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

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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 A 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, piropo 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; Mendelssohn & 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 Diamondiferous Provinces of the Minas Gerais State as defined by Penha et al. (2000) in geographic terms: Alto Paranaíba (samples ESRB), West São Francisco (samples TRA and SGRA) 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 Mendelssohn & Milledge (1995).

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

Tab. 1 - Spectral classification of diamonds

TYPE	CHARACTERISTICS	DEFECT	IR LINE (cm^{-1})
IIa	Up to 20 atomic ppm nitrogen	-	-
IIb	Up to 20 atomic ppm nitrogen, contains Boron	-	-
Ib	Single substitutional N	C (or N)	1130
IaA	Two adjacent substitutional N	A	1282
IaB	Four tetrahedrally arranged substitutional N	B	1175
IaAB	IaA + IaB, most of natural diamonds	A and B	1282 and 1175
platelets	{001} planar structures	D	~1365
voidites	Inclusions with N	-	-

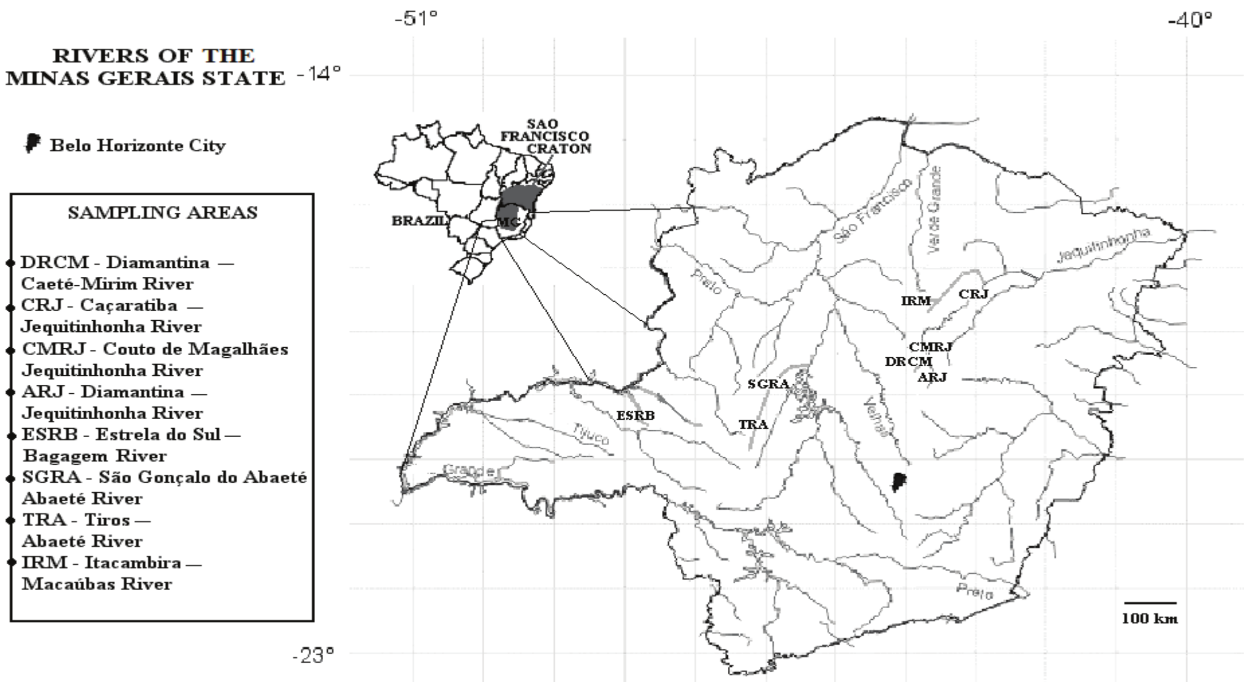

Fig. 1- Rivers of the Minas Gerais (MG) State and diamond sampling areas.

Raman spectra were obtained by using a triple-monochromator DILOR XY equipped with an Olympus microscope and 514.5nm 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.

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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.

