

Patrick C. Hayman · Maya G. Kopylova
Felix V. Kaminsky

Lower mantle diamonds from Rio Soriso (Juina area, Mato Grosso, Brazil)

Received: 30 August 2004 / Accepted: 4 February 2005 / Published online: 4 May 2005
© Springer-Verlag 2005

Abstract The morphology, colour, fluorescence, cathodoluminescence, nitrogen content and aggregation state, internal structure and mineral inclusions have been studied for 69 alluvial diamonds from the Rio Soriso (Juina area, Mato Grosso State, Brazil). Nitrogen in most diamonds (53%) is fully aggregated as B centres, but there is also a large proportion of N-free stones (38%). A strong positive correlation between nitrogen and IR-active hydrogen concentrations is observed. The diamonds contain (in order of decreasing abundance) ferropericlase, CaSi-perovskite, magnetite, MgSi-perovskite, pyrrhotite, ‘olivine’, SiO₂, perovskite, tetragonal almandine-pyrophe phase and some other minerals represented by single grains. The Rio Soriso diamond suite is subdivided into several subpopulations that originated in upper and lower mantle of ultramafic and mafic compositions, with the largest subgroup forming in the ultramafic lower mantle. Analysed ferropericlase grains are enriched in Fe ($Mg\# = 0.43\text{--}0.89$), which is ascribed to their origin in the lowermost mantle. The Juina kimberlites may be unique in sampling the material from depths below 1,700 km that ascended in a plume formed at the core–mantle boundary.

Electronic Supplementary Material Supplementary material is available for this article at <http://dx.doi.org/10.1007/s00410-005-0657-8>

Communicated by T.L. Grove

P. C. Hayman · M. G. Kopylova (✉)
Department of Earth and Ocean Sciences,
University of British Columbia, 6339 Stores Road,
Vancouver, BC, Canada, V6T 1Z4
E-mail: mkopylov@eos.ubc.ca
Tel.: +1-604-8220865
Fax: +1-604-8226088

F. V. Kaminsky
KM Diamond Exploration Ltd., 2446 Shadbolt Lane,
West Vancouver, BC, Canada, V7S 3J1

Introduction

Diamonds and the minerals trapped within them provide a unique opportunity to directly study materials from great depths (>150 km). Less than 1% of diamonds worldwide contain minerals that are predicted by experiments to exist only in the lower mantle (>660 km) (Stachel 2001). The Juina area, Brazil (Fig. 1a) has historically produced the highest proportion of diamonds containing lower mantle inclusions (Wilding 1991; Harte and Harris 1994; Hutchison 1997; Harte et al. 1999; Kaminsky et al. 2001), with diamonds from these studies having mostly been recovered from streams that feed into the Rio Cinta Larga (Fig. 1b). This study examines 69 diamonds from alluvial deposits of the Rio Soriso (Fig. 1b) mined by Diagem International Resource Corporation.

A range of techniques was employed to divide the Rio Soriso suite into paragenetic subgroups. We examined crystal morphology, colour, fluorescence (FL), cathodoluminescence (CL), nitrogen concentration and aggregation, internal morphology and mineral inclusion chemistry of the diamonds. We also modified the traditional methodology of studying diamond inclusions (DI) to enable a check on the primary or secondary origin of included grains and to increase the rate of DI recovery.

The results from this study significantly expand the database for lower mantle mineral compositions. Following previous studies of Juina samples, we found that most Rio Soriso diamonds formed in the lower mantle. We propose that Fe-enriched ferropericlase found among Rio Soriso inclusions represents ferropericlase from the lowermost mantle, which could be the natural analogue to either the low-spin Fe ferropericlase produced experimentally and predicted theoretically (Badro et al. 2003), or ferropericlase that equilibrated with post-perovskite at the base of the mantle (Murakami et al. 2004a).

Local geology of the Juina area

The Juina area (Mato Grosso State, Brazil) is located in the Amazonian Craton (Fig. 1a), which is surrounded by Neoproterozoic orogenic belts and is divided into several geochronological provinces. Juina is situated in the Rio Negro-Juruena Province (1.55–1.8 Ga) and is bounded by older rocks towards the north and northeast, and by younger rocks towards the southwest (Tassinari and Macambira 1999). The basement rocks of the Rio Negro-Juruena Province are mostly composed of granitic gneisses and granitoids of tonalitic and granodioritic composition (Tassinari and Macambira 1999).

There are a number of kimberlites in the area (Fig. 1b), two of which have been dated at 92–95 Ma (U/Pb dating of zircons from kimberlitic breccia) (Herman et al. 1998). Kimberlites are located near the southwestern margin of the Amazonian Craton and are mostly emplaced in the Permo-Carboniferous sedimentary rocks of the Fazenda da Casa Branca Formation, while some intrude the older Rio Negro-Juruena Province (Tassinari and Macambira 1999). No kimberlites are currently being mined, though some of them are of subeconomic importance. It is unclear if they are the source for all the diamonds recovered from local rivers.

Analytical methods

Sixty-nine diamonds ranging in weight from 0.015 carats to 2.02 carats (0.003–0.404 grams) are studied. Their morphology, surface features, body colour, fluorescence, cathodoluminescence, nitrogen content and aggregation state, and inclusions are documented in Electronic Supplementary Table 1 (eTable 1).

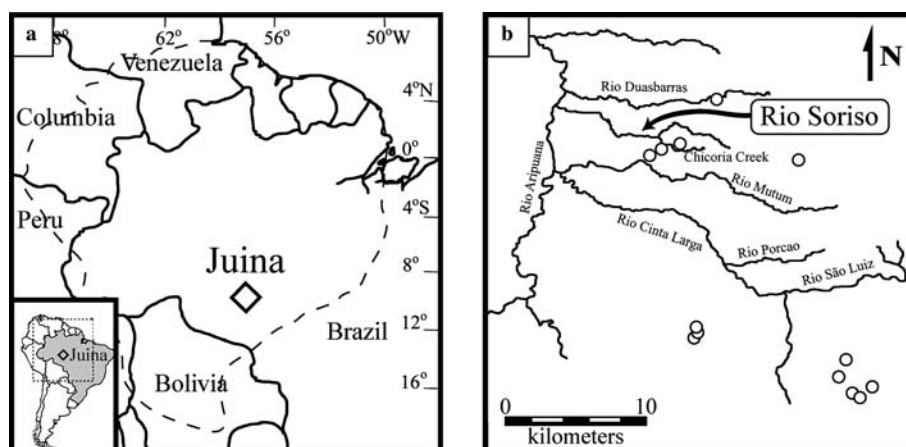
Diamond FL was examined using a 100 W light source with a UV exciter filter (360 ± 20 nm) and barrier filter (420 nm) attached to a Leica MZ FLIII optical microscope. Photographs were collected for each dia-

mond using a fixed exposure time of 20 s so that FL intensity could be compared between stones.

Optical CL characteristics of 47 rough and 14 cut diamonds were examined using a Cambridge Instruments Cathode Luminescence (CITL 8200 mK4) system attached to an optical microscope. Cut diamonds were embedded in carbon putty so as to reduce internal reflections. Photographs were collected with a $2.5\times$ objective at 15 kV and $300 \mu\text{A}$. Quantitative CL data were collected for several diamonds using an Electron Optics Service CL spectrometer attached to a Philips XL 30 scanning electron microscope. The spectrometer has a high sensitivity 2,048 charge coupled device with selected grating optimised for 360–1,000 nm spectral coverage and was operated at 20 kV and $100 \mu\text{A}$.

The concentration and aggregation state of nitrogen in diamond was measured using two different methods. Bulk infrared (IR) was done on all rough diamonds by selecting one point for analysis so that the IR beam passed through the core region of the diamond and thus measured an integrated IR spectrum of several growth zones. Detailed IR spectroscopy was done on 14 cut diamonds by selecting numerous points ($\sim 100 \times 100 \mu\text{m}$) across the polished surface. IR points in distinct growth zones were located using CL and optical microphotographs. IR spectra were collected over the range $650\text{--}4,000 \text{ cm}^{-1}$ on a Nicolet Fourier Transform Infrared spectrometer with a liquid- N_2 -cooled detector. Spectra were collected in transmission mode using a resolution of 8 cm^{-1} by averaging the signal of 256 scans. Spectra were manipulated using Omnic version 6.0a software and de-convoluted into A (pairs of N atoms), B (four N atoms) and D (platelets) components using least square techniques similar to those described in Clark and Davey (1984). Nitrogen concentrations (in ppm) were determined by calculating the absorption at $1,282 \text{ cm}^{-1}$ for both A centres (Boyd et al. 1994: 16.5 ± 1) and B centres (Boyd et al. 1995: 79.4 ± 8). The overall precision of this method is estimated at 19 and 23% for A and B centres, respectively, which agrees well with the 10–20%

Fig. 1 a Location of Juina area in Brazil. Dashed line indicates approximate outline of Amazonian craton (Tassinari and Macambira 1999) (inset of South America). b Detailed map of Juina area with Rio Soriso and other rivers indicated. Open circles represent kimberlite occurrences



precision estimates reported (e.g. Kaminsky and Khachatryan 2001; Stachel et al. 2002). The estimated minimum detection limits (MDL) are 12 and 20 ppm N for A and B centres, respectively. Based on the concentration of nitrogen and its aggregation state, diamonds are divided into Type I (stones with >20 ppm N) or II (stones with no measurable N). This division is arbitrary and relates more to the detection limits of the spectrometer used. Type I diamonds are further subdivided into Type Ib (N occurs only as single atoms), Type IaA (pairs of N atoms) and Type IaB (four N atoms) as well as into transitional groups (Type Ib-IaA and IaAB). The conversion of N from Type Ib to IaA and Type IaA to IaB is largely controlled by time and temperature and has been quantified (Taylor et al. 1990). Relative hydrogen concentrations were calculated by measuring the difference between the base and peak height at $3,107\text{ cm}^{-1}$ after baseline correction and diamond thickness calibration. The error for hydrogen values reported is estimated at 2.6% relative and the MDL is estimated at 0.03 cm^{-1} absorption coefficients (a.c.) for a diamond of 1-cm thickness.

