Carbon and Nitrogen Compositions and Physical Characteristics of Transition Zone and Lower Mantle Diamonds from São Luiz, Brazil

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ABSTRACT

The São Luiz alluvial deposit, Brazil, possesses the most extensive known population of transition zone and lower mantle diamonds. The physical and chemical characteristics of these diamonds and the syngenetic inclusions they contain provide information on the composition of the deep Earth and conditions for diamond formation in an environment far removed from the lithosphere.

São Luiz diamonds have undergone eventful histories. The dominance of irregular and dodecahedral morphologies and complex cathodoluminescence patterns indicate multiple stages of growth, resorption and precipitation. Diamonds have also been subjected to high levels of physical deformation evidenced by the large proportion of brown diamonds, common occurrence of stones which contain fractures and / or plastic deformation lamellae; especially those which also contain platelets. Deformation characteristics are interpreted as being due to the conditions of shear prevalent in the diamonds' source regions and the large internal pressures which build up around inclusions on exhumation from such depths.

Nitrogen is especially depleted in lower mantle diamonds compared to transition zone stones; lower mantle diamonds are almost always Type II as determined by FTIR. Additionally, although transition zone stones are aggregated in nitrogen (> 42 % IaB), where nitrogen appears in lower mantle diamonds it is > 94% IaB supporting a relatively higher ambient temperature or longer residence time in the lower mantle. Carbon isotopic compositions of transition zone stones range from -4.63 ‰ to -12.42 ‰. In contrast, lower mantle diamonds cluster tightly around -5‰ (with ion-probe measurements showing a wider variation on a fine scale within individual stones), which is typical for lower mantle diamonds from elsewhere and indicates a well-mixed lower mantle within the regions sampled.

Keywords: diamond, $d^{13}C$, nitrogen, nitrogen aggregation, lower mantle, transition zone, São Luiz

1 INTRODUCTION

Diamonds from the São Luiz alluvial deposit have yielded syngenetic mineral inclusions whose mutual associations within single stones and compositional characteristics are evidence for many diamonds having an origin within the Earth's transition zone (TZ) and lower mantle (LM) (Harte and Harris, 1994 and Hutchison, 1997). A total of six distinct mineral inclusion associations have been identified (Hutchison *et al.*, in prep.) which are summarised as follows:

- Upper Mantle (UM) peridotitic association of Cr-poor Group 2 (Stephens and Dawson, 1977) lherzolitic clinopyroxene and garnet formed at ~ 120–180 km depth (following Ellis and Green, 1979).
- Transition zone (TZ) association of omphacite, majoritic garnet and pyrrhotite from ~ 120–180 km depth (following Irifune and Ringwood, 1987).
- Lower mantle boundary (LM/UM) association of (Mg,Fe)O periclase-wüstite (termed ferropericlase or 'fPer'), $(Mg,Fe)_2SiO_4$ inclusions thought to have initially adopted a ringwoodite structure and a tetragonally structured pyrope-almandine composition phase termed TAPP (Harris *et al.*, 1997). This association is believed to have formed at ~ 670 km depth (following Jeanloz and Thompson, 1983) where there is a limited depth range where olivine and fPer composition phases can coexist.
- Lower mantle (LM I) association of fPer, $(Mg,Fe)SiO_3$ (termed Type I) composition inclusions understood to have originally adopted a perovskite structure and TAPP from > 670 km depth (following Jeanloz and Thompson, 1983).
- Lower mantle (LM II) association of fPer, corundum (var. ruby) and aluminous $(Mg,Fe)SiO_3$ inclusions with ~ 10 wt% Al_2O_3 (Type II) from ~ 750 to 1000 km in depth (following Irifune *et al.*, 1996).
- Lower mantle boundary (LM III) association of fPer inclusions, Al, Na and Ca-rich $(Mg,Fe)SiO_3$ inclusions (~ 8 to 13 wt% Al_2O_3, ~ 5 wt% CaO and ~6 wt% Na_2O, termed Type III), in addition to a further aluminous phase of one or other of TAPP or low Ca- garnet with a small (3.07 Si cations per 12 O anions) majoritic component. This association is thought to have formed at very close to 670 km depth, perhaps even into the upper mantle, following experimental work of Gasparik (1996) and Jeanloz and Thompson (1983).

All lower mantle associations are thought to have crystallised in association with varying quantities of perovskite structured $CaSiO_3$, principally because of the very low trace element concentrations present in coexisting phases and the identification of a $CaSiO_3$ inclusion from the same diamond as an fPer (Hutchison, 1997). Furthermore, the term 'LM' association is used to refer to diamonds yielding combinations of fPer, TAPP and $CaSiO_3$ inclusions which cannot unambiguously be assigned to a single one of the above lower mantle associations.

As a result of their unusually deep origin, the physical and chemical characteristics of São Luiz diamonds offer an important opportunity not only to infer ambient conditions of diamond growth in the deep mantle, but also to understand post-formation history. Given the danger of assuming any similarity with lithospheric populations, a range of analytical techniques were employed to investigate as many features of the diamonds' composition on as wide a size scale as possible. Subsequently, carbon isotopic composition, nitrogen concentration and

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aggregation and the presence of additional I.R. active species were all measured on scales ranging from mm to ~30 μm. Furthermore, nitrogen concentration was not only measured by conventional FTIR spectroscopy but also by gas combustion and secondary ion mass spectrometry to preclude the possibility of nitrogen being present in non-I.R. active states. Features of diamond growth and deformation were also observed by both optical and high resolution imaging techniques and cathodoluminescence in order to compare physical and compositional characteristics, assess the possibility of inclusion alteration (Hutchison, 1997) and infer the ambient physical and chemical environment on diamond precipitation and exhumation. Comparison is also made throughout with the small number of deep mantle (transition zone and lower mantle) diamonds from other localities world-wide in order to investigate scales of global trends and inhomogeneities.

2 SAMPLES AND METHODS

Diamonds from the São Luiz alluvial deposit are given sample numbers prefixed by 'BZ' and 'JH'. Most São Luiz diamonds studied were crushed to release their mineral inclusions. In addition to these broken stones, two parallel faces were polished onto each of eight diamonds (four of these, BZ251, BZ252, BZ254, BZ255, are of lower mantle association) in order to expose inclusions on one surface, clearly view the inclusions' environment in diamond, observe diamond growth stratigraphy and facilitate high resolution chemical analysis. An additional twelve diamonds (BZ261 - BZ272) were studied but left unbroken. Due to the possibility of sample label mixing in a preliminary analytical study involving diamonds with 'BZ' numbers less than 200 (Wilding, 1991), only results from subsequent study of post-BZ200 and JH diamonds are presented herein.

Prior to any inclusion release, observations of diamond colour, morphology and features of plastic and brittle deformation were made. Stones were then classified according to inclusion association and thus depth of origin, and diamond fragments and unbroken stones exhibiting deep mantle associations were subjected to chemical analysis as follows.