Sample	Sampling area	a.u. at $1282cm^{-1}$ (A)	a.u. at $1175cm^{-1}$ (B).	a.u. at $1365cm^{-1}$ (D)	B/A	N (A) (atomic ppm)	N (B) (atomic ppm)	N total (atomic ppm)	Spectral classification
ARJ3		5.254	2.522	0.452	0.480	841	0	841	IaA
ARJ4		2.476	1.078	0.000	0.435	396	0	396	IaA
ARJ5	Diamantina -	3.240	1.829	1.352	0.565	518	110	628	IaAB
ARJ6	Jequitinhonha River	0.613	0.348	0.065	0.568	98	21	119	IaAB
ARJ7		0.748	0.526	0.522	0.703	120	32	152	IaAB
ARJ8		2.650	2.155	1.086	0.813	424	129	553	IaAB
CMRJ1	Couto de Magalhães –	2.590	1.083	0.548	0.418	414	0	414	IaA
CMRJ2	Jequitinhonha River	0.674	0.420	0.334	0.623	108	25	133	IaAB
CRJ1		0.560	0.550	0.458	0.982	90	33	123	IaAB
CRJ2		1.048	0.560	0.180	0.534	168	34	202	IaAB
CRJ3		1.136	1.172	1.465	1.032	182	70	252	IaAB
CRJ4		0.762	0.495	0.453	0.650	122	30	152	IaAB
CRJ5	Caçaratiba –	0.376	0.300	0.215	0.798	60	18	78	IaAB
CRJ6	Jequitinhonha River	0.216	0.136	0.033	0.630	35	8	43	IaAB
CRJ7		2.276	1.268	0.685	0.557	364	76	440	IaAB
CRJ9		2.476	1.381	0.638	0.558	396	83	479	IaAB
CRJ11		0.428	0.311	0.144	0.727	68	19	87	IaAB
CRJ12		0.086	0.033	0.000	0.384	14	0	14	IaA
CRJ13		3.170	1.456	0.227	0.459	507	0	507	IaA
DRCM3		1.046	0.542	0.216	0.518	167	33	200	IaAB
DRCM4		0.497	0.226	0.065	0.455	80	0	80	IaA
DRCM5		1.249	1.244	1.381	0.996	200	75	275	IaAB
DRCM7		2.424	1.625	1.158	0.670	388	98	486	IaAB
DRCM8		0.635	0.449	0.422	0.707	102	27	129	IaAB
DRCM9	Diamantina –	3.340	1.968	1.424	0.589	534	118	652	IaAB
DRCM10	Caeté Mirim River	3.080	2.350	2.219	0.763	493	141	634	IaAB
DRCM11		2.410	1.098	0.105	0.456	386	0	386	IaA
DRCM12		3.450	1.610	0.362	0.467	552	0	552	IaA
DRCM13		2.720	1.690	1.171	0.621	435	101	536	IaAB
DRCM14		0.206	0.174	0.053	0.845	33	10	43	IaAB
DRCM15		3.890	2.500	1.880	0.643	622	150	772	IaAB
ESRB4		0.084	0.189	0.000	2.250	13	11	24	IaAB
ESRB6		0.136	0.188	0.062	1.376	22	11	33	IaAB
ESRB7	Estrela do Sul –	0.765	0.345	0.000	0.451	122	0	122	IaA
ESRB8	Bagagem River	1.120	0.618	0.142	0.552	179	37	216	IaAB
ESRB9		0.547	0.254	0.030	0.464	87	0	87	IaA
ESRB10		0.049	0.072	0.008	1.477	8	4	12	IaAB
ESRB11		0.413	1.149	0.000	2.782	0	70	70	IaB
IRM1		3.041	1.479	0.600	0.486	487	0	487	IaA
