Spectroscopic analysis of microdiamonds in ophiolitic chromitite and peridotite

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ABSTRACT

Microdiamonds ~200 µm in size, occurring in ophiolitic chromitites and peridotites, have been reported in recent years. Owing to their unusual geological formation, there are several debates about their origin. We studied 30 microdiamonds from 3 sources: (1) chromitite ore in Luobusa, Tibet; (2) peridotite in Luobusa, Tibet; and (3) chromitite ore in Ray-Iz, polar Ural Mountains, Russia. They are translucent, yellow to greenish-yellow diamonds with a cubo-octahedral polycrystalline or single crystal with partial cubo-octahedral form. Infrared (IR) spectra revealed that these diamonds are type Ib (i.e., diamonds containing neutrally charged single substitutional nitrogen atoms, Ns) with unknown broad bands observed in the one-phonon region. They contain fluid inclusions, such as water, carbonates, silicates, hydrocarbons, and solid CO2. We also identified additional microinclusions, such as chromite, magnetite, feldspar (albite), moissanite, hematite, and magnesiochromite, using a Raman microscope. Photoluminescence (PL) spectra measured at liquid nitrogen temperature suggest that these diamonds contain nitrogen-vacancy, nickel, and H2 center defects. We compare them with high-pressure–high-temperature (HPHT) synthetic industrial diamond grits. Although there are similarities between microdiamonds and HPHT synthetic diamonds, major differences in the IR, Raman, and PL spectra confirm that these microdiamonds are of natural origin. Spectral characteristics suggest that their geological formation is different but unique compared to that of natural gem-quality diamonds. Although these microdiamonds are not commercially important, they are geologically important in that they provide an understanding of a new diamond genesis.

INTRODUCTION

During recent years, yellow cubo-octahedral diamonds ranging from 0.2 to 0.5 mm have been discovered in ophiolitic chromitite and peridotite deposits in Tibet and the polar Ural Mountains (Polar Urals; Yang et al., 2014). Models of formation for these new sources have been proposed by many (Yang et al., 2014, 2015; Howell et al., 2015; Robinson et al., 2015; Xiong et al., 2015; Xu et al., 2015; Griffin et al., 2016). However, their unusual geological occurrence and appearance, similar to industrial HPHT synthetic diamond grits, have raised concerns among many researchers, who have tried to prove, using a variety of methods, that these diamonds occur in nature.

We studied microdiamonds found in Luobusa (Tibet) and Ray-Iz (Polar Urals) ophiolites using Fourier transform infrared (FTIR) and Raman microscopy. We have characterized their diamond type, inclusions, and defects. Our goal is to identify the origin of these diamonds, and determine if they are of natural or synthetic origin. We have solely focused on the identification of these diamonds, and propose no model of formation.

MATERIALS AND METHODS

Sizes of microdiamonds in this study range from 200 to 250 µm in width (Fig. 1). Most of the microdiamonds are crystal fragments, containing cubo-octahedral facets. They were discovered in Luobusa and Ray-Iz ophiolites (Fig. 2). We examined 30 samples: 10 from Luobusa chromitite, 10 from Luobusa peridotite, and 10 from Ray-Iz chromitite. We also collected spectra for 10 yellow HPHT synthetic industrial diamond grits with sizes ranging from 250 to 300 µm; they are from an unknown manufacturer and are compared with microdiamonds. All samples were cleaned in an ultrasonic cleaner with acetone, then cleaned again with deionized water in ultrasonic cleaner. Subsequently, the samples were heated at 70 °C for 30 min to remove moisture.

The Thermo Scientific Nicolet iN 10 FTIR-microscope with an attached liquid nitrogen–cooled MCT (mercury-cadmium-telluride) detector was used to collect IR spectra. The spectra for each sample are collected with 1 cm−1 spectral resolution and 100 × 100 µm aperture size from 700 to 4000 cm−1 spectral range for 256 scans. We tested for possible contaminations, such as moisture and CO2 in the FTIR system and for grease on the glass slide. By measuring the IR spectrum of a gem-quality type IIa diamond (i.e., contains no detectable nitrogen defects using FTIR) with the same conditions of collection for the microdiamonds, we eliminated the possibility of such errors.

