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## Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity

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**Abstract** Three new mineral associations have been discovered within diamonds from the Juina district of Brazil. These include a previously unrecorded Na-Al-(Mg, Fe)SiO<sub>3</sub> phase associated with ferropicrinite and the tetragonal almandine pyrope phase, TAPP. Also reported are an association of corundum with aluminous-pyroxene and an olivine composition phase associated with ferropicrinite. The minerals in each association often occurred within the same diamonds in addition to being recovered from individual diamonds in different combinations. High-pressure experimental data indicate that these associations formed at different depths within a region ca. 60 km on either side of the upper-mantle/lower-mantle boundary. Mineral compositions show that for the regions sampled, the deep transition zone and lower mantle are chemically distinct and inhomogeneous. Importantly, in the shallow lower mantle, Al is not solely accommodated within perovskite-structured (Mg, Fe)SiO<sub>3</sub> as some recent experimental studies have suggested.

### Introduction

As more diamonds containing inclusion phases indicative of sublithospheric origins are discovered (Hutchison 1997 and references therein; Davies et al. 1999; Harte et al. 1999; Joswig et al. 1999; McDade and Harris 1999), it is clear that diamond encapsulation is the primary means to obtain information on likely mineral assemblages and compositional characteristics of regions of the deep mantle (mantle transition zone and lower mantle). The alluvial deposits of the Juina district, centred on the Rio São Luiz, Mato Grosso State, Brazil, have provided the greatest number and widest compositional range of deep mantle-origin inclusions in diamond. Two mineral associations have been previously described (Wilding 1991; Hutchison 1997; Harte et al. 1999). One association derived from the transition zone (TZ) comprises diopside with majoritic garnet inclusions which contain pyroxene in solid solution (Irifune and Ringwood 1987). The second association (termed type I, Table 1) comprises (Mg, Fe)O (ferropicrinite or 'fPer'), tetragonal almandine-pyrope phase (TAPP, Harris et al. 1997) and (Mg, Fe)SiO<sub>3</sub> is interpreted to represent a stable assemblage in the lower mantle that formed by pressure-induced disassociation of upper-mantle ringwoodite ((Mg, Fe)<sub>2</sub>SiO<sub>4</sub>). The inclusions with pyroxene chemistries are believed to have initially crystallised with perovskite structures but now exist as atmospheric-pressure polymorphs (Hutchison 1997). Thus, it is the chemistry rather than the present structural state of inclusions which provides evidence for deep-mantle origins. In this paper we present three new inclusion associations recovered from São Luiz diamonds which appear to have formed close to the boundary region between the upper and lower mantle. Such syngenetic inclusions in diamonds are particularly important as knowledge of chemical compositions within this region is crucial to our understanding of whether the upper and lower mantles convect separately and whether they are compositionally different (Davies and Richards 1992). Furthermore, we

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**Table 1** Deep-mantle mineral associations from São Luiz diamonds. *Letters* refer to suffixes to diamond names identifying individual inclusions. *TAPP* Tetragonal almandine pyrope phase (Harris et al. 1997); *Ol* originally spinel-structured (Mg, Fe)<sub>2</sub>SiO<sub>4</sub>; *I-px* type-I originally perovskite-structured (Mg, Fe)SiO<sub>3</sub>; *fPer*

(Mg, Fe)O periclase-wüstite; *Maj* low-Ca majoritic garnet; *II-px* Type-II originally perovskite-structured Al (~10 wt% Al<sub>2</sub>O<sub>3</sub>) (Mg, Fe)SiO<sub>3</sub>; *III-px* type-III originally garnet-structured Na, Ca, Al (Mg, Fe)SiO<sub>3</sub>; *BZ241Acor* discrete ruby inclusion found in diamond BZ241

Association	Diamond	TAPP	Ol	I-px	fPer	Association	Diamond	Maj	TAPP	II-px	III-px	Ruby	fPer
LM/UM	BZ243	A	C		B	Type II <sup>c</sup>	BZ210 BZ214			B			A
Type I <sup>e</sup>	BZ120 BZ207 BZ251 BZ254	A <sup>d</sup>		C C <sup>d</sup> B A	A B A	Type III <sup>e</sup>	BZ241 BZ237 BZ242 BZ246 BZ259	C <sup>b</sup>		B1 <sup>a</sup> ,B2	A1-8,6 <sup>b</sup> B A B <sup>c</sup>	A Acor, C <sup>a</sup>	A A
									A1,A2 <sup>c</sup>				

<sup>a</sup>, <sup>b</sup>, <sup>c</sup>, <sup>d</sup>Constituents of a single composite inclusion

<sup>e</sup>Although not so far found within the same diamonds, REE compositions suggest association with perovskite-structured CaSiO<sub>3</sub>

present new data pertaining to the controversial role of aluminium in the lower mantle (O'Neill and Jeanloz 1994; Irifune et al. 1996).