IRM2		0.084	0.167	0.000	1.988	13	10	23	IaAB
IRM3		5.643	2.754	0.156	0.488	903	0	903	IaA
IRM4		0.178	0.282	0.195	1.582	29	17	46	IaAB
IRM5		0.209	0.157	0.127	0.749	33	9	42	IaAB
IRM6		1.066	1.536	2.092	1.441	171	92	263	IaAB
IRM7		3.201	1.509	0.377	0.471	512	0	512	IaA
IRM9		1.942	0.992	0.483	0.511	311	60	371	IaAB
IRM11		0.392	0.186	0.052	0.474	63	0	63	IaA
IRM14		1.619	1.039	0.773	0.642	259	62	321	IaAB
IRM15		1.362	0.993	0.628	0.729	218	60	278	IaAB
IRM16		2.689	1.664	1.071	0.619	430	100	530	IaAB
IRM17		0.960	0.448	0.029	0.467	154	0	154	IaA
IRM18		1.076	1.273	1.465	1.183	172	76	248	IaAB
IRM19	Itacambira –	1.302	0.660	0.310	0.507	208	40	248	IaAB
IRM20	Macaúbas River	0.928	0.951	1.056	1.025	148	57	205	IaAB
IRM21		1.424	0.697	0.390	0.489	228	0	228	IaA
IRM22		3.408	2.176	1.427	0.639	545	131	676	IaAB
IRM23		2.430	1.940	2.030	0.798	389	116	505	IaAB
IRM24		0.508	0.406	0.335	0.799	81	24	105	IaAB
IRM25		5.475	2.207	0.136	0.403	876	0	876	IaA
IRM26		0.346	0.310	0.261	0.897	55	19	74	IaAB
IRM27		1.346	1.880	2.692	1.397	215	113	328	IaAB
IRM28		1.395	0.790	0.177	0.566	223	47	270	IaAB
IRM29		1.674	2.255	2.042	1.347	268	135	403	IaAB
IRM30		1.523	1.230	1.155	0.808	244	74	318	IaAB
IRM31		5.474	3.219	0.827	0.588	876	193	1069	IaAB
IRM32		0.556	0.448	0.224	0.805	89	27	116	IaAB
IRM33		0.166	0.200	0.236	1.203	27	12	39	IaAB
IRM34		0.872	0.632	0.561	0.724	140	38	178	IaAB
IRM35		2.575	1.365	0.321	0.530	412	82	494	IaAB
IRM36		0.109	0.096	0.064	0.881	17	6	23	IaAB
SGRA1		0.618	0.514	0.448	0.832	99	31	130	IaAB
SGRA2		2.703	1.457	0.773	0.539	433	87	520	IaAB
SGRA5		0.133	0.128	0.100	0.962	21	8	29	IaAB
SGRA7		3.747	1.960	1.067	0.523	599	118	717	IaAB
SGRA8	São Gonçalo do	2.984	2.488	2.046	0.834	477	149	626	IaAB
SGRA9	Abaeté –	0.604	0.925	0.866	1.532	97	56	153	IaAB
SGRA10	Abaeté River	0.481	0.398	0.287	0.829	77	24	101	IaAB
SGRA11		0.180	0.116	0.056	0.644	29	7	36	IaAB
SGRA12		0.503	0.391	0.175	0.777	80	23	103	IaAB
SGRA13		0.199	0.144	0.065	0.727	32	9	41	IaAB
SGRA15		4.587	2.095	0.776	0.457	734	0	734	IaA
TRA1	Tiros –	0.743	1.500	1.236	2.018	119	90	209	IaAB
TRA2	Abaeté River	2.266	1.160	0.539	0.512	363	70	433	IaAB
TRA4		2.238	1.926	1.344	0.860	358	116	474	IaAB

