Investigations of Diamonds from Minas Gerais (Brazil) by Vibrational Spectroscopy

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Received em 23 de agosto de 2010 / Aceito em 2 de fevereiro de 2011

Abstract

Type Ia and type II diamonds have been described among 91 investigated stones from Minas Gerais State (Brazil) through infrared activity of nitrogen centres. Four different type Ia diamond populations have been defined from their nitrogen aggregation histories. The discrimination method is based on fact that platelet (D defect) develop as centres evolve to B centres in mantle under very well controlled conditions of time and energy. Ratio B/A versus D diagram seems to indicate that nitrogen aggregation behavior of each group can be mathematically described by a first degree equation. Additionally, pyrope and forsterite included in diamonds have been analyzed by Raman spectroscopy and revealed peridotitic mantle mineralogy under the southern São Francisco Craton.

Keywords: diamond, nitrogen, mineral inclusions, vibrational spectroscopy, Minas Gerais.

Resumo

Diamantes do tipo Ia e tipo II foram encontrados em Minas Gerais (Brasil) dentre um total de 91 pedras investigadas através da atividade infravermelha dos centros de nitrogênio. Quatro diferentes populações de diamantes tipo Ia foram definidas a partir de suas histórias de agregação de nitrogênio. O método de discriminação se baseia no fato de que platelets (defeitos D) desenvolvem-se à medida que centros A evoluem para centros B no manto sob condições muito bem controladas de tempo e energia. Diagrama das razões B/A versus D parece indicar que o comportamento da agregação de nitrogênio de cada grupo pode ser descrito matematicamente por uma equação de primeiro grau. Adicionalmente, pirope e forsterita inclusos nos diamantes foram analisados por espectroscopia Raman, revelando uma mineralogia peridotítica do manto sob o Cráton São Francisco Meridional.

Palavras-chave: diamante, nitrogênio, inclusões minerais, espectroscopia vibracional, Minas Gerais.

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1. Introduction

In the last 70 years, considerable progress has been made in the investigation and interpretation of optically active structural defects (centres) in diamond by vibrational spectroscopy (e.g. Woods, 1986; Evans, 1992; Mendelsohn & Milledge, 1995). Nitrogen is the most common impurity in natural diamonds and it causes many of these defects. Historically, diamond has been grouped into two types, I and II (Robertson et al., 1934). On the basis of the ultraviolet and infrared (IR) absorption, type-I diamond contains nitrogen in a number of different forms, whereas type-II diamond (IIa and IIb) is considered a nitrogen-free variety (less than 20 atomic ppm nitrogen, which is not detected by IR). Type-I diamond was further subdivided into type Ia (IaA, IaAB and IaB) and type Ib depending on the arrangement that the nitrogen takes within the structure of the crystal.

Rare in natural diamonds, type Ib absorbance indicates the presence of a C centre, a single substitutional N atom (type C defect). This is considered to be the state in which nitrogen is initially incorporated into diamond (Dyer et al., 1965), but C centres are unstable at mantle temperatures and N atoms rapidly diffuse to form pairs (A centres). The aggregation of nitrogen in type Ia diamond proceeds from A to B defects (Chrenko et al., 1977; Evans & Qi, 1982). The A centre consists of two adjacent substitutional N atoms (Kaiser and Bond, 1959). The B centre is thought to consist of four N atoms tetrahedrally arranged around a vacancy (Jones et al., 1982).

The diffusion-controlled process of aggregation from A to B centres is promoted by high temperatures, time, high concentrations of nitrogen defects and plastic deformation (Evans, 1992). Most natural type Ia diamonds contain a component of both A and B defect structures (IaAB).

A further result of nitrogen aggregation from A to B centres is the development of platelets (type-D defect), which are nanometric to micrometric {001} enigmatic planar structures found only in type Ia diamonds.

Platelets are destroyed by high temperatures and are sometimes absent in highly aggregated IaB diamonds. The degradation of platelets results in dislocation loops and voidites (Woods, 1986; Evans et al., 1995). Voidites are nanometric octahedral {111} faceted defects that occur in the cubic {100} plane in association with dislocation loops (Woods, 1993). The spectral classification of diamonds recorded by IR is summarized in the Table 1.