We used a Renishaw inVia Raman microscope to measure Raman and photoluminescence (PL) spectra. The Raman spectra for inclusions were collected with a range from 100 to 1200 cm−1 at room temperature, using 514.5 and 830.0 nm lasers. The laser spot sizes of the 514.5 nm and 830.0 nm lasers (using a Leica 50x objective) are 1.14 and 1.84 µm, respectively. PL spectra were measured with 514.5, 632.8, and 830.0 nm laser excitations at liquid nitrogen temperature. Samples were submerged in the liquid nitrogen double-layer bath method.
RESULTS AND DISCUSSION

Optical Characteristics and Surface Features

The microdiamonds are yellow to greenish-yellow, semitransparent to translucent, and both polycrystalline and single crystal diamonds can be observed. The surfaces have etch features, similar to step-like markings, usually found on natural rough diamonds (Fig. 1).

Inclusions Identified by FTIR Spectra

The diamond intrinsic absorption band observed in the IR spectrum confirms that these samples are diamond (Fig. 3); it also reveals the presence of water, hydrocarbons, carbonates, silicates, and solid CO₂ (Fig. 3). The fluid inclusions are nanometer-sized (<1 µm) solid phases intergrown with minor amounts of hydrous solution and gas bubbles (Kopylova, 2010). They were trapped during the diamond formation. These syngenetic inclusions represent the composition of diamond-forming fluids, containing water and carbonates as the main volatile components.

Water and carbonates were first observed in cuboid diamonds using FTIR by Chrenko et al. (1967). Mantle-derived fluids (or volatile-rich melt) can be trapped as homogeneous, high-density fluids. During ascending and cooling, fluid inclusions are formed as a secondary phase (i.e., the separation of immiscible fluids), and low-density fluids can be trapped inside them. FTIR is a useful tool to study such fluid inclusions, and it can also measure the bulk content.

Water

The presence of water is confirmed by broad peaks with various positions from 3286 to 3377 cm⁻¹ (OH stretching; Fig. 3) and a peak at ~1740 cm⁻¹ (H₂O bending; Fig. 3) observed in all microdiamonds studied. The 1740 cm⁻¹ peak is associated with a 1660 cm⁻¹ peak at its shoulder.

Water has been reported in fibrous and coated cuboid diamonds (De Corte et al., 1998; Kagi et al., 2000; Zedgenizov et al., 2006; BenDavid et al., 2007; Kopylova, 2010). Water can be observed as hydroxyl groups inside fibrous diamonds. Thus, diamond can carry hydrous components directly from the Earth’s mantle. Kagi et al. (2000) showed evidence for water as solid inclusions in the form of ice VI (i.e., high-pressure form of water) inside cuboid diamonds.

Hydrocarbons

IR spectra confirm the presence of hydrocarbon peaks in the microdiamonds (Fig. 3). All these peaks are slightly broad and they are located approximately at 2854, 2872, 2925, and 2958 cm⁻¹. A peak at 2854 cm⁻¹ is caused by symmetric stretching, and a peak at 2925 cm⁻¹ is caused by asymmetric stretching of CH₂ hydrocarbons (Titus et al., 2005). CH₃ hydrocarbons contribute to the symmetric and asymmetric stretching bands at 2880 and 2960 cm⁻¹, respectively (Titus et al., 2005). However, we do not observe individual hydrocarbon inclusions under the Raman microscope, suggesting that they are fluid inclusions of <1 µm.

Hydrocarbon fluid inclusions of ~20 µm have been reported in natural diamonds from placers of Yakutia, Russia (Tomilenko, 2008). The Raman and IR spectroscopy confirms the existence of water-nitrogen-hydrocarbon (CH₄-rich) high-density fluids in these diamonds. Tomilenko (2008) proposed that hydrocarbons are the source of carbon as well as carbon carriers during diamond formation; however, this theory is still debated.

Hydrocarbons have also been reported in fibrous cuboid diamonds from the Democratic Republic of the Congo (Kopylova, 2010). It...
has been proposed that hydrocarbons occurred by deuteric reaction between trapped CO\(_2\) and hydrogen, released from the formation of secondary OH-bearing minerals. The intensity of hydrocarbon peaks in cuboid diamonds is much stronger than OH-stretching bands, very similar to hydrocarbons bands observed in our samples. The hydrocarbon peaks, OH-stretching, and carbonate bands show a positive correlation consistent with that of natural formation of diamond.

**Carbonates**

All of the microdiamonds contain a carbonate peak at \(\sim 1460\) cm\(^{-1}\), which is an asymmetric stretching band (Fig. 3). The abundance of carbonate fluid inclusions suggests that carbonate high-density fluids are involved in the diamond growth process. Zedgenizov et al. (2004) proposed that diamond growth was caused by precipitation of free carbon in carbonatitic melt or through carbonate-silicate interaction.

