Mineral inclusions in diamonds from Chapada Diamantina, Bahia, Brazil: a Raman spectroscopic characterization

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Abstract

The Chapada Diamantina, located in the central region of the State of Bahia, is of important historical significance due to its diamond occurrences. Discovered in the nineteenth century, comprehensive research about the regional diamonds and their origins are still limited, demanding more investigation in the matter. Looking for insights about their genesis, mineral inclusions in 23 alluvial diamonds from 4 *garimpos* located in the Chapada Diamantina were analyzed through the use of Raman micro spectroscopy. Additionally, the characteristics of nitrogen aggregation of the host diamonds were measured using Fourier-transform infrared spectroscopy (FTIR). The diamonds from Chapada Diamantina consist mainly of well-formed crystals, with dominant dodecahedral habits, characterized by faint to very light yellow body colors, typically with green and brown radiation spots on their surface. The main surface textures observed are related to processes that took place in the late stage resorption and during the residence of the diamonds in placer environments. The diamonds are predominantly type IaAB, with a significant occurrence of poorly aggregated nitrogen (Type IaA diamond). The main mineral assemblages of the studied peridotitic inclusions refer to a harzburgitic paragenesis.

Keywords: diamonds, Chapada Diamantina, mineral inclusions, Raman spectroscopy.

1. Introduction

The discovery of diamonds in the State of Bahia occurred in the Chapada Diamantina region, in 1821, nearly a century after the first finds in Brazil, which took place in the State of Minas Gerais (Leonardos, 1937). From 1844 onwards, Bahia had a remarkable production of diamonds and carbonados (Barbosa, 1991), which has gradually declined until today. The mining regions around the municipalities of Lençóis, Andaraí and Mucugê, within the surroundings of the established National Park of Chapada Diamantina boundaries, produced the greatest economic impact on Bahia's diamond production (Sampaio, 1994).

The exploration of diamonds occurs mainly in alluvial deposits of the Paraguaçu, Santo Antônio and São José rivers, in which the diamonds are considered a product of disintegration and reworking of the Mesoproterozoic Tombador Formation conglomerates (Bonfim and Pedreira, 1990). The primary source of

such diamonds is unknown; due to the absence of typical satellite minerals, the diamond's genesis in Chapada Diamantina, as well as in all the Espinhaço range, is still controversial (Chaves *et al.*, 1998; Almeida-Abreu and Renger, 1999).

The oldest known primary source of diamonds in the São Francisco craton is the Neoproterozoic kimberlites of Brauna Field (642+/-6 Ma, U-Pb in perovskite, Donatti Filho *et al.*, 2012), located northeast of the State of Bahia, and the Mesoproterozoic kimberlites of Salvador Field (1.152 Ga, Rb-Sr in phlogopite, Williamson and Pereira, 1991), located northwest of Chapada Diamantina (Nannini *et al.*, 2017).

The upper limit for the sedimentation of the Tombador Formation is suggested as 1394+/-14 Ma (U-Pb in zircons) (Gruber *et al.*, 2011). In this way, the kimberlitic affinity intrusions known in the State of Bahia are younger than the primary sources required for the diamonds

present in the Tombador Formation conglomerates (Pereira and Fuck, 2005; Pereira, 2007).

The study of inclusions in diamonds has changed and shaped our understanding about diamond genesis, and is the only means to determine the process of diamond formation (Stachel and Harris, 2008).

Studies of diamonds and their associated mineral inclusions in Brazil are surprisingly scarce. One exception is the diamonds from the Juína area, in the State of Mato Grosso, widely studied due to their superdeep paragenesis (Kaminsky *et al.*, 2009). The Juína diamonds are unique in comparison to other Brazilian diamond populations (Meyer and Svisero, 1975; Chaves *et al.*, 2005; Tappert *et al.*, 2006).

On the other hand, mineral inclusions in diamonds from Chapada Diamantina have never been widely studied. The only records we were able to find are in the works of Meyer and Svisero (1975)

and Svisero (1978), when they studied mineral inclusions in Brazilian diamonds.

The present study presents data from the analysis of syngenetic mineral inclu-

sions and their assemblage in 23 diamonds from Chapada Diamantina, Bahia, and also emphasizes the morphological and infrared spectroscopic characteristics of

the diamond hosts. Data about the aggregation state of nitrogen in the diamonds from Chapada Diamantina have not been found in literature.