- Diamond shards (0.05 mg and 2.5 mg) were examined by Fourier Transform Infra-Red Spectroscopy (FTIR) for N content and aggregation, plus any other IR-active species (such as C-H or CO_2), at the Laboratoire de Geochimie et des Isotopes Stables (Université de Paris VII). A Nicolet Magna Bench 550 coupled with an IR Plan Spectratech microscope equipped with MCT(A) detector apparatus was employed. Absorption coefficients used in the deconvolution are given by Boyd *et al.* (1994a and 1995a).
- In the same laboratory, all samples were burned for $\delta^{13}C$ analysis and, for selected samples, $\delta^{15}N$ analysis. Methodology followed that of Boyd *et al.* (1995b), results being expressed in the conventional delta notation in per mil deviation relative to PDB carbonate standard (Craig, 1957) for $\delta^{13}C$ and relative to atmospheric nitrogen for $\delta^{15}N$ with accuracies of +/- 0.1 and ~ 0.5 ‰ respectively. The quantity of resulting nitrogen was measured as ppm wt using a capaticance manometer with a precision of +/- 5 ‰. Given the low diamond nitrogen contents, $\delta^{15}N$ analyses presented in Table 3 are blank corrected (4×10^{-9} gN) with a $\delta^{15}N$ taken between -10 and +10 ‰.
- FTIR spectra were also obtained from a number of *unbroken* stones from the BZ215-BZ272 suite at the Diamond Trading Company Research Centre in Maidenhead using a Nicolet Magna-IR 750 Spectrometer.

Cathodoluminescence (CL) characteristics were determined for the eight polished lower mantle diamonds, mounted in indium to reduce internal reflection. Apparatus used was a CITL CCL 8200 Mk3A source combined with Nikon Optiphot optics of the University of Edinburgh operating at ~800 μA and 12-15 kV at 8 Pa. CL intensity was determined by photographic spot metering. Subsequent discrete measurements on BZ251, BZ252, BZ254 and BZ255 were made as follows:

- $\delta^{13}C$ composition was determined by Cameca ims-4f ion microprobe of the University of Edinburgh / N.E.R.C. to a precision of ~ 1.7 ‰ at 2σ. Analyses were carried out using a 14.5 keV $^{133}Cs^+$ primary beam with a 8nA beam current. Field aperture 3, 150 μm contrast aperture, 150 μm image field and ± 12.5 eV energy slits were selected. Reference was made throughout to synthetic standard SYNAT supplied by J.W.H.. Methodology followed that of Harte and Otter (1992).
- Absolute N content was determined by the same ion microprobe using an 8nA beam current, contrast aperture 3, a small field aperture (aperture 2) and narrow energy slits (± 25 eV). Methodology is described in Hutchison (1997).
- FTIR spectra from cuboid volumes close to ion probe pits were obtained at the Diamond Trading Company Research Centre, Maidenhead.
- Scanning electron microscopy (SEM), atomic force microscopy (AFM; Digital Instruments Nanoscope III), scanning probe microscopy (SPM; Nanovision) and electron probe (Cameca Camebax) analysis of inclusion-related fracture zones was conducted at the University of Edinburgh down to resolutions of 1 nm.

3 RESULTS

3.1 Morphology and Colour

São Luiz diamonds of deep mantle origin exhibit octahedral, dodecahedral, irregular or macle morphologies but cubic forms are absent (Table 1). Furthermore, dodecahedra are significantly more common than octahedra, where dodecahedral morphology is regarded as being a resorption form of the octahedron. Indeed all octahedral stones show either evidence of plastic deformation (lamenation lines) or resorption (surface pitting or etch features such as trigons and stepped morphology, Harris 1992). Amongst lower mantle diamonds, irregular stones are particularly common. Table 2 shows that, although the numbers of diamonds involved are small, morphological characteristics of São Luiz diamonds

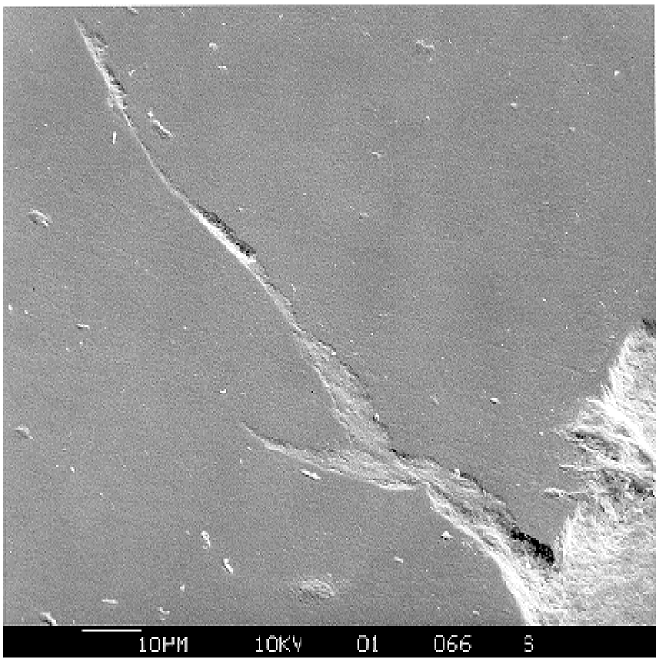

Figure 1. Augen fracture feature in lower mantle diamond BZ251.

Table 1 Distribution of morphology, colour, visible signs of brittle and plastic deformation amongst post BZ214 and JH- series São Luiz diamonds.

	All stones	**L.M. †**	**T.Z. ‡**	**Other ¥**		**All stones**	**L.M. †**	**T.Z. ‡**	**Other ¥**
Dodecahedral	28%	19%	38%	33%	**p.d.**	77 %	74 %	75 %	79 %
Octahedral	18%	12%	25%	22%	**Brown + p.d.♥**	89 %	76 %	100 %	100 %
Irregular	41%	54%	0%	41%	**C/less + p.d.♣**	60 %	56 %	50 %	67 %
Macle	13%	15%	38%	4%	**External I**	15 %	13 %	12 %	17 %
Colourless	41%	35%	50%	44%	**External II**	3 %	9 %	0 %	0 %
Cloud	2%	0%	0%	4%	**Internal**	55 %	39 %	38 %	72 %
Brown	57%	65%	50%	52%					
No. of stones	61	26	8	27	**No. of stones**	61	26	8	27

† Stones of lower mantle associations, i.e. of L.M., LM I, LM II, LM III and LM / UM association.
‡ Stones of transition zone (TZ) association.
¥ Stones of upper mantle and unknown associations. Unbroken diamonds are assigned to the 'other' suite unless a positive identification of LM or TZ paragenesis has been made by XRD (e.g. BZ257) or EPMA (e.g. BZ251).
♥ The percentage of brown diamonds which, additionally, show plastic deformation (p.d.) lamellae.
♣ The percentage of colourless diamonds which, additionally, show plastic deformation (p.d.) lamellae.
External I fractures are observed to reach the surface of the diamond but do not involve the inclusion(s) of interest.
External II fractures show communication between the diamond surface and the inclusion(s) of interest. These fractures often show a brown oxidised colouration.
Internal fractures are systems which are seen to be wholly encapsulated within the stone.

Table 2 Features of deep mantle association diamonds from the literature.

