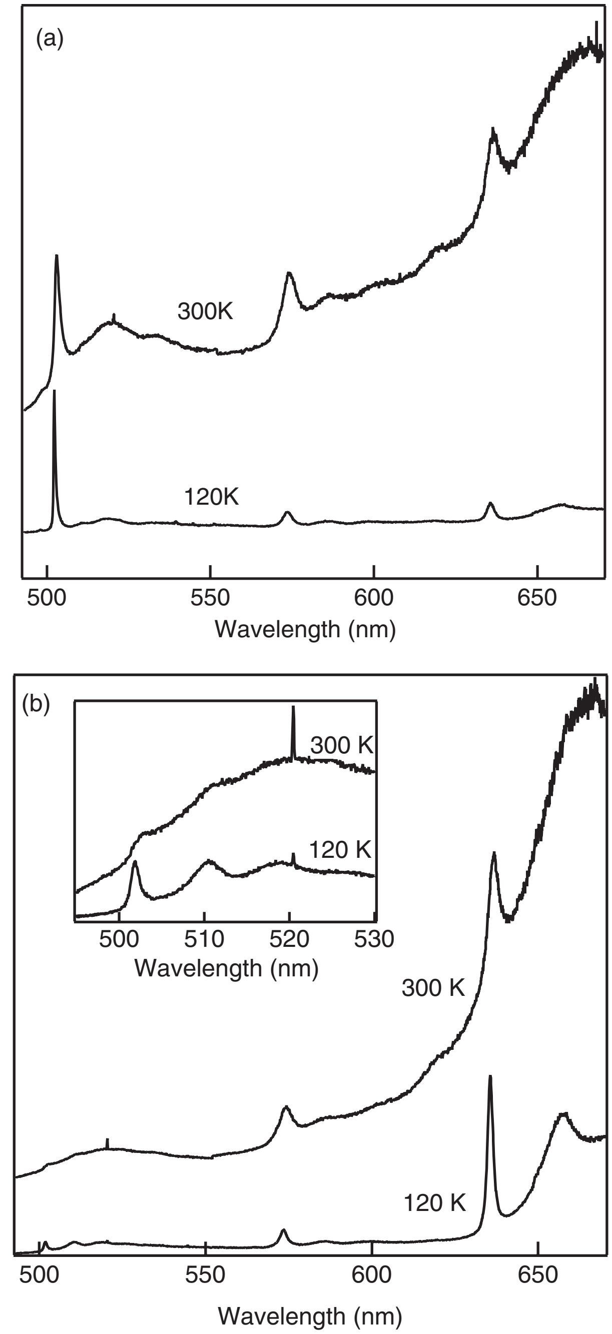

FIGURE 2. Photoluminescence (PL) spectra of two types of carbonado observed at 300 and 120 K. (**a**) Group-A carbonado. (**b**) Group-B carbonado. The inset shows enlarged spectrum. Fine structures in the side band differ between Group-A and Group-B. From features in the side band structure, PL spectra of Group-A can be assigned to the 3H center and those of Group-B to the H3 center.

and the C-isotopic compositions ranging from –26 to –24‰ with an instrumental precision of ±0.29‰. The present results are in fairly good agreement with the previously published range of C-isotopic compositions of CAR carbonado.

Cathodoluminescence images

Figure 3 shows monochromatized CL images of Group-A carbonado. Characteristic CL halos are visible in Figure 3a, for which the image was obtained at 600 nm. On the other hand, Figure 3b shows that those CL halos are not visible at a wavelength of 430 nm. This contrast strongly suggests that the CL halos result from the zero phonon line at 575 nm and its phonon side bands extending to the higher wavelength. A CL image of Group-B carbonado monochromatized at 600 nm also exhibited similar halos. A comparison of CL images of Group-A and Group-B carbonado taken at 600 nm is displayed in Figures 4a and 4b. No marked difference is visible in these photographs.

The carbonado surface was polished carefully for the CL measurements in this study. Using coolant liquid, particular care was taken not to increase the surface temperature. However, considerable changes in PL spectra were observed after polishing. Samples that initially exhibited PL spectra typical of Group-A with a 3H center changed to show the Group-B-like feature without the strong and sharp zero phonon line at 504 nm after the treatment. This finding suggests that the PL and CL of Group-A diamonds can easily change, and great care must be taken in preparing polished samples of carbonado for optical observations.