2. Geological Setting

The Chapada Diamantina, located in the central part of the State of Bahia, is inserted in the geological context of the São Francisco Craton, which consists of an Archean/Paleoproterozoic basement and Paleomesoproterozoic and Neoproterozoic covering sediments of the Espinhaço and São Francisco Supergroups, respectively (Figure 1). The basement rocks are mainly composed of medium to high grade metamorphic rocks of the Gavião Block and granitoids associated with metamorphic-migmatitic events (Barbosa *et al.*, 2012a).

The covering rocks begin with a succession of continental and marine metasedimentary and metavolcanic

rocks of the Espinhaço Supergroup, which comprises, from base to top, according to Guimarães *et al.* (2012), the Serra da Gameleira Formation, Rio dos Remédios Group (composed of Novo Horizonte, Lagoa de Dentro and Ouricuri do Ouro Formations), Paraguaçu Group (composed of Mangabeiras and Açuruá Formations), Chapada Diamantina Group (composed of Tombador and Caboclo Formations) and Morro do Chapéu Formation.

The carbonatic and siliciclastic rocks of the São Francisco Supergroup rest on an erosional unconformity of regional character overlaying the crystalline basement rocks, the Chapada Diamantina Group

and the Morro do Chapéu Formation. The São Francisco Supergroup comprises the Bebedouro and Salitre Formations, which are covered by Cenozoic surficial deposits.

The most important diamond occurrences of Chapada Diamantina are related to the Tombador Formation. This formation includes 3 siliciclastic lithofacies associations, being the lower and the intermediate composed of metarenites and metaconglomerates; the latter carry detrital diamond. Diamonds are mostly recovered in colluviums and alluviums due to erosion and subsequent reworking of diamondiferous conglomerates of the Tombador Formation (paleoplacer) (Barbosa *et al.*, 2012b).
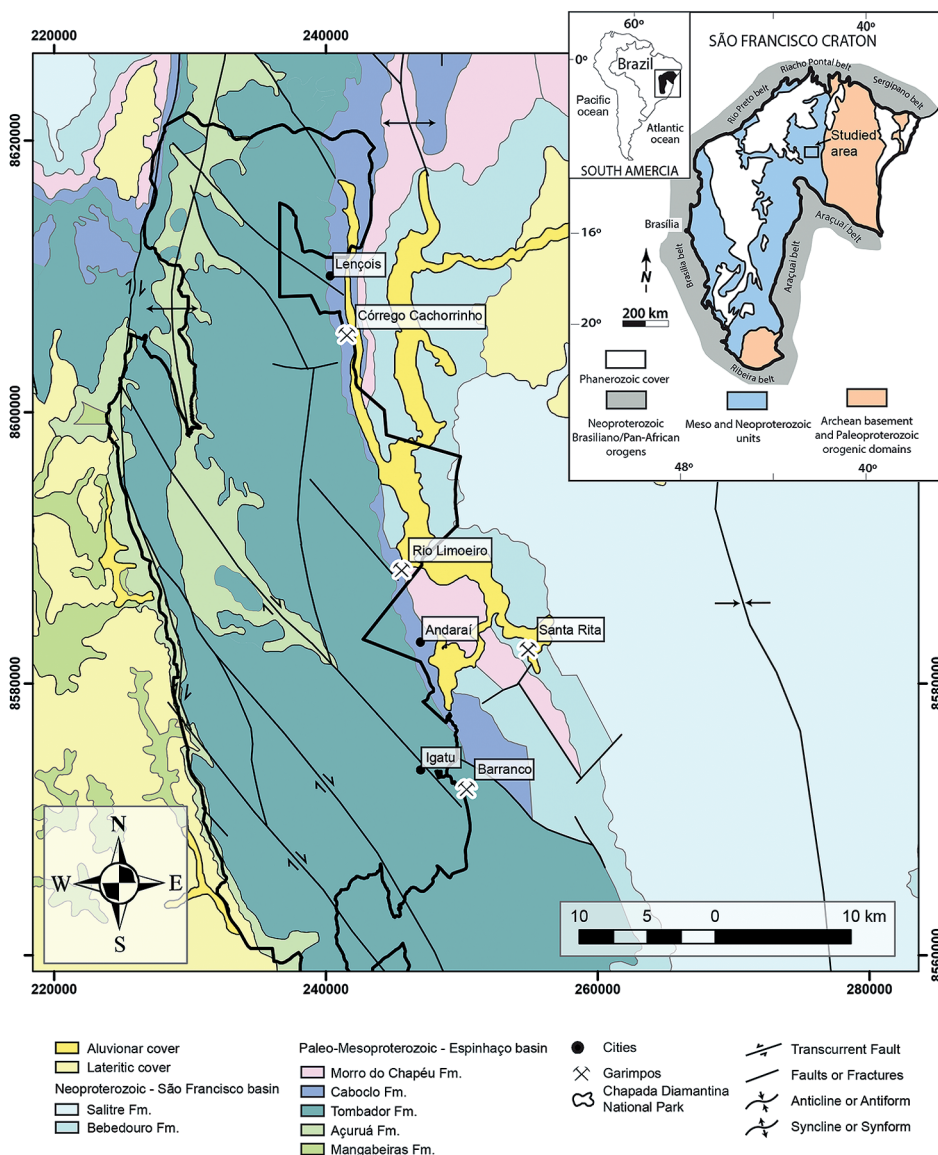

