

Cathodoluminescence investigations on the Popigai, Ries, and Lappajärvi impact diamonds

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ABSTRACT

Twenty impact diamond samples from the Popigai, Ries, and Lappajärvi astroblemes were analysed using cathodoluminescence (CL) at room temperature (RT). Five of the samples were further investigated at liquid nitrogen temperature (LNT). Cathodoluminescence images allowed for the discrimination of diamond from graphite, thus contributing to a better understanding of the reciprocal relationships between these carbon polymorphs and their overall textural features.

Cathodoluminescence spectral measurements of the diamonds revealed emission bands and peaks located at 1.8 eV (688 nm), 2.23 eV (556 nm), 2.32 eV (534 nm), 2.39 eV (519 nm), 2.49 eV (498 nm), and 2.8–2.9 eV (443–427 nm). The bands at 2.8–2.9 eV and at 1.8 eV, observed at RT, were related respectively to vibronic levels (involved in electronic transitions), located at dislocation defects and to dislocations. Regarding the other lines, which were only visible at LNT, there may be a relationship between the peaks at 2.32 eV, 2.23 eV, and 2.39 eV, and the content of amorphous carbon phases.

Some spectral features may be considered a possible signature of impact diamonds. In particular, the band at 1.8 eV, which is uncommon in terrestrial natural diamonds, and the peaks at 2.23 eV and 2.32 eV, are present in all the samples studied.

INTRODUCTION

The relationship between diamond and pressure has been well known since the carbon phase-diagram was established; however, in nature almost all diamonds are related to persistent high-pressure conditions in the mantle, where they originated. Consequently, most of our knowledge about them derives from studies of this typical kind of diamond.

Impact diamonds represent another important type. Such diamonds constitute mineralogical evidence of shock metamorphism and give unique information about impact processes. Nevertheless, in spite of their importance and the progress that has been made in their study, some genetic aspects of impact diamonds are still not completely clear. The cathodoluminescence (CL) technique is effective in studying diamonds, but very few impact diamonds from terrestrial impactites (rocks being affected by impacts resulting from collisions of planetary bodies) have been studied by this method (Val'ter et al. 1992).

The first discovery of impact diamond was made in 1888, in the Novo Urei, Russia, ureilite (Yerofeev and Lachinov 1888). Soon after this, Foote (1891) found diamonds in fragments of the Canyon Diablo, Arizona, iron meteorite. But it was only in the 1950s that Ninger (1956) considered a shock origin for the diamonds of the Canyon Diablo meteorite. Later, his hypothesis was confirmed by Lipschutz and Anders (1961), who established that these diamonds were of impact origin. At the same time, De Carli and Jamieson (1961) reported the first

shock synthesis of diamond. After these studies, knowledge about the formation of diamonds by shock pressure and impact processes rapidly increased and many impact diamonds were found in meteorites (Vdovykin 1967, 1970).

It was only in the 1970s that Masaitis discovered the first occurrence of impact diamonds in the rocks of a terrestrial meteoritic crater, at the Popigai astrobleme in Russia (Masaitis et al. 1972). Other Russian scientists soon made further important contributions to this subject by discovering and describing high-pressure polymorphs of carbon in the impact glass of the Ries crater, Germany (Rost et al. 1978). A few years later, impact diamond discoveries were also made at other sites. These include the Kara (Ezersky 1982) and Puchezh-Katunski (Marakushev et al. 1993) impact structures of Russia; the Obolon, Il'inty, Terny, and Zapadny craters of the Ukraine (Gurov et al. 1995; Val'ter et al. 1992; Val'ter and Er'omenko 1996); and the Lappajärvi astrobleme (Masaitis et al. 1998a) in Finland. Occurrences of impact diamonds have also been reported recently from the suevitic breccias of the Onaping Formation (Sudbury, Canada impact structure: Masaitis et al. 1999), the "catastrophic layer" of the 1908 Tunguska impact event (Kvasnitsa et al. 1979) and the Yanis-jarvi impact structure (Vishnevsky and Pal'chik 2002), both in Russia.

In addition to in situ findings in the impactites of terrestrial meteorite craters, redeposited impact diamonds are also known to occur in unconsolidated Cenozoic sediments. Around the Popigai crater, for example, some of them were disseminated to form strewn fields (Vishnevsky et al. 1997). Strewn fields also occur around the Chicxulub crater. At Arroyo El Mumbra,

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Mexico, microdiamonds have been found in the K-T impactoclastic layer with the iridium anomaly (Hough et al. 1995a, 1997). Some other diamonds were derived from diamond-bearing impact structures by means of fluvial and other surface processes (Yurk et al. 1973). In situ or redeposited impact diamonds are also reported in eclogites in the related metamorphic complexes (Holovnya et al. 1977). In this connection, Vishnevsky and Raitala (2000) showed that impact diamonds may be preserved after exposure to high-grade regional metamorphism.

The findings described above are usually considered to be the so-called paramorphs (a particular kind of pseudomorph when the transformation has involved no change in chemical composition of the material, but only in the crystalline structure and physical properties) impact diamonds (PIDs), derived from either parental graphite or coal (Ezersky 1986; Masaitis et al. 1990; Val'ter et al. 1992; Vishnevsky and Pal'chik 1975; Vishnevsky et al. 1997). There are several examples in which such evidence is clearly demonstrated. These include grain morphology, preferred orientation of crystallites, the occurrence of lonsdaleite (a high-pressure polymorph of carbon with hexagonal close-packed structure), associations with target rock inclusions (material exposed at the site of an impact before crater formation), and occurrence within large bodies of impact melt rocks such as tagamites (impact melt rocks; term used in Russia). However, a new interpretation of the origin for some xenomorphic polycrystalline diamonds from Popigai—possible condensation from impact vapor—has been hypothesized recently by Langenhorst and Masaitis (1996), although this morphological type of diamond also may be explained by shock fragmentation of parental graphite segregations (Vishnevsky et al. 1997). Moreover, it is difficult to explain the diamond-bearing tagamites as condensation products.