Of the three new associations:

1. The lower-mantle/upper-mantle boundary association (LM/UM) comprises fPer, (Mg, Fe)<sub>2</sub>SiO<sub>4</sub>, and TAPP;
2. Type-II association consists of (Mg, Fe)SiO<sub>3</sub> inclusions with an Al<sub>2</sub>O<sub>3</sub> component, fPer and Al<sub>2</sub>O<sub>3</sub> (var. ruby);
3. Type-III association comprises TAPP/majoritic garnet, fPer, (Mg, Fe)SiO<sub>3</sub> with Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> components (Gasparik and Hutchison 2000).

Although some of these phases have been reported previously as separate inclusions (e.g. Harte et al. 1999), discoveries of new occurrences either all within the same diamond or in different combinations within a number of stones (Table 1) allow mineral associations to be recognised. Type-II and type-III association phases comprise both touching and non-touching inclusion pairs of similar composition, suggesting equilibrium and importantly also suggesting that associations are the same as those formed on initial crystallisation. Although the LM/UM association does not include touching grains, minerals of this association have all been recovered from the same diamond which shows no obvious evidence for multiple growth. The LM/UM (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> is unusually Fe rich compared with upper-mantle olivines. As touching inclusions in São Luiz diamonds rarely show evidence of re-equilibration to low-pressure assemblages (Wilding 1991; Hutchison 1997; Harte et al. 1999), exhumation was probably rapid and so further diamond precipitation at shallower depths is considered unlikely. Thus, the Fe-rich LM/UM (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> is considered to reflect a deep mantle paragenesis.

### Analytical procedures

The inclusions discussed were all recovered using a purpose-built steel anvil from diamonds that showed

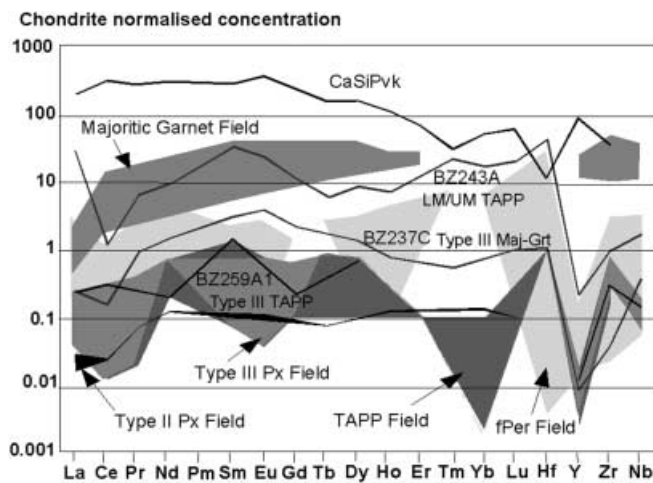
no visible fractures between the inclusions and the surface of the diamond hosts. Inclusions were mounted in brass tubes in epoxy resin and polished with 1/4- $\mu$ m diamond paste for major-element analysis by Cameca Camebax electron microprobe (University of Edinburgh), and for trace-element analysis using a Cameca ims-4f (University of Edinburgh/N.E.R.C.). Electron microprobe analysis was undertaken using a 20-kV and 15-nA beam with calibration against well-characterised natural and synthetic standards and correction following the ZAF procedure. Analytical procedures for ion microprobe analyses are described in Harte et al. (1999). Major and minor element concentrations for representative inclusions are presented in Table 2. Additional data (see Electronic Supplementary Material) and trace element compositions are shown in Fig. 1. Single grains of type-II and type-III pyroxene compositions were mounted on glass fibres for structural analysis. Cell dimensions and intensity data were recorded at 293 K following Danapoulos et al. (1991) using a FAST TV area detector diffractometer mounted at the window of a rotating molybdenum anode ( $\lambda$ Mo K $\alpha$ =0.71069 Å) operating at 50 kV, 55 mA at the University of Wales, Cardiff. The crystal-to-detector distance was 50 mm and the detector  $2\theta$  swing angle was 20°. Slightly more than one hemisphere of data was recorded with space groups determined by normal data processing. Structures were solved by direct methods (Sheldrick 1990) and refined anisotropically by full matrix least squares (Sheldrick 1993) based on F<sup>2</sup>.

### Inclusion chemistry and structure

Many aspects of the compositions of the phases from the new associations distinguish them from their counterparts in other mantle settings and, in some cases, from otherwise similar phases from São Luiz. As is characteristic of all TAPP inclusions, the CaO content of the LM/UM TAPP inclusion is very low (<0.15 wt%, Table 2). However, rare-earth element concentrations in this phase are relatively high and are similar to garnet

**Table 2** Representative major-element analyses of deep-mantle inclusions from the region of the upper-mantle/lower-mantle boundary (data are presented as wt% of oxide)