Figure 1
Geology and tectonic features of Chapada Diamantina and the São Francisco Craton with locations of the studied garimpos (Modified from Dalton de Souza *et al.*, 2003).

3. Materials and methods

This study presents the results of the analysis of inclusions in 23 diamonds (Figure 2) from 4 *garimpos* in the Chapada Diamantina region, being 12 from *Garimpo* Santa Rita, Andaraí; 7 from *Córrego* Cachorrinho, Lençóis; 3 from *Garimpo* Barranco, Igatu; and 1 from the Limoeiro river, Andaraí (Figure 1). The samples were kindly ceded by Diamond Brazil Project from the Geological Survey of Brazil (CPRM).
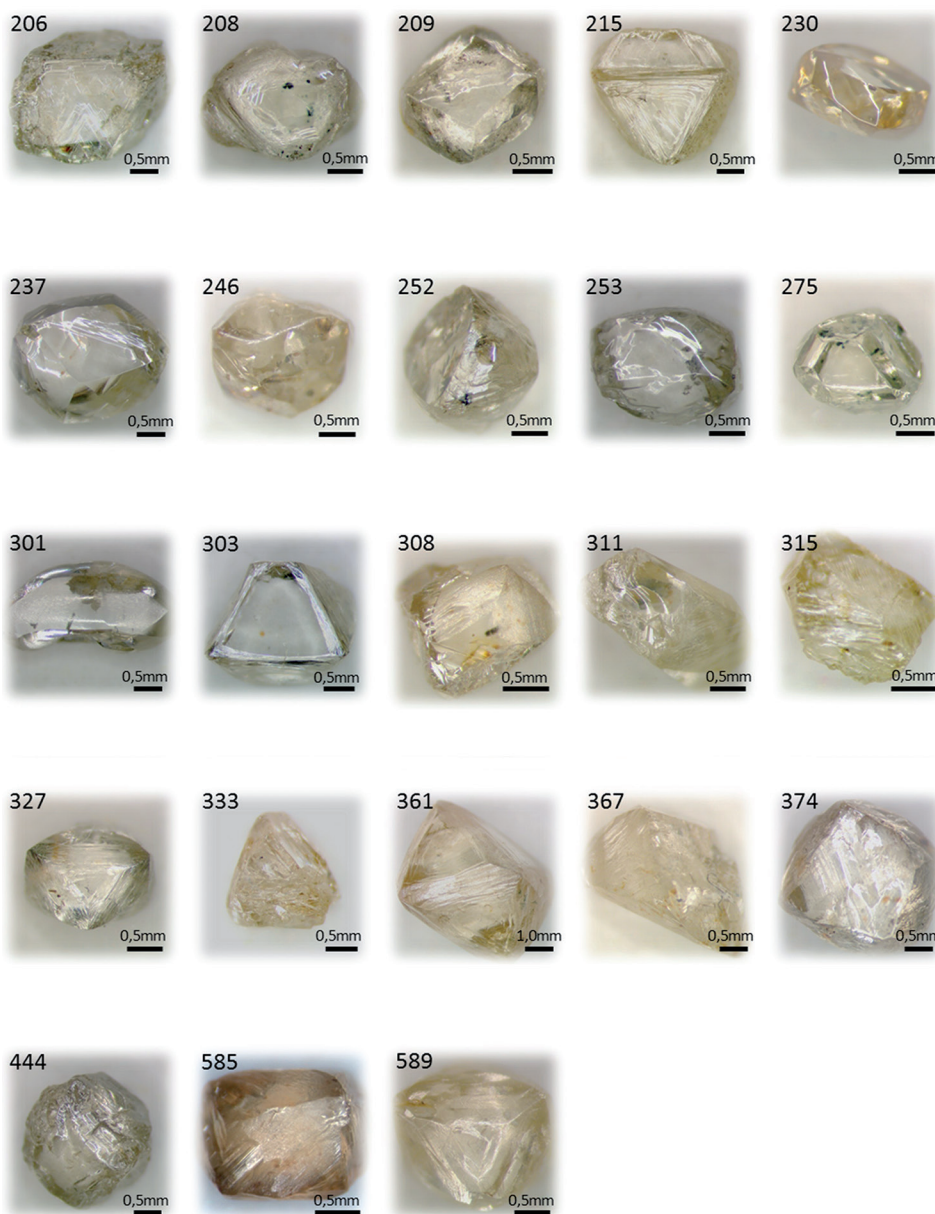

Figure 2
Pictures of the 23 diamonds analyzed in this study. The numbers in the upper left corner of the pictures are the codes of the samples. The characteristics of the diamonds can be ascertained in Table 1.