Sample	**Ass'n**	**M**	**C**	**$\delta^{13}C$**	**FTIR**	**IaB**	**N**	**Sample**	**Ass'n**	**M**	**C**	**$\delta^{13}C$**	**FTIR**	**IaB**	**N**
Jagersfontein, R.S.A. §								**Pipe DO-27, Lac de Gras, Canada** ¤							
J22	T.Z.	i	c/l	-20.19	II			98 22	L.M.	D	B	-2.54	IaAB	95	1950
J23	T.Z.	dm	c/l	-18.94	IaAB	98	65	98 9A	L.M.	D	c/l	-5.01	II		
J25	T.Z.	i	c/l	-24.39	II			97 14H	L.M.	d	b ‡	-4.32	II		
J27	T.Z.	o	c/l	-22.20	II			97 14A	L.M.	d	B	n.d.	II		
J32	T.Z.	tm	c/l	-19.43	II			97 15B1	L.M.	i	B	-3.17	II		
Birim Field, Ghana £								**Koffiefontein, R.S.A.** *							
G303	T.Z.	d	c/l	n.d.	II			K30	L.M.	i	B	-4.99	II		
Letseng-la-Terai, Lesotho ¢								K33	L.M.	o	C	-5.15	IaB	100	33
llt 32	L.M.	i	y ‡	-3.87	II			K34	L.M.	d	b ‡	-5.04	II		
Kankan District, Guinea ¥															
GU4	L.M.	d	c/l	-5.11	II										

Ass'n :- Association
M :- Morphology; d :- dodecahedron; i :- irregular; dm :- flattened dodecahedral macle; tm :- triangular macle
C :- Colour; c/l :- colourless; y :- yellow; b :- brown; ‡ :- shows evidence for plastic deformation
n.d. :- not determined
IaB :- %IaB
N :- Nitrogen content in ppm;
§ :- Deines *et al.* (1991); £ :- Stachel and Harris (1997); ¢ :- McDade and Harris (this volume); ¥ :- Hutchison (1997); ¤ :- Sample names prefixed by DO-27-, data from Davies *et al.* (this volume); * :- Deines *et al.* (1991)

compare favourably with those of deep mantle diamonds recorded in the literature. Transition zone diamonds from elsewhere are mostly irregular or dodecahedral and lower mantle diamonds are dominantly dodecahedral (Deines *et al.*, 1991; Stachel and Harris, 1997; Hutchison, 1997; McDade and Harris, this volume; Davies *et al.*, this volume).

Colourless and, in particular, brown diamonds dominate the sample population from São Luiz (Table 1) and yellow stones are unrecorded. Furthermore, brown colouration, which is believed to be synonymous with plastic deformation (Robinson et al., 1986), is particularly common amongst lower mantle association stones compared to those of the transition zone population. Of at least 38 diamond localities for which detailed study of diamond colour has been made, only three other sources show such a dominance of brown colouration; being Argyle (Hall and Smith, 1984), Venetia (Robinson *et al.*, this volume) and Guinea (Sutherland 1993). Comparison with samples from other localities shows that, in contrast to São Luiz stones, all transition zone diamonds recorded from elsewhere are colourless (Table 2; Deines *et al.*, 1991; Stachel and Harris, 1997). This may be a reflection of the fact that most populations exhibit a colour dependence on the basis of diamond size, however in the absence of size data for non-São Luiz diamonds, this cannot be stated definitively. As for São Luiz, lower mantle diamonds from elsewhere are usually brown (Table 2).

3.2 Deformation

A significant proportion of São Luiz diamonds (55%), particularly those from the lower mantle compared to the transition zone, show obvious features of brittle deformation of various forms (Table 1). The most common brittle deformation feature is wholly internal fracturing, in particular surrounding inclusions. Large fractures running to the outer surface of the diamond are uncommon (~15%) and even fewer stones (<10%) contain fractures connecting mineral inclusions to the diamond surface. Under high magnification, observations carried out on manually broken fragments from JH11 show that fractures propagated under atmospheric conditions have sharp edges, imperceptibly fine terminations and often show 70° orientations to each other, strongly controlled by the diamond's cleavage (Field, 1979). In contrast, the unbroken diamonds of lower mantle origin (BZ251, BZ252, BZ254 and BZ255) usually exhibit sinuous fracture morphologies with 'augen' features (Fig. 1) and show a range of termination types from blunt (4 µm) to sharp (Fig. 2). Additionally, some fractures are observed to terminate prior (20 µm) to intersection with other fractures (e.g. in BZ254).

A yet larger large proportion of São Luiz diamonds (77%) show fine, parallel, surface lamination lines characteristic of plastic deformation (Table 1). Furthermore, as observed world-wide (Robinson et al., 1986), a strong positive correlation exists between diamonds showing evidence for plastic deformation and exhibiting a brown colouration; irrespective of inclusion association, almost all brown stones are plastically deformed.

3.3 Cathodoluminescence

The cathodoluminescence of all eight São Luiz diamonds investigated is lower in intensity than is common for world-wide diamonds. Colouration is in blues of varying saturation with the exception of a single diamond (BZ253) showing a purplish tinge in parts. Variation of cathodoluminescence intensity over polished surfaces was found to be extremely and unusually complex (Figs. 3 & 4). Both diffuse and sharp irregular boundaries between regions of CL intensity were observed and, in some diamonds (BZ253, BZ254, BZ255 and BZ258), regions of sharply bounded concentric zonation typical of lithsopheric diamonds (e.g. Bulanova *et al.*, 1998) were noted (Fig. 4). In one diamond (BZ255), concentric zonation was observed to be centred around a single inclusion; however, in no case does any concentric region surround the central point of a stone. Three diamonds (BZ251, BZ252, BZ255) show external straight edges cutting across CL

Table 3 Compositional characteristics of BZ-200 and JH series diamonds from São Luiz

Sample	**Assoc'n**	**δ^{13}C**	**δ^{15}N**	**Error**	**N †**	**FTIR ¥**	**%B**	**N ‡**
BZ201	L.M.	-5.3				II		
BZ202-1	U.	-4.71				II		
BZ202-2	U.	-4.73				II		
BZ203	U. ¢	-4.46				II		
BZ204-1	U.	-4.22				II		
BZ204-2	U.	-4.56				II		
BZ205-1	L.M.	-5.57				II		
BZ205-2	L.M.	-4.99				II		
BZ206	L.M.	-5.00				II b		
BZ207-1	L.M. I	-4.85				II s, b		
BZ207-2	L.M. I	-5.00	n.d.	-	-	II		
BZ208-1	U.	-5.22				¤ b		25 ?
BZ209-1	T.Z.	-12.42				IaAB s	89	311
BZ209-2	T.Z.					IaAB s	89	252
BZ210	L.M. II	-4.90				II b		
BZ211-1	U.	-12.96				IaA? b?	?	311
BZ211-2	U.					IaA s, b	?	
BZ212-1	U.	-8.54				IaAB s	?	47
BZ213-1	U.M.	-5.27				IaAB s	78	252
BZ213-2	U.M.					II ¤		
BZ214	U.	-11.56				II b		
BZ215-1	T.Z.	-8.85	+1.3	1.0	166	IaAB s	71	289
BZ216	T.Z.	-6.23						
BZ217-1	T.Z.	-8.64	+1.2	1.05	62	IaAB s, b (13)	42 - 66	76 – 127
BZ218-1	T.Z.	-7.90				II (2)		
BZ221	T.Z.	-4.95				II		
BZ222	T.Z.	-12.12				II		
BZ223	T.Z.	-4.63				II ¤		
BZ226-2	L.M.	-4.02	n.d.	-	-	II ¤ (2)		
BZ226-1,3,4,5	L.M.					IaAB s, b (12)	94 - 98	≤ 222
BZ227-1	U.	-4.99	-0.3	0.9	63	II ¤		71
BZ227-2	U.	-4.41	n.d.	-	-	II		
BZ231	T.Z.	-7.77				II		
BZ233-1	L.M.	-5.45				II		
BZ233-2	L.M.					II		
BZ235-1	U.	-10.83				IaAB s, b (3)	92 - 93	≤ 212
BZ235-2	U.	-10.62	-1.2	0.85	54			
BZ237-1	L.M. III	-4.93	-6	0.65	262	IaB s	100	152
Sample	**Assoc'n.**	**δ^{13}C ♦**	**δ^{15}N**	**Error**	**N †**	**FTIR ¥**	**%B**	**N ‡**
BZ237-2	L.M. III	-5.25	-5.2	0.8	70	IaAB s	95	145
BZ239	L.M.	-5.25				II s		
BZ240	L.M.	-5.43				II		
BZ241	L.M. II	-5.30				II		
BZ242-1	L.M. III					II		
BZ242-2	L.M. III	-5.24				II		
BZ243-1	L.M. / U.M.	-5.34				II		
BZ243-2	L.M. / U.M.					II		
BZ244	L.M.	-4.82				II		
BZ245	L.M.	-4.58				II		
BZ246	L.M. III	-8.31				II		
BZ250-1	L.M.	-5.28				II ¤ (2)		
BZ251	L.M. I	-4.09			≤ 223	IaB (11)	100	≤115
BZ252	L.M.	-3.47			≤ 186	IaB (5)	100	≤ 69
BZ254	L.M. I	-5.05			≤ 3.7	II		
BZ255	L.M.	-4.78			≤ 8.5			
BZ257	L.M.					II		
BZ258	U.					II (3)		
BZ259	L.M. III	-4.70				II		
BZ260	L.M.	-4.84				II ¤		
BZ261	U. (T.Z.) §					IaB	100	12
BZ262	U. (T.Z.) §					IaAB	94	935
BZ263	U.					IaB (2)	100	≤ 46
BZ264	U.					II (3)		
BZ266	U. (T.Z.) ♥					IaAB	68	26
BZ267	U. (T.Z.) ♥					IaAB	68	71
BZ268	U. (T.Z.) ♥					IaAB	52	24
BZ269	U. (T.Z.) ♥					IaAB	69	40
BZ270	U. (L.M.) ♣					IaB	100	7
BZ271	U.					IaB ¤	100	
BZ272	U. (U.M.)♠					IaAB	56	336
JH2	L.M.	-4.83				II		
JH6-1	L.M.	-4.57				II		
JH7	L.M.	-4.57				II		
JH11	L.M.	-5.09				II		
JH12	L.M.	-4.89				II		
JH17	L.M.	-5.22				II		