The main goal of this study is to investigate the nitrogen aggregation states of diamonds from southern São Francisco Craton situated at Minas Gerais, Brazil (Fig. 1), by IR spectroscopy as well as its mineral inclusions by Raman spectroscopy to know the evolution of the nitrogen aggregation of distinct diamond populations and the mantle mineralogy under the southern Craton. A method to discriminate Ia diamond populations by using IR is also proposed.

2. Samples and Methods

Methods used are based on IR and Raman vibrational spectroscopy. IR absorption spectra were measured for 91 whole diamonds from secondary sources (sampled rivers in figure 1) situated at the three main Diamoniferous Provinces of the Minas Gerais State as defined by Penha et al. (2000) in geographic terms: Alto Paranaiba (samples ESRB), West São Francisco (samples TRA and SGRB) and Espinhaço (samples ARJ, DRCM, CMRJ, CRJ, and IRM). IR data represent averages of total nitrogen contents and aggregation states for individual whole stones.

Spectra were obtained using a NICOLET FTIR spectrometer equipped with a microscope, MCT detector and KBr beam splitter. Spectra were normalized by the value of the absorption at 1992 cm⁻¹ to determine the nitrogen contents and aggregation states by using the method proposed by Mendelsohn & Milledge (1995).

In order to baseline spectra, the absorption was measured at 4000 cm⁻¹ and at the minimum in the region 1600-1400 cm⁻¹, and the linear baseline
defined by these two values was extrapolated to 900 cm\(^{-1}\). IR spectra were recorded over the range from 4000 to 650 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\).

**Tab. 1 - Spectral classification of diamonds**

<table>
<thead>
<tr>
<th>TYPE</th>
<th>CHARACTERISTICS</th>
<th>DEFECT</th>
<th>IR LINE (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>Up to 20 atomic ppm nitrogen</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IIb</td>
<td>Up to 20 atomic ppm nitrogen, contains Boron</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ib</td>
<td>Single substitutional N</td>
<td>C (or N)</td>
<td>1130</td>
</tr>
<tr>
<td>IaA</td>
<td>Two adjacent substitutional N</td>
<td>A</td>
<td>1282</td>
</tr>
<tr>
<td>IaB</td>
<td>Four tetrahedrally arranged substitutional N</td>
<td>B</td>
<td>1175</td>
</tr>
<tr>
<td>IaAB</td>
<td>IaA + IaB, most of natural diamonds</td>
<td>A and B</td>
<td>1282 and 1175</td>
</tr>
<tr>
<td>platelets</td>
<td>Inclusions with N</td>
<td>D</td>
<td>(~1365)</td>
</tr>
<tr>
<td>voidites</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Raman spectra were obtained by using a triple-monochromator DILOR XY equipped with an Olympus microscope and 514.5 nm line from Ar-Kr laser. Raman spectra database (RSD) from site http://rruff.geo.arizona.edu/rruff/ has been used to constrain studied inclusions. Raman and FTIR equipments are located at the Department of Physics of the ICEX-UFMG.

**Fig. 1- Rivers of the Minas Gerais (MG) State and diamond sampling areas.**

From all samples seven diamonds were identified as type II (samples ARJ2, CRJ8, CRJ10, ESRB5, IRM10, IRM12, SGRA6) and type Ib diamond was not found in this study. The majority of the further samples can be classified as type IaAB as shown in the Tab. 2.
Table 2 - IR results for diamonds of selected areas of Minas Gerais State. a.u. = absorption units, N(A) = A centre nitrogen, N(B) = B centre nitrogen, Ntotal = total nitrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampling</th>
<th>a.u. at 1282 cm⁻¹ (A)</th>
<th>a.u. at 1177 cm⁻¹ (B)</th>
<th>a.u. at 1365 cm⁻¹ (D)</th>
<th>B/A</th>
<th>N(A)</th>
<th>N(B)</th>
<th>Ntotal</th>
<th>Spectral classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB001</td>
<td>Córrego</td>
<td>1.150</td>
<td>1.040</td>
<td>0.220</td>
<td>0.38</td>
<td>0.35</td>
<td>0.35</td>
<td>0.68</td>
<td>IA</td>
</tr>
<tr>
<td>AB002</td>
<td>Itacambira</td>
<td>0.674</td>
<td>0.420</td>
<td>0.210</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.68</td>
<td>IA</td>
</tr>
<tr>
<td>AB01</td>
<td>Diamantina</td>
<td>2.434</td>
<td>2.238</td>
<td>2.016</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>1.94</td>
<td>IA</td>
</tr>
<tr>
<td>AB02</td>
<td>Itacambira</td>
<td>0.674</td>
<td>0.420</td>
<td>0.210</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.68</td>
<td>IA</td>
</tr>
<tr>
<td>AB03</td>
<td>Diamantina</td>
<td>2.434</td>
<td>2.238</td>
<td>2.016</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>1.94</td>
<td>IA</td>
</tr>
</tbody>
</table>