Inclusions were extracted from 29 diamonds by mechanical crushing in an enclosed steel cracker. Chips from the cracked diamonds were then mounted on stubs and examined using a scanning electron microscope (SEM) to find small and colourless inclusions that would not be visible otherwise. The surfaces of unpolished inclusions were further investigated under higher magnification to screen out secondary minerals often observed as polycrystalline aggregates. Only homogeneous grains with fresh, non-pitted and non-flaky cleavage surfaces or crystal faces were further analysed. The most prospective inclusions identified by SEM were then transferred to other stubs for electron probe microanalysis (EPMA).

Mineral analyses were obtained using the CAMECA SX-50 electron microprobe in wavelength dispersion mode (Earth and Ocean Sciences Dept., University of British Columbia), employing the 'PAP' $\phi(\rho Z)$ correction procedure (Pouchou and Pichoir 1985). The operating conditions were: excitation voltage, 15 kV; beam current, 20 nA; peak count time, 20 s; background count time, 10 s; and beam diameter, 1 μm . For elements Y, Zr, Ce, La, Pr, Nd and Gd, peak count time was 40 s and background count time was 20 s. A variety of well-characterized minerals and synthetic phases were used as standards. The minimum detection limits for most oxides are less than 0.06 wt%. Exceptions to this include Cr_2O_3 (0.16 wt%), FeO (0.08 wt%), MnO (0.08 wt%) and NiO (0.10 wt%). The analytical errors depend on the absolute abundances of each element. Relative errors, at the 2σ confidence level, are estimated to be <2% at the >10 wt% level, 5–10% at the ~ 1 wt% level, 10–25% at the 0.2–1 wt% level, and 25–50% at the <0.1 wt% level.

Physical and chemical characteristics of Rio Soriso diamonds

Most diamonds are broken and possess only remnant primary growth faces. The crystals are strongly resorbed, with 52% of stones falling between classes 1–3 on the resorption scale of McCallum et al. (1994), and thus most are dodecahedroids and tetrahexahedroids, while 13% exhibit non-uniform resorption. Single crystals make up 87% of the population whereas aggregates (7%) and unknown crystals (6%) make up the remainder of the suite. Etching features such as trigons, hexagons, tetragons and etch channels are observed on most diamonds. Deformation laminations (DeVries 1975) are visible on at least 20% of the diamonds. Frosting and hillocks are present on less than half of the stones and weak signs of mechanical abrasion through erosion in the surficial environment are observed on one grain.

The majority of diamonds (93%) have uniform body colour, while the remainder are heterogeneous. Body colours observed include colourless (43%), grey (20%), yellow (13%), brown (10%), pink (3%) and milky (3%). Plastic deformation laminations are visible on many of the brown diamonds and on all of the pink stones. One diamond displays fairly weak green radiation damage that occurs as a spot approximately 0.25 mm in diameter.

Diamonds fluoresce in shades of blue (80%), turquoise (15.5%), green (3%) and brown (1.5%) but fluorescence tends to be weaker than what is common for worldwide diamond suites. One diamond does not fluoresce and ten diamonds have heterogeneous FL colours. Two correlations between diamond FL and body colour are observed (Fig. 2). Firstly, green and turquoise FL colours are commonly associated with brown and yellow stones, thus indicating that the defects responsible for brown and yellow body colour also have control on FL colours. A similar pattern was noted by Collins and Mohammed (1982). Secondly, the FL colour distributions for both grey and colourless diamonds are remarkably similar, which corroborates previous suggestions that grey colouration is a result of numerous microscopic inclusions in an otherwise colourless diamond (e.g. Orlov 1977; Robinson 1979; Titkov et al. 2003).

The examined 47 rough stones cathodoluminesce various shades of blue (38%), turquoise (38%), green (13%) and purple (11%). CL spectroscopy indicates that green and blue CL colours have two broad peaks between 435–445 nm and 483–512 nm, with a shift to higher numbers for green CL. Absorption at 440 nm is found in many different diamonds worldwide with a variety of nitrogen concentrations and aggregation states (Pratesi et al. 2003). The stronger peak observed in this study for diamonds with green CL (~ 510 nm) may be related to H3 centre strain (Zaitsev 2000). Analysis of a thick green rim on one diamond indicates that it contains aggregated nitrogen.

Total nitrogen concentrations in the crystals examined are low, with a mean of 72 ppm and mode of 36 ppm. Nitrogen concentration ranges from 0 ppm to 541 ppm for total nitrogen, 0–116 ppm for A centres, and 0–541 ppm for B centres. Most of the stones are Type Ia (62.3%) while the remainder are Type II. Type Ia stones are further subdivided into Type IaA (1.5%), IaAB (7.2%) and IaB (53.6%). Very few diamonds contain platelets (absorption at $\sim 1,365\text{ cm}^{-1}$). Due to the high N aggregation state for most Rio Soriso diamonds, it is not surprising that most are irregular (Woods 1986), as any platelets that may have existed have since degraded. Spectra from 71% of the diamonds studied show a hydrogen peak at $3,107\text{ cm}^{-1}$ that varies in intensity from 0.03 to 6.06 (a.c.). There is a strong positive correlation between total nitrogen concentration and relative hydrogen concentration, which is seen within the suite in general (Fig. 3) and within individual diamonds (Fig. 3 inset). Two explanations for this correlation are: (1) conditions favouring the incorporation of N equally favour the incorporation of H, and (2) N and H enter diamond as an N–H complex. Rondeou et al. (2004) report a similar strong correlation between N and H and propose that H, C and aggregated N often form a defect in diamond together. The relative hydrogen concentration, however, reflects only IR-active H (Sellschop 1992) and there may be significant quantities of IR-inactive H.

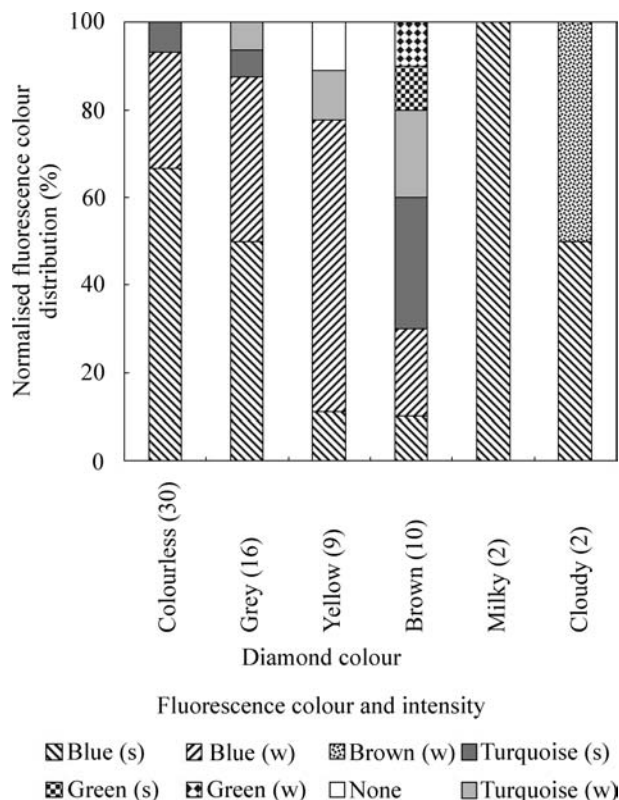


Fig. 2 Normalised histograms of fluorescence colours in Rio Soriso diamonds plotted by diamond body colour. Numbers in brackets indicate sample size. *s* strong, *w* weak

The internal structure of diamond, revealed through examination of cut diamonds under CL, provides information about the diamond's history, such as growth conditions, deformation and resorption. Internal structures are absent in seven diamonds while the rest show concentric structures (four diamonds; Fig. 4a), complex morphology (one diamond), and sectoral zoning (two diamonds; Fig. 4b). For diamonds with concentric internal structures, nitrogen concentrations decrease from core to rim. Episodic resorption and growth are visible in several crystals (Fig. 4a) and most diamonds have experienced a final episode of resorption before exhumation, which is reflected in the number of tetrahedra and dodecahedra observed. Two diamonds have a green/yellow CL rim, one of which comprises Type IaAB diamond (250- μm thick) while the other is too thin for IR analysis ($< 10\text{ }\mu\text{m}$). Evidence of plastic deformation is observed in some diamonds, occurring as either parallel laminations of blue or yellow CL of varying intensity. Local patches of yellow CL are observed on three diamonds, forming mostly around inclusions and have been interpreted by others as indicating areas of low N with intrinsic defects (Davies 1998). Diamond fracturing followed by diamond growth is thought to be evident in one crystal, where a bright CL feature appears broken into several pieces that now occur as disjointed segments within a zone of weak CL.