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 $1175cm^{-1}$ (B) and $1282cm^{-1}$ (A) normalized absorptions *versus* the absorption of the line corresponding to platelets defects (D - $1365cm^{-1}$) 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 925cm^{-1}), typical of ultramafic suite, was found inside sample SGRA5. Finally, graphite (Raman line 1583cm^{-1}) was observed inside sample SGRA8.

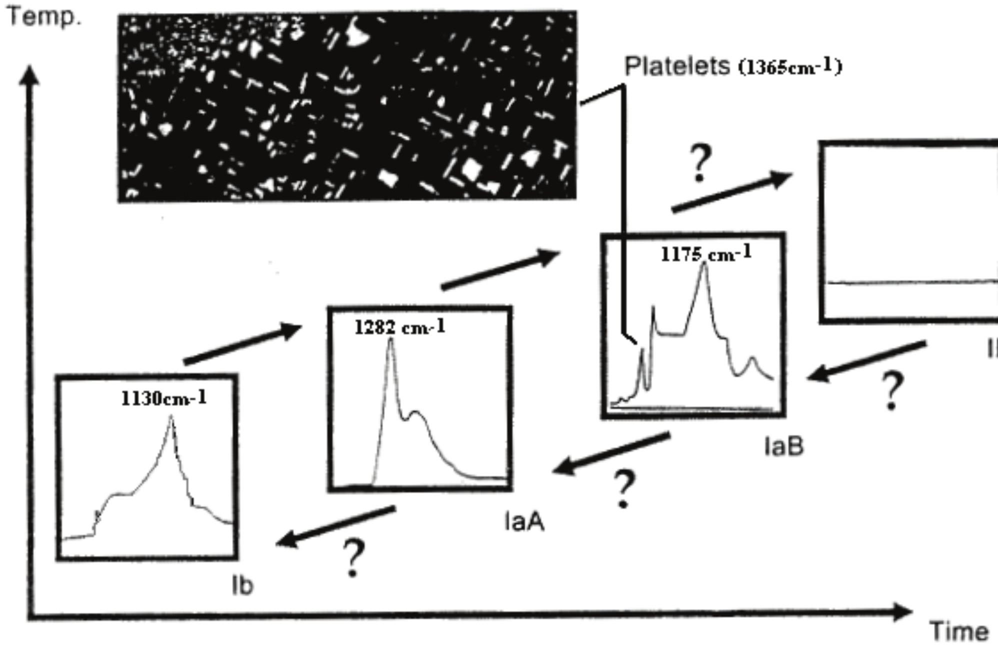

Figure 2 - Temperature versus time schematic representation of the evolution of nitrogen aggregation from C centres (Ib diamonds) to A (IaA diamonds) and B centres (IaB diamonds). Platelets seem to appear during A to B centres transformation. Squares show the infrared absorption envelopes corresponding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

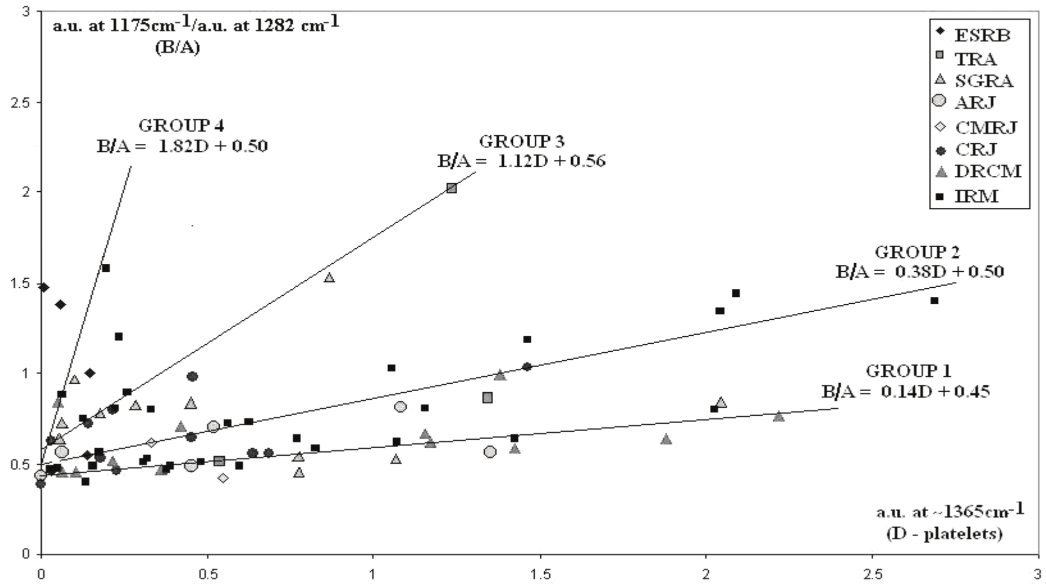

Figure 3 - The ratio between normalized absorption of the 1175cm^{-1} (B) and 1282cm^{-1} (A) lines versus the platelets (D) absorption of diamonds from Minas Gerais.