DISCUSSION

Background on luminescence spectroscopy and thermal history of carbonado

Before giving details regarding the PL spectra obtained on carbonado, the PL spectra of diamonds will be summarized briefly. Collins (1999) reviewed recent progress in peak assignments of the optical spectra of diamond. Radiation damage introduced by high-energy particles from radioactive elements,

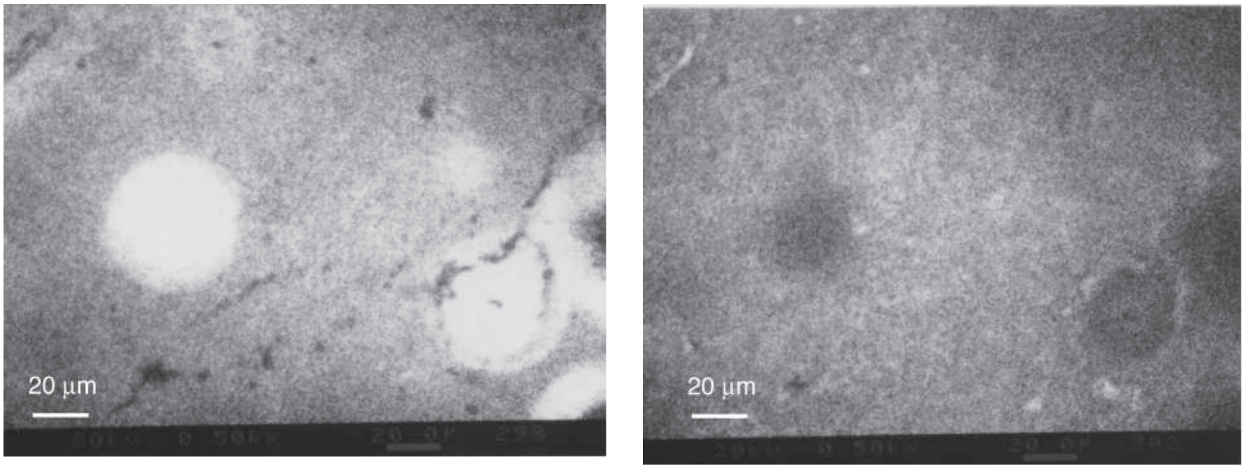

FIGURE 3. Cathodoluminescence (CL) images of Group-A carbonado monochromatized by the spectrometer at (**left**) 600 and (**right**) 430 nm. Note that the circular CL halos are bright at 600 nm, but not at 430 nm.

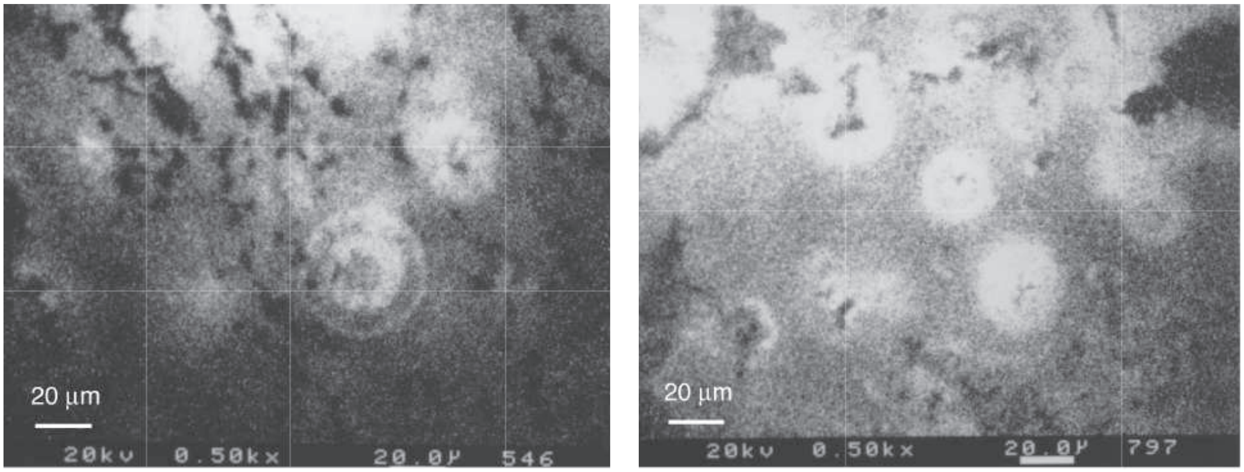

FIGURE 4. Cathodoluminescence (CL) images of carbonado monochromatized by the spectrometer at 600 nm for (**left**) Group-A carbonado and (**right**) Group-B carbonado.