Results of this study are similar to previous morphological, CL and IR studies on Juina diamonds (Hutchison et al. 1999; Hutchison 1997; Kaminsky et al.

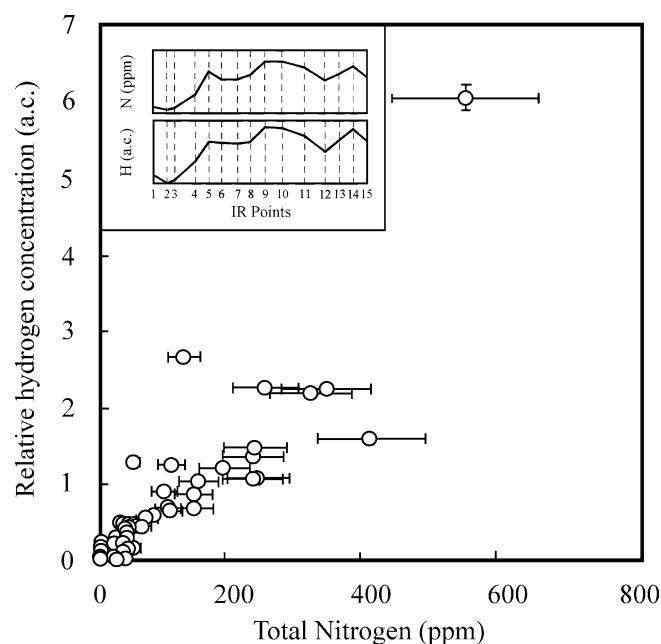


Fig. 3 Total nitrogen concentration (ppm) versus relative hydrogen concentration (a.c., absorption coefficients for diamond normalised to 1-cm thickness) for rough Rio Soriso diamonds. Error bars are 20% for total nitrogen concentration and 2.6% for relative hydrogen concentration. An IR transect across polished diamond 1–4 (inset) shows a remarkable N–H positive correlation

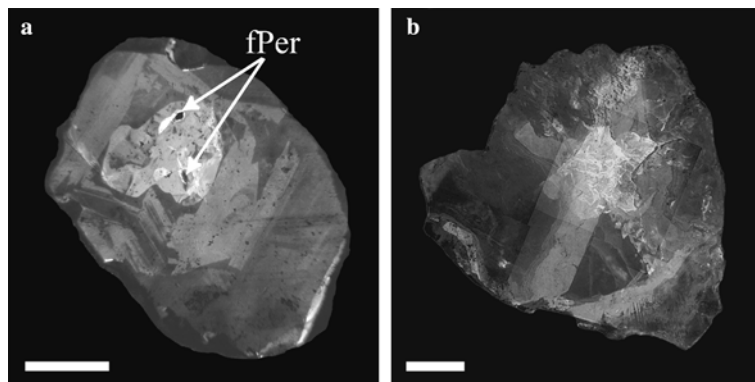


Fig. 4 Cathodoluminescence images of cut diamonds. **a** Internal structure of diamond 3–5. Note the strongly resorbed bright CL core with fPer inclusions indicated, episodic octahedral growth and dissolution events and the general weakening of CL from core to rim. **b** Internal structure of diamond 1–4. The variation in CL intensity is a function of nitrogen concentration, which in turn is controlled by the growth face developing. Bright CL arms radiating from the bright core indicate growth on octahedral faces, while the dark zones between these arms indicate growth on cubic faces. Scale bars are 1 mm

2001; Araujo et al. 2003). All studies noted an abundance of complex and irregular crystal forms, a high proportion of broken crystals, the presence of a small population of twins and aggregates, the absence of cubes, the abundance of deformation laminations, similarities in diamond and CL colours, the abundance of Type II and IaB diamonds, the general absence of platelets in Type I diamond and similar internal structures. For the first time for Juina, we report pink and Type IaA diamonds, and diamonds with bright green CL colours and sectoral zoning.

Mineral inclusions

Most syngenetic mineral inclusions recovered from Rio Soriso diamonds are phases considered stable only in the lower mantle. From the 29 diamonds cracked, 11 different phases have been analysed, comprising 204 separate grains (Table 1, eTable 1). The high recovery rate is a consequence of the technique employed and not a reflection of analysis of several chips from one inclusion. Confidence in the number of grains recovered is strengthened by the fact that most grains were found embedded in diamond and that many have a euhedral form. Listed in order of decreasing abundance, the inclusions recovered include: ferropericlase, CaSiO_3 , magnetite, $(\text{Mg,Fe})\text{SiO}_3$, pyrrhotite, $(\text{Mg,Fe})_2\text{SiO}_4$, SiO_2 , perovskite, tetragonal almandine-pyrope phase (TAPP), garnet, titanate and native Fe. Most inclusions occur in isolation, but there are also nine touching pairs and one three-phase composite.

We will refer to most grains of $(\text{Mg,Fe})\text{SiO}_3$ and to all CaSiO_3 found in Rio Soriso diamonds as MgSi- and CaSi-perovskites, respectively, even though they likely have reverted to a pyroxene ($(\text{Mg,Fe})\text{SiO}_3$) and pyrox-

enoid (CaSiO_3) structure during exhumation (Liu and Ringwood 1975; Joswig et al. 1999). Composition of these inclusions provides strong evidence in support of an initial perovskite structure. Analysed $(\text{Mg,Fe})\text{SiO}_3$ contains no Ni suggesting it was in equilibrium with ferropericlase at lower mantle conditions (Kesson and Fitz Gerald 1991). Furthermore, analysed $(\text{Mg,Fe})\text{SiO}_3$ contains more than 1 wt% Al_2O_3 , comparable with Al content in MgSi-Prv detected in natural samples from the lower mantle (Harte et al. 1999; Davies et al. 1999a; Stachel et al. 2000; Kaminsky et al. 2001) and reproduced experimentally (Kesson et al. 1995; Irifune et al. 1996). Orthopyroxene (stable up to ~ 300 km depth) inclusions in diamond, on the contrary, typically contain < 1.00 wt% Al_2O_3 and > 0.1 wt% NiO (Meyer 1987). Finally, all $(\text{Mg,Fe})\text{SiO}_3$ grains but one occur in association with ferropericlase; this association is only stable in the lower mantle (Fig. 5). Among CaSiO_3 polymorphs, only CaSi-perovskite (CaSi-Prv) is stable with mantle minerals and it occurs only at depths > 580 km (Fig. 5).

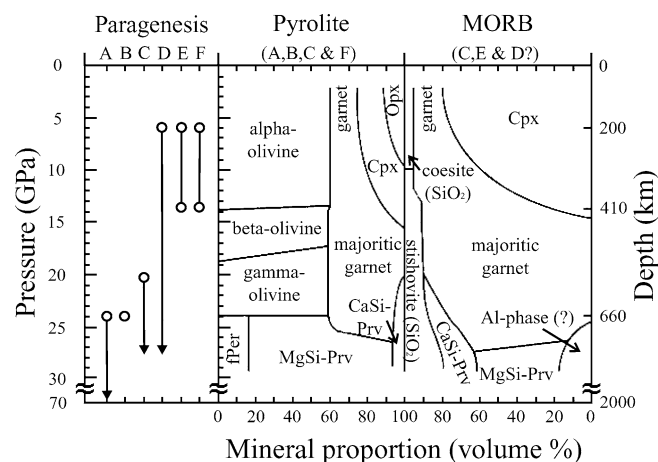


Fig. 5 Depths of origin and compositions for six paragenetic groups identified in Rio Soriso diamonds and the modal mineralogy (vol%)-depth profiles of pyrolite and MORB (Fei and Bertka 1999). Group D has non-ultramafic parent rocks, Groups A, B and F are ultramafic, Group E is mafic, and Group C could come from either of these parental rocks. See text for further discussion of subgroups