Association Name Phase No. <sup>a</sup>	LM/UM			Type II			Type III			
	BZ243A TAPP 3	BZ243B fPer 1	BZ243C Olivine 3	BZ241A fPer 3	BZ241B2 II-px 3	BZ241C Ruby 4	BZ237A <sup>b</sup> III-px 30	BZ237C Maj.-grt 5	BZ259A1 TAPP 2	BZ259B III-px 14
SiO <sub>2</sub>	42.24	0.03	40.50	0.05	52.63	0.78	57.07	43.37	42.24	55.75
TiO <sub>2</sub>	0.04	0.01	0.01	0.04	0.01	0.05	0.01	0.01	0.03	0.01
Al <sub>2</sub> O <sub>3</sub>	24.17	0.08	0.04	0.11	9.86	89.94	8.34	21.47	23.12	10.11
Cr <sub>2</sub> O <sub>3</sub>	2.41	1.14	0.19	1.00	1.16	8.66	3.14	2.96	2.38	1.29
FeO	5.19	29.43	11.88	28.63	5.37	0.71	3.18	6.02	4.45	3.62
MnO	0.90	0.40	0.10	0.42	1.26	0.06	0.47	0.89	0.67	1.13
NiO	0.02	1.01	0.41	1.49	0.01	0.01	0.01	0.02	0.02	0.02
Na <sub>2</sub> O	0.09	0.52	0.05	0.12	0.87	0.00	6.21	0.27	0.15	5.95
MgO	24.36	64.57	46.40	68.21	27.54	0.44	16.13	22.20	26.01	16.46
CaO	0.11	0.01	0.00	0.01	0.70	0.01	5.07	1.72	0.10	5.32
K <sub>2</sub> O	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.03
Total	99.54	97.20	99.60	100.08	99.42	100.68	99.63	98.95	99.16	99.70

<sup>a</sup>Number of analyses for average<sup>b</sup>Average taken from analyses on eight separate broken fragments probably from a single original inclusion**Fig. 1** Trace-element compositions of São Luiz inclusions. Concentrations are ratioed to chondritic values of Sun and McDonough (1989)

compositions from the TZ association (Harte 1992; Fig. 1). The LM/UM fPer contains ~30 wt% FeO, a composition typical of this mineral from São Luiz (Harte et al. 1999). The LM/UM olivine is relatively Mg poor (Mg# ( $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ) of 0.87) compared to inclusions in diamonds from other localities (Harris and Gurney 1979).

The type-II pyroxenes with ~10 wt% Al<sub>2</sub>O<sub>3</sub> (Table 2) reflect the presence of a significant garnet component. The rubies are characterised by 8.5 wt% Cr<sub>2</sub>O<sub>3</sub> and ~0.3% FeO. The type-II fPers are typical of those recovered throughout the São Luiz inclusion population (Hutchison 1997).

In view of the presence of ~5 wt% CaO and Na<sub>2</sub>O and > 8 wt% Al<sub>2</sub>O<sub>3</sub>, type-III pyroxenes are compositionally distinctive and have not been recorded from

other localities. The closest analogies are a significantly more calcic, aluminous, relatively low-pressure pyroxene with a small amount of Na from the Western Ross Embayment, Antarctica (Salviullo et al. 1997). In contrast, the type-III TAPP grains are similar to other São Luiz TAPP inclusions. The majoritic garnet has unusually low Ca (1.72 wt%) and rare earth element contents compared with majoritic garnets from the São Luiz transition-zone association (Harte 1992; Fig. 1).

An additional feature that distinguishes the deep-mantle São Luiz association from other mantle minerals is that all phases show unusual chondrite-normalised ratios of Y/Ho less than unity (Fig. 1).

X-ray diffraction of type-II aluminous pyroxene composition inclusion BZ241B2 revealed an orthorhombic Pbca structure with cell dimensions of  $a = 8.740(11) \text{ \AA}$ ,  $b = 5.203(11) \text{ \AA}$  and  $c = 18.27(2) \text{ \AA}$ . This is a typical orthopyroxene structure. On the basis of 787 reflections, type-III Na, Al, Mg – silicate inclusion BZ242B was found to have a monoclinic C2/c pyroxene structure. Crystal data and refinement for BZ242B are presented in Tables 3, 4 and 5. Fitting cation values from compositional data in Table 2 on the basis of a pyroxene structure and six O anions (Table 6; see Electronic Supplementary Material) confirms that the type-III pyroxenes are unusual. Most inclusions show a slight deficiency of Si at the tetrahedral site which is compensated for by Al. With the remaining Al assigned to the M1 site, this requires some Mg (and possibly also Fe<sup>2+</sup>) to be assigned to M2, giving a formula unit of (Na, Ca, Mg, Mn)(Mg, Al, Fe, Cr)(Si, Al)<sub>2</sub>O<sub>6</sub>. Both these assignments preclude type-III pyroxenes from belonging to the omphacite or aegirine-augite compositional ranges. The compositional and structural data indicate that type-III pyroxene can be regarded as a new mineral phase.