Recently, a new type of condensation/nucleation impact diamonds (CNIDs), of nano- and micrometer size, has been found in association with impactoclastic material of the K-T boundary layer in Canada (Carlisle and Braman 1991; Gilmour et al. 1992) and with impactites from the Ries crater (Hough et al. 1995b).

Diamond formation in the Ries crater took place at ~30–140 GPa and ~700–4000 K (Vishnevsky et al. 1997), as revealed by experimental shock synthesis data (De Carli and Jamieson 1961; Hannemann et al. 1967; and others) and petrographic observations of shock metamorphism of enclosing rocks, a method commonly used to estimate the pressure-temperature conditions for the origin of impact diamond paramorphs probably derived from graphite (Vishnevsky and Pal'chik 1975; Masaitis et al. 1990). In a study of shock-induced graphite-diamond phase transition in the gneiss of the Ries impact crater, El Goresy et al. (2001) showed that the characterization of diamond and its relationship with graphite also help to provide information about formational mechanism(s), as well as estimating the pressure and temperature of the impact process. As for impact diamond paramorphs derived from coal, their origin took place in the Kara impact structure at ~25–60 GPa and residual temperatures of <3000 K (Ezersky 1982, 1986).

Most of the investigations listed above consider that, apart from CNIDs, impact diamonds are paramorphs that originated from shock and were derived from precursor graphite or coal by means, respectively, of a martensitic (a diffusionless solid-

state transformation involving a change in volume, shape, and structure but no change in concentration) or diffusion (involving fluid or any short-order range amorphous state of the source material) transformation; nevertheless, in spite of the progress that has been made, the origin of the diamonds found at impact sites is still not completely clear. As for CNIDs, their origin is even more obscure and debatable, as our knowledge of these minerals is still very poor. This group combines several types of diamonds that derive from various formation mechanisms and environments. Hough et al. (1995b) suggested that the Ries skeletal micro-diamonds may have originated by chemical vapor deposition (CVD) of carbon atoms from a plasma-like fireball. Masaitis et al. (1998b) suggested that the CNIDs were the result of the dissolution of PIDs in high-temperature impact melts. Vishnevsky and Raitala (2000) hypothesized that the Ries skeletal micro-diamonds and North American astrobleme-related nano diamonds originated through a mechanism of homogeneous nucleation.

Another intriguing aspect is the possible relationship between impact diamonds and parental graphite. For the Popigai diamonds in particular, Masaitis et al. (1998b) suggested that a back-inversion of diamond to graphite may occur, so that it remains generally unclear whether the graphite that coexists with the diamond is residual primary graphite or was formed by retrograde mineral transformation from diamond at high post-shock temperatures (Pratesi et al. 2002).

Concerning the mechanism of carbon transformation, Erskine and Nellis (1992), Val'ter et al. (1992), De Carli (1995), and Langenhorst and Masaitis (1996) proposed that the phase transformation was of the martensitic type. According to Vishnevsky et al. (1997), PIDs derived from graphite may originate from martensite, if the resulting paramorphs have preferred orientation of crystallites, or from diffusion, if the crystallites of the paramorphs have either weak orientation or no preferred orientation at all. Diamonds derived from coal may form by diffusion only (Vishnevsky et al. 1997). As for the presence of lonsdaleite, it has to originate first, but then may be partially or completely annealed to a cubic diamond while still in a shock-loaded state (Val'ter et al. 1992). De Carli (1998) emphasized the role of the initial crystallinity of carbon, so that a highly ordered graphite may be transformed to diamond at pressures above ~15 GPa and simultaneous temperatures above 1300 K. Conversely, Hirai et al. (1995) suggested that phase transformation in dynamic conditions is much easier at low graphite crystallinity.

Impact diamonds are important mineralogical evidence and give unique information about impact processes. Nevertheless, in spite of their importance and the effectiveness of the CL technique in investigating them (Klein et al. 1995; Marinelli et al. 1998; Iakoubovskii and Adriaenssens 2000a; Panczer et al. 2000; Sauer et al. 2000; Takeuchi et al. 2001; Zaitsev 2001), only a few studies have been done on diamond in meteorites (Grady et al. 1994; Bischoff et al. 1999; Grund and Bischoff 1999) and only one on diamond in terrestrial impactites (Val'ter et al. 1992). More frequently, Raman or infrared spectroscopy has been used to study impact diamonds in both meteorites and impactites (Koeberl et al. 1995; El Goresy et al. 2001).

The present study refers to paramorphs of Popigai (Arctic

Russia), Ries (Germany), and Lappajärvi (Finland) impact diamonds, deriving from parental graphite in the crystalline target rocks. Using optical microscopy, scanning electron microscopy (SEM), CL microscopy, and CL spectroscopy, impact diamonds from these three localities were investigated to define their CL spectral features, color, morphology, as well as their origin.

SAMPLES

Twenty diamonds were separated by thermochemical (alkaline fusion) treatment of impact melt rocks from the astroblemes listed above following the procedure of Rost et al. (1978) and Vishnevsky et al. (1997, 1999). The diamond samples are relatively small grains (Popigai 170–320 μm ; Ries 140–260 μm ; Lappajärvi 120–220 μm) of various colors, ranging from pale-yellow to yellow, yellowish-gray, gray, brownish-gray, and black. Each grain is a polycrystalline aggregate of diamonds that range in size from less than 0.1 to 1 μm . Graphite impurities sometimes occur as other components of these diamonds. We analyzed ten grains from the Popigai crater and ten from the Lappajärvi and Ries craters using SEM and CL methods.