The abundance of carbonate fluid inclusions inside natural diamond is well known. There are many detailed studies about carbonate inclusions (e.g., De Corte et al., 1998; Zedgenizov et al., 2004, 2006).

**Silicates**

Silicate peaks are detected at 967 and 1085 cm\(^{-1}\) in all of the microdiamonds studied (Fig. 3). Silicate fluid inclusions have been previously discovered in cuboid and fibrous-coated diamonds (Yelisseyev et al., 2004; Zedgenizov et al., 2004; Ben-David et al., 2007). In the diamond stability field, silicate, carbonatic, and hydrous melts and/or fluids are fully miscible, and they can be trapped inside diamond as highly concentrated fluids. Sheet silicates can be formed as secondary minerals from the trapped fluids.

The presence of silicates is further confirmed by the discovery of two feldspar inclusions in Ray-Iz diamonds (discussed in the following).

**Solid CO\(_2\)**

Carbon dioxide is the most abundant volatile component in the Earth’s mantle (Schrauder and Navon, 1993). Solid CO\(_2\) inclusions can be observed in a few samples, two from Luobusa (chromitite), three from Luobusa (peridotite), and four from Ray-Iz (Fig. 4). The peaks at 2375, 2513, 3687, and 3748 cm\(^{-1}\) are related to solid CO\(_2\). Natural diamonds containing this fluid inclusion have been reported previously. Schrauder and Navon (1993) discovered solid CO\(_2\) in a brownish-yellow diamond. The IR spectrum revealed solid CO\(_2\) peaks at 650 (\(v_1\)), 2376 (\(v_3\)), 3620 (\(v_1+2v_2\)), and 3752 (\(v_1+v_3\)) cm\(^{-1}\). These are shifted toward higher peak positions from one atmosphere pressure, caused by internal pressure of 5 GPa. The peaks observed in the microdiamonds are located at even higher positions at 2513 and 3687 cm\(^{-1}\), possibly caused by intense internal pressure. The pressure during diamond formation can be much higher than the internal pressure measured at room temperature (Schrauder and Navon, 1993). Evidence of high internal pressure suggests that fluid inclusions have been trapped during diamond growth.

**Inclusions Identified by Raman Spectra**

We identified 22 microinclusions, with sizes ranging from 5 to 20 \(\mu\)m, using a Raman microscope. They are chromite, magnetite, feldspar (albite), moissanite, hematite, and magnesiochromite (Table 1). Most of them are individual inclusions, but a few are nontouching monomineralic or polyminalic assemblages (Table 2). All of the inclusions are located below the surface, with the exception of one of seven chromite inclusions and a hematite inclusion that break on the surface. We also observed multiple inclusions of <1 \(\mu\)m under the Raman microscope. Since they are smaller than laser spot size, we cannot identify them. However, the identification of 22 inclusions in these microdiamonds is important, providing strong evidence of the natural origin.

**Figure 3. Infrared (IR) spectra of microdiamonds.** (A) Fluid inclusions of water, hydrocarbon, carbonate, and silicate are shown. Arrows indicate various peak positions of water (OH stretching). The solid CO\(_2\) was not shown here. (B) Detailed IR spectral region from 700 to 1800 cm\(^{-1}\); water (H\(_2\)O bending) at 1740 cm\(^{-1}\) and its associated peak at 1660 cm\(^{-1}\), carbonate and silicate inclusions, nitrogen defects, and unknown peaks. Spectra are normalized and vertically shifted for clarity. a—Luobusa chromitite; b—Luobusa peridotite; c—Ray-Iz chromitite.

**Figure 4. Infrared (IR) spectra of a few microdiamonds showing solid CO\(_2\) inclusion.** Spectra are vertically shifted for clarity. a—Luobusa chromitite; b and c—Ray-Iz chromitite; d—Luobusa peridotite; ACO\(_2\)—atmospheric CO\(_2\) at 2365 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>TABLE 1. LIST OF IDENTIFIED MICROINCLUSIONS</th>
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<tbody>
<tr>
<td>Inclusions</td>
</tr>
<tr>
<td>chromite</td>
</tr>
<tr>
<td>magnetite</td>
</tr>
<tr>
<td>feldspar</td>
</tr>
<tr>
<td>moissanite</td>
</tr>
<tr>
<td>hematite</td>
</tr>
<tr>
<td>magnesiochromite</td>
</tr>
</tbody>
</table>