## Origin of inclusion associations

### LM/UM association

The seismic discontinuity at approximately 670 km in depth is widely believed to be primarily the result of the reaction of (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> (ringwoodite) to form (Mg, Fe)O plus perovskite-structured (Mg, Fe)SiO<sub>3</sub> (MgSiPvk) (Ito and Takahashi 1989; Akaogi et al. 1998). Phase relations in the MgO-FeO-SiO<sub>2</sub> system show that this reaction occurs over a range of pressures equivalent to the very deepest regions of the upper mantle where ringwoodite can coexist with fPer (Ito and Takahashi 1989; Akaogi et al. 1998; Fig. 2). These observations have

a particular bearing on determining the crystallisation depths of the LM/UM association. The (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> and fPer inclusions have Mg# of 0.87 and 0.80 respectively. Comparison with phase relations (Ito and Takahashi 1989; Akaogi et al. 1998) therefore places the formation of the LM/UM association in the range 23–24.5 GPa (Fig. 2) dependent on temperature. Furthermore, the (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> inclusion would originally have been ringwoodite. There is some debate over the temperature of the mantle, principally being dependent on whether the mantle convects singly or as two separate layers (Jeanloz and Richter 1979; Solheim and Peltier 1993). However, extrapolation of phase relations to the highest estimates of ~2,100 K (Jeanloz and Richter 1979) would force the pressure of formation to no lower than

**Table 3** Structural data for type-III inclusion BZ242B after release from diamond: unit cell and analysis data

Type	Value	Type	Value
Crystal system	Monoclinic	$\beta$ (°)	108.33(4)
Space group	C2/c (no. 15)	Formula weight	209.15
a dimension (Å)	9.587(4)	Calculated density (mg m <sup>-3</sup> )	3.344
b dimension (Å)	8.699(6)	Data/parameters	6.6
c dimension (Å)	5.247(4)	R1 (I > 2 $\sigma$ I)	0.0516
Volume (Å <sup>3</sup> ), Z	415.4(5), 4	wR2 (all data)	0.1247
Reflections	787	Goodness of fit	0.553
Independent reflections	309	Largest difference peak (eÅ <sup>-3</sup> )	0.775
Theta range (°)	3.24 to 24.60	$\mu$ (mm <sup>-1</sup> )	1.811 mm <sup>-1</sup>

**Table 4** Structural data for type-III inclusion BZ242B after release from diamond: positions and thermal parameters. All atoms were refined with anisotropic thermal parameters. The anisotropic displacement factor exponent takes the form

$-2\pi^2[h^2a^*^2U_{11} + \dots + 2hka^*b^*U_{12}]$ . *M(1)* 46% Mg<sup>2+</sup>, 43% Al<sup>3+</sup>, 6% Fe<sup>3+</sup>, 5% Cr<sup>3+</sup>. *M(2)* 39% Mg<sup>2+</sup>, 31% Na<sup>+</sup>, 16% Ca<sup>2+</sup>, 6% Fe<sup>3+</sup>, 4% Mn<sup>2+</sup>. *Si(1)* 96% Si<sup>4+</sup>, 4% Al<sup>3+</sup>

Atom	Site	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
M(1)	4e	0	0.9049(6)	0.2500	15(2)	15(3)	26(3)	0	14(2)	0
M(2)	4e	0	0.2847(6)	0.2500	18(3)	21(3)	12(3)	0	2(2)	0
Si(1)	8f	0.2933(3)	0.0924(4)	0.2456(7)	12(2)	10(2)	22(2)	1(2)	10(2)	0(2)
O(1)	8f	0.1137(7)	0.0860(9)	0.1368(14)	10(4)	22(4)	19(5)	10(4)	12(3)	-3(4)
O(2)	8f	0.3674(9)	0.2554(9)	0.3261(15)	30(5)	25(5)	32(5)	1(4)	13(4)	-16(4)
O(3)	8f	0.3546(8)	0.0078(11)	1.0264(18)	24(4)	48(6)	39(6)	-11(4)	15(4)	-29(5)

**Table 5** Structural data for type-III inclusion BZ242B after release from diamond: interatomic distances (Å) and angles (°). Symmetry transformations used to generate equivalent atoms: #1  $x-1/2, y+1/2, z$  #2  $-x+1/2, y+1/2, -z+1/2$  #3  $-x, -y+1, -z$  #4  $x, -y+1, z+1/2$  #5  $-x, y+1, -z+1/2$  #6  $x, y+1, z$  #7  $-x, -y+1, -z+1$  #8  $-x, y, -z+1/2$  #9

$x-1/2, -y+1/2, z-1/2$  #10  $-x+1/2, -y+1/2, -z+1$  #11  $-x+1/2, y+1/2, -z+3/2$  #12  $x-1/2, y+1/2, z-1$  #13  $x, y, z-1$  #14  $x, -y, z-1/2$  #15  $x, y-1, z$  #16  $x+1/2, y-1/2, z$  #17  $x, y, z+1$  #18  $x, -y, z+1/2$  #19  $x+1/2, y-1/2, z+1$