Table 1 Inclusions recovered from Rio Soriso diamonds

Inclusion species	No. of diamonds	No. of inclusions	No. of touching phases	Depth of paragenesis (km)	Bulk composition	Paragenetic code ^a
CaSi-Prv	3	8	0	>580	unknown	C
fPer	8	60	0	>660	ultramafic	A
magnetite	2	9	0	?	non-ultramafic	D
'olivine'	1	1	0	<410 ^b	peridotitic	F
pyrrhotite	1	2	0	<410 ^b	eclogitic	E
CaSi-Prv, perovskite	2	4,4	4 ^c	>580	unknown	C
CaSi-Prv, fPer	3	12,6	0	>660	ultramafic	A
CaSi-Prv, titanite	1	5,2	0	>580	unknown	C
Garnet, CaSi-Prv	1	1,2	0	<250 and >580 ^d	eclogitic	E and C
magnetite, SiO ₂	1	13,1	0	?	non-ultramafic	D
'olivine', (Mg,Fe)SiO ₃ (Opx?), pentlandite	1	1,1,1	0	<410 ^b	peridotitic	F
fPer, MgSi-Prv, 'olivine'	1	7,6,2	1 ^e	~660	ultramafic	B
fPer, MgSi-Prv, retrograde 'olivine'	1	5,2,1	1 ^f	>660	ultramafic	A
native Fe, pyrrhotite, SiO ₂	1	1,9,7	0	<410 ^b	eclogitic	E
fPer, MgSi-Prv, 'olivine', TAPP	1	7,2,2,2	2 ^g	~660	ultramafic	B
CaSi-Prv, fPer, MgSi-Prv, 'olivine', TAPP	1	1,12,4,3,1	2 ^h	~660	ultramafic	B

^a Letters correspond to subpopulations described in the discussion

^b Shallow origin (<410 km) supported by IR data

^c There are four composite grains of CaSiO₃ and perovskite (CaTiO₃)

^d These phases are not in equilibrium (garnet does not have a majoritic component)

^e There is one composite of 'olivine' and fPer

^f The 'olivine' touching (Mg,Fe)SiO₃ in this diamond is considered retrograde (described further in the discussion)

^g There is one composite of (Mg,Fe)SiO₃ and TAPP and one three phase composite of MgSiO₃, TAPP and 'olivine' (x2)

^h There is one composite of (Mg,Fe)SiO₃ and 'olivine' and another of (Mg,Fe)SiO₃ and TAPP

Below, (Mg,Fe)₂SiO₄ inclusions are labelled as 'olivine' because they most likely have olivine structure, but their composition provides little insight into what initial phase (α -olivine, β -olivine, γ -olivine) the inclusions represent or if they have a retrograde origin.

Although 12 grains of SiO₂ have been identified in the suite, we do not consider them syngenetic and drop them from further discussion. When examined under SEM, all grains are polycrystalline and fine-grained (Fig. 6h), in stark contrast to coherent, euhedral crystals of most other Rio Soriso inclusions (Fig. 6a, b). A secondary origin assigned to these grains is further supported by the abundance of SiO₂ found on fracture surfaces of several cracked diamonds.

Ferropericlasite

Ferropericlasite (fPer) is the most abundant mineral inclusion recovered from Rio Soriso diamonds. Ninety-seven individual grains of fPer are identified in 15 diamonds under SEM; this is more than all ferropericlasite reported in literature (94; Liu 2002).

Most grains (20–250 μ m) are euhedral with cubo-octahedral habit (Fig. 6a) and are brown/black in colour, although some exceptionally thin grains appear pale orange and purple. Ferropericlasite occurs alone or in association with MgSi-Prv, CaSi-Prv, 'olivine' and TAPP, and there is one occurrence of fPer in direct contact with 'olivine' (Fig. 6d). There is a wide variation in Mg-number (0.45–0.89, average 0.68, Table 2), and fPer in association with 'olivine' and TAPP tend to be richer in MgO (Fig. 7). Oxides of Ni, Cr, Mn and Na are present in amounts up to 1.2–1.5 wt%, but a coupled Na–Cr substitution (Stachel et al. 2000) is not observed.

Grains of fPer released from two diamonds have abundant small blebs, which are generally <2 μ m in diameter (Fig. 6b). Blebs are observed only on the inclusion surface, absent inside cracked fPer grains and tend to form in a linear pattern. SEM analysis shows that they are essentially a pure Fe–Ni (Fe > Ni) alloy. Ferropericlasite grains recovered from another diamond are covered locally by secondary magnetite–magnesian-ferrite (Fig. 6c). Micrograins of Fe–Ni alloy and magnetite–magnesian-ferrite were known to exist in Juina ferropericlasite (Hutchison 1997).

MgSi-perovskite, CaSi-perovskite, 'olivine'

MgSi-perovskite (MgSi-Prv) (14 grains in four diamonds) is found to be colourless and range in size from 15 μ m to 150 μ m (Fig. 6k, l). The Mg-numbers of four MgSi-Prv grains varies from 0.91 to 0.94 (Table 3), which are among the highest Mg-numbers reported for MgSi-Prv in Juina (0.86–0.94; Harte et al. 1999; Kaminsky et al. 2001) but lower than those reported globally (0.93–0.95; Davies et al. 1999a; Stachel et al. 2000). The only abundant trace oxide is Al₂O₃ (1.60–2.54 wt%).

CaSi-perovskite (CaSi-Prv) (32 grains in 11 diamonds) is identified in the suite, which is considerably more than the number of grains (~20) previously reported in DI studies. Grains are colourless to milky in appearance and range in size from 10 μ m to 120 μ m (Fig. 6i). Inclusions are almost pure CaSi-Prv (97.53–99.92%), with minor amounts of FeO (0–1.14 wt%, average 0.26 wt%). One of the CaSi-Prv grains contains an elevated concentration of TiO₂ (2.13 wt%), and another has high Na₂O (0.48 wt%) content (Table 3).

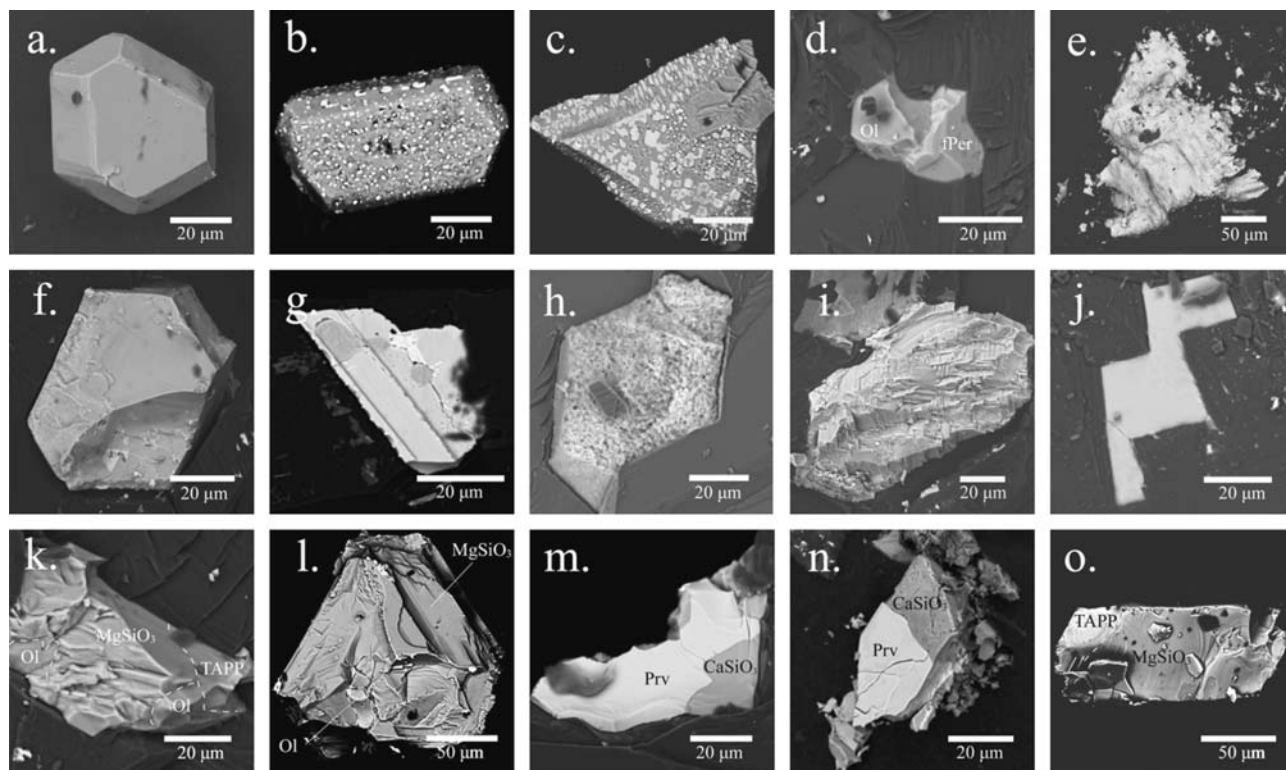


Fig. 6 BSE-SEM images of representative mineral inclusions recovered from Rio Soriso diamonds. **a** Cubo-octahedral habit of fPer grain (sample no. 5–10E), **b** fPer with blebs of Fe–Ni (small bright spots) (3–5D), **c** fPer with spots of secondary magnesioferrite (3–6K), **d** touching inclusions of ‘olivine’ (Ol) (4–3K1) and fPer (4–3K2), **e** native Fe (2–11E), **f** cubo-octahedral habit of magnetite grain (2–6K), **g** heterogeneous sulphide with a composition mostly of pyrrhotite (2–11P), **h** SiO₂ inclusion with a polycrystalline flaky appearance suggestive of a secondary origin (2–11C), **i** CaSi-Prv (3–2L), **j** ‘olivine’ (6–8A), **k** touching MgSi-Prv (1–5J1), TAPP (1–5J3) and ‘olivines’ (1–5J2 on left and 1–5J4 on right), **l** touching MgSi-Prv (3–5G1) and ‘olivine’ (3–5G2), **m** touching CaSi-Prv (2–8L1) and perovskite (2–8L2), **n** touching CaSi-Prv (3–7A1) and perovskite (3–7A2), and **o** touching MgSi-Prv (1–5A1) and TAPP (1–5A2).