Note: This shows the total number of inclusions observed in each location.
Chromite

Raman shifts observed for the translucent to opaque, reddish-orange chromite inclusions are located at 550, 692, and 723 cm$^{-1}$ (Fig. 5). These are most abundant in Ray-Iz diamonds, but two of them are observed in Luobusa (peridotite) samples. Most inclusions are single crystals; one Ray-Iz sample contains three chromite inclusions. One chromite is associated with magnetite and hematite inclusions in the Luobusa (peridotite) sample (Table 2).

Chromite is a mantle-derived mineral, and it is indicative of peridotitic paragenesis. It has been observed as a macro-inclusion in natural diamonds (McKenna et al., 2004). It can also be found as microinclusions, e.g., ~50 µm inclusions in microdiamonds from kimberlites in the Yakutia (Sobolev et al., 2004). Chromite microinclusions have also been observed in fibrous diamonds (Zedgenizov et al., 2004). The composition of chromite grains obtained from kimberlites in central India confirmed that they can occur in the diamond stability field (Mainkar et al., 2004).

Magnetite

We confirmed opaque black crystals as magnetite with Raman shifts at 544 and 671 cm$^{-1}$ (Fig. 5). These are individual inclusions, and one crystal is associated with chromite and hematite found in the Luobusa (peridotite) sample.

Magnetite inclusions can be syngenetic and have been observed in natural diamonds from around the world (Gorshkov et al., 1997; Sobolev et al., 1998; Titkov et al., 2003; Hayman et al., 2005; Jacob et al., 2009).

Feldspar

Two of the Ray-Iz microdiamonds contain translucent, gray feldspar inclusions: one is individual, and the other is associated with moissanite. Their Raman shifts can be located at 292, 411, 478, 510, 761, and 817 cm$^{-1}$ (Fig. 5). Feldspar inclusions, such as sanidine, can be observed in natural diamonds, as reported in Siberian and Venezuelan diamonds (Meyer, 1985; Novgorodov et al., 1990; Sobolev et al., 1998). However, the Raman spectrum of our feldspar inclusion is very similar to the reference spectrum of albite.

Feldspar, however, is not stable in the diamond stability field. It can be formed inside cracks or fractures by secondary fluids. Both of the feldspar (albite) inclusions in the microdiamonds are completely enclosed inside the host diamond. However, we do not observe any healed fractures around them. The time required to completely enclose an inclusion inside diamond by fracture healing, i.e., the age of feldspar inclusions, would take at least few hundred years if not thousands of years. The age of feldspar is important in our research (discussed herein).

Moissanite

Gray to black opaque moissanite inclusions are present in diamonds from all three sources. However, they are most abundant in the Luobusa (chromitite) samples. Their Raman peaks are located at 150, 765, 786, and 966 cm$^{-1}$ (Fig. 5). The Raman spectra indicate that they are most likely 6H SiC crystals. The moissanite is included as single crystals with the exception of the Ray-Iz diamond where it is associated with feldspar inclusions (Table 2).

Moissanite inclusions can also be observed in natural diamonds from Western Australia, South Africa, North America, and China (Jaques et al., 1989; Moore and Gurney, 1989; Otter and Gurney, 1989; Leung, 1990; Gorshkov et al., 1997; Field et al., 2008). Leung (1990) discovered three moissanite inclusions in an octahedral diamond from Fuxian, China. Observed in one inclusion, 6H SiC crystals were enclosed in a colorless grain of 3C SiC. Three moissanite inclusions were surrounded by a thin layer of

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**Table 2. Inclusions Observed in Individual Diamonds**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inclusions</th>
</tr>
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<tbody>
<tr>
<td>KCr2</td>
<td>moissanite</td>
</tr>
<tr>
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<td>moissanite</td>
</tr>
<tr>
<td>KCr5</td>
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</tr>
<tr>
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<td>moissanite</td>
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<td>KCr7</td>
<td>moissanite</td>
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<tr>
<td>KCr2</td>
<td>magnetite</td>
</tr>
<tr>
<td>KY4</td>
<td>chromite, magnetite, hematite</td>
</tr>
<tr>
<td>KY6</td>
<td>chromite</td>
</tr>
<tr>
<td>KY7</td>
<td>magnetite</td>
</tr>
<tr>
<td>KY9</td>
<td>moissanite</td>
</tr>
<tr>
<td>WP1</td>
<td>chromite</td>
</tr>
<tr>
<td>WP11</td>
<td>magnetite</td>
</tr>
<tr>
<td>WP6</td>
<td>chromite, chromite, chromite</td>
</tr>
<tr>
<td>WP8</td>
<td>feldspar</td>
</tr>
<tr>
<td>WP9</td>
<td>feldspar, moissanite</td>
</tr>
<tr>
<td>WP10</td>
<td>chromite</td>
</tr>
</tbody>
</table>