All diamonds were examined microscopically to determine visible morphological features, surface textures and colors. Subsequently, the diamonds had a face polished for better visualization of the inclusions. The concentration and aggregation state of nitrogen impurities in the diamonds were determined by Fourier transform infrared (FTIR) spectroscopy, using a Perkin-Elmer Spectrum 400 instrument, equipped with a 5x beam condenser, from the Gemological Research Laboratory of the Center for Mineral Technology (CETEM). Raman spectra were recorded in back-scattering geometry with a Raman microspectrometer (Horiba model LabRam HR) from the Technological Characterization Sector of CETEM, with a laser beam of 632.8 nm. The recording times were in the order of 7 minutes.

4. Results and discussion

Diamond characteristics

The 23 studied diamonds have a weight range of 0.02 to 0.13 carats, with the exception of one crystal of 1.10 ct. Their characteristics are presented in Table 1. The majority of the diamonds have faint and very light yellow body colors, sometimes with a brownish hue. The dominant shape is the dodecahedron, which comprises more than half of the studied diamonds; the presence of macles is also notable. Transition forms between octahedron and dodecahedron, as well as fragmented crystals, also occur.

Sample	Origin	Weight (ct)	Color	Shape	Type	Spots	Assemblage
206	G. Sta Rita	0.099	FY	Flat	IaAB	Green, Brown	Ol
208	G. Sta Rita	0.050	FY	Tran	IaAB	Green, Brown	Ol
209	G. Sta Rita	0.031	VLY	Dod	IaAB	Brown	Ol
215	G. Sta Rita	0.081	VLY	Twin	IaAB	Green	Ol+Prp
230	G. Sta Rita	0.028	VLY	Dod	IaAB	Brown	Ol
237	G. Sta Rita	0.076	FY	Dod	IaAB	Brown	En
246	G. Sta Rita	0.038	VLB	Dod	IaA	Brown	Ol
252	G. Sta Rita	0.050	FY	Tran	IaA	Green, Brown	Ol
253	G. Sta Rita	0.033	FY	Dod	IaA	Green	Ol
275	G. Sta Rita	0.025	NC	Twin	IIa	Green	Ol
301	C. Cachorrinho	0.056	FY	Dod	IaB	Brown	Ol+En+Prp
303	C. Cachorrinho	0.079	FY	Oct	IaB	Brown	Ol
308	C. Cachorrinho	0.032	VLB	Dod	IIa	Brown	Chr
311	C. Cachorrinho	0.057	VLY	Dod	IaAB	Green	Ol
315	C. Cachorrinho	0.027	FY	Und	IaAB	Brown	Ol
327	C. Cachorrinho	0.030	FY	Tran	IaAB	-	Ol
333	C. Cachorrinho	0.052	VLY	Und	-	-	Ol
361	G. Barranco	1.104	VLY	Tran	IaAB	Green, Brown	Ol+En
367	G. Barranco	0.109	FB	Dod	IaAB	Brown	Ol+En
374	G. Barranco	0.129	VLY	Dod	IaAB	Brown	Ol
444	Limoeiro River	0.074	FY	Und	IaA	-	Ol+En
585	G. Sta Rita	0.028	LB	Dod	IaAB	Brown	Ol
589	G. Sta Rita	0.087	VLB	Dod	IaAB	-	Ol

Colors are classified according to the classification scheme of GIA: C = colorless, NC = near colorless,

FY = faint yellow/ FB = faint brown, VLY = very light yellow/ VLB = very light brown, LY = light yellow/ LB = light brown.

Dod = dodecahedroid, Tran = transitional, Oct = octahedron, Und = undefined

Ol = olivine, Prp = pirope, En = enstatite, Chr = chromite.

Table 1
Characteristics of the diamonds from Chapada Diamantina studied in this work.

The surface textures observed in the diamonds are mainly related to processes that took place in the late stages of resorption in the kimberlitic melt (enhanced luster), and during the residence in a placer environment (network patterns). The first developed possibly due to a late-stage high-temperature (~1000°C) etching (Phaal, 1965); and the second is related to a natural etching in placer environment due to a preferential attack linked to a minor dislocation of carbon atoms along octahedral planes (Emara and Tolansky, 1957).