Diamonds BZ201-BZ214 were broken by JWH (Harte and Harris, 1994) and BZ215-BZ250, BZ259, BZ260 and 'JH' stones were broken by MTH (Hutchison, 1997).

Assoc'n :- Association as defined in section 1; ¢:- A fPer inclusion was noted but not confirmed by analysis; U :- Unbroken diamond cannot be definitively assigned to an association; § :- Appears to contain an orange (majoritic) garnet, probably of T.Z. origin; ♥ :- Appears to contain a sulphide inclusion, probably of T.Z. origin; ♣ :- Appears to occlude a ferropericlase inclusion, probably of L.M. origin; ♠ :- Appears to occlude a purple garnet / clinopyroxene composite inclusion, probably of U.M. origin

♦: - Values for BZ251, BZ252, BZ254 and BZ255 averaged from ion microprobe spot analyses

n.d. :- no nitrogen detected on combustion

Error :- ‰ error in δ^{15}N

† :- N concentration ppm atomic recalculated from ppm wt determined by combustion mass spectrometry and by ion microprobe for BZ251, BZ252, BZ254 and BZ255

¥ :- Nitrogen aggregation and additional absorption due to bonded hydrogen by FTIR. Number of spectra obtained are displayed in brackets if greater than one; b :- absorption at 2840 and 2905 cm^{-1} due to C-H bending; s :- absorption at 3107 cm^{-1} due to C-H stretching; ? :-indistinct; ¤ :- some small concentration of N may be present but is too small to be deconvoluted

‡ :- N concentration in ppm atomic as determined by deconvolution of FTIR spectra

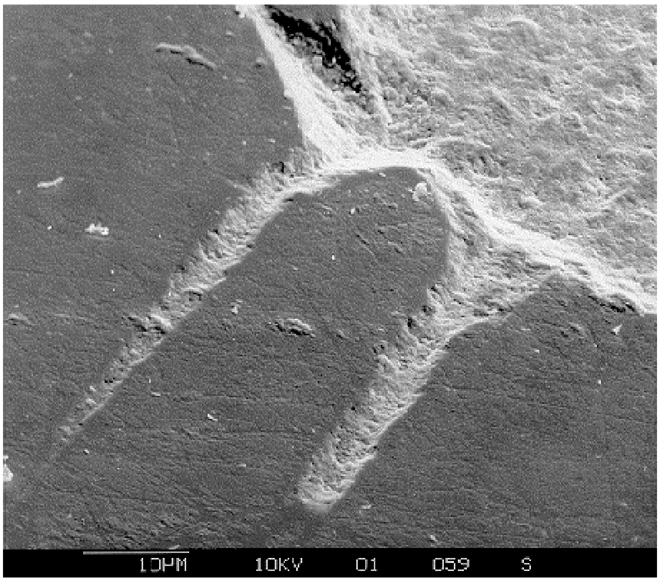

Figure 2. Differing fracture termination morphology in BZ251. Being in the same general direction and growth zone (as determined by CL), there is no crystallographic control to explain the differences in fracture termination. It is concluded that the two fractures occurred within different fracturing events, the sharper under a régime dominated by brittle failure, and the blunter within a more plastic régime.

Figure 3. Complex cathodoluminescence zonation in diamond BZ252. The bright semi-circle across the inclusion is a result of internal reflection of an inclined fracture.

zones suggesting that they are fragments of once larger stones.

3.4 Carbon isotopic compositions

3.4(a) Carbon isotopic composition of broken stones by combustion mass spectrometry

The nine transition zone diamonds studied show a broad range of δ^{13}C (-12.42 to -4.63 ‰, σ = 2.61 ‰, Fig. 5) similar to the range in δ^{13}C often seen within individual eclogitic suites (e.g. Koffiefontein, Deines *et al.*, 1991 and Argyle, Jaques *et al.*, 1989) and occasionally amongst peridotitic suites (Premier, Deines *et al.*, 1989 and Orapa, Deines *et al.*, 1993) from the upper mantle. The number of diamonds involved, however, is too few to be able to say whether the distribution is skewed to negative values or represents two different populations. Transition zone diamonds from São Luiz are less depleted than diamonds containing similar majoritic garnet inclusions from Jagersfontein (Deines *et al.*, 1991). Jagersfontein diamonds show a clearer negatively skewed distribution ranging from δ^{13}C of -18.94 to -24.39 ‰ (Table 2 and Fig. 5). In contrast, δ^{13}C shows a very tight distribution amongst lower mantle diamonds (Fig. 6) with the exception of BZ246 (-8.31 ‰) of at least very shallow lower mantle, if not upper mantle origin (Hutchison, 1997). Values range from -3.47 to -5.57 ‰. It is striking to note the similarity in the tight δ^{13}C cluster of lower mantle diamonds from São Luiz with diamonds of lower mantle origin from elsewhere (Table 2 and Fig. 6).

3.4(b) Carbon isotopic composition of polished diamond flats by ion microprobe

The δ^{13}C values of the four polished lower mantle diamonds at the 30 µm scale show a wider range in comparison to bulk (mm scale) analyses of diamonds from the same depth of origin. The distribution is negatively skewed with a mean of -4.28‰ (1 σ = 1.82 ‰, Fig. 7). This mean is ~ 0.8 ‰ less depleted than the average for bulk analyses of the lower mantle diamonds and is considered to be a reflection of the much smaller sample size measured by ion microprobe. The ranges of δ^{13}C composition of individual stones all lie outwith analytical error of ~ 0.8 ‰ at 1 σ (however the distributions within BZ251 and BZ255 lie only marginally outwith the 2 σ error of ~ 1.7 ‰). BZ254 shows the widest range of δ^{13}C for an individual diamond (-1.30 to -10.24 ‰, Fig. 7). It is concluded that there is a detectable zonation of δ^{13}C within the lower mantle diamonds analysed although this is probably small.