EXPERIMENTAL TECHNIQUES

The single diamond grains were picked up with a thin needle and placed on a glass slide within a circular hollow recessed area. All of the samples were studied with optical microscopy so as to evaluate their colors and compare them with spectral measurements. Subsequently, they were put into a small metal cup and inserted into the electron microscope vacuum column. The samples were not coated, because the aim of the work was to study not only diamonds but also graphite remnants and the relationships among them.

The SEM used was an Oxford Instruments Leica Stereoscan mod. 420 ($E_{\text{max}} = 30 \text{ keV}$, $I_{\text{beam}} = 1 \text{ pA} - 1 \text{ }\mu\text{A}$) equipped with the MONO-CL system at the Department of Inorganic Chemistry, University of Turin (Italy). This CL system operates in both monochromatic (MC) and panchromatic (PC) modes.

In the MC mode, luminescence emitted from the sample is focused into a spectrometer consisting of a monochromator with a plane diffraction grating for light dispersion (spectral range 300–900 nm). Wavelength resolution is on the order of a few nanometers, depending on the entrance and exit slit aperture

after the monochromator that is used. Outgoing light is focused into a HAMAMATSU R376 photomultiplier tube with a fused silica window (spectral range 160–800 nm). The spectral range of the resulting apparatus is effectively 300–800 nm. In the PC mode, light is focused directly into the photomultiplier without passing through the monochromator, so that all wavelengths are collected and the signal is increased (Vittone et al. 2001).

Cathodoluminescence maps were acquired in both panchromatic mode (to select luminescence zones) and monochromatic mode (as the wavelength was the same as that of the main peaks). To compare photon emission from different diamond grains, spectra were collected using the same magnification (i.e., the same electron scanning area of about $30 \times 22 \text{ }\mu\text{m}$), a probe current of 200 pA for high luminescent grains and 1000 pA for low luminescent grains, and a voltage of 5 keV, and selecting the flattest regions to reduce sample geometry photon-collecting problems. The measured spectra were corrected for the spectral response of the instrument (based on data obtained by using calibrated sources both for wavelength and intensity), and peak locations were obtained through smoothing and fitting procedures using general purpose software (Microcal Origin Professional). All measurements were carried out at room temperature.

To verify the presence of other peaks and to improve the spectral analyses, additional data were collected on five grains by using a SEM Cambridge Stereoscan mod. 360 equipped with the Oxford MONO-CL system at CNR-IMEM Institute Parma (Italy). These measurements were carried out at liquid nitrogen temperature (LNT), using the same operative conditions of the previous RT measurements.

RESULTS

Optical microscopy observations

As shown in Table 1, although the grains exhibit several colors, the color is homogeneous within in each grain. Yellow grains with several shades ranging from pale-yellow to yellowish-gray are present in samples from all three craters investigated. Based upon data by Val'ter et al. (1992), the yellow hue of impact diamonds correlates with the amount of lonsdaleite that occurs as inclusions: the greater the amount, the more intense the color. According to those authors, lonsdaleite is easily annealed in a shock-compressed state; hence, the longer the duration of this state (i.e., the larger the impact crater), the smaller the amount of lonsdaleite. Never-

TABLE 1. CL analyses of diamonds at room temperature

	Grain	Color	A-band position (eV)	A-band FWHM (eV)	A-band area (a.u.)	B-band area (a.u.)	B-band / A-band
RIES	1	Yellowish – Gray	2.89 ± 0.02	0.50 ± 0.03	0.49	0.13	0.27
	2	Brownish – Gray	2.89 ± 0.01	0.43 ± 0.02	0.37	0.10	0.28
	3	Pale Yellow	2.82 ± 0.01	0.42 ± 0.01	1.40	3.54	2.53
	4	Brownish – Gray	2.90 ± 0.01	0.43 ± 0.02	0.27	0.09	0.33
	5	Pale Yellow	2.82 ± 0.01	0.46 ± 0.01	1.43	4.88	3.20
LAPPAJARVI	1	Irregular Gray Color	2.90 ± 0.02	0.46 ± 0.05	0.58	0.97	1.7
	2	Pale Yellow	2.86 ± 0.02	0.46 ± 0.01	0.82	3.96	4.9
	3	Pale Yellow	2.83 ± 0.01	0.39 ± 0.03	0.64	0.41	0.6
	4	Pale Yellow	2.84 ± 0.02	0.41 ± 0.02	0.86	0.74	0.9
	5	Pale Yellow	2.81 ± 0.02	0.41 ± 0.03	0.52	0.40	0.8
	"	"	2.84 ± 0.01	0.44 ± 0.01	>4	>13	
POPIGAI	1	Yellowish	2.81 ± 0.01	0.40 ± 0.01	0.68	1.63	2.41
	2	Yellowish	2.81 ± 0.01	0.40 ± 0.01	1.59	3.86	2.43
	3	Yellowish	2.81 ± 0.01	0.44 ± 0.01	1.26	1.94	1.54
	4	Yellowish - Gray	2.82 ± 0.02	0.42 ± 0.03	0.44	0.25	0.58
	5	Yellowish - Gray	"	"	"	"	"
	6	Yellowish - Gray	"	"	"	"	"
	7	Gray	2.84 ± 0.02	0.39 ± 0.03	0.28	0.29	1.03
	8	Gray	2.88 ± 0.02	0.45 ± 0.03	0.68	2.52	3.73
	9	Black	2.90 ± 0.02	0.46 ± 0.02	0.43	0.27	0.63
	10	Black	2.91 ± 0.02	0.52 ± 0.03	0.31	0.00	0.00

Notes: List of analyzed grains with position, FWHM and area of band-A (obtained using a gaussian fit). Area of B-band was obtained by subtracting band-A area from total spectrum area, because a gaussian fit could not be used due to band irregularity. Last column only indicates contribution to spectrum from A and B bands. Measurements performed at 200 pA are not highlighted; those performed at 1000 pA are shown in bold.

theless, as discussed below, the color of these diamonds also may be caused by the presence of trace amounts of nitrogen or other impurities.