Another feature observed, but not related to any specific feature of the dissolution conditions, are the hillocks, which Khokhryakov and Pal'yanov (2015) suggest to be related to strong deformation in the diamond crystals.

Percussion marks on the crystal's surface have not been observed; such absence is not directly related to the distance of transport from the kimberlitic source, but most likely to the stream-bed gradient and the stream-bed lithology (Robinson, 1979).

A common feature is the presence of green and brown radiation spots on the crystal surface. According to Vance et al. (1973), the radiation damage on diamonds can be caused by the presence of radioactive element-rich minerals or solutions in contact with diamonds in placer environments or in the kimberlite.

Raal (1969) recognized that the diamonds from the uranium rich sediments of Witwatersand are all colored in various shades of green. Diamonds with green and brown coats are characteristically associated with pre-Cambrian conglomerates, as in the case of some deposits in Africa, Brazil and Venezuela (Vance *et al.,* 1973).

Only a small parcel of diamonds in kimberlites present radiation spots; the presence of spots in diamonds of kimberlites seems to be directly associated with the weathering mantle (Harris *et al.,* 1977).

In the case of Chapada Diamantina, the vast occurrence of spotted diamonds strongly suggests that such irradiation has occurred during the long-term residence of the diamonds in the conglomerates of the Tombador Formation. The radioactive elements are present in minerals such as zircon, known to occur in the sediments of Tombador Formation. (Svisero, 1978; Gruber *et al.*, 2011).

The presence of brown spots points to a thermal event in the diamond's history following the irradiation damage. It is widely accepted that the green radiation spots turn brown in response to heating at about 550 - 600°C (Vance *et al.*, 1973; Nasdala *et al.,* 2013; Eaton-Magaña and Moe, 2016). The coexistence of green and brown spots in the same diamond indicates that, after heating, the diamond subsequently received additional radiation damage (Vance *et al.,* 1973).

However, in all the Espinhaço range, metamorphism does not exceed greenschist facies (Sussenberger *et al,* 2014). Haralyi and Rodrigues (1992)

suggest that locally the diamondiferous conglomerates may have reached higher temperatures than those of the regional metamorphism. Anyway it is still an unsolved question.

Nitrogen concentrations range from 16.6 to 172 atomic ppm, and 2 diamonds have no detectable nitrogen, being classified as type IIa, according to the classification scheme of Robertson *et al.* (1934). The observed aggregation states are variable (Figure 3); more than half of the diamonds are type IaAB (Figure 3a), which means that they have similar concentrations of nitrogen as A and B centers, indicated by the 1282 and 1175 cm^{-1} absorbance peaks, respectively (Breeding and Shigley, 2009). The other diamonds show a predominance of poorly aggregated nitrogen (A centers) (Figure 3b).

The infrared spectra of 16 diamonds also reveal a 3107 cm^{-1} peak (Figures 3a, 3b and 3c), which is related to an impurity of hydrogen strongly linked to carbon and weakly linked to nitrogen (Fritsch *et al.,* 2007).