as well as artificially accelerated electrons and ions, produces vacancies that are stable at room temperature. A zero phonon line (luminescence line not associated with a vibrational transition, i.e., a purely electronic transition) at 504 nm is called as 3H center and is related to self-interstitials in diamond (Steeds et al. 1999a; Zaitsev 2001). When annealing diamonds at high temperature, self-interstitials become mobile at lower temperatures and then vacancies become mobile at higher temperatures; in N-containing diamonds, vacancies become trapped at the location of N atoms to produce new color centers (Davies et al. 1992). The presence of N, the major impurity in natural diamonds, is fundamental for controlling the color and luminescence spectra of diamonds. In Type Ib diamonds (Clark et al. 1992), which contain isolated substitutional N atoms, a vacancy (= □) trapped at a single N produces a negatively charged (N-□)$^-$ center with a zero phonon line at 638 nm. A neutral N-□ center causes a zero phonon line at 575 nm. In Type Ia diamonds, which contain aggregated N impurities, a vacancy trapped at the nearest neighbor substitutional pairs (so-called A aggregates) produces an H3 center, causing a zero phonon line at 504 nm (Collins 1999; Collins et al. 2000). These luminescence lines are specific to the structure of color centers. Among the centers of interest to the present study, the 3H and H3 centers give rise to zero phonon lines at 504 nm. As described in this paper, these two centers are easily distinguishable at low temperature by observing the fine structure of phonon side bands resulting from the vibronic transition extending to higher wavelengths in the PL spectra (Kanda et al. 2003).

The presence of a 3H center in diamonds suggests the absence of substantial heating because the 3H center vanishes upon heating to 400–500 °C for 1 h (Kagi et al. 1994). In contrast, annealing at high temperature forms the H3 center. Spectral assignments of these two centers depict the thermal history of carbonado. A 3H center was detected in the Group-A carbonado but an H3 center was detected in the Group-B carbonado (see Fig. 2). These observations confirm that Group-B carbonado experienced higher temperatures than did Group-A, which had been reported in our previous papers (Kagi et al. 1991, 1994). It is also noted that both groups of carbonado contain N-□ centers at 575 nm and 638 nm. The presence of these centers implies that isolated N atoms are contained in the both types of carbonado samples. The coexistence of 3H centers and N-□ centers is very rare and needs further consideration. This is because N-□ centers are believed to form at high temperatures after the disappearance of 3H centers. The present result suggests that the formation of N-□ centers by thermal annealing followed by natural irradiation, which formed the 3H centers. However, further spectral measurements are needed, including FTIR measurements, to clarify the state of the N impurity in carbonado.

Residual stress in carbonado

Collins and Robertson (1985) reported that the width of zero phonon line at 575 nm in CL spectra correlates with the internal stress in artificially sintered diamonds. Similar estimations were reported from observations of other PL lines (Davey et al. 1984; Evans et al. 1984). According to those authors, all the zero phonon lines in luminescence spectra exhibited strain-broadening phenomena. Furthermore, the width of CL and PL spectra can be a measure of internal strain of artificial sintered diamonds. They concluded that the sintering process produced considerable internal strain in diamond grains and that the amount of strain depended on both the grain size of the diamonds and sintering temperature. We have applied this methodology to the CAR samples.

The full-width at half-maximum (FWHM) of the zero phonon line at 575 nm in the PL spectra measured at low temperature is shown in histograms (Fig. 5). Group-A carbonado exhibit an average line width of 3.80 nm with a standard deviation of 0.54 nm, whereas Group-B carbonado exhibit an average line width of 2.80 nm with a standard deviation of 0.38 nm. When applying these results to the relationship between the width of 575 nm zero phonon line and residual stress established by Collins and Robertson (1985), the average residual stresses of 1.5 and 1.0 GPa are obtained, respectively, for Group-A carbonado and Group-B carbonado. The absolute numbers of the residual stress might not be applicable because the widths of the 575 nm zero phonon line for CL and PL spectra might not coincide. However, a relative comparison of residual stress between the two groups of carbonado is possible.