As presented in Introduction, increasing temperature and/or time can lead A centres to evolve to B centres in association to platelet development (Fig. 2). In order to understand the evolution of nitrogen aggregation from A to B centres in type Ia diamonds from Minas Gerais rivers, the ratio B/A between the 1175 cm⁻¹ (B) and 1282 cm⁻¹ (A) normalized absorptions versus the absorption of the line corresponding to platelets defects (D - 1365 cm⁻¹) was plotted.

Four sample groups aligned in four different linear curves (Fig. 3), which indicate that nitrogen aggregation behavior of each group should be mathematically described by the first degree equation.
B/A = aD + b (a = slope; b = intersection with B/A axis).

The composition of some mineral inclusions were determined for diamonds SGRA8 (Group 1), CMRJ2 (Group 2), IRM32 (Group 3) and SGRA5 (Group 4) by Raman spectroscopy. Forsterite (Raman lines 824 to 826 cm⁻¹ and 856 to 858 cm⁻¹) was found in diamonds from all groups (Figs. 4 and 5). Lilac pyrope garnet (Raman line 925 cm⁻¹), typical of ultramafic suite, was found inside sample SGRA5. Finally, graphite (Raman line 1583 cm⁻¹) was observed inside sample SGRA8.

Figure 2 - Temperature versus time schematic representation of the evolution of nitrogen aggregation from C centres (Ib diamonds) to A (IaA diamonds) and B centres (IaB diamonds). Platelets seem to appear during A to B centres transformation. Squares show the infrared absorption envelopes corresponding to each nitrogen aggregation state (modified from Mendelssohn & Milledge, 1995).

Figure 3 - The ratio between normalized absorption of the 1175 cm⁻¹ (B) and 1282 cm⁻¹ (A) lines versus the platelets (D) absorption of diamonds from Minas Gerais.
4. Discussions and Conclusions

Different histories of nitrogen aggregation were responsible for distinct linear curves shown by four Ia diamond groups from Minas Gerais. Platelet (D defect) development seems to be controlled by very well defined conditions of time and energy in mantle and it occur as A centres evolve to B centres. Therefore, the diagram of figure 3 represents an useful tool to define diamond populations as B/A ratio is related to D defect IR absorption. However, this method to discriminate nitrogen signatures of diamond populations must be tested by using a large number of stones from distinct populations around the world to measure its efficiency.

Based on IR data, samples from Group 1 presented the lowest B centres aggregation related to total nitrogen content.
This fact in association to the presence of graphite seem to indicate that diamonds from Group 1 were formed at shallow mantle (lowest temperature and pressure among 4 groups, ~1150°C and ~45 Kbar), near the limit of graphite/diamond stability field (~150 km depth). Diamonds of this group have probably had the shortest residence time within the mantle.

From Group 2 to 4 the diamond formation depth is increasing and in the last one ESRB samples keeps diamonds generated at highest temperature and pressure among the studied groups. Under these conditions, platelets were partially destroyed and eventually are absent in IaB diamond found in low N samples from Group 4 (see table 2). Diamonds of this group have probably had the longest residence time within mantle.

The presence of forsterite inclusions in diamonds from all groups links them to ultramafic suite. This observation reveals a peridotitic mantle underlaying São Francisco Craton. It is important to remark that samples of a same group are not necessarily from same sampling geographic area.

Acknowledgements
Thanks go to CNPq for the first author’s Post Doctoral research support, to Center for Development of Nuclear Technology (CDTN-CNEN) and Department of Physics of UFMG, where the work was developed with unrestricted support. Special thanks to Roberto Luiz Moreira (IR lab.), Marcos Pimenta (Raman lab.), and Maximiliano Martins (UFMG).

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RSD - RAMAN SPECTRADATA BASE - available at http://rruff.geo.arizona.edu/rruff/.