### Interatomic distances (Å) and angles (°)

M(1)-O(2)#1	1.946(10)	M(1)-O(2)#2	1.946(10)	Si(1)-O(2)	1.583(8)		
M(1)-O(1)#3	1.981(7)	M(1)-O(1)#4	1.981(7)	Si(1)-O(1)	1.635(6)		
M(1)-O(1)#5	2.105(9)	M(1)-O(1)#6	2.105(9)	Si(1)-O(3)#13	1.624(10)		
M(2)-O(1)#8	2.222(8)	M(2)-O(1)	2.222(8)	Si(1)-O(3)#14	1.653(9)		
M(2)-O(2)#9	2.215(8)	M(2)-O(2)#10	2.215(8)				
M(2)-O(3)#11	2.461(10)	M(2)-O(3)#12	2.461(10)				
O(2)#1-M(1)-O(2)#2	96.1(5)	O(2)#1-M(1)-O(1)#3	93.0(3)	O(1)#8-M(2)-O(1)	77.8(4)	O(1)#8-M(2)-O(2)#9	88.3(3)
O(2)#2-M(1)-O(1)#3	90.1(3)	O(2)#1-M(1)-O(1)#4	90.1(3)	O(1)-M(2)-O(2)#9	77.5(3)	O(1)#8-M(2)-O(2)#10	77.5(3)
O(2)#2-M(1)-O(1)#4	93.0(3)	O(1)#3-M(1)-O(1)#4	175.4(5)	O(1)-M(2)-O(2)#10	88.3(3)	O(2)#9-M(2)-O(2)#10	161.9(5)
O(2)#1-M(1)-O(1)#5	90.7(3)	O(2)#2-M(1)-O(1)#5	171.1(3)	O(1)#8-M(2)-O(3)#11	137.6(3)	O(1)-M(2)-O(3)#11	119.3(3)
O(1)#3-M(1)-O(1)#5	95.3(3)	O(1)#4-M(1)-O(1)#5	81.2(3)	O(2)#9-M(2)-O(3)#11	131.5(3)	O(2)#10-M(2)-O(3)#11	65.5(3)
O(2)#1-M(1)-O(1)#6	171.1(3)	O(2)#2-M(1)-O(1)#6	90.7(3)	O(1)#8-M(2)-O(3)#12	119.3(3)	O(1)-M(2)-O(3)#12	137.6(3)
O(1)#3-M(1)-O(1)#6	81.2(3)	O(1)#4-M(1)-O(1)#6	95.3(3)	O(2)#9-M(2)-O(3)#12	65.5(3)	O(2)#10-M(2)-O(3)#12	131.5(3)
O(1)#5-M(1)-O(1)#6	83.1(4)	O(2)-Si(1)-O(3)#13	111.3(5)	O(3)#11-M(2)-O(3)#12	75.9(3)	O(2)-Si(1)-O(1)	117.3(4)
O(3)#13-Si(1)-O(1)	108.2(4)	O(2)-Si(1)-O(3)#14	103.3(5)	O(3)#13-Si(1)-O(3)#14	106.6(3)	O(1)-Si(1)-O(3)#14	109.5(4)

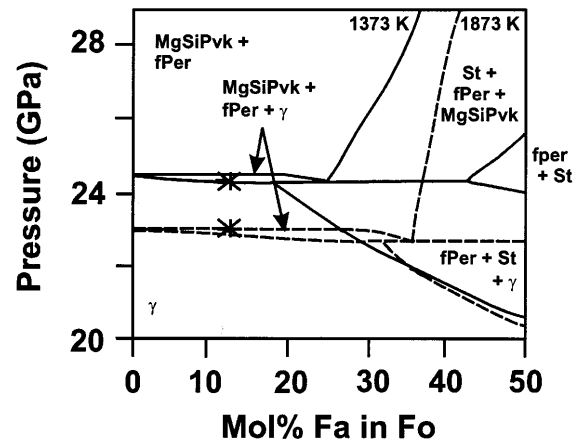
**Table 6** Cation assignments for type-III pyroxenes assuming C2/c pyroxene structure. Cations calculated on the basis of six O anions

	Inclusion	
	237A	259B
Si site	2.000	2.000
Si	2.000	1.957
Al	0.000	0.043
M1 site	1.000	1.000
Mg	0.475	0.483
Al	0.345	0.375
Fe <sup>2+</sup>	0.023	0.027
Fe <sup>3+</sup>	0.070	0.080
Cr	0.087	0.036
M2 site	0.995	1.018
Ca	0.190	0.200
Ti	0.000	0.000
Ni	0.000	0.000
K	0.000	0.001
Mg	0.368	0.378
Na	0.422	0.405
Mn	0.014	0.033

22.5 GPa. Furthermore, the absence of Al substitution into fPer and (Mg, Fe)Si<sub>2</sub>O<sub>4</sub> indicates that the presence of TAPP in the association has no effect on the stability range of the fPer and (Mg, Fe)Si<sub>2</sub>O<sub>4</sub>. Indeed, given that TAPP is probably restricted to the base of the upper mantle (Harris et al. 1997), its occurrence corroborates a depth of origin that can be placed confidently within a range of 630–680 km (PREM, Dziewonski and Anderson 1981). The inferred bulk composition of Mg# > 0.80 is consistent with the Fe-rich end of the compositional range of the majority of peridotitic mantle models (Anderson and Bass 1986). This is also implied by the relatively high rare-earth element concentrations in LM/UM TAPP (Fig. 1), suggesting that the source rock is Ca-poor and does not involve the REE-phyllitic perovskite-structured CaSiO<sub>3</sub> (CaSiPvk).