SEM observation

Most of the diamonds studied were rectangular flattened plates or shapeless-xenomorphic grains (Figs. 1a and 1b). According to previous findings (Vishnevsky et al. 1997), flattened grains are the result of phase transformation and fragmentation of thin plates of precursor graphite, whereas volume-xenomorphic grains are the result of the same process in thick aggregates of the parental graphite. The isotopic composition of carbon in impact diamonds is usually inherited from the precursor graphite (Vishnevsky et al. 1974, 1997).

Some of the impact diamonds examined, especially those from the Ries and Lappajärvi craters, exhibit traces of intensive dissolving corrosion on the grain surfaces (Fig. 2a), which probably took place in a host high-temperature impact melt, possibly due to the action of OH^- , Na, K, and free O (Vishnevsky and Raitala 2000).

CL spectral measurements at room temperature

Diamond is a semiconductor with a band gap of 5.45 eV. In pure diamond, only one weak-edge CL peak (band-to-band recombination) is typically observed. Impurities or lattice defects create intra-gap energy levels that may be related to other CL peaks. In nature, the main impurity element is nitrogen, which is why the commonly used natural diamond classification system is based on the presence of this element (Zaitsev 2000).

A clear inverse correlation exists between the intensity of

CL observed in impact diamonds and the amount of carbonaceous material present (Fig. 2b, Table 1). This correlation is easily explained by the fact that the paler diamonds undergo a strong charge effect with respect to the darker ones. Thus, it may be argued that black material inside the less-luminescent grains is graphite, which prevents the charge effect and simultaneously decreases the total amount of luminescence.

Several peaks were observed in our diamonds: a blue-A band at 2.8–2.9 eV (443–427 nm), a broad B-band at about 1.8 eV (688 nm), and a weak band at 2.3 eV (539 nm) (see Figs. 3 and 4). The presence of the last band is rather intriguing, as it was only detected in the two least luminescent diamond samples from Lappajärvi (grains 1 and 2). The blue-A band was observed in all grains; its position was located from 2.81 to 2.91 eV. Lower-energies were observed in high-luminescence grains from all impact sites. Instead, higher-energies were measured in black and brownish grains, which were also less luminescent (Fig. 5, Table 1). The average measured FWHM of this band was about 0.4 eV.

Besides blue-band A, all grains showed a strong contribution from the B band at 1.8 eV, a broad band with an FWHM of 0.4–0.5 eV and an asymmetric tail at high energies. This contribution was higher in yellowish grains, where the B-band area is greater than that of the A-band, although an exact correlation was not observed (see Table 1).

Using the MC mode for light collection, we also acquired CL maps from the A-band (monochromator fixed at 444 nm) and B band (monochromator fixed at 610 nm due to higher quantum efficiency than at 689 nm). As shown in Figure 6, the photons emitted at 610 nm came from the same region, indicating that centers responsible for these bands are highly correlated with one another.

CL spectral measurements at liquid nitrogen temperature (LNT)

Five samples (namely Popigai grain 2, Ries grains 4 and 5, and Lappajärvi grains 1 and 5) were chosen from the twenty impact diamonds and were analysed at liquid Ni temperature (LNT). The spectra acquired at LNT, in the ranges 1.7–2.2 eV and 2.6–3.2 eV, strongly resembled those collected at RT, as both the blue-A band and the B-band were still present. In ad-

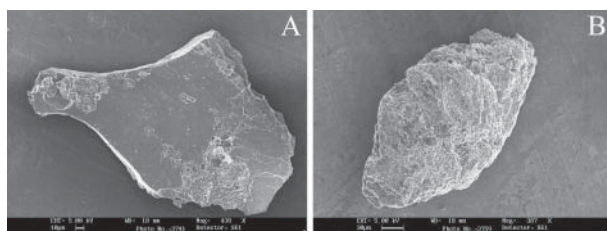


FIGURE 1. SEM images of grain 2 (a, left) and grain 9 (b, right) from Popigai.

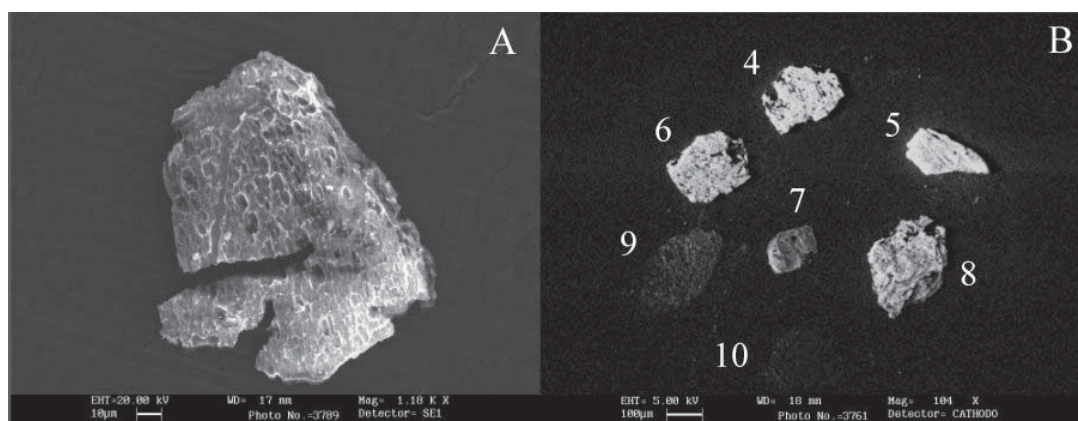


FIGURE 2. (a, left) SEM image of grain 2 from Lappajärvi; (b, right) panchromatic CL image of grains 4–10 from Popigai (probe current 150 pA).

dition, some new peaks appeared in the range 2.2–2.6 eV when the spectra were collected at LNT (Fig. 7).