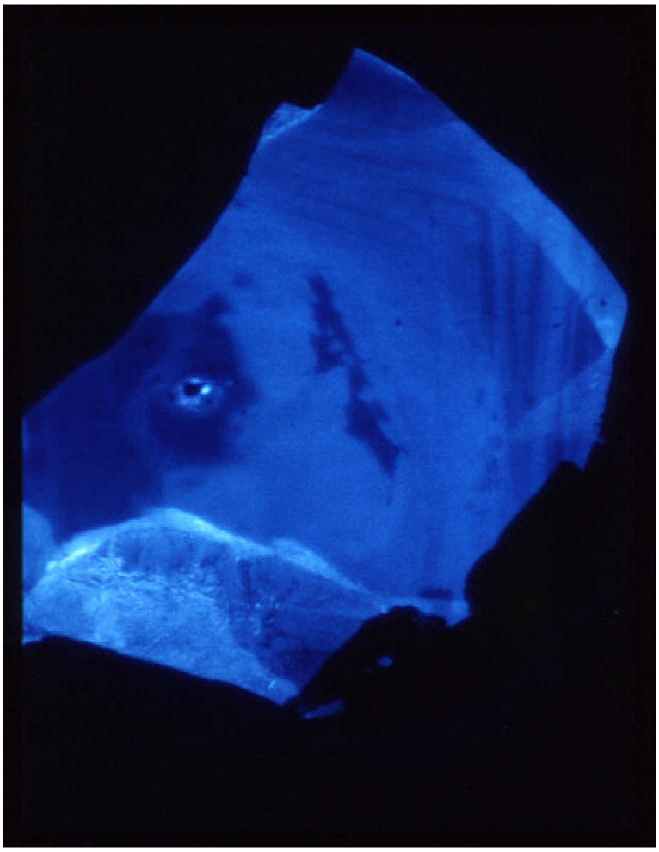

Figure 4. Concentric zonation in cathodoluminescence intensity in BZ255 showing embayment and termination of CL zones.

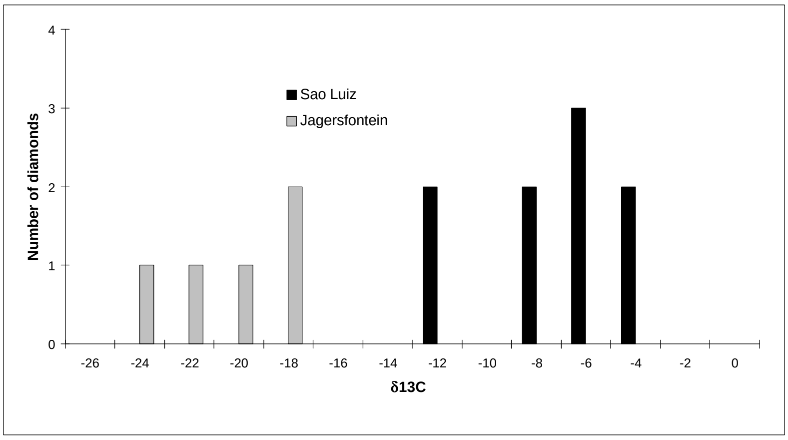

Figure 5. Distribution of δ^{13}C composition for transition zone diamonds from São Luiz in comparison with transition zone diamonds from Jagersfontein (Deines *et al.*, 1991).

3.5 Nitrogen

3.5(a) Nitrogen Concentration and aggregation by FTIR

In general, São Luiz diamonds have unusually little nitrogen in an infra-red active state (Table 3). FTIR spectra collected from volumes of ~ 0.075 mm^3 within broken fragments, show that most deep mantle stones are Type II (30 of 37) with an average of < 20 ppm atomic of nitrogen. Of the few nitrogen-bearing diamonds, many show the characteristic of being both plastically deformed and having significant platelet absorption at about 1370 cm^{-1} (BZ215, BZ262, BZ268 and BZ272).

Of the eight TZ association diamonds analysed only three contain nitrogen, although nitrogen was also detected in six unbroken diamonds of possible transition zone origin over larger, ~ 2 mm^3, volumes (Table 3). All spectra were of Type IaAB (with 42 - 71% IaB) with significant platelet absorption. Nitrogen contents, where detectable in broken stones, were found to be variable between 90 and 289 ppm. Similar observations are made for transition zone diamonds from Jagersfontein (Deines *et al.*, 1989, Table 2).

Amongst lower mantle diamonds, nitrogen appears to be even more commonly absent and, where it is present, is more aggregated than in transition zone diamonds; 25 of 29 diamonds analysed were determined to be Type II and amongst the exceptions, significant platelets and variable amounts (< 20 to 222 ppm) of highly aggregated (> 95% IaB) nitrogen were observed (e.g. see BZ251, Fig. 8). As with São Luiz, deep mantle diamonds from all other world-wide localities are Type II or at least contain very small quantities of nitrogen (Deines et al., 1991; Davies et al., this volume; Hutchison, 1997; McDade and Harris, this volume; Table 2). The single exception is a Lac de Gras diamond with 1950 ppm N (Davies *et al.*, this volume).

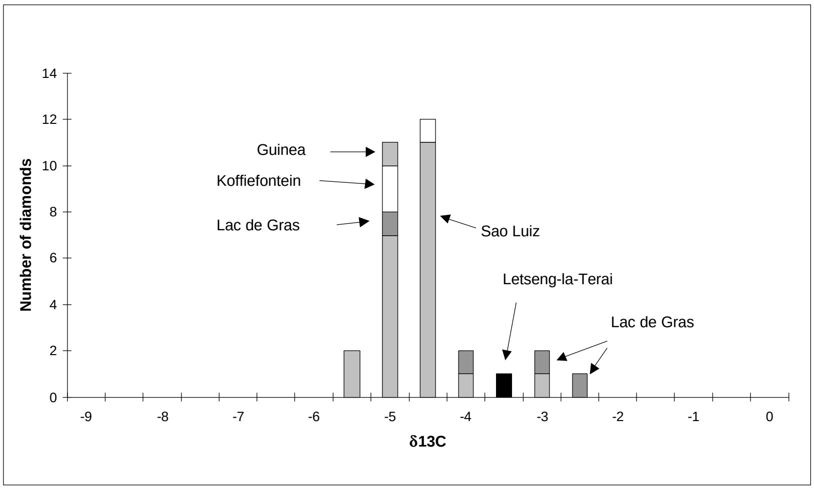

Figure 5. Distribution of 13C composition for transition zone diamonds from São Luiz in comparison with transition zone diamonds from Jagersfontein (Deines et al., 1991).

3.5(b) Nitrogen concentration by combustion mass spectrometry

Two fragments with Type II FTIR spectra (BZ207-2 and BZ227-2) yielded no detectable nitrogen by gas combustion and fragments indicating a small but non-deconvolutable amount of nitrogen by FTIR (BZ226-2 and BZ227-1) gave very little, if any, nitrogen on combustion either (Table 3). Furthermore, of the other fragments analysed, the quantities of nitrogen calculated by deconvolution compare well with those observed by combustion bearing in mind the variability of nitrogen on a small scale and the volume difference between the two analytical techniques. The São Luiz diamonds therefore, are genuinely depleted in nitrogen rather than having nitrogen 'hidden' in non-IR active sites such as voidites (Hirsch *et al.*, 1986).