#### Type-II association

Although the compositions of type-II pyroxene inclusions have some similarities with those recorded from crustal granulites (particularly for Al), association with fPer and Al<sub>2</sub>O<sub>3</sub> (ruby) places its origin at significantly higher pressure, within the lower mantle (Irifune et al. 1996). Thus, it originally existed with a perovskite structure rather than the present orthopyroxene structure. Discovery of the type-II association represents a resolution of what has been a contentious issue – whether Al can be wholly dissolved into MgSiPvk throughout the lower mantle or whether Al stabilises a separate phase. Early experimental work on pyrolite and MORB under lower-mantle conditions suggested the presence of an Al-rich phase which could not be identified (Irifune and Ringwood 1987). More recently, Al has been shown experimentally to be incorporated into MgSiPvk (O'Neill and Jeanloz 1994; Kesson et al. 1995), although other workers suggest that a separate Al-rich phase of either corundum (Irifune et al. 1996) or an



**Fig. 2** Phase relations within the forsterite–fayalite composition system determined at 1,373 and 1,873 K (Akaogi et al. 1998) and for pressures relevant to the LM/UM association. Two phase fields involve fPer and (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> coexisting. The stars indicate the composition of the olivine composition inclusion BZ243C, implying that the LM/UM association formed at around 22.5–24.5 GPa, dependent on temperature. MgSiPvk Perovskite-structured (Mg, Fe)SiO<sub>3</sub>; fPer (Mg, Fe)O. St Stishovite;  $\gamma$  ringwoodite; Fo forsterite composition (MgSi<sub>2</sub>O<sub>4</sub>); Fa fayalite composition (Fe<sub>2</sub>SiO<sub>4</sub>)

Al-rich calcium ferrite-structured phase (e.g. Kondo and Yagi 1998) coexists with mildly aluminous MgSiPvk. The type-II association of Al<sub>2</sub>O<sub>3</sub> (var. ruby) and aluminous MgSiPvk is consistent with the latter argument that a phase field of MgSiPvk and Al<sub>2</sub>O<sub>3</sub> exists in the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system over a restricted pressure interval (Irifune et al. 1996) before complete solid solution of MgSiO<sub>3</sub> and Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> is stabilised at higher pressure (Kesson et al. 1995). Phase relations place the São Luiz MgSiPvk – Al<sub>2</sub>O<sub>3</sub> assemblage between lower-mantle pressures of 26.5 and ~30 GPa (1,773 K) depending on bulk composition (Irifune et al. 1996).

The fact that corundum inclusions are recovered rather than the aluminous calcium ferrite-structured phase observed by some workers may indicate that the latter is a metastable phase. Indeed, in experiments by Yagi (personal communication) the Al-rich phase and aluminous pyroxene compositions were extrapolated from electron microprobe data of sub-micron grains. Thus, it could have equally been concluded that the most Al-rich phase present was in fact corundum. It could also be argued from assessing the experimental phase relations that the bulk composition of Al<sub>2</sub>O<sub>3</sub> required to form this association would be atypical for mantle rocks. However, the minimum garnet component in MgSiPvk in the work of Irifune et al. (1996) was determined to be ~55%, compared to a ~40% component in type-II pyroxene inclusions considered here. This difference can most likely be accounted for by deviations from a MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> bulk composition in the natural assemblage, as the addition of Fe is known to restrict Al solubility within MgSiPvk (O'Neill and Jeanloz 1994). Furthermore, the low rare-earth element concentrations in the Mg-silicate phase (Fig. 1) indicates that it is associated with CaSiPvk. This further supports a lower-mantle origin for the

type-II association. The phase relations indicate that the type-II association formed at  $\sim 730$  km (Dziewonski and Anderson 1981) in a bulk composition of at least 40% garnet component in pyroxene. This bulk composition is similar to the type-I association (Wilding 1991; Hutchison 1997; Harte et al. 1999) where TAPP is the Al phase rather than  $\text{Al}_2\text{O}_3$  and  $(\text{Mg}, \text{Fe})\text{SiO}_3$  is sub-aluminous ( $< 3$  wt%  $\text{Al}_2\text{O}_3$ ). The type-I association is likely therefore to be a lower-pressure form of the type-II association.