At 2.23 eV, there is a slight shoulder in grain 5 from Ries and a better defined shoulder in grain 2 from Popigai, and grain 5 from Lappajärvi. In grain 4 from Ries and grain 1 from Lappajärvi, it grows to become a pronounced peak, with a FWHM of about 0.1 eV. In all of the samples that we analysed, an important new peak can be seen at 2.32 eV (FWHM \sim 0.05 eV). This peak is particularly intense in the Lappajärvi and Popigai samples, whereas it is less pronounced in the Ries samples. The above-mentioned peaks represent the most important feature in the gray and brownish-gray grains. Furthermore, grain 1 from Lappajärvi and grain 4 from Ries show less luminescence and a further shoulder at 2.39 eV that can be also seen in grain 2 from Popigai. Finally, the more luminescent samples show a slight band at 2.49 eV, which is easily visible in grain 2 from Popigai and grain 5 from Lappajärvi, but is merely outlined in grain 5 from Ries. This line is missing in the less-luminescent samples, grain 1 from Lappajärvi and grain 4 from Ries.

DISCUSSION

Grain texture and luminescence

Cathodoluminescence is a powerful method for investigating diamond distribution and the graphite-diamond transformation process, especially when coupled with secondary electron image analysis. It allows CL properties and their distribution within materials to be studied.

On the basis of our observations, no evident relationship seems to exist between the intensity of luminescence and the shape of the grains, as both flattened plates (which preserve the form of the precursor graphite) and shapeless grains ex-

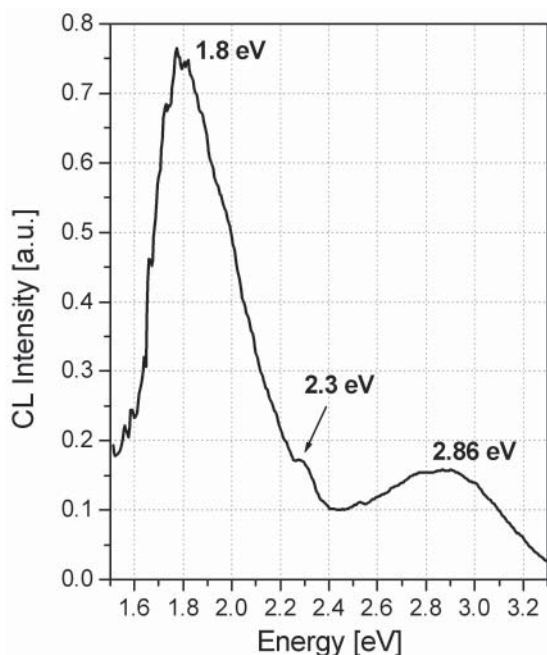


FIGURE 3. CL spectra of grain 2 from Lappajärvi (probe current 1000 pA).

hibit luminescence. In some cases, the former exhibit strong luminescence and in others, none at all (Fig. 8). Luminescence is also present in grains that show traces of dissolving corrosion, however, the CL emission appears not to be related to the texture of the corrosion (Fig. 9). Therefore, if any relation exists between luminescence (amount of diamond in the grain) and the initial crystallinity of the graphite (as suggested by De Carli 1998), it depends exclusively on crystallite size and not on crystal size or shape.

Luminescence spectral measurements

As reported by Zaitsev (2000), more than 500 electronic optical centers have been detected in the absorption and luminescence of diamond, many of which are due to nitrogen impurities. Following a well-established physical classification, diamonds are divided into Types I and II.

Type I includes diamonds in which the optical and para-

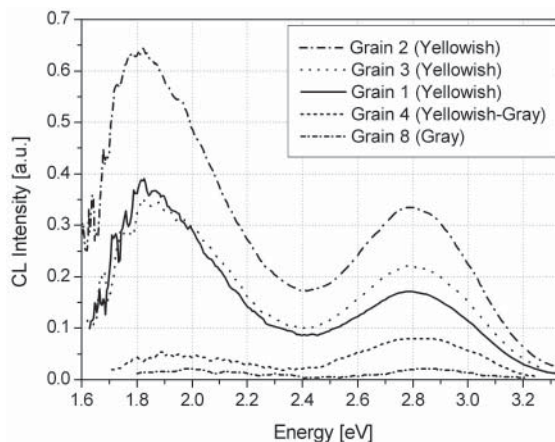


FIGURE 4. CL spectra of five grains from Popigai (probe current 200 pA).

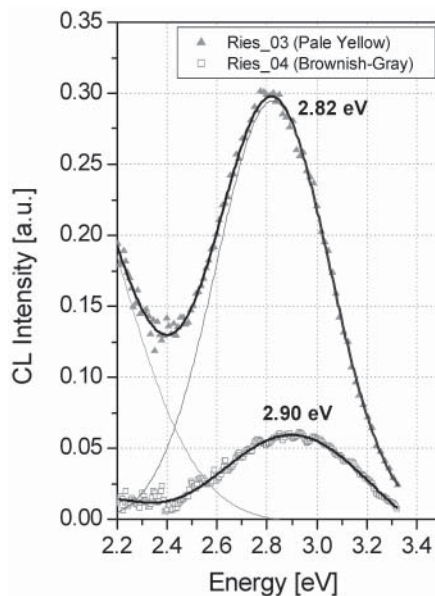


FIGURE 5. Blue band A of grain 3 (pale yellow) and grain 4 (brownish-gray) from Ries (probe current 1000 pA). Symbols from experimental data and lines from fits.