3.5(c) Nitrogen concentration of polished flats by ion microprobe

Nitrogen concentration was also determined on the diamond sections for volumes estimated at ~ 8x10^{-7} mm^3 selected to cover the range of CL intensities in each stone and, in addition, to provide comparison with δ^{13}C measurements (section 5.2). Results compare well with FTIR point analyses (c.f. Fig. 8 and Fig. 9) and, as for δ^{13}C composition (c.f. Fig. 6 and Fig. 7), larger variations in nitrogen concentration were found within individual stones than for bulk determinations amongst the lower mantle population as a whole. The brightest cathodoluminescing diamond, BZ251, shows the widest range of nitrogen concentrations (0.1 to 260 wt ppm, Fig. 9), the other diamond sections being generally nitrogen-poor with the exception of two points within surface fractures in BZ252 (543 ppm) and BZ254 (128 ppm, Table 3). Such elevated nitrogen in fractures is believed to be due to atmospheric nitrogen trapped amongst remnant polishing material, thus making such data spurious (J. Craven, *1997 personal communication*).

In all cases, nitrogen concentration appears to correlate positively with cathodoluminescence intensity (e.g. BZ255, Fig. 10). This correlation is not, however, linear perhaps due to the otherwise inconsequential influence of additional causes of CL (such as additional species or crystallographic defects) becoming relatively important at low nitrogen concentrations.

3.5(d) Nitrogen Isotopic Composition

Due to the paucity of nitrogen-bearing diamonds from the deep mantle throughout the São Luiz sample, the choice of suitable diamonds for δ^{15}N analysis was limited. Furthermore, lower mantle diamonds BZ207 and BZ226 which appeared to contain nitrogen by FTIR, failed to yield nitrogen by gas combustion above detection limit (131 and 22 ppm wt respectively). A lower mantle / upper mantle boundary stone (BZ237) did, however, yield two negative values within error of each other of about 0.5 ‰ (Table 3). In contrast, two transition zone diamonds (BZ215 and BZ217) gave positive δ^{15}N compositions (+1.3 and +1.2‰), within the range that can be expected from δ^{13}C, δ^{15}N, N covariations (Cartigny *et al.*, this volume).

3.6 Additional atomic species in São Luiz diamonds

Absorption due to bonded hydrogen (C-H bending at 2840 & 2905 cm^{-1}, Krot *et al.*, 1994 and C-H stretching at 3107 cm^{-1}, Woods and Collins, 1983 and Kiflawi *et al.*, 1996) was observed amongst a significant number of São Luiz diamonds (3 of 8 transition zone diamonds and 6 of 21 lower mantle diamonds for which spectra were collected in the 2 and 3 phonon regions, Table 3). No relationships between the presence of C-H bending and inclusion association or nitrogen concentration were observed. However, with the exception of a small peak in a fragment of BZ239 (Table 3), Type II stones do not show C-H stretching absorption. A similar result was obtained in a study by Woods and Collins (1983) where amongst a population of Ia stones, they found C-H stretching absorption in all spectra but never in Type II stones.

4 DISCUSSION

4.1 Ambient physical conditions of growth and exhumation

Highly aggregated nitrogen, brown colouration, complex CL and deformation characteristics cannot be used as evidence for a deep origin for São Luiz diamonds as all these features can be found, although usually in smaller proportions, amongst lithospheric diamond suites. However, the striking prevalence of such features together amongst São Luiz diamonds containing this unusual inclusion suite (Harte and Harris, 1994 and Hutchison, 1997) is *consistent* with the extreme physical conditions expected to prevail in the deep regions of the Earth where they form. Transition zone and lower mantle diamonds from São Luiz have clearly experienced tortuous histories. The concentric stepped CL which is typical of diamonds from world-wide lithospheric sources, suggests that, for at least some São Luiz diamonds, part of their growth occurred in an environment where all ambient physical conditions were within the stability field of diamond. However random truncations of concentric CL zones apparent in all the stones analysed suggests that the diamonds were also subjected to periods of resorption followed by re-precipitation. As inclusions are surrounded by diamond with a variety of CL styles and intensities, it would appear that inclusion growth and encapsulation was not confined to a single stage of diamond growth. Additionally, diamonds seem to have witnessed a number of deformation events, both plastic, as evidenced by visual observations of deformation lamellae and brown colouration, and brittle, as supported by the ragged edges of CL features, interfering fracture systems and the variations in fracture termination morphology. Such deformation would also appear to be unusually intense; the presence of rare diamonds showing both plastic deformation and platelet absorption from São Luiz (similar to those described by Chinn *et al.*, 1995) suggests that shear stresses may have been greater than 0.5 - 0.6 GPa (for 1200 K following Evans and Wild, 1965). Such shear stresses may be related to mechanical stresses in the convective régimes around the upper mantle / lower mantle boundary. Throughout the whole São Luiz population, it is clear by the presence of straight, sharply terminated fractures, that the final deformation was in a brittle régime probably occurring during the initial stages of depressurisation on eruption of the host kimberlite (from ~90 km as determined by thermoelastic modelling of diamond / inclusion systems, Hutchison, 1997). Final deformation within a brittle régime is consistent with studies of diamond deformation (e.g. Weidner *et al.*, 1994). Indeed, most of the smaller internal fracture systems extending from