‘Olivine’ (ten grains in six diamonds) is found as colourless, generally small (10–100 μm) and mostly anhedral grains (Fig. 6j). Most ‘olivine’ inclusions are Fo₈₀, but one grain is more magnesian (Fo₉₅; Table 3). Inclusions also contain up to 0.80 wt% Al₂O₃ and trace amounts of NiO, TiO₂ and MnO.

Garnets, magnetite, sulphides, native Fe

Tetragonal almandine-pyrope phase (TAPP) occurs as three small (10–60 μm) inclusions in two diamonds. The phase is never found as an isolated crystal, but always in contact with larger inclusions of MgSi-Prv (Fig. 5k, o) in diamonds that also host ‘olivine’ and fPer. Chemical data are available for only one grain and show that it has garnet stoichiometry. The composition, however, is atypical for mantle garnets, i.e. low in Ca and Cr and high in Ti (Table 3). Similar compositions of garnet

found only in Juina were reported to have tetragonal structure and therefore termed TAPP (Harris et al. 1997). The Si/Al ratio of the Rio Soriso TAPP grain is within the range of ‘typical’ mantle garnets without evidence of a majorite component. Two origins of TAPP are proposed in literature: (1) a retrograde origin from the transformation of γ -olivine to β -olivine plus TAPP (Brenker et al. 2002), and (2) a primary origin in the uppermost levels of the ultramafic lower mantle (Harris et al. 1997). A primary origin of the Rio Soriso TAPP grains is supported by the association of TAPP with ‘olivine’, MgSi-Prv and fPer, which occur together only at the upper mantle/lower mantle boundary. We reject the retrograde origin because it is unlikely that the precursor γ -olivine could have accommodated all the Ti measured in TAPP (4.71 wt%), and because ‘olivine’ is either absent or a minor phase in the composite TAPP grains.

Eclogitic garnet found as two grains in a single diamond is Ca-rich and Cr-poor. Quantitative chemical data are available for one large (120 μm), pale orange inclusion (Table 3). The grain contains minor amounts of TiO₂ (0.92 wt%), MnO (0.32 wt%) and Na₂O (0.17 wt%), with no evidence for a majoritic component. The composition is similar to published data for eclogitic garnets from a variety of worldwide sources (Meyer 1987).

Magnetite (22 grains in three diamonds) occurs as black inclusions, 10–60 μm in size, and most with cubo-octahedral habit (Fig. 6f). The grains are rich in Al₂O₃ (3.44–6.92 wt%), TiO₂ (1.50–3.61 wt%), MgO (1.46–3.58 wt%) and Cr₂O₃ (< 3.03 wt%). Magnetite is a rare

Table 2 Averaged microprobe analyses of ferropericlasite inclusions in Rio Soriso diamonds (wt%)

Sample	1-2H	1-2I	1-2J	1-2L	1-2M	1-2P	1-2V	1-2Y	1-2AF	1-2AI	1-2AJ	1-5D	1-5F
Inclusion Assemblage	fPer											fPer+MgSi-Prv+Ol+TAPP	
Average of	3	3	2	1	3	3	1	3	3	2	2	3	3
Paragenesis	A	A	A	A	A	A	A	A	A	A	A	B	B
SiO ₂		0.09	0.06	0.08	0.10	0.08	0.09	0.22	0.10	0.09	0.24	0.07	0.09
Al ₂ O ₃										0.08			
Cr ₂ O ₃	0.17		0.20	0.16	0.17	0.19	0.18	0.22	0.17	0.21	0.16	0.35	0.39
FeO	59.93	58.38	58.49	55.67	59.51	59.54	59.56	57.59	59.22	59.07	55.28	37.56	36.42
MnO	0.31	0.29	0.30	0.38	0.32	0.27	0.38	0.43	0.37	0.35	0.37	0.30	0.32
NiO	0.22	0.20	0.20	0.18	0.21	0.20	0.30	0.17	0.26	0.26	0.23	1.18	1.20
MgO	37.63	39.94	40.42	45.19	39.38	39.75	37.38	40.44	38.70	37.99	43.70	58.97	60.94
CaO													
Na ₂ O	0.12	0.14	0.11		0.13	0.11	0.16	0.48	0.45	0.42	0.10	0.11	
K ₂ O													
Total	98.38	99.04	99.78	101.66	99.82	100.14	98.05	99.55	99.27	98.47	100.08	98.54	99.36
Mg/(Mg + Fe)	0.53	0.55	0.55	0.59	0.54	0.54	0.53	0.56	0.54	0.53	0.58	0.74	0.75

Sample	1-5G	1-5K	2-2E	2-7A	2-7C	2-7O	3-2A	3-2F	3-2G	3-2J	3-5E
Inclusion Assemblage	fPer+MgSi-Prv+Ol+TAPP		fPer+CaSi-Prv	fPer			CaSi-Prv+fPer+MgSi-Prv+Ol+TAPP				fPer+MgSi-Prv+Ol
Average of	3	1	3	1	1	1	2	1	3	2	1
Paragenesis ^a	B	B	A	A	A	A	B	B	B	B	A
SiO ₂	0.08	0.09	0.15	0.06	0.12		0.14		0.08	0.11	0.11
Al ₂ O ₃			0.11								0.06
Cr ₂ O ₃	0.41	0.32	0.50	0.47	0.42	0.57	0.36	0.40	0.35	0.38	0.76
FeO	35.58	37.25	33.90	28.86	27.56	28.94	25.69	25.43	24.67	25.27	48.97
MnO	0.28	0.23	0.26	0.36	0.43	0.38	0.25	0.24	0.22	0.27	0.79
NiO	1.14	1.13	1.35	1.32	1.07	1.28	1.39	1.17	1.36	1.34	0.31
MgO	62.13	61.86	64.63	66.68	67.49	68.45	71.45	73.67	72.41	71.30	50.34
CaO					0.27						
Na ₂ O	0.49	0.23	0.49	0.19	0.41	0.29		0.67	0.18	0.18	0.34
K ₂ O					0.28	0.06					
Total	100.11	101.11	101.39	97.94	98.05	99.97	99.28	101.58	99.27	98.85	101.68
Mg/(Mg + Fe)	0.76	0.75	0.77	0.80	0.81	0.81	0.83	0.84	0.84	0.83	0.65

^a Letters correspond to subpopulations described in the discussion

Blank entries, below detection limit. TiO₂ below detection limit

Abbreviations for minerals in Inclusion Assemblage and Paragenesis are listed in text

Sample	3-6D	3-6J	3-6K	3-6L	3-9H	3-9I	3-9J	3-10C	3-10H	3-10AA
Inclusion Assemblage	fPer				fPer			fPer+CaSi-Prv		
Average of	2	3	3	3	3	3	3	3	2	2
Paragenesis	A	A	A	A	A	A	A	A	A	A
SiO ₂	0.12		0.06	0.10	0.11	0.25	0.20		0.13	
Al ₂ O ₃		0.08	0.13	0.10		0.08	0.06	0.18	0.20	0.17
Cr ₂ O ₃					0.35	0.22	0.33	1.30	1.27	1.24
FeO	53.97	57.35	59.38	59.28	38.37	18.00	37.05	64.97	58.39	65.09
MnO	0.23	0.18	0.20	0.19	0.34	0.16	0.30	1.46	1.35	1.33
NiO	0.24	0.30	0.22	0.15	1.01	0.92	0.97	0.13	0.11	0.12
MgO	46.84	41.39	39.17	41.34	59.77	81.24	60.77	30.35	39.59	30.02
CaO										
Na ₂ O				0.06	0.14		0.73	0.64	0.56	1.20
K ₂ O										
Total	101.40	99.30	99.16	101.22	100.09	100.87	100.41	99.03	101.60	99.17
Mg/(Mg + Fe)	0.61	0.56	0.54	0.55	0.74	0.89	0.75	0.45	0.55	0.45