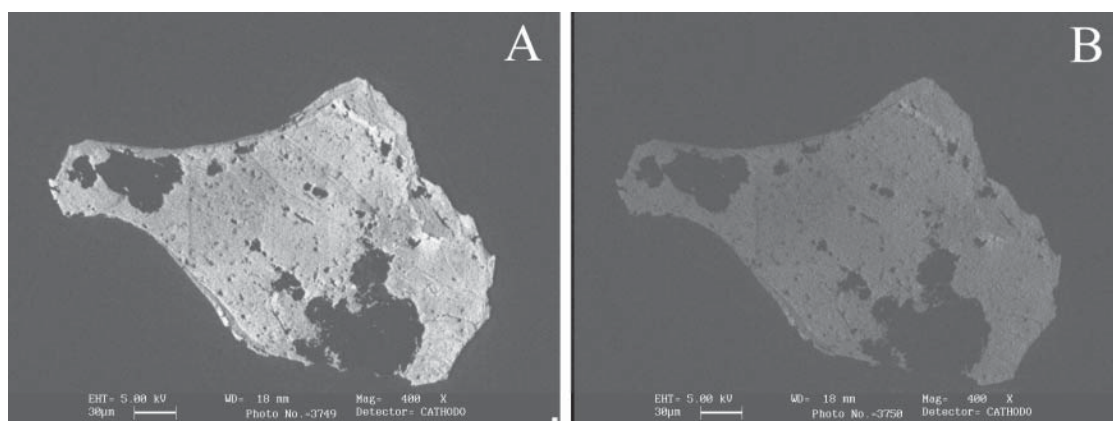


FIGURE 6. Monochromatic images of grain 2 from Popigai centered on blue-band A (a, left) and B band (b, right).

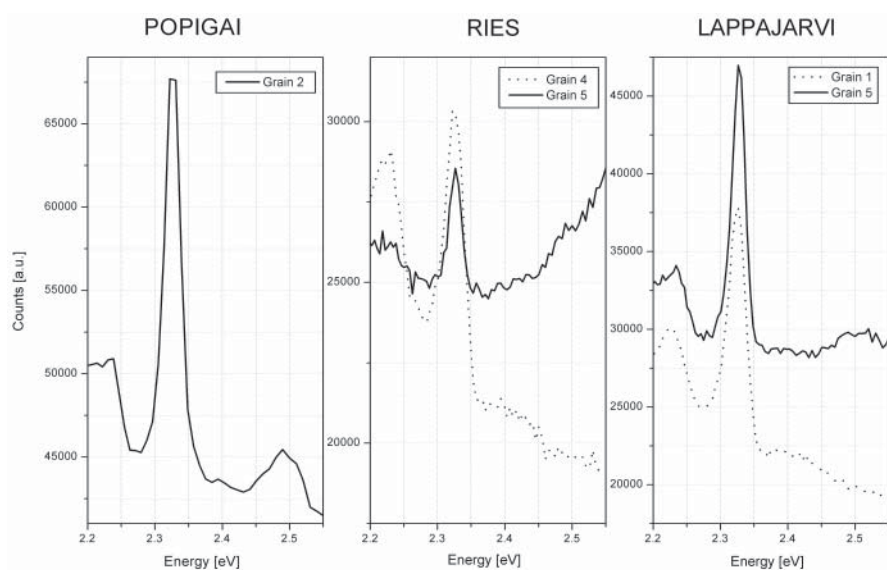


FIGURE 7. CL spectra of impact diamonds collected at liquid nitrogen temperature. Figure shows the spectral range from 2.20 to 2.55 eV where appeared new features with respect to the spectra collected at room temperature.

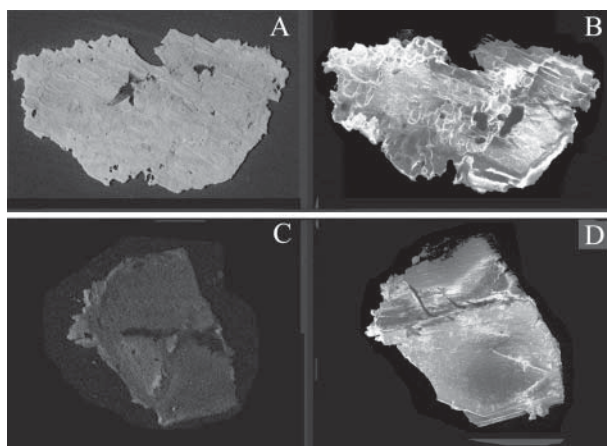


FIGURE 8. Panchromatic CL image (a) and SEM image (b) of grain 5 from Ries; panchromatic CL image (c) and SEM image (d) of grain 4 from Ries. Probe current 1000 pA.

magnetic absorption features are mainly due to nitrogen-related defects. Although about 98% of natural diamonds contain some nitrogen, however, only 74% have a nitrogen content high enough to be classified as Type I. This type can be split up into several subclasses: IaA, containing A centers, which are believed to be N_S-N_S pairs; IaB, containing B centers, related to four substitutional nitrogen atoms arranged in a tetrahedral configuration around a lattice vacancy $[4N_S-V]^\ominus$ (Davies 1999); IaB', containing diamonds with B'-defects (platelets); Ib, containing nitrogen (typically 40–200 ppm), mostly as single substitutional atoms (N_S or C centers); and Ic, including diamond with high concentrations of dislocations. The subclass Ib is very rare. In fact, only about 1 in 1000 natural diamonds are of this type. This rarity is because nitrogen atoms aggregate to form A centers (type IaA diamond) and B centers during the long-term upper mantle residence period experienced by most diamonds (Taylor et al. 1996).