### Type-III association

Gasparik and Hutchison (2000) have undertaken a series of high-pressure/temperature experiments and have synthesised type-III pyroxene composition phases at 22–25 GPa, 1,700–2,000 °C. Under these conditions the type-III pyroxene is garnet structured and thus is unlike pyroxene composition inclusions from the type-I and type-II associations, which are believed to initially have crystallised with perovskite structures. Despite their present monoclinic structure (Tables 3, 4 and 5), type-III pyroxene inclusions are therefore concluded to originally have been garnet structured and this explains their unusual compositions. Cation concentrations calculated from type-III pyroxene compositions give good fits to a typical garnet structure (see Electronic Supplementary Material) and are further improved by assuming that, of the small amount of iron, some of the ferric iron resides at the octahedral site. The average ratio of  $\text{Fe}^{3+}/\text{total Fe}$  required to give the best fit is 0.75, similar to values obtained by Mössbauer on other São Luiz phases (McCammon et al. 1997). Furthermore, perovskite-structured Mg silicates are not considered able to accommodate the high CaO contents present in type-III pyroxenes, as in this phase field CaO is more likely to be accommodated wholly within  $\text{CaSiPvk}$  (e.g. Irifune and Ringwood 1987). The lower-pressure/temperature experiments of Gasparik and Hutchison (2000) are also compatible with mantle geotherms, assuming no steep thermal gradient between upper and lower mantle (Solheim and Peltier 1993), whereas all their experiments are compatible with a mantle with a steep thermal boundary (Jeanloz and Richter 1979). So, depending on the thermal state of the mantle, the type-III association can be concluded to have formed between 22 GPa (618 km, Dziewonski and Anderson 1981) and 25 GPa (694 km).

Additionally, the regression to a low-pressure polymorph is not unusual for inclusions in diamond. As compositional data show, exhumation was probably rapid, and significant internal pressure can be retained around inclusions because of the differences in expansivity relative to diamond (e.g. Harris et al. 1970). However, with large free-energy differences and pressure release aided by plastic deformation of the diamonds, high-pressure polymorphs are rarely retained. It is as a result of the absence of high-pressure structures that mineral chemistry must be relied upon to assess the conditions of origin of inclusion associations in diamonds.

In addition to the phase relations evidence, the presence of TAPP and the lower-pressure majoritic garnet in association with type-III pyroxenes also supports an origin within the deepest regions of the upper mantle for the type-III association. Although there is no direct experimental evidence for TAPP or majoritic garnet coexisting with type-III garnet-structured pyroxene, the experiments of Gasparik and Hutchison (2000) have crystallised a K-hollandite phase with three times as much Al as the associated type-III garnet at 1,900 °C, 24 GPa. The stability of the K-hollandite phase is clearly a result of the high K content of the starting material and is not necessarily applicable to the type-III inclusion association. However, it does demonstrate that the type-III garnet-structured phase does not have to be the most aluminous phase present. Furthermore, Gasparik (personal communication) has observed two-garnet phase fields at high pressure in some experiments. It is proposed that the pyroxene component of the garnet composition phase in association with type-III pyroxene reflects a fine-scale variation of depth of formation of the association. As the phase field of perovskite-structured  $\text{CaSiO}_3$  expands with increasing pressure, TAPP would be stabilised as the most aluminous phase in preference to majoritic garnet (Harris et al. 1997). As with the LM/UM association, the occurrence of fPer is not inconsistent with an origin of 618–694 km for the type-III association. For the shallower part of the depth range, fPer would be associated with ringwoodite and, subsequently in the lower mantle, with perovskite-structured  $\text{MgSiO}_3$  (Gasparik and Hutchison 2000) as the garnet phases continue to break down. Further evidence is provided by trace-element compositions of type-III association phases. Ferropericlase exhibits subchondritic concentrations of rare-earth element concentrations because its crystal structure is unable to accommodate relatively large radii ions. No such crystallographic control is likely for TAPP (Harris et al. 1997) or garnet-structured phases. Thus, the depletion in Ca and trace elements in BZ237C (Table 2, Fig. 1), compared with transition-zone association majoritic garnets, and the low rare-earth element concentrations in type-III pyroxenes support equilibration with the extremely REE-phyllitic (Kato et al. 1988)  $\text{CaSiPvk}$ . This phase is only stable at pressures in excess of 17 GPa, depending on bulk composition (Irifune and Ringwood 1987).

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### Discussion and conclusions

One of the most critical questions relating to the interpretation of deep-mantle inclusions revolves around their relevance to the mantle on a larger scale. The inclusion associations are clearly representative of their own protoliths as the inclusions grew syngenetically with their diamond hosts. For example, the presence of  $\text{Al}_2\text{O}_3$  inclusions, both singly and within a touching association consistent with high-pressure phase relations (Irifune et al. 1996), shows that  $\text{Al}_2\text{O}_3$  can be a free phase in the