Sample	4-3B	4-3J	4-3Q	4-3R	5-10A	5-10E	6-1B	6-1E	6-2A	6-9A	6-9C
Inclusion Assemblage	fPer+MgSi-Prv+Ol				fPer		fPer		fPer	fPer	
Average of	1	2	1	2	1	2	2	3	2	3	2
Paragenesis	B	B	B	B	A	A	A	A	A	A	A
SiO ₂	0.06	0.14	0.12	0.07	0.14	0.34	0.13	0.08	0.16	0.08	0.11
Al ₂ O ₃	0.11	0.10	0.10	0.08	0.08	0.07	0.22	0.41			
Cr ₂ O ₃	0.83	0.98	1.01	1.18	0.54	0.51	0.44	0.40	0.29	0.25	0.21
FeO	24.21	24.71	26.19	27.57	28.09	28.94	36.95	37.21	44.39	48.03	46.38
MnO	0.22	0.23	0.20	0.23	0.28	0.36	0.40	0.38	0.12	0.12	0.12
NiO	1.28	1.41	1.46	1.26	1.07	1.21	0.91	0.93	0.39	0.26	0.24
MgO	73.29	72.82	68.35	68.98	68.33	67.52	60.93	60.97	56.34	51.35	51.22
CaO											
Na ₂ O	0.49	0.89	0.92	0.57		0.08	0.06	0.23		0.08	
K ₂ O											
Total	100.49	101.28	98.35	99.94	98.53	99.03	100.04	100.61	101.69	100.17	98.28
Mg/(Mg + Fe)	0.84	0.84	0.82	0.82	0.81	0.81	0.75	0.74	0.69	0.66	0.66

inclusion in diamond found only in Juina (Hutchison 1997), Guaniamo, Venezuela (Sobolev et al. 1998), Sloan, USA (Meyer and McCallum 1986) and several localities on the Siberian platform (Sobolev et al. 1981; Sobolev 1984). Only minerals of eclogitic paragenesis have been found in association with magnetite (Sobolev 1984).

Sulphides (12 grains in three diamonds) are found as dark/black, small (<30 µm), anhedral grains that are heterogeneous in composition (Fig. 6g). Semi-quantitative EPMA of three grains show that they contain Fe, S, Ni (<3.6 wt%), Cu and Co and are similar in composition to eclogitic pyrrhotites reported by Bulanova et al. (1996). Another sulphide grain contains appreciable Ni (~35 wt%) and Co and is similar in composition to peridotitic pentlandite inclusions (Bulanova et al. 1996).

The single Fe inclusion found in this study occurs in association with eclogitic pyrrhotite. Native iron is a rare diamond inclusion and has been reported in peridotitic diamonds from Siberia (Sobolev et al. 1981; Bulanova et al. 1998), Wellington, Australia (Davies et al. 1999b), and in diamonds of an unknown paragenesis from Colorado-Wyoming (Meyer and McCallum 1986).

Perovskite and titanite

Perovskite (CaTiO₃) grains are dark grey/black, 10–80 µm in size and only occur in contact with CaSi-Prv (Fig. 6m, n). SEM analysis shows that all grains also contain Si, Al and Ce. Quantitative chemical data are only available for one of the four perovskite grains identified (Table 3). The perovskite is characterized by: (1) high REE and HFSE contents, (2) the prevalence of Ce over La, and (3) relatively high (1–2 wt%) Al₂O₃ and SiO₂ contents. Such an ambiguous chemical signature is difficult to interpret. The prevalence of Ce over La may suggest a secondary origin related to kimberlite fluids (Kopylova et al. 1997), as Ce enrichment is typical for kimberlitic perovskite (Mitchell and Reed 1988). However, high Al and Si may be indicators of deep (>250 km) perovskites as similarly elevated contents of these elements were found in perovskite associated with majoritic garnet (Kaminsky et al. 2001), which is only stable at 250 to ~700 km depths. The ubiquitous association of perovskite with CaSi-Prv in this study suggests an even deeper (>580 km) origin from a retrograde reaction involving CaSi-Prv. Experiments have shown that perovskite at these depths forms a complete solid solution with CaSi-Prv (Kubo et al. 1997), while at lower pressures and temperature Ca and Ti are accommodated in majorite and clinopyroxene (Ringwood 1991; Canil 1994). Ca(Si,Ti)O₃ perovskite breaks down into CaTiO₃ perovskite and CaSiO₃ wollastonite below ~9 GPa (280 km) (Kubo et al. 1997). We propose that composite grains of perovskite + CaSi-Prv resulted from a breakdown of the CaTiO₃-CaSiO₃ solid solution upon ascent.

Two small (~20 µm) grains of titanite (CaTiSiO₄) were recovered from one diamond that also contained inclusions of CaSi-Prv. There are no quantitative chemical data for these inclusions. They may be primary, or represent a retrograde product from the breakdown of CaSi-Prv to larnite and titanite (Joswig et al. 1999) in the transition zone during exhumation. Titanite was recovered from another Juina diamond by Kaminsky et al. (2001).

Discussion

Origin of ferropericlasite

Correlation of fPer composition with the presence or absence of 'olivine' is the key pattern providing an insight into the formation and origin of fPer. Ferropericlasite released from diamonds containing 'olivine' tends to be more Mg-rich (Fig. 7). When plotted in $X\text{Fe}^{2+}_{\text{fPer}} - X\text{Fe}^{2+}_{\text{MgSi-Prv}}$ space these Mg-rich fPer grains lie close to the regression line determined from experimentally equilibrated fPer and MgSi-Prv at $P=240\text{--}300$ Kb (Fig. 8). Eight out of 11 pairs of fPer and MgSi-Prv found in lower mantle diamonds plot on the line (McCammon et al. 2004b) that defines the distribution coefficient $K_D\text{Fe}^{2+} = (\text{Fe}^{2+}\#\text{Pv}\cdot\text{Mg}\#\text{fPer}) / (\text{Fe}^{2+}\#\text{fPer}\cdot\text{Mg}\#\text{Pv}) = 0.28 \pm 0.14$. The Rio Soriso data

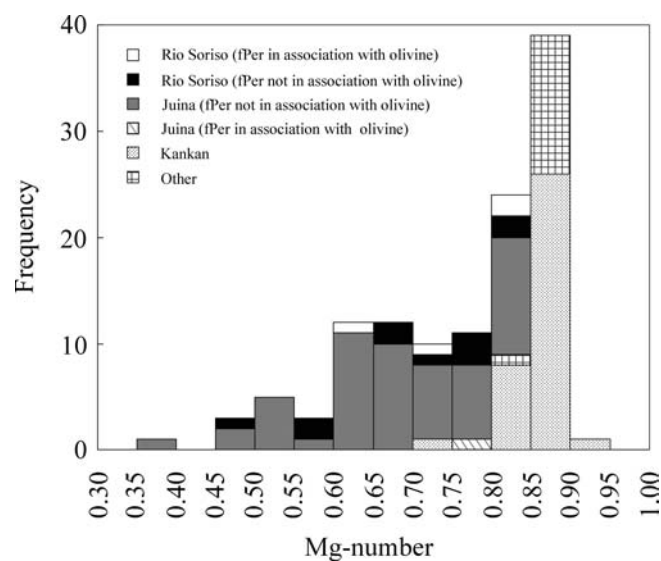


Fig. 7 Histogram of Mg-number ($\text{Mg}\# = \text{Mg}/(\text{Mg} + \text{Fe}_{\text{TOT}})$, moles) for fPer inclusions in diamond. The data for: Juina are from Hutchison (1997), Kaminsky et al. (2001) and this study; Kankan are from Hutchison (1997) and Stachel et al. (2000) and; Other are from Scott-Smith et al. (1984), Otter and Gurney (1989), Kopylova et al. (1997), Stachel et al. (1998), McDade and Harris (1999), Davies et al. (1999) and Kaminsky et al. (2000). The Mg-number represents an average of all fPer analyses for diamonds containing more than one fPer grain

suggest the distribution coefficient $K_D\text{Fe}^{2+} = 0.16\text{--}0.25$ ¹ for grains at reduced conditions, and 0.20–0.31 for grains at higher oxygen fugacities ($f\text{O}_2$). Mg-rich fPer grains from Rio Soriso have clearly equilibrated with MgSi-Prv in uppermost lower mantle.

Ferropericlase in ‘olivine’-free diamonds tends to be richer in Fe ($\text{Mg}\# = 0.45\text{--}0.66$, Fig. 7) and in some cases, is so Fe-rich that the grains, by definition, are magnesio-wustite. Similarly Fe-rich fPer is also found in one diamond (3–5) with ‘olivine’ and MgSi-Prv; unfortunately, only semi-quantitative analyses are available for these inclusions. The analyses suggest that the extreme Fe-enrichment in fPer is not matched by a respective Fe enrichment in coexisting MgSi-Prv. These fPer-MgSi-Prv pairs plot to the left of the experimental regression line of Fig. 8, having much lower distribution coefficients $K_D\text{Fe}^{2+}$ (0.04–0.12 for reduced conditions, and 0.05–0.15 at oxidized conditions, eTable 2). Ferropericlase similarly enriched in Fe relative to coexisting MgSi-Prv was previously reported from other locations in Juina (Harte et al. 1999; Kaminsky et al. 2001).