Type II is rare in nature and comprises only 1–2% of natural diamonds. It includes diamonds in which nitrogen-related

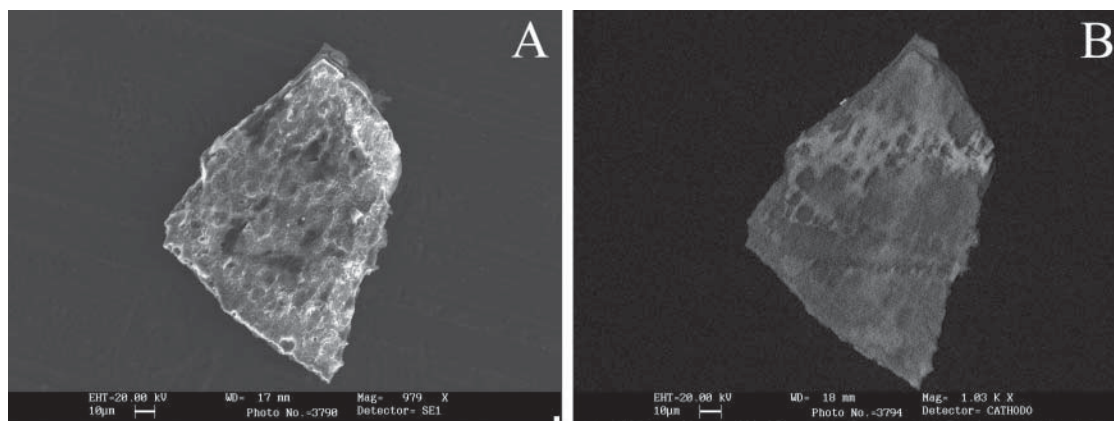


FIGURE 9. SEM image (a) and panchromatic CL image (b) of grain 1 from Lappajärvi. Probe current 1000 pA.

defects are not responsible for optical and paramagnetic absorption. Type II has three subclasses: IIa, which does not show the IR absorption band related to boron and hydrogen impurities; IIb, showing optical absorption due to boron impurities; and IIc, consisting of diamonds with hydrogen-related absorption.

Due to the lack of luminescence studies on impact diamonds, their optical properties and physical classification are poorly understood. Only Koeberl et al. (1995), in their study of the Popigai diamonds, observed that the IR spectra are distinctly different from those of Ib (with dispersed N atoms) and IaB diamonds. According to these authors, the bands are similar but not identical to those of type IaA diamonds (with paired N-centers).

As noted previously, the CL spectra collected during this study show several bands and peaks (Figs. 3, 4, and 7). Among them a strong band at 2.8 eV is present in all samples. In some cases, this band may be related to the presence of the A center, which is typical of type IaA, but it is also present in other types of diamonds (Iakoubovskii and Adriaenssens 2000b). The band at 2.8 eV is a common characteristic of natural and artificial diamond grown by Carbon Vapor Deposition (CVD) and High Pressure High Temperature (HPHT). The presence of the band at 2.8 eV is thus a good way of identifying a diamond phase. According to Hanley et al. (1977), the A-band is the main CL feature of type IIa diamonds. This observation is confirmed by other authors (Lang 1977; Zaitsev 2001), who state that the A-band is especially strong in low-nitrogen diamonds. Moreover, following Yokota et al. (1992), nitrogen impurities greatly quench dislocation A-band luminescence. However, the peak at 2.8 eV is a classic feature of many diamonds (Panczer et al. 2000), and its origin and significance has long been debated but are still not understood completely. Before improvements in the CVD technique, which permitted diamonds to be grown with few impurities, Dean (1965) ascribed this band to the recombination of the donor-acceptor pair, with randomly distributed B as the acceptor.

Since 1990, inconsistencies between the model proposed by Dean (1965) and CVD experimental data have progressively increased, and many alternative explanations have been proposed. In particular, Graham and Ravi (1992) and Marinelli et

al. (1996) suggested that the A-band was related to a structural defect such as a dislocation, even if, in a given sample, not all dislocations were luminescent (Pennycook et al. 1980; Kiflawi and Lang 1974) and there is, however, no correlation between A-band and those dislocations (Yamamoto et al. 1984). Kawarada et al. (1988) pointed out that {100} sectors are more commonly blue, and Iyer et al. (1997) stated that {111} sectors are always green. Iyer et al. (1997) also suggested that blue (band-A) emission is related to vibronic levels located in dislocation defects. In contrast, Marinelli et al. (1998) observed that the highest band-A emission in CVD diamond film occurs when competition exists between the {111} and {100} growth sectors. They therefore excluded the possibility that the relative optical center could be located in either sector. Lastly, Takeuchi et al. (2001), considering that an sp^2 -like structure behaves like a defect in the network of sp^3 , proposed that band-A emission be attributed to sp^2 defects at incoherent grain boundaries and/or dislocations where localized states occur. A further problem arises with the N3 center, consisting of the substitution of three nitrogen atoms with a vacancy, which induces absorption at 2.98 eV. Its contribution may thus overlap those of the others.

The assignment of the 2.23 eV line to a particular transition is difficult. In fact, it cannot be related to any center identified so far. It is nevertheless worth mentioning that this line became more evident in the less-luminescent samples and, moreover, that it appears to be related to the 2.32 eV line.