Figure 3
Infrared spectra of the diamonds 374 (a), 253 (b), 301 (c) and 308 (d). The absorbance from 1000 to 1500 cm^{-1} is related to nitrogen defects, which allows classifying the diamond as type Ia ((a), (b) and (c) spectra) or, lacking absorption in this region, as type IIa ((d) spectrum). The spectrum (a) is of a type IaAB diamond, which contains nitrogen aggregated both as A center (1282 peak) and B center (1175 peak). The spectrum (b) is of a type IaA diamond, and the (c) of a type IaB diamond. The (d) spectrum shows no absorption in the nitrogen region, being classified as type IIa. The indicated 3107 cm^{-1} is related to the presence of hydrogen.
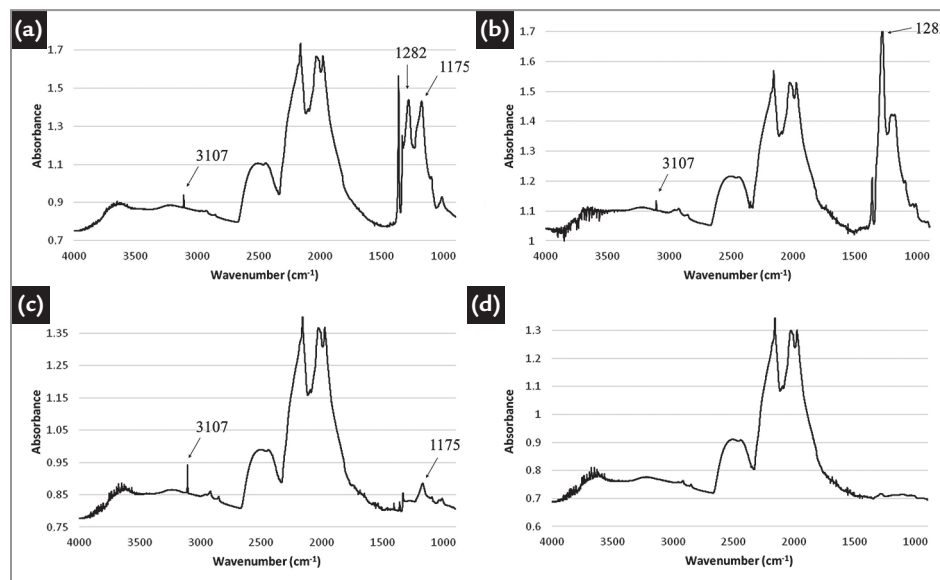
The aggregation from A center (two nitrogens) to B center (four nitrogens surrounding a vacancy) occurs at low rates. Curiously, all 4 diamonds classified as type IaA were from the Andaraí region, and the 2 diamonds classified as type IaB were from Lençóis. The characteristic of nitrogen aggregation in diamonds can be used to identify distinct time temperature populations among pipe and alluvial diamonds, as the degree of aggregation depends on the mantle residence time of diamond, its nitrogen content, and the temperature history (Taylor *et al.*, 1990).

Mineral inclusions

Inclusion studies are currently the only means to determine the source paragenesis and the physical and chemical conditions of diamond formation (Stachel and Harris, 2008). The syngenetic mineral inclusions analyzed in situ by Raman micro spectroscopy were identified based on Raman peak positions, which allowed the estimation of the major element composition of the minerals: forsterite, enstatite, pyrope and chromite (Figure 4). Such minerals belong to the peridotitic suite (Meyer and Tsai, 1976), which indicates a mantle source origin consistent with the majority of other Brazilian diamonds (Meyer and Svisero, 1975, Chaves *et al.,* 2005; Tappert *et al.*, 2006).

Figure 4
In situ Raman spectra of mineral inclusions from Chapada Diamantina diamonds: (a) – Forsterite inclusion, coexistent with enstatite, in a diamond from Igatu; (b) – Enstatite inclusion, coexistent with olivine and pyrope, in a diamond from Lençóis; (c) – Pyrope inclusion, coexistent with olivine, in a diamond from Andaraí; (d) – Single chromite inclusion in a diamond from Lençóis.
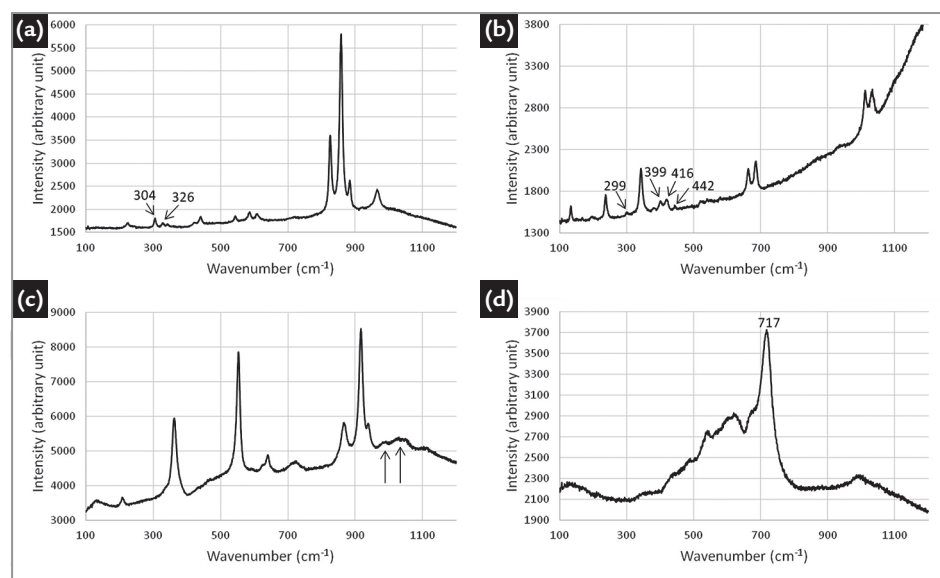
Olivine is the most common mineral inclusion found in diamonds from Chapada Diamantina, occurring in almost all analyzed samples. Forsterite occurs as single and non-touching inclusions combined with enstatite, pyrope or both (Figure 5a).