Several explanations can account for high-Fe character of fPer from Juina. The grains can be metasomatically enriched in Fe and thus be out of equilibrium with their source rocks. Another model ascribes low and highly variable $\text{Mg}\#$'s of fPer to its genesis in a decarbonation reaction in the lower mantle (Liu 2002). This reaction produces diamond and fPer by reduction of the Fe-rich end-member of magnesite ((Mg,Fe) CO_3). In this model, fPer is not in equilibrium with MgSi-Prv or any other lower mantle phases, but attained its wide range of compositions through a repeated decarbonation with increasing pressure (Liu 2002). The third explanation for the Fe-rich character of fPer is by contamination of lower mantle with core material at the D'' layer at the core–mantle boundary (Harte et al. 1999). There is also a possibility that the fPer could be equilibrated with MgSi-Prv in the lowermost mantle at depths greater than 1,700 km, where a transition from high-spin to low-spin state of Fe in fPer depletes MgSi-Prv of its Fe and concentrates Fe in fPer (Badro et al. 2003, 2004). Finally, fPer may have originally been in equilibrium with post-perovskite (Murakami et al. 2004a) at $P > 115$ GPa. The distribution of Fe significantly changes at the post-perovskite phase transition, and iron partitions predominantly into ferropericlase (Murakami et al. 2004b).

We cannot accept the former two models. Secondary Fe enrichment of fPer or its origin as a by-product of a decarbonation reaction does not explain why Fe-rich

fPer preferentially occurs in grains not associated with ‘olivine’. Also, the decarbonation reaction requires very high temperatures incompatible with the mantle adiabat (Isshiki et al. 2004). And furthermore, magnesite is stable only in rare oxidized regions of the lower mantle and converts to diamond in the more common ultramafic lower mantle (Luth 1999). Further experiments on the stability of magnesite in an ultramafic system at $f\text{O}_2$ of the lower mantle (between IW and Re- ReO_2 buffers, McCammon et al. 2004b) are needed to test the decarbonation model.

Both preferred models advocate the origin of Fe-rich fPer in the lowermost mantle. A significant contamination of the lower mantle with core Fe would result in a simultaneous increase of Fe content in MgSi-Prv and fPer. This is observed in diamond 1–5, but not in diamond 3–5 (eTable 2). However, the assumed core contamination of the D'' layer is no longer required to explain the Fe-rich character of fPer after recent high- P high- T experiments demonstrated that the lower part of the lower mantle (1,700–2,900 km's) may have a different mineralogy as compared to its upper portion. The end result of the changes in electronic and crystal structures of the lower mantle minerals is enrichment of ferropericlase in Fe (Badro et al. 2003; Murakami et al. 2004b). If this is true, then the Juina area is unique in sampling lower mantle material from below 1,700 km.

Relative proportions of fPer, MgSi-Prv and CaSi-Prv inclusions

The observed ratio of fPer/MgSi-Prv/CaSi-Prv (68/10/22) is not in agreement with the predicted ratio for these minerals in the lower mantle of pyrolite or mafic composition (Fig. 5). The disproportional abundance of fPer in Rio Soriso diamonds is not representative of the lower mantle assemblage and can be explained in two ways. Diamond may preferentially nucleate on and include fPer (Liu 2002; Davies, personal communication), in the same way that they are selectively associated with sulphides in the upper mantle (Bulanova 1995). Alternatively, diamonds with fPer may preferentially survive over diamonds with other lower mantle inclusions. The survival of diamond is controlled by internal diamond stress caused by the different volume changes of inclusions and their diamond hosts on ascent, and by the absence or presence of polymorph transformations within the crystal lattice of diamond inclusions.

The relative expansion of inclusions in diamond is quantified by the pressure preservation index (PPI) and is a function of the P – T path diamond takes during exhumation (Barron 2003). The model predicts that diamonds that include fPer in the lower mantle (230 Kb and 1,400–1,500°C) should contain ~80 Kb of remnant pressure at surface (Barron 2003). MgSi-Prv, on the contrary, expands less than diamond on a similar P – T path and would form a pressure cavity

¹Coefficients $X\text{Fe}^{2+}$ were estimated (eTable 2) taking into account content of Fe^{3+} in fPer and MgSi-Prv (McCammon et al. 2004a). Ferric iron estimates in fPer depend on oxygen fugacity (McCammon et al. 2004a) and vary from negligible at reduced conditions to 0.03–0.08 cations per formula units (cpfu) at oxidizing conditions (eTable 2). In contrast, Fe^{3+} estimates in MgSi-Prv depend only on Al_2O_3 content (McCammon et al. 2004a). Al-rich MgSi-perovskite of Rio Soriso contains 0.02–0.03 Fe^{3+} (cpfu) (eTable 2).

Table 3 Averaged microprobe analyses of other inclusions in Rio Soriso diamonds (wt%)

Mineral	Magnetite	Magnetite	MgSi-Prv	TAPP	MgSi-Prv	'Olivine'	Magnetite	Magnetite	CaSi-Prv	CaTiO ₃	CaSi-Prv	CaSi-Prv
Sample	1-4I	1-4K	1-5A1	1-5A2	1-5J1	1-5J2	2-6B	2-6K	2-8L1	2-8L2 ^b	3-1A	3-1E
Inclusion Assemblage	fPer+MgSi-Prv+Ol+TAPP								CaSi-Prv+CaTiO ₃		CaSi-Prv+fPer	
Average of Paragenesis	3 D	2 D	3 B	3 B	3 B	2 B	1 D	4 D	3 C	3 C	3 A	3 A
SiO ₂	0.16	0.16	57.31	39.99	54.92	38.03	0.17	0.28	52.59	2.06	50.31	52.11
TiO ₂	1.50	2.36	0.16	4.71	0.17	0.05	3.61	2.97	0.07	52.41		0.21
Al ₂ O ₃	5.56	4.75	1.91	19.03	2.22	0.12	6.92	3.44		1.48		0.21
Cr ₂ O ₃			0.21	2.74	0.20		3.03	2.10				
FeO	28.33	30.80	6.34	6.87	6.15	10.24	29.48	30.16	0.42	0.17		0.28
Fe ₂ O ₃ ^a	60.11	58.21					51.74	56.91				
MnO	0.61	0.58	0.13	0.14	0.13	0.12	0.62	0.53				0.29
NiO												
MgO	2.85	1.46	33.91	25.75	35.68	48.46	3.58	2.04			0.12	0.08
CaO		0.15	0.06	0.04	0.04				46.61	38.78	47.94	45.50
Na ₂ O								0.11	0.16			0.10
K ₂ O									0.14		0.04	
Total	99.13	98.46	100.03	99.26	99.51	97.02	99.15	98.53	99.98	98.67	98.42	98.79
Mg/(Mg+Fe)			0.91	0.87	0.91	0.89						

Mineral	MgSi-Prv	CaSi-Prv	'Olivine'	CaSi-Prv	MgSi-Prv	'Olivine'	MgSi-Prv	MgSi-Prv	CaSi-Prv	Garnet	CaSi-Prv	CaSi-Prv
Sample	3-2II	3-2L	3-2S	3-4E	3-5G1+Q ^e	4-3C	4-3D	4-3E	4-7E	4-10A	4-10G	7-1A
Inclusion Assemblage	CaSi-Prv+fPer+MgSi-Prv+Ol			CaSi-Prv + titanite	fPer+MgSi-Prv+Ol	fPer+MgSi-Prv+Ol			CaSi-Prv+Garnet			
Average of Paragenesis	2 B	3 B	3 B	4 C	2 A	2 B	3 B	2 B	2 C	4 E	1 C	3 C
SiO ₂	58.19	52.18	39.42	49.15	55.7	42.74	55.36	56.73	52.40	40.04	52.05	51.91
TiO ₂	0.20			2.13	0.1	0.07	0.21	0.21		0.92	0.10	
Al ₂ O ₃	1.60			0.26	3.1	0.80	2.54	2.36		21.52		
Cr ₂ O ₃	0.22				0.2		0.20	0.20				
FeO	4.21		11.15		6.6	4.61	4.29	4.25	0.12	17.15	1.14	0.08
Fe ₂ O ₃ ^a												
MnO	0.14		0.12		0.3	0.15	0.10	0.10		0.32	0.17	
NiO			0.31									
MgO	33.43	0.05	48.85	0.05	33.2	51.96	36.30	34.41		10.39	0.35	
CaO	0.04	46.97	0.07	47.15					47.74	8.87	46.32	47.94
Na ₂ O		0.09					0.07	0.08		0.17	0.48	
K ₂ O											0.08	
Total	98.01	99.30	99.93	98.74	99.3	100.33	99.08	98.35	100.27	99.38	100.69	99.93
Mg/(Mg+Fe)	0.93		0.89		0.92	0.95	0.94	0.94		0.52		

^a Fe₂O₃ from stoichiometry^b Grain also contains Ce₂O₃ (1.33 wt%), La₂O₃ (0.49 wt%), Y₂O₃ (0.13 wt%), ZrO₂ (0.60 wt%), Pr₂O₃ (0.29 wt%), Nd₂O₃ (0.72 wt%) and Gd₂O₃ (0.21 wt%)^c Analysis represents an average of two inclusions and has a higher analytical uncertainty

Blank entries, below detection limit

Abbreviations for minerals in Inclusion Assemblage and subgroups in Paragenesis are listed in text

thus enabling the inclusion to invert to lower P – T polymorphs. This prediction is supported by studies on lower mantle diamonds as no (Mg,Fe)SiO₃ inclusion occurring in association with fPer has ever been found with the perovskite structure (Kaminsky et al. 2001; Hutchison et al. 2001). This model does not explain the observed ratio of fPer to MgSi-Prv inclusions as fPer is the only inclusion that could exert pressure on the host and thus have the potential to shatter diamond.