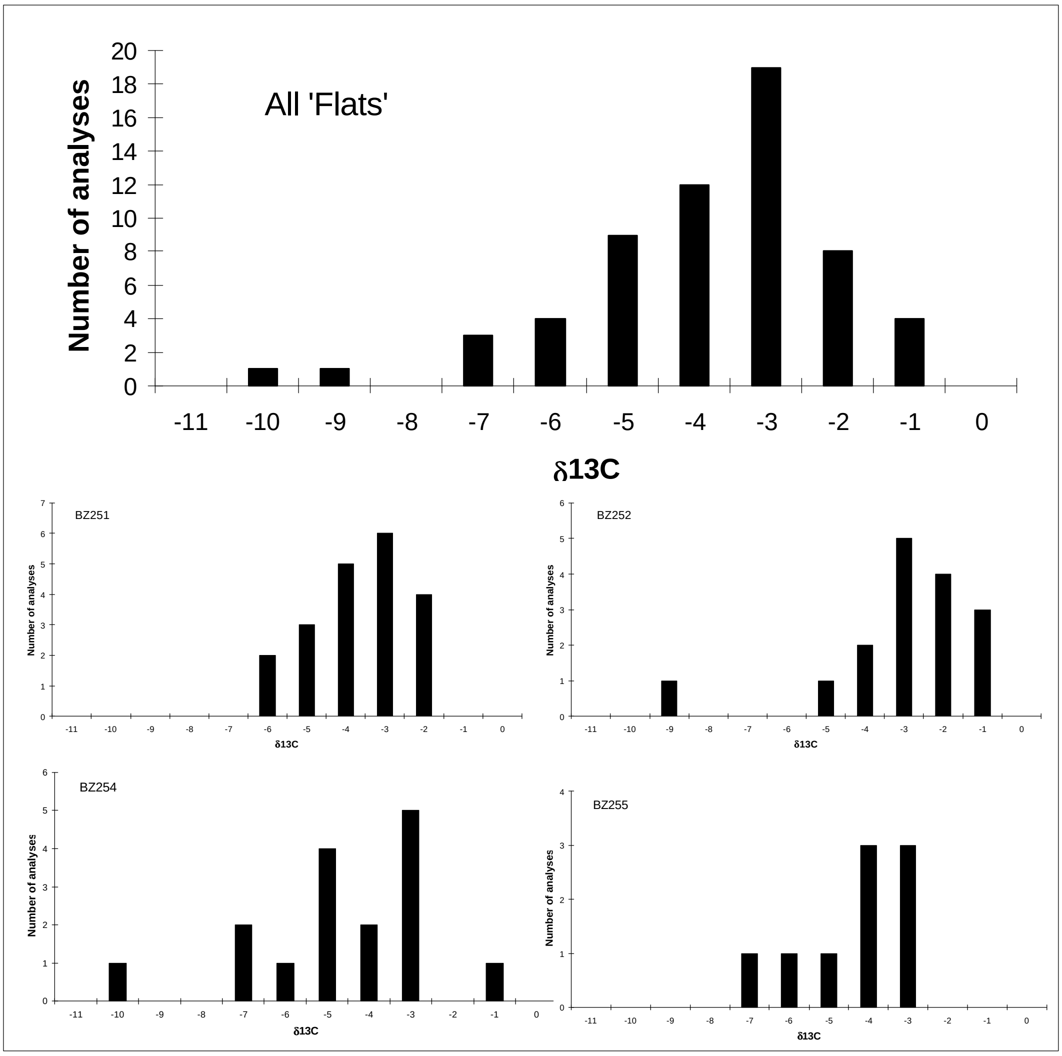

Figure 7. Distribution of $\delta^{13}C$ for polished 'flats' of lower mantle diamonds as determined by ion microprobe. For each individual stone, the range of data points lie outwith the maximum error of the mean of 2‰ at 2σ and show a wider range in composition than observed by combustion mass spectrometry for bulk diamonds of similar origin. Given the contrasting homogeneity of diamond sampled from larger volumes, the range within individual stones are believed to either reflect very localised inhomogeneity, subsequently precipitated diamond at shallower regions in the Earth or else be a product of an as yet unknown fractionation process.

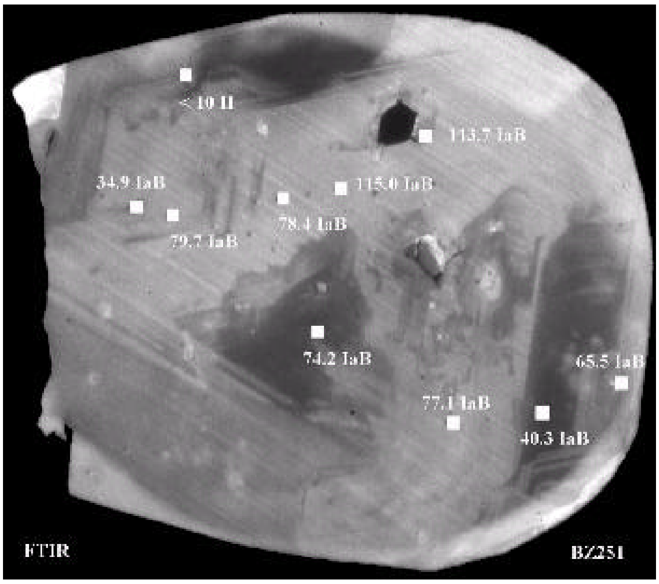

Figure 8. Nitrogen concentration as determined by high resolution FTIR for lower mantle diamond slab BZ251. Concentrations are given in ppm atomic and show significant variation over the surface of the diamond. All nitrogen was found to be aggregated as 100 % IaB. BZ251 shows a wider variation in nitrogen than most lower mantle stones, significantly more marked on a local scale than for analyses taken for larger volumes by FTIR and gas combustion mass spectrometry.

inclusion diamond interfaces are interpreted to have occurred at this time as it is here that diamond hosts will be subject to the most internal pressure imposed by their inclusions (Hutchison, 1997). World-wide, the percentage occurrence of gem quality stones is higher amongst alluvial rather than kimberlite production due to the mechanical action of alluvial transportation (e.g. Jaques et al., 1986). The rarity of large surface penetrating fractures within São Luiz stones, particularly those involving inclusions, is perhaps unsurprising, therefore, because such stones are likely to be very weak and few would survive alluvial transportation.

Another strong parameter calling for a difference between São Luiz and more common lithosphere derived diamonds is the highly advanced aggregation state of nitrogen. It is well established that the four main nitrogen-bearing defects; A (IaA diamond with N occuring as pairs), B (IaB, probably involving four N atoms plus a vacancy), C (Ib diamond with single substituted N) and D (unknown structure), (Davies, 1976; Woods, 1986; and Jones *et al.*, 1992); are linked by second order kinetic diffusion processes. These processes depend on mantle residence time, temperature and total nitrogen content and start from an aggregation of C to A defects followed by A to B and D defects (e.g. Chrenko et al., 1977 and Evans and Qi, 1982). The second order kinetic implies that the higher the nitrogen content, the higher the rate of nitrogen aggregation. Accordingly, São Luiz diamonds with generally low total nitrogen contents together with extremely advanced aggregation states imply long mantle residence times and / or higher temperatures (the absence of cubic forms, Giardini and Tydings, 1962, are also consistent with high temperature). Nitrogen measurements, therefore, suggest independently of inclusion arguments, that some São Luiz diamonds originate from deeper regions than lithospheric stones, particularly given the fact that temperature plays a more important role on nitrogen aggregation state than mantle residence time (Evans and Harris, 1989 and Taylor *et al.*, 1990).

Differences in colour, morphology and nitrogen aggregation between transition zone diamonds and lower mantle stones may also reflect the differing physical conditions we understand to be present in these distinct regions. The facts that lower mantle diamonds are more commonly brown, irregular and have more aggregated nitrogen than transition zone stones, are taken as a reflection of the greater shear (most likely along the lower mantle upper mantle boundary) and the greater temperature to which lower mantle diamonds will have been subjected.

4.2 Chemical conditions of diamond growth

The Si contents of included majoritic garnets from transition zone diamonds (up to 3.30 Si cations per 12 O anions, Wilding, 1991 and Hutchison, 1997) reflect a variety of depths of formation amongst the São Luiz sample (after Irifune and Ringwood, 1987). As there is no clear relationship between Si content of majoritic garnets and $\delta^{13}C$ composition of occluding diamond however (contrary to Deines *et al.*, 1991, on Jagersfontein diamonds), the present evidence suggests that the observed range in $\delta^{13}C$ compositions do not reflect a depth stratification in the upper mantle but rather supports the existence of localised pods of differing isotopic composition. Furthermore, the markedly different $\delta^{13}C$ compositions of Jagersfontein stones (Deines *et al.*, 1991) to the São Luiz diamonds also suggests that the transition zone is inhomogeneous in terms of $\delta^{13}C$ composition over a trans-continental scale.