The Raman spectrum of forsterite (Figure 4a) can be divided into two wavenumber regions, up to 400 cm^{-1} and from 400 to 1000 cm^{-1}. The last region consists mainly of internal SiO$_4$ vibrations. The low wavenumber region shows mixed modes of external SiO$_4$ and Mg vibrations; the indicated peaks at 304 and 326 cm^{-1} have the largest Mg character (Kolesov and Geiger, 2004). This region presents strong differences compared to the spectrum of fayalite (Chopelas, 1991).

The studies of Svisero (1978) revealed, for the olivine inclusions of Chapada Diamantina, forsterite numbers ((Mg x 100) / (Mg + Fe)) around 92, and CaO contents of 0.03 wt%.

Orthopyroxene was the second most common mineral inclusion identified. Enstatite occurs either as single inclusion, and associated with olivine (plus pyrope in one case). Olivine + enstatite is the most common inclusion pair among the studied diamonds (Figure 5b).

The most prominent vibrational modes in Raman spectrum of Figure 4b are consistent with the orthopiroxene end-member enstatite; the observed frequencies decreases with iron content, as in the case of olivines (Huang *et al.*,

2000). All the enstatites analyzed showed strong fluorescence. The two main modes bellow 600 cm^{-1} are characterized by metal-oxygen stretching modes. The two modes in the range from 600 to 700 cm^{-1} are related to Si-O-Si bend, and the ones from 900 to 1100 cm^{-1} are generally assigned Si-O stretching vibrations (Huang *et al.*, 2000). The indicated peaks at 299, 399, 416 and 442 cm^{-1} are characterized by Mg-O stretching, that usually appear in Mg rich samples (Huang *et al.*, 2000).

Svisero (1978) found Mg numbers of 93.8, CaO contents of 0.14 wt%, and Cr$_2$O$_3$ contents of 0.62 wt% for a single enstatite inclusion in a diamond from Chapada Diamantina.

Pyrope garnet was only found in two diamonds, one from Andaraí and another from Lençóis. The first occurs associated with olivine (Figure 5c), and the second with olivine and enstatite (Figure 5a).

In the Raman spectrum of the pyrope garnet (Figure 4c), the peaks observed at higher energies correspond to SiO$_4$ internal stretching modes, and the others, at medium and lower frequencies, are related to SiO$_4$ internal bend modes. Stretching frequencies of pyrope often occur at higher energies, when compared to other garnets (Hofmeister and Chopelas, 1991).

No assessment could be made about major elements, but some coincidence with additional bands related to increased TiO$_2$ content (Gillet *et al.,* 2002), indicated by the arrows in Figure 4c, was ob-

served. According to Stachel and Harris (2008), TiO$_2$ contents in garnet exceeding 0.04 wt % point to metasomatic reenrichment, since the titanium should have been largely removed during the intense melt depletion inferred for cratonic peridotites.

The hypothesis of possible high TiO$_2$ contents are not consistent with the data of Svisero (1978) for a pyrope garnet from Chapada Diamantina associated with olivine. The studies of Svisero (1978) revealed TiO$_2$ contents <0,01 wt%, and also Cr$_2$O$_3$ contents of 9.34 wt%, Mg numbers between 88.43 and CaO contents of 5.09 wt%.