Note: KCr—Luobusa chromitite; KY—Luobusa peridotite; WP—Ray-Iz chromitite.
glass, which also contained calcium carbonate and calcium sulfate crystals. Therefore, it was concluded that moissanite inclusions originated from the mantle.

Segregation of Fe-Ni-Si-C alloy liquid can facilitate the crystallization of diamond and/or moissanite in the lower mantle (Dasgupta, 2013). Because moissanite is a highly reduced mineral, Leung (1990) proposed that it can occur in geological environments with extremely low F/O₂ values or conditions at depths >250 km. Thus, moissanite can be a potential carbon source for diamond formation, therefore, it can be trapped as inclusions during diamond formation.

**Hematite**

A translucent, orange-red hematite crystal is breaking the surface in a Luobusa (peridotite) diamond. It is associated with chrome and magnetite crystals. The Raman shifts are located at 223, 289, 405, and 608 cm⁻¹ (Fig. 5).

Hematite inclusions are observed in diamonds from Jericho kimberlites in Canada and in gray Siberian diamonds (Titkov et al., 2003; De Stefano et al., 2009). Hematite inclusions (>5 μm) associated with magnetite were observed in frame sites (i.e., polycrystalline diamond aggregates) from the Orapa Mine in Botswana (Jacob et al., 2009). Hematite is currently assigned to unknown or uncertain diamond paragenesis. Hematite is not a primary mineral in the mantle, and it is possibly formed after low-nickel sulfides (Szabó and Bodnar, 1995).

**Magnesiochromite**

Two magnesiochromite inclusions are identified in one diamond from Luobusa (chromitite). They are translucent, pale orange crystals. Raman shifts are located at 529 and 692 cm⁻¹ (Fig. 5).

Magnesiochromite can be observed as abundant inclusions in placer diamonds from Brazil (Tappert et al., 2006). They are indicative of peridotite paragenesis, and diamond formation temperature can be extrapolated as 1210–1340 °C (Tappert et al., 2006).

**Defects Detected by FTIR Spectra**

The nitrogen defect (C center) can be detected at 1344 cm⁻¹ in all samples (Fig. 3). This defect can also be detected at 1131 cm⁻¹ in some of the diamonds. The C center–containing diamonds can be classified as type Ib, and they are very rare in nature (<1% of natural gem-quality yellow diamonds). We decided not to measure the concentration of nitrogen because of the presence of unusual broad bands observed in the one-phonon region, which may cause potential errors. A positively charged nitrogen atom, N⁺, at 1332 cm⁻¹ can be observed in all samples (Fig. 3).

Two peaks at 1365 and 1378 cm⁻¹ are detected in the microdiamonds (Fig. 3). They are similar to plateau peaks, which can be detected from spectral range 1358 to 1380 cm⁻¹ (Zaitsev, 2001). The plateau is a [100] planar defect containing carbon interstitials and nitrogen atoms (Woods, 1986). However, they coexist and are linearly correlated with the B center (i.e., nitrogen aggregates) in natural diamonds. The microdiamonds do not show the B center at 1175 cm⁻¹, although there are broad peaks at ~1155 and ~1185 cm⁻¹ (Fig. 3). These broad peaks are possibly masking the B center. Considering this fact and the clear nature of the peaks, the 1365 and 1378 cm⁻¹ peaks are most likely attributed to plateau defects.

Additional unknown peaks were also detected at 1209, 1245, 1275, and 1311 cm⁻¹ in the one-phonon region, and 1495 cm⁻¹ in the two-phonon region (Fig. 3; some peaks are not shown). These broad bands are possibly masking nitrogen A aggregates at 1282 cm⁻¹ and N⁺ at 1131 cm⁻¹ in some diamonds.