In contrast, the tight clustering of carbon isotopic values from lower mantle-sourced São Luiz diamonds, around $\delta^{13}C$ of -4.5 to -5 ‰ (Fig. 6), appears to be global (Table 2). Fractionation of carbon isotopes during diamond precipitation under lithospheric conditions are believed to be restricted to a few parts per thousand (Deines, 1980) and increases in temperature is known to decrease fractionation factors (e.g. Bottinga, 1969). It follows that, given the elevated temperatures in the lower mantle compared to shallower depths, a restricted range of $\delta^{13}C$ values in lower

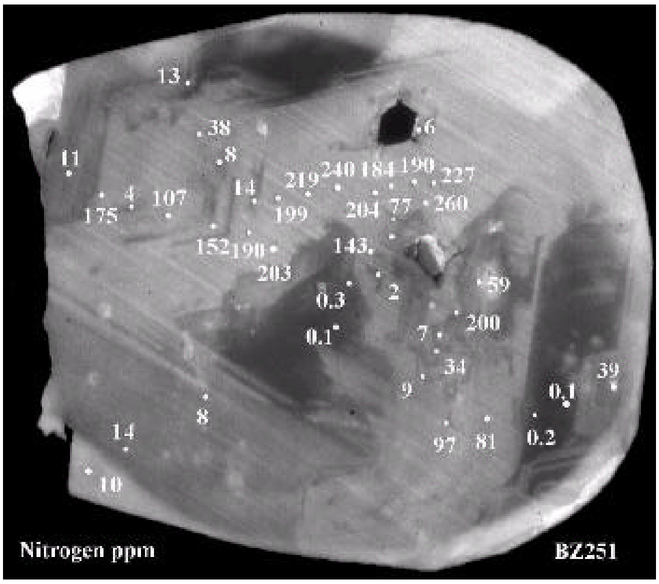

Figure 9. Nitrogen concentration as determined by ion microprobe for lower mantle diamond BZ251. Concentrations are given in ppm wt (~1.166 x ppm atomic) and show a significant variation over the surface of the diamond correlating positively with cathodoluminescence intensity (lighter shading). The results of ion microprobe analyses also correlate well with the results of FTIR (Fig. 8) and support the conclusion that São Luiz diamonds genuinely are nitrogen-poor, rather than holding nitrogen in non-IR active sites.

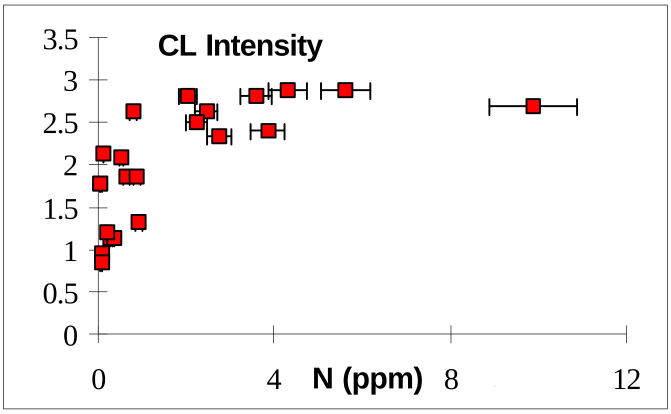

Figure 10. Variation of cathodoluminescence intensity against nitrogen concentration for BZ255. Cathodoluminescence intensity is presented as the reciprocal of the exposure time recommended by Optiphot instrumentation for spot metering from 50 µm areas. Nitrogen concentration in ppm atomic is presented with 10% error bars on each analysis.

mantle diamonds (see Table 2) is to be expected and further implies that a reservoir of constant $\delta^{13}C$ is available for diamond precipitation. Unlike in the transition zone, the tight cluster of $\delta^{13}C$ compositions for lower mantle diamonds therefore suggests that the lower mantle is homogeneous in $\delta^{13}C$ composition. Such a homogenisation may have come about either because the lower mantle accreted with a restricted $\delta^{13}C$ composition, or else because it became well-mixed by the time the diamonds formed. There is more variation in $\delta^{13}C$ values within individual stones than the population as a whole, however, as the average composition of stones is so constant, the distributions probably reflect restricted local variations in composition. An additional explanation is that some of the variation in $\delta^{13}C$ may also be due to diamond precipitating later, in the transition zone or even at shallower depths in the mantle.

In theory, the environment of diamond precipitation, whether by fractional or equilibrium crystallisation, or component mixing can be distinguished using models based on the carbon isotopic composition and nitrogen contents of diamond (e.g. van Heerden, 1993). The method principally uses nitrogen as an indicator of the degree of crystallisation (highest nitrogen relates to primary crystallised diamond) where its relationship to $\delta^{13}C$ composition varies with crystallisation environment. No crystallisation model, however, produced reasonable trends for either the transition zone or the lower mantle populations from São Luiz, or for individual lower mantle diamonds where N was detected, apart from the general observation that the most depleted carbon does correlate with the lowest nitrogen contents. This lack of a good correlation (like CL) suggests that São Luiz diamonds have grown in a number of régimes of crystallisation involving complex processes where each precipitating reservoir has a different initial nitrogen concentration.

The relative lack of nitrogen in deep mantle diamonds is particularly striking, especially for lower mantle samples compared to those from shallower depths. The only exception to the lower mantle observations (Davies *et al's*., this volume, Lac de Gras diamond) is believed to have obtained its signature on later precipitation of additional diamond in the upper mantle. Several hypotheses can be advanced to account for the general type II character of, in particular, the lower mantle diamonds. Either some mechanism prevents the accommodation of nitrogen within precipitating diamond or the lower mantle is free of nitrogen. The former scenario could arise because diamond growth is slow (e.g. Boyd et al., 1994b). Although slow growth may appear to be contradictory to the elevated temperature in the deep mantle in comparison with the lithosphere (possibly up to 1000K e.g. Richter and McKenzie, 1981) and the likely sufficient supply of chemical reactants (Huss and Lewis, 1995), unknown differences in the oxygen fugacities of growth medium and diamond may cause slow growth. Alternatively N may be trapped within a separate phase. It is considered unlikely that one such suggested phase, osbornite (TiN, Javoy, 1997) exists as a free phase in the mantle although it is possible that such a component could be dissolved into pyroxene composition phases. The latter hypothesis, where nitrogen is absent in the lower mantle, would appear to be at odds with mainstream models which describe the lower mantle as an undegassed reservoir (e.g. Herzberg, 1984). A significant quantity of nitrogen may, however, have been lost to the core on accretion, in a similar way to the fate of some of the more abundant mantle carbon (Wood, 1993).

5 CONCLUSIONS

It is not only the unusual assemblages of mineral inclusions recovered from São Luiz diamonds which makes them unique. Although taken separately, the diamonds' physical and chemical properties are not unrecorded from lithospheric stones, it is the dominance of these characteristics in the population and the fact that they occur together that makes the São Luiz diamonds *themselves* unique. The irregular morphologies, brown colouration, deformation and in particular the presence of plastically deformed stones with platelets are all concluded to be a reflection of the extreme degrees of pressure and shear that São Luiz diamonds have encountered during growth within, and exhumation from, the Earth's transition zone and lower mantle. Furthermore, the highly aggregated nitrogen, where present, is considered to be due to a combination of high temperature and long residence time (especially for the lower mantle stones). Taken together, therefore, the inclusion and diamond characteristics provide even more compelling evidence for a deep mantle source to many of the São Luiz diamonds than constituent features can provide and represent a data base which must be considered as a whole when considering any alternative explanation for a depth of origin.

Additionally, the compositional characteristics of lower mantle diamonds suggest that some differences exist between the lower mantle and upper mantle, at least within the regions sampled. Nitrogen is almost completely absent from lower mantle diamonds which have carbon isotopic contents suggesting that the lower mantle is globally homogeneous at $\delta^{13}C \sim -5$ ‰. In contrast the transition zone sampled represents a less mixed variable carbon isotopic reservoir. These observations are concurrent with the evidence from inclusion assemblages (Hutchison, 1997) of a compositional difference between lower and upper mantle *rocks* and the presence of a thermal boundary between the two regions with an appropriate density contrast to support separate convection (cf. Anderson, 1989 and Richter and McKenzie, 1981).

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