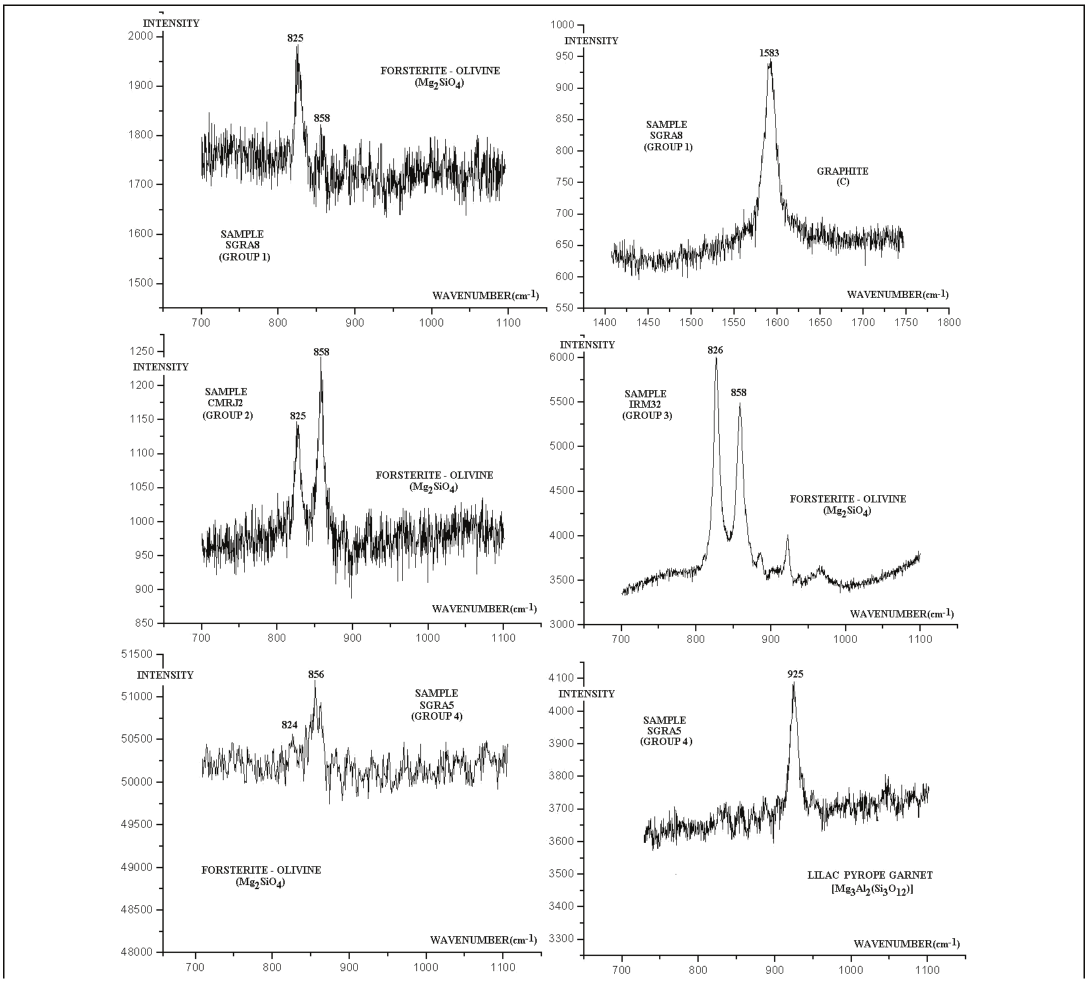

Figure 4 - Raman spectra of mineral inclusions for diamonds from all groups.

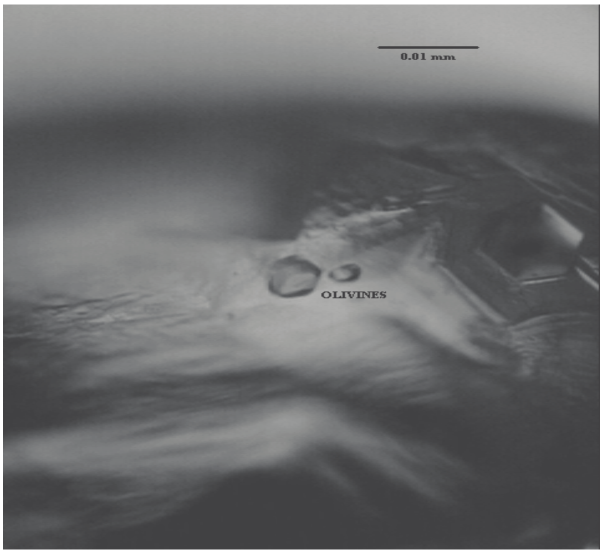

Figure 5 -Two olivine crystals (forsterite) within diamond of IRM sampling area.

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.

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