At LNT, the center at 2.32 eV appears as a well-defined, narrow peak, with FWHM of ~ 0.05 eV. However, at RT, some of the lesser-luminescent samples showed a weak and broader band at 2.3 eV (Fig. 3). In both CVD and HTHP synthetic diamonds (Zaitsev 2001), the so-called green band encompasses this energy range. This band is well-known in boron-doped synthetic diamonds, although increasing boron concentrations do not necessarily give rise to this peak (Iyer et al. 1997). Even if the green band is usually broad (FWHM from 0.4 to 0.8 eV), it consists of two components: A at 2.34 eV and B at 2.39 eV. Iakoubovskii and Adriaenssens (2000b) observed that the first peak correlates with recombination in the amorphous carbon phases, whereas in CVD films, the second one increases with surface hydrogenation. Val'ter et al. (1992) suggested that the

peak observed in impact diamond samples is more probably related to the H3 center, due to a vacancy trapped between two neighboring nitrogen atoms $[N_5-V-N_5]^0$. This center may originate either by migration of two nitrogen atoms to form a nearest-neighbor pair (typically in HPHT synthesis) or by direct incorporation of N_2 , followed by capture of a vacancy (Iakubovskii 2000, and references therein). Lastly, according to Zaitsev (2001) an optical band occurs at 2.30 eV in hydrogenated CVD diamond films: it is stimulated by electron irradiation in the KeV range.

A relationship among the 2.23, 2.32, and 2.39 eV lines has to be found if a clearer interpretative scheme is to be constructed. In light of this aim, it is again worth emphasizing that these lines are more evident in the grains that have lower luminescence, and therefore, with smaller amount of diamond. From an interpretative point of view, Bergman et al. (1993, 1994), reported that the intensity of the broadband luminescence (at 565–800 nm) is correlated linearly with the amount of amorphous hydrogenated carbon material that possesses a random network of sp^2 - and sp^3 -bonding configuration. Following other authors (Field 1992; Jorge et al. 1983; Mohammed et al. 1982), a luminescence emission can be observed around 2.4 eV in natural brown diamonds. Concerning impact samples, Langenhorst et al. (1999) observed an amorphous carbon phase in shocked Lappajärvi and Popigai gneisses. Recently, transparent and hard, very dense carbon platelets, which lack the Raman characteristic feature of diamond, have been found in the Ries crater (El Goresy et al. 2001) and in shocked gneiss from Popigai crater (El Goresy et al. 2002). Apart from the meaning of the presence of an amorphous carbon phase (which may, however, represent a transition phase) in impact craters, and considering the results of other researchers (see the above-mentioned references), we can now propose a relationship between the lines observed at 2.23, 2.32, and 2.39 eV and the amorphous carbon phase.

The band at 2.49 eV may be related to a center, called the B-line, that has been observed in natural brown diamonds at 2.48 eV by Field (1992) and Mohammed et al. (1982).

The band at 1.8 eV is present in all samples except grain 10 from Popigai, which has very low luminescence. This band makes a strong contribution to the CL of the samples and is characterized by an FWHM of 0.4–0.5 eV. This quite rare band (Panczer et al. 2000) has been observed in terrestrial brown natural diamonds and type II diamonds (Wight et al. 1971; Zaitsev 2001) and, although Grund and Bischoff (1999) detected it in several ureilite meteorites, they did not offer any explanation for its presence. A possible interpretation for the band at 1.8 eV is suggested by other authors (see Zaitsev 2001, and references therein), who called this band B-band and relate it to dislocations. The FWHM of the band observed in the present study is 0.4–0.5 eV, and it is thus very similar to the FWHM reported for the B-band by the authors mentioned above.

Cause of color

The presence of color in these impact diamonds possibly may be related to their lonsdaleite content (Val'ter et al. 1992), but is more probably due to optical absorption on single sub-

stitutional nitrogen atoms. Although on the basis of CL spectral features the nitrogen content seems to be low, according to Collins (1982) and Nassau (1993), a concentration of dispersed nitrogen as low as 10–30 ppm may cause yellow coloration, whereas following Anthony and Banholzer (1992), merely 1 ppm of nitrogen is sufficient to give such a color. According to Shelkov et al. (1998), however, a nitrogen content typically less than 20 ppm can be suggested for the studied impact diamonds; such an amount is, therefore, sufficient to provide the observed coloration.

SUMMARY REMARKS

Cathodoluminescence spectra from twenty impact diamond samples from the Popigai, Ries, and Lappajärvi craters show substantial similarities but also some slight differences. The assignment of optical bands is not always straightforward; however, a reasonable explanation has been suggested for some samples. In particular, the peak at 2.8 eV may be related to vibronic levels that correspond with dislocation defects. A relationship is suggested between, on the one hand, the most prominent line visible at 2.32 eV in all of the spectra collected at LNT, and the 2.23 eV and 2.39 eV lines that are particularly pronounced in the less-luminescent grains that, in room light, show a gray or brownish-gray color, and, on the other hand, the content of amorphous carbon phases. Moreover, the 1.8 eV band is related to dislocations.

The intensity of luminescence, and the modulation of color from pale-yellow to black, is influenced by the presence of parental graphite and its relationships with diamond. The color seems to be a function of the presence of trace amounts of single nitrogen atoms in the diamonds.

Although it was not possible to define exactly the aggregation status of nitrogen atoms, the CL spectra suggest a low content of nitrogen in impact diamonds and give some indications for distinguishing impact diamonds from terrestrial diamonds. In particular, some spectral features (e.g., the band at 1.8 eV) are uncommon in terrestrial diamonds but were revealed in all the impact diamonds that were investigated. Considering that the 1.8 eV band relates to dislocations, it may be distinctive of impact diamonds, as such dislocations are probably due to the shock wave pressure induced by impact. Furthermore the 2.23 and 2.32 eV lines, observed at LNT in all the impact diamonds studied, can be also regarded as a possible signature.

Finally, a vibrational analysis will be necessary to improve knowledge of the optical properties of impact diamonds. Such an analysis would also contribute to their physical classification and is the subject of a further paper now in preparation.

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