lower mantle. The question which subsequently arises is, how representative of the mantle is this observation? It is true to say that the volume of material available for study is small and it is not entirely clear how unusual are the processes that lead to the crystallisation of diamond in the deep mantle. It is observed that by far the most common mineral phases included in shallow-mantle diamonds are sulphides, and this association is typically out of equilibrium with mantle olivine (Deines and Harris 1995). Much diamond precipitation at shallow depth is therefore not in equilibrium with 'normal' shallow-mantle material. However, for deep-mantle diamonds, it is empirically observed that ferropericlase is the principal inclusion in diamond (e.g. Hutchison 1997; Davies et al. 1999; Harte et al. 1999). As ferropericlase constitutes a very significant proportion of the lower mantle for a large range of bulk compositions (e.g. Irfune and Ringwood 1987), it is not unreasonable to suppose that diamond formation, at least in the lower mantle, is in equilibrium with 'normal' lower-mantle bulk compositions. We expect that inclusions in deep-mantle diamonds are not atypical of the deep mantle per se. Whether the significance of the mineral associations can be taken a stage further to use as a tool for assessing large-scale mantle dynamics is a more difficult question. The evidence presented for a variety of different bulk compositions from similar depth suggests inhomogeneity of mantle protoliths. This is consistent with geodynamic models of the mantle, for example, those involving the ponding of subducted slabs (Davies and Richards 1992). Indeed, if the mantle did reach a state of physical equilibrium, then it is believed that it would rapidly stratify on the basis of the Fe composition of constituent phases (Anderson 1977). It is also important to recognise that the Juina samples constitute the majority of deep-mantle material available for direct study. It would be foolish to disregard their potential implications for mantle composition and dynamics.

The presence of majoritic garnet and jadeitic diopside indicates that the source of the transition-zone association is eclogitic. By contrast, the dominance of fPer and type-I (Mg, Fe)SiO<sub>3</sub> inclusions, which are equivalent to an olivine component, indicates that the lower-mantle type-I protolith is peridotitic. Such a distinct compositional difference between upper- and lower-mantle protoliths is also supported by the compositions of the diamonds. Lower-mantle stones are strongly depleted in nitrogen and show a far more restricted and generally heavier  $\delta^{13}\text{C}$  composition than transition-zone diamonds (Deines et al. 1991; Hutchison et al. 1999). Perhaps not surprisingly, the inclusion associations presented here suggest that the compositions of these mantle regions are not so simple. The range in mineral compositions of the associations reported show that a complexity of bulk compositions exists across the 670-km boundary region. Despite similar depths of origin for the LM/UM and type-III associations, they clearly arise from different bulk compositions. For example, the type-III association is much more calcic, as evident from the compositions of

the pyroxene and garnet composition phases and from the trace-element evidence for an association with Ca-SiPvk. In contrast, none of the LM/UM phases contain significant Ca, and trace-element considerations preclude the significant presence of the most likely Ca-bearing phase, CaSiPvk. Such differences possibly reflect a fertile subducted protolith for the type-III association and a more peridotitic protolith for the LM/UM association. This implies that the mantle was poorly mixed at deep upper-mantle depths when the São Luiz diamonds formed and is consistent with present-day geophysical observations (e.g. Morgan and Shearer 1993). Despite these inhomogeneities and the more restricted depth range sampled, the new associations do however still indicate differences between upper-mantle and lower-mantle protoliths sampled. In particular, Na has a significant presence in phases of both the TZ (Wilding 1991; Hutchison 1997) and type-III associations. However, it is relatively depleted in the slightly deeper LM/UM association (with 0.5 wt% in fPer). Furthermore, even if the lower-mantle protoliths contain as much as 40 mol% fPer (typically with <0.2 wt% Na<sub>2</sub>O, Hutchison 1997) it can still be concluded from the mineral inclusions discussed here that there is a significant Na depletion in the lower-mantle compared with upper-mantle protoliths. The complexity of the mineral associations described are consistent with the popular concept of intermixing at the upper-mantle/lower-mantle boundary with occasional ponding of subducted material and the upwelling of lower-mantle plumes (Davies and Richards 1992).

All possible ion probe interferences were carefully accounted for in SIMS analyses collected over a number of different sessions and yet a chondrite-normalised Y/Ho ratio of less than unity (0.9–0.01) was observed for all phases (Fig. 1). As Y and Ho both exist as trivalent ions (except under very exceptional conditions for Ho) and have similar ionic radii (Shannon 1976), mantle rocks exhibit a small range of chondrite-normalised ratios from 0.7 to 1.3 (Burnett et al. 1989). It is unlikely that the inclusions presented in this paper crystallised under sufficiently extreme oxidising or reducing conditions for Ho to have adopted an unusual oxidation state. Also, the differences in crystal field energy between the two ions are unlikely to produce a large effect. The remaining method to significantly fractionate Y from Ho lies in their differing volatility. Yttrium is more refractory than Ho and thus, in planetary condensation settings, Y and Ho can fractionate significantly. Burnett et al. (1989) observed substantially lower Y than the norm in studies of meteorites, and Yoneda et al. (1990) found chondrite-normalised Y/Ho ratios ranging from 0.06 to 0.58 for group-II inclusions in Allende. It is concluded therefore that the standard chondritic ratio of Ho to Y is not entirely applicable to the region of the deep mantle sampled and a slightly different or variable meteoritic composition may apply to these deep regions of the Earth.

In summary, if the mineral associations can be considered representative of significant portions of the mantle, compositional differences across the upper-

mantle/lower-mantle boundary inferred further support separate mantle convection, whereas if the shallower assemblages discussed represent ponded subducted material their presence supports at least a transient upper/lower-mantle boundary.

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