Chromite inclusions were found in only one diamond from Lençóis (Figure 5d). To our knowledge, this is the first report of chromite in diamonds from Chapada Diamantina; according to Svisero (1978) chromite inclusions are not abundant in Brazilian diamonds. Raman spectra of chromites usually consist of a major broad peak near 685 cm^{-1}, and a few other less intense ones; according to Wang *et al.* (2004), this feature is generated by the vibration of the A^{3+}O$_6$ (A = Cr^{3+}, Fe^{3+}, Al^{3+}) octahedron. However, the Raman spectrum obtained in this study shows the main peak strongly shifted (Figure 4d). The abnormally high wavenumber position of this peak is recognized for high chromium content in mantle chromites (Wang *et al.*, 1994). Some of the most Cr-rich chromite grains found in nature are found as inclusions in diamond (Barnes and Roeder, 2001).
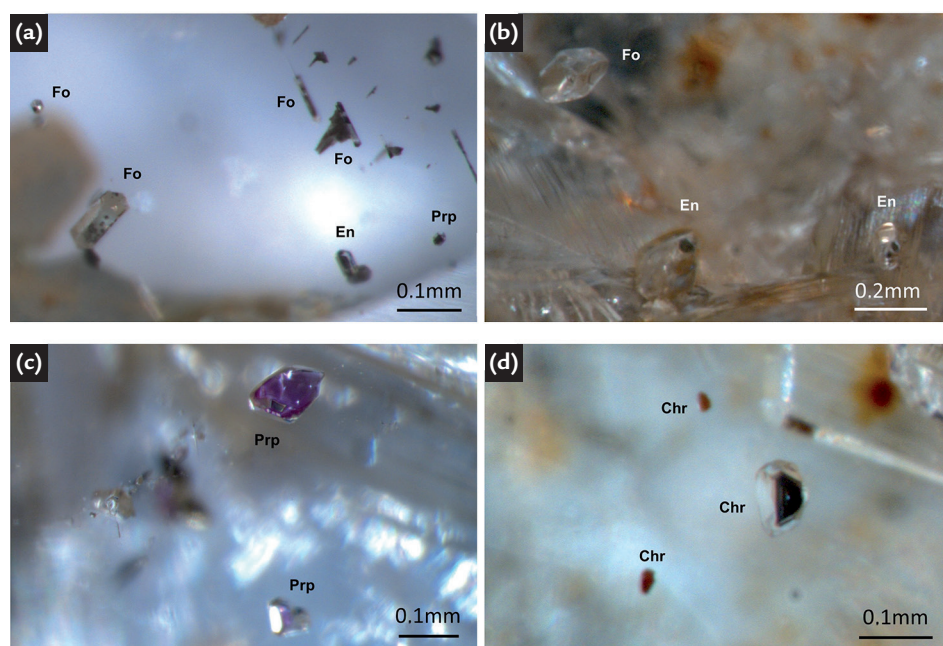

Figure 5
Peridotitic mineral inclusions in the diamonds from Chapada Diamantina (Fo = forsterite; En = enstatite; Prp = pirope; Chr = chromite).
(a) - inclusions of forsterite, enstatite and pirope coexistent in the diamond 301.
(b) – forsterite + enstatite inclusion pair in the diamond 367.
(c) – pirope coexistent with forsterite in the diamond 215.
(d) – chromite inclusions in the diamond 308.

The Mg rich character of forsterite and enstatite inferred by Raman

spectroscopy, the typical mineral assemblages of the analyzed diamonds

(Forsterite + Enstatite; Forsterite + Pyrope; and Forsterite + Enstatite +

Pyrope) and the absence of clinopyroxene, that also have not been reported in previous studies as inclusions in diamonds from Chapada Diamantina, largely indicate a harzburgitic source rock for the studied diamonds (Stachel and Harris, 2008). The correlation with the high Mg numbers and low calcium contents of forsterite and enstatite, and the composition of the garnets analyzed for Svisero (1978), corroborate that such peridotitic diamonds may have formed in depleted harzburgitic sources (Boyd and Finnerty, 1980, Stachel and Harris, 2008).

5. Conclusions

The analyzed alluvial diamonds from Chapada Diamantina have characteristically faint to very light yellow body colors, typically with green and/or brown radiation spots on their surface. A common feature is the network pattern, which reflects the long-term residence in placer environments of such diamonds. The high abundances (>80%) of spotted diamonds is evidence of a long time exposure to radiation. The absence of diamond indicator minerals, the sorting of diamonds by size, shape, and quality, and the surface textures, all indicate that the Chapada Diamantina diamonds have been reworked in sedimentary environments, suggesting farther primary sources, which may have been obscured by erosion and sedimentation.

Based on the analytical data obtained in this work, it is not possible to distinguish between different diamond populations by using morphological criteria, which may be a result of the small number of samples examined. The noticeable relationship between the aggregation state of nitrogen and the studied deposits, despite the small number of samples, suggests that a population of diamonds may have experienced a higher temperature and/or longer storage in the mantle than others.

The diamonds contain abundant olivine inclusions, followed by enstatite, pyrope and chromite. The coexistence of olivine with pyrope and/or enstatite, besides the absence of clinopyroxene, allows to conclude that such minerals belong to the harzburgitic paragenesis, which resemble results from other Brazilian deposits (Meyer and Svisero, 1975, Chaves *et al.,* 2005; Tappert *et al.,* 2006) and corroborates the studies of Svisero (1978), in which chemical data are consistent with depleted harzburgitic source rocks.

The non-destructive character of this study precluded further comprehension on the conditions of diamond formation in the sublithospheric mantle under the São Francisco craton. Nevertheless, the current indications are that diamonds from the São Francisco craton have similar origins to those demonstrated on other cratons elsewhere in the world; these are most predominantly harzburgitic in origin, dodecahedral in shape and faint yellow in color. In addition, the diamonds from Chapada Diamantina should have probably originated under the same conditions and as products of the same process.

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