**Defects Detected by PL Spectra**

**Nitrogen-Vacancy Centers**

Nitrogen-vacancy (NV) centers are detected at 575 (NV⁰) and 637 (NV⁻) nm with broad phonon sidebands ranging from 647 to 804 nm (Fig. 6). The NV⁻ has a higher intensity than the NV⁰ center. The width of NV centers is slightly broad with average FWHM (full width at half maximum) values of 2.18 nm for NV⁰ and 2.75 nm for NV⁻ centers.

Broad NV centers with a similar ratio (637 > 575) and phonon sidebands can be observed in yellow coated diamonds from Snap Lake–King Lake kimberlites in Canada (Yelisseyev et al., 2004). It has been proposed that strain from nickel-related defects was contributing broad NV peaks. We confirmed the presence of nickel-related defects in our samples by detection of the 882–884 nm doublet (Fig. 6). Therefore, nickel defects are most likely causing broad NV peaks in microdiamonds. The NV centers can be caused by exposure to postgrowth ionizing irradiation with natural low-temperature annealing (Yelisseyev et al., 2004). The similar NV ratio and broad sidebands have also been observed in natural ABC (i.e., diamonds containing A, B, and C nitrogen centers; A = aggregate of two nitrogen atoms; B = aggregate of four nitrogen atoms) and type Ib diamonds (Hainschwang et al., 2006, 2013).

**Nickel Defect**

Nickel-related peaks at 882 and 884 nm in diamonds can be observed in diamonds from all sources, but their intensity is source dependent.

![Figure 6. Photoluminescence (PL) spectra of microdiamonds and high-pressure–high-temperature (HPHT) synthetic diamond grit. (A) Excited with 514 nm laser at liquid nitrogen temperature (LNT), showing nitrogen-vacancy (NV) centers and phonon sidebands. (B) PL spectra excited by 830 nm laser at LNT. It shows 882–884 nm doublet, H₂ center, and peaks at 909 and 953 nm for microdiamonds from chromeitite, and 865 and 871 nm peaks for HPHT synthetic diamonds. (C) PL spectra excited by 633 nm laser at LNT. The 657 nm peak is detected in all diamonds. A triplet at 683 nm can be observed in HPHT synthetic diamond. Spectra are normalized and vertically shifted for clarity. a—Ray-Iz chromitite; b—Luobusa peridotite; c—Luobusa chromitite; d—HPHT synthetic diamond; AR—artifact.](https://pubs.geoscienceworld.org/gsa/lithosphere/article-pdf/4032822133.pdf)
The ratio between the 882 and 884 nm doublet and the diamond Raman peak is reversely related between chromitite and peridotite sources; in the Luobusa (chromitite) and Ray-Iz diamonds, they are stronger than the diamond Raman peak but broad and weak in the Luobusa (peridotite) diamonds (Fig. 6). Therefore, microdiamonds from both chromitite sources are nickel rich.

The nickel defect is commonly observed in HPHT synthetic diamond grown with nickel catalyst, but it can be rarely seen in natural type Ib diamonds. Nickel defects, such as Ni-N complexes, have been reported in yellow coated diamonds from Snap Lake–King Lake kimberlites in Canada (Yelisseyev et al., 2004). Diamonds from Siberia, Canada, and Australia may also contain nickel defects (Yelisseyev et al., 2004). The 882–884 nm doublet can also detected in natural type Ib diamonds along with the Y center defect at 799.4 nm (Hainschwang et al., 2013).

Nickel can enhance a faster nitrogen aggregation process (Fisher and Lawson, 1998). However, we do not see any clear peaks for A and B aggregates in microdiamonds. Instead, unknown broad bands are observed in the nitrogen spectral region from 1000 to 1400 cm⁻¹. These broad bands are probably masking the A and B centers (Fig. 3).

### H2 Center

The H2 center defect is detected at 986 nm in all microdiamonds (Fig. 6), except a few of them that did not show it. This defect is a negatively charged nitrogen-vacancy-nitrogen (N-V-N) center, and is located along the <110> direction (Zaitsev, 2001).

The H2 center can be observed in natural yellow and brown ABC diamonds, and type Ib orange diamonds (Hainschwang et al., 2006 and 2013) in the absorption spectrum. Our samples are too small to measure ultraviolet-visible spectra. However, the presence of the H2 center is confirmed using PL spectroscopy.

### 657 Center

The 657 nm peak can be observed in all microdiamonds (Fig. 6). This peak has been reported in natural diamonds (Adams and Payne, 1974), and nickel-rich, type IaA orange-yellow diamond (Hainschwang and Notari, 2004).