The contrast in residual pressure between Group-A and

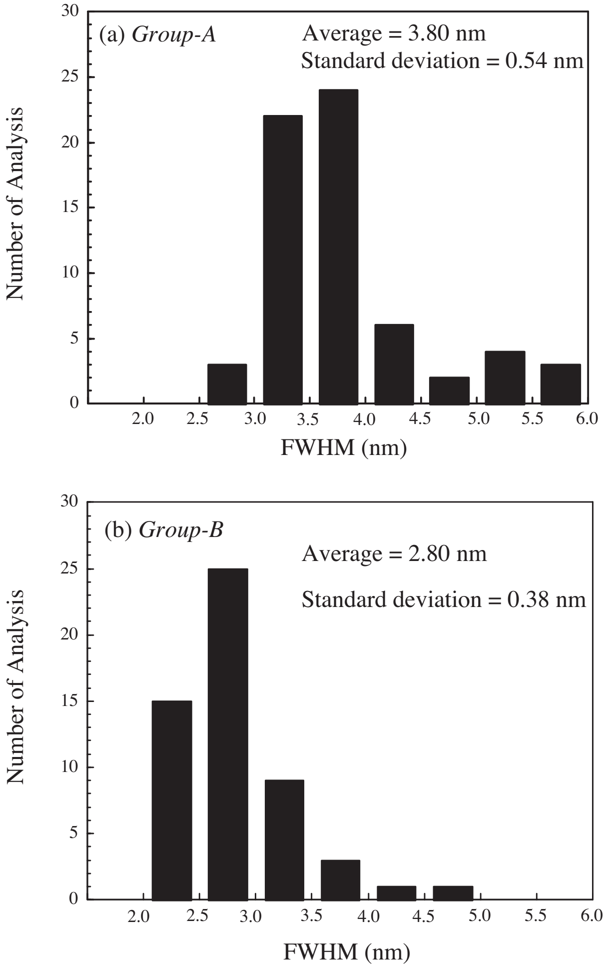

FIGURE 5. Histogram of the width of the 575 nm zero phonon line. (**a**) Group-A carbonado. (**b**) Group-B carbonado.

Group-B could be due to two causes. First, the grain sizes of diamond crystallites in the two types of carbonado differ from each other. In artificial sintered diamonds, the smaller the average grain size of the starting diamond powder, the larger the residual stress. If this were the case, then Group-A carbonado would be composed of smaller diamond crystals compared with Group-B. However, according to the thermal analysis reported by Kagi et al. (1994), oxidation occurs at much lower temperatures for Group-B carbonado than for Group-A. This result suggests that Group-B carbonado has a higher surface area or consists of diamonds with smaller diameters than Group-A. Consequently, the results from the thermal analysis and spectroscopic observation are inconsistent. Moreover, SEM images for sliced carbonado samples revealed no systematic microtextural difference between Group-A and Group-B (data not shown).

Second, the difference in annealing temperature can engender differences in the residual stress. Even if the two types of carbonados comprise diamond crystallites with similar sizes, annealing at higher temperature can cause relaxation of residual stress while enhancing plastic deformation at the grain boundaries. The PL spectra suggested a high-temperature origin of Group-B, as described before. The relatively low residual pressure for Group-B carbonado is consistent with the assumption that Group-B carbonado underwent annealing at higher temperature. Different thermal histories of Group-A and Group-B are most likely the cause of the difference in the residual stress.