### Unknown Defects

Additional defects were detected at 909 and 953 nm (Fig. 6). These are observed in the nickel-rich Luobusa (chromitite) and Ray-Iz diamonds, but not in the nickel-poor Luobusa (peridotite) diamonds. Their assignments are unknown.

### Comparison with Industrial Diamond Grits

There are three types of diamond used for drill bits in the oil and gas industry: polycrystalline diamond compact (PDC), HPHT-grown synthetic diamond grits (used for grit hot-pressed inserts), and natural bort diamonds. They are applied to drill bits without moving parts and are called fixed cutters. HPHT synthetic grits have similar size and crystal form compared to the microdiamonds. Therefore, we decided to examine three HPHT synthetic diamond grits of unknown manufacture using the same instruments and measurement parameters. The samples are ~300 µm yellow, cubo-octahedral crystals.

### Raman Spectral Analysis

Elongated or irregularly shaped microinclusions, containing methane, hydrocarbons, carbon dioxide, water, and amorphous carbon clusters, can be found in HPHT synthetic diamonds, grown in the Fe-Ni-C system (at 60 kbar and 1350–1400 °C), and the carbonate-carbon system (at 70 kbar and 1700–1750 °C) (Tomilenko, 2008). These can be detected by Raman spectroscopy.

However, we did not observe Raman-active water and CO₂-rich microinclusions in both microdiamonds and HPHT synthetic diamonds. Instead, we found metallic flux inclusions in the HPHT synthetic grits, as reported in previous studies (Shigley et al., 2004).

### PL Spectral Analysis

NV centers are detected at 575 (NV⁰) and 637 (NV⁻) nm in HPHT synthetic diamonds (Fig. 6). NV centers can be observed in irradiated and annealed HPHT synthetic diamonds (Lawson et al., 1998). The ratio of NV centers and phonon
The intensity is higher than the diamond Raman (Fig. 6). This peak was reported in Chatham syn-
which is grown in Fe-Ni-C system and annealed Luobusa (peridotite) diamond. (G) Luobusa (peridotite) diamond. (H, I) Luobusa (chromitite) diamonds.

Nickel defects can be detected at the 882 and 884 nm doublet (Fig. 6). The intensity is much weaker compared to microdiamonds from chromitite sources. Nickel alloy has been widely used in growing commercial HPHT synthetics. Consequently, single nickel atoms (most likely interstitial Ni⁺) can be introduced into the diamond lattice in {111} growth sectors during HPHT synthesis (Collins, 2000). Nickel defects can be observed in HPHT synthetic diamond, which is grown in Fe-Ni-C system and annealed above 1700 °C (Yelisseyev et al., 2004).

The H2 center is detected at 986 nm (Fig. 6). The intensity is higher than the diamond Raman peak. This center can be produced by irradiation and annealing at ~1700 °C in type Ib synthetic diamonds (Mita et al., 1990). This defect is observed in microdiamonds from all three sources (Fig. 6). However, the H2 peak has relatively higher intensity in synthetic diamond than in the microdiamonds. Natural diamonds can also contain the H2 defect (Hainschwang and Notari, 2004).

Peaks at 565, 865, and 871 nm, and the 693 nm system (691-692-693 triplet; Fig. 6) are also observed in HPHT synthetic diamond grits. However, none of these peaks were detected in microdiamonds. The 565 nm peak is commonly observed in natural, gem-quality type Ib diamonds. The assignments of aforementioned peaks are unknown.

Possible Contamination

Samples were cleaned by soaking in acetone for 30 min, and air-dried for another 30 min. After observing strong hydrocarbon and water peaks in the IR spectra, we suspected a possible contamination of the samples. We performed additional cleaning using acetone and deionized water inside ultrasonic cleaner. We then dried the samples with a low heat.

In order to confirm that the FTIR microscope system was working properly, we tested a gem-quality, type Ia diamond parallel to measuring microdiamonds. The IR spectrum of the gem-quality diamond did not show hydrocarbon, water, and other fluid-inclusion peaks (Fig. 7). When we resumed measuring IR spectra for microdiamonds, these peaks appeared again.

The microdiamonds were placed on a glass slide to measure spectra. We also collected the IR spectrum of the glass slide and it showed a flat line, with only two broad peaks at 816 and 1271 cm⁻¹ (Fig. 7). These broad peaks are not observed in any of the microdiamonds.

Using this confirmation, we can conclude that the IR absorption peaks of fluid inclusions are real, and not caused by contamination from either the samples or the FTIR system.

Cubo-octahedral and Dodecahedroid Form

The microdiamonds are cubo-octahedral polycrystalline crystals or single crystals with partial cubo-octahedral form, with the exception of one Luobusa (peridotite) diamond that shows flat dodecahedroid form (Fig. 8).

Cubo-octahedral diamonds have been reported in nature. Diamonds from the Swartruggens dike in the Helam Mine, South Africa, exhibit cubo-octahedral growth sectors (McKenna et al., 2004). Octahedral diamonds from Yakutian kibberlites have cube-octahedral growth bands (Bulanova, 1995). This growth pattern can also be observed in natural gem-quality diamonds, suggesting that diamonds are essentially crystallized as cubo-octahedra in the early stages of formation.

Cubo-octahedral inclusions are frequently observed in natural diamonds. Cubo-octahedral magnetite grains of 10–60 µm can be observed in lower mantle diamonds from Rio Soriso in Brazil (Hayman et al., 2005). These diamonds also have cubo-octahedral growth sectors, indicative of lower crystallization temperatures compared to octahedral diamonds.

Although most natural diamonds crystallize in the octahedral form, some diamonds may have cuboid or cube or complex growth forms. Cuboid-octahedral diamonds, along with cubes and other unusual shapes from the Jwaneng Mine in Botswana were reported by Welbourn et al. (1989). Natural cubo-octahedral diamonds were discovered from ultramafic belts of Armenia (Pavlenko et al., 1974). De Corte et al. (1998) reported and analyzed 16 ~200–380 µm cubo-octahedral alluvial diamonds from the Kokchetav massif, northern Kazakhstan. Four cubo-octahedral diamonds were found in the Swartruggens dike in the Helam Mine, South Africa (McKenna et al., 2004). Cubo-octahedral diamonds can be formed at intermediate growth rates, between the low growth rate of octahedra and the high growth rate of cubes.

One of the diamonds from the Luobusa (peridotite) shows a flat dodecahedroid form (Fig. 8). Dodecahedroid diamonds can be found in nature. Five dodecahedroid diamonds were discovered in Yakutian kibberlites (Bulanova, 1995). One of them is a flat dodecahedroid, similar to the
diamond can be transformed into dodecahedron form in the later stages of crystallization (Bulanova, 1995). Dodecahedroid diamonds can also be found in alluvial deposits from the ultramafic belts of Armenia (Pavlenko et al., 1974).

Natural Versus Synthetic Origin: Why They Cannot Have Originated from Drill Bits

Both natural and HPHT synthetic diamonds can contain nitrogen defects. However, the presence of fluid inclusions in microdiamonds is critical to our identification process. Although hydrocarbons can be contained in HPHT synthetic diamonds, IR-active water, solid CO2, and carbonate and silicate fluid inclusions have never been reported in HPHT synthetic diamonds. The HPHT synthetic grits in this study do not show fluid inclusion–related peaks in their IR spectra. Therefore, these fluid inclusions strongly suggest that the microdiamonds are natural in origin.

The microdiamonds from Luobusa and Ray-lz are natural diamonds. Our conclusion is supported by the following observations.

- Inclusions of these minerals have been reported in HPHT synthetic diamonds.
- Defects in PL spectra, such as NV, nickel, H2, and 657 nm do not provide a conclusive evidence for identification. However, we observed clear differences between the microdiamonds and HPHT synthetic diamonds. Peaks at 565, 865, 871, and triplet at 693 nm are exclusive to the HPHT synthetic diamonds. Two peaks at 909 and 953 nm can be detected in the microdiamonds from chromite sources, but are not observed in HPHT synthetic diamonds.
- The detection of chromite, magnetite, hematic, magnetite, and magnesiochromite are natural diamond inclusions. They cannot be formed in HPHT synthetic diamonds.

Feldspar, which is the youngest of the observed microinclusions, predates the invention of HPHT synthetic diamond grits used for drill bits in the mining industry.

The inclusions and defects observed in the microdiamonds suggest that they originated from an unusual geological environment compared to that of gem-quality diamonds. This makes them unique, although they are very small. They are not commercially important, but they are geologically important. This research will help provide a greater understanding of diamond genesis.

ACKNOWLEDGMENTS

We thank Yildirim Dilek and an anonymous reviewer for their constructive comments, and Kurt Stuwee for editorial handling.

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