Formation stage determining PL spectra and possible mechanism for carbon isotope fractionation

This study has revealed that Group-A and Group-B carbonado exhibit considerably different C-isotopic compositions and have diverse properties relating to their thermal histories. The coexistence of the (N-□) center at 575 nm and the $(\text{N-}\square)^-$ center at 637 nm for both Group-A and Group-B carbonado demonstrates the presence (trace) of isolated N atoms in carbonado (Chrenko et al. 1977; Evans and Qi 1982). In general, the isolated N impurities in diamond aggregate with each other and form N pairs or, eventually, N platelets at high temperature on a geological time scale. The presence of isolated N atoms in carbonado means that sufficient time and temperature to aggregate N atoms had not been provided since the formation of the diamonds. This fact is consistent with the rapid crystallization of diamond, quenching from source materials oversaturated with C, which resulted in a high nucleation density that produced small diamond crystallites with a high dislocation density as recorded by TEM observations (De et al. 1998). However, we must consider the results of PL spectroscopy, which is a very sensitive method for detecting optical centers and irradiation to diamonds containing highly aggregated N atoms that result in the formation of N-□ centers (e.g., Collins 1999). Consequently, the presence of N-□ centers in carbonado does not necessarily mean that the dominant N impurity is in the isolated form. Infrared absorption spectra will clarify this ambiguity.

It is important to consider whether the PL features present in carbonado are syngenetic or epigenetic with respect to the crystallization of diamond. As conjectured by many researchers, carbonado genesis is sufficiently complex that it probably was a multi-stage process. The PL and CL of natural diamonds are derived from radiation-induced damage introduced by high-energy particles from radioactive elements located at the center of CL halos. Mendelssohn et al. (1979) suggested that the internal radioactive halos in natural diamonds result from the decay series of Th and U. CL halos from CAR carbonado also have been reported (Magee 2001). Recently, Fukura et al. (2005) reported that a pore can be found in the center of radiation haloes and suggested that the pore had been filled with radioactive inclusions.

The close relationship between the genesis of carbonado and irradiation from U and Th was indicated by the detection of fissiogenic noble gases (Ozima et al. 1991). Radiation-induced crystallization of diamond was proposed as a possible origin of carbonado (Daulton and Ozima 1996). The fissiogenic origin of diamond also has been supported by Pb-isotope systematics (Ozima and Tatsumoto 1997). The CL halos can provide direct evidence of the interaction between radioactive nuclides and diamond. The radius of CL halos is up to ~30 μm, and some halos have structures consisting of two or more rings, suggesting that several radioactive nuclides with different emission energies were located in the center of the halo (Mendelssohn et al. 1979).

Figure 6 displays an SEM image taken in the same area as the CL image shown in Figure 3a. A comparison of these two images reveals that the CL halos are larger than the crystallite size of the carbonado. In other words, the CL halos radiate beyond the grain boundaries of carbonado. This geometrical relationship suggests a secondary origin for the radiation damage, i.e., radiation damage occurred after the aggregation of the carbonado. It had been hypothesized that high-energy particles induced formation of carbonado diamonds in the crust from organic carbon with low δ^{13}C (Kaminskii 1987). Our present results do not support the radiation-induced formation of carbonado. Considering these circumstances, it is our opinion that diamond crystals in carbonados have a high-pressure origin.

Enigma of C-isotopic composition

Our present results have shown that Group-A carbonado having a 3H center exhibits a ^{13}C-rich isotopic composition compared with Group-B carbonado with an H3 center. As described already, Group-A carbonado samples emit light-green luminescence

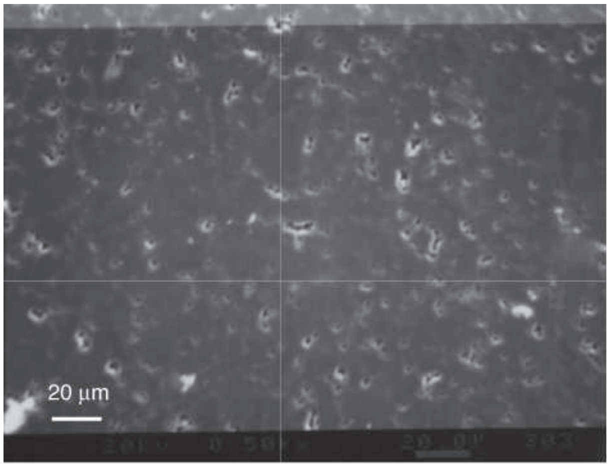

FIGURE 6. SEM image of Group-A carbonado in the same area as in Figure 3a.

mainly because of the 3H center, and Group-B samples emit orange luminescence mainly because of the 575 nm center. On the other hand, De et al. (2001) reported results opposite to the present study in terms of the relationship between CL color and C-isotopic compositions. According to their conclusions, the euhedral crystals that luminesced green exhibited mean $\delta^{13}C$ values of –26.5‰ ±0.2‰, whereas the red luminescent anhedral yielded mean $\delta^{13}C$ values of –24.4‰ ±0.2‰. Carbon-isotopic compositions were obtained from the bulk analysis in the present study, whereas those in De et al. (2001) were obtained from ion-probe microanalysis with a 20 μm diameter beam. Moreover, the sensitivity of each luminescence line might differ greatly between PL and CL. It is possible therefore that the colors of PL in the present study do not correspond to those of CL images observed by De et al. (2001). The PL measurements were performed on unpolished specimens in the present study, whereas the CL images in De et al. (2001) were obtained on a polished surface. As described above, we also tested mechanical polishing for the carbonado samples. According to our experience, even if the polishing procedure is very gentle, the luminescence intensity of 3H centers weakened considerably. This heat-induced change in PL intensity also was observed following laser irradiation. We suggest that the difference in the sample preparation procedures in both studies can be the cause of the difference in the colors of PL and CL. It is worth noting that polishing a diamond can substantially anneal color centers such as 3H, which can anneal out at relatively low temperature. Despite some discrepancies, these two studies suggest independently that the structure of radiation damage corresponding to CL and PL correlates with C-isotopic compositions of carbonado.

The observed difference in the C-isotopic composition between Groups-A and Groups-B carbonado samples can be interpreted in at least three ways. The first possibility is to attribute the differences in C-isotopic composition to the starting materials of the two types of carbonado. This explanation is very simple, but it is insufficient to provide a meaningful reason for the contrast in physical and chemical properties between the two groups. In particular, differences in thermal-analysis patterns (Kagi et al. 1994) and in residual stresses that were found in this study are difficult to explain solely by the difference in the source material.

Second, systematic differences in C-isotopic compositions might originate from Rayleigh fractionation at different temperatures. It has been suggested that oxidation of carbonaceous material during metamorphism could lower the $\delta^{13}C$ values, if temperatures are higher than 500 °C and if an oxidizing condition is present (Eiler et al. 1997). The isotope-fractionation coefficient between diamond and CO_2 is 1.01 at 500 °C, and diamond therefore would be depleted in ^{13}C compared with CO_2 (Bottinga 1969; Polyakov and Kharklashina 1995). Partial oxidation can result in lowered $\delta^{13}C$ values, if this were the case for carbonado. For Rayleigh fractionation during diamond oxidation, the isotopic composition of diamond crystallites comprising carbonado must be equilibrated with coexisting oxidant phases. This process requires C atoms to diffuse in the diamond crystallites at a rate similar to surface oxidation. One can justify this process by comparing the self-diffusion constant of diamond and the oxidation rate at a given oxygen fugacity and temperature. However, no reliable self-diffusion constant has been reported for diamond, so we cannot make a precise evaluation of Rayleigh fractionation during the oxidation of carbonado. Although the extremely low expected diffusion constant in diamond would seem to rule out that hypothesis (De et al. 2001), Rayleigh fractionation can account for all the experimental results obtained in this study without inconsistency. Furthermore, our spectroscopic information suggests that Group-B carbonado once had experienced temperatures higher than 400–500 °C. Given that the oxidation reaction occurred in this temperature range, the oxidation rate might be sufficiently slow to allow for self-diffusion in diamond. It would be almost impossible to account for the light C isotopes only by Rayleigh fractionation during the formation of the carbonado, but slight fractionation is explainable by Rayleigh fractionation.

The third possibility involves exchange during alteration with a hydrothermal fluid having a different C-isotopic compositions. If Group-B carbonado interacted with a fluid at higher temperature having a light C isotopic composition compared with Group-A carbonado, the relationship between thermal history and C isotopic composition could be explained. This scenario could reconcile the discrepancy in the relationship between luminescence and C-isotopic composition found in the present results and in De et al. (2001), if we assume hydrothermal fluid with different C-isotopic compositions.

The ^{13}C-depleted isotopic composition cannot solely demonstrate that the source material of carbonado is biogenic C because some kimberlitic diamonds also show very low $\delta^{13}C$ values (Smirnov et al. 1979). Carbonado with heavy C-isotopic compositions could be discovered in the future.

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