The preferential survival of diamonds with fPer may be partly controlled by the absence of its lattice transformation over P = 0–250 Kb. In contrast, (Mg,Fe)SiO₃ has to convert from high-pressure to low-pressure polymorphs at least five times during ascent from lower mantle depths, incrementally increasing its volume by 22% (Fei and Bertka 1999; Chopelas 1999). The structural changes that CaSiO₃ experience over the same P – T path would result in a 33% volume increase (Varghese and Dubrovinsky 1997) in three major steps. The gradual rather than sudden changes in the internal pressure in diamonds hosting fPer may be the main factor ensuring their survival.

Diamond subpopulations

Thirty two of the Rio Soriso diamonds are divided into six paragenetic subgroups based on several of the following characteristics: mineral inclusion data, N content and aggregation, diamond morphology, body colour, FL, CL, and internal structure (Fig. 5, eTable3). The six paragenetic subgroups are:

- Ultramafic diamonds from the lower mantle from depths > 660 km (12 diamonds)
- Ultramafic diamonds from ~660 km depth (3 diamonds)
- Diamonds from depths > 580 km (6 diamonds)
- Non-ultramafic diamonds from unknown depths (3 diamonds)
- Eclogitic upper mantle diamonds from depths < 410 km (4 diamonds)
- Peridotitic upper mantle diamonds from depths < 410 km (3 diamonds)

The remaining 37 diamonds are either Type II or Type IaB (20–335 ppm N) and likely belong to one of the deep subgroups (A, B and/or C) as their N charac-

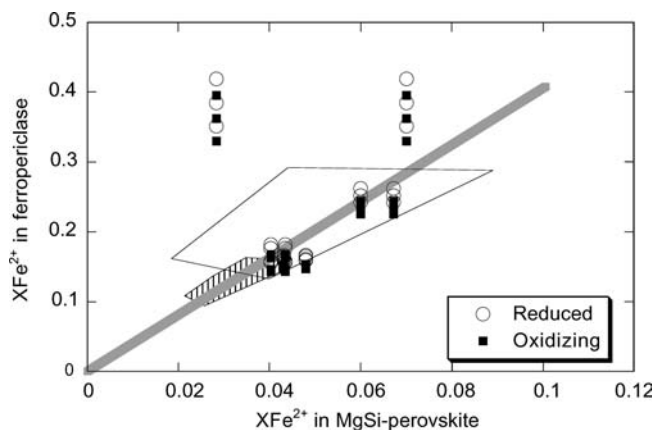


Fig. 8 Fe^{2+} —Mg partitioning between coexisting MgSi-perovskite—fPer inclusions in diamond. Rio Soriso Fe^{2+} -numbers $\text{Fe}^{2+}\# = \text{Fe}^{2+} / (\text{Fe}^{2+} + \text{Mg})$ are estimated using Eqs. 1 and 2 of McCammon et al. (2004a). $\text{Fe}^{2+}\#$ for fPer are calculated for two extreme redox states: reduced, close to IW buffer (open dot) and oxidizing, close to Re-ReO₂ buffer (solid square). Patterned field shows data from Kankan and Koffiefontein inclusions, open field represents data from Sao Luiz (Juina) inclusions (McCammon et al. 2004b). The thick line indicates the best fit regression line determined from experimental data at pressures and temperatures equivalent to those near the top of the lower mantle and at $\text{Mg}\# > 0.75$ (McCammon et al. 2004a)

teristics are similar to those for all other deep diamond populations (e.g. Harte and Harris 1994; Hutchison et al. 1999; Kaminsky et al. 2001; Davies et al. 1999a). All but two diamonds with multiple inclusions contain equilibrium assemblages of minerals and can be unambiguously assigned to a paragenetic subgroup. Multiple growth events, evident from examination of internal structures, can explain incompatible mineral inclusions.

Ultramafic diamonds from the lower mantle (> 660 km)

Diamonds are classified into the lower mantle subgroup based on the presence of fPer (that tends to be Fe enriched) in the absence of primary ‘olivine’. One diamond (No. 3–5) contains Fe-rich fPer ($\text{Mg}\# = 0.65$) and is classified to this subgroup even though the diamond includes ‘olivine’ (Fig. 5l), which must have either a retrograde origin (from the reaction $\text{fPer} + \text{MgSi-Prv}$) or been trapped later at a shallower depth. Four diamonds in this subgroup also contain CaSi-Prv. Diamonds are more resorbed (resorption categories 1 or 2) than in any other subgroup, occurring as tetrahedra and dodecahedra. Plastic deformation laminations are observed on half of the diamonds, which is significantly higher than the percentage observed on the population as a whole. All diamonds in this subgroup have weak blue FL colours. Diamonds are either Type II or IaB, similar to all ferropericlase-bearing diamonds from other studies (e.g. Hutchison et al. 1999; Davies et al. 1999a; Stachel et al. 2000; Kaminsky et al. 2001), with nitrogen concentrations ranging from 0 ppm to 400 ppm N (average of 60 ppm N). Fully aggregated

nitrogen (Type IaB) is an indicator of high mantle residence temperatures and/or long mantle residence times. Using the N-aggregation thermo-chronometer (Taylor et al. 1990), our calculations show that 95% of A centres are converted to B centres in less than 10 Ma for a diamond residing at ~410 km depths. This conversion would occur even quicker in deformed diamonds (Evans 1992) and at greater depths.

Ultramafic diamonds from ~660 km

Three diamonds are grouped here based on the distribution of Fe^{2+} and Mg between fPer and MgSi-Prv characteristic of the uppermost lower mantle. Diamonds also contain ‘olivine’, which is only in equilibrium with fPer and MgSi-Prv at a narrow depth range straddling the upper mantle/lower mantle boundary. Most ‘olivine’ grains have $\text{Mg}\# = 0.89$, compatible with the experimentally determined $\text{Mg}\#$ of γ -olivine at the 660 km discontinuity (Irifune 1994). Two diamonds also contain TAPP and one contains CaSi-Prv. Diamonds are Type IaB, with N concentrations ranging from 32 ppm to 211 ppm. Diamonds fluoresce blue and are generally well resorbed broken crystals.

Diamonds from > 580 km

Six diamonds have been included in this subgroup based on the presence of CaSi-Prv inclusions in the absence of fPer and MgSi-Prv. The diamonds must have formed deeper than 580 km since at this depth CaSi-Prv becomes part of the deep mantle assemblage (Fig. 5). The observed high abundance of CaSi-Prv, not matched by respective occurrences of other minerals from the transition zone and the lower mantle, is enigmatic and unlikely to occur by chance alone. The absence of MgSi-Prv may be ascribed to diamond crystallisation at 580–660 km depths where MgSi-Prv is not stable, but this hypothesis fails to explain the absence of majorite. The inclusion data do not allow for constraints on bulk composition of the diamondiferous rocks; the diamonds could belong to either mafic or ultramafic paragenesis. CaTi-Prv is found in two diamonds in this subgroup. Diamonds are Type II or IaB with nitrogen concentrations less than 225 ppm. They exhibit a variety of FL and CL colours and tend to show moderate signs of resorption and are generally broken crystals.

Non-ultramafic diamonds of unknown depth

Three diamonds are assigned to this subgroup based on the presence of magnetite inclusions. Magnetite is absent in cratonic peridotite, but occurs in more silicic rocks, including cratonic eclogite (Pearson et al. 2003). All three diamonds are Type IaB, two of which contain unusually high concentrations of nitrogen for this study (233 and 541 ppm N). Diamonds have intense blue and turquoise FL and CL colours, which is likely a reflection

of the higher N concentrations of these stones. The growth mechanism of diamonds belonging to this subgroup might differ from the rest of the subgroups as the only diamond with sectoral zoning of N (Fig. 4b), interpreted as indicating cubo-octahedral growth, belongs to this paragenesis. Cubo-octahedral growth suggests lower crystallization temperatures than those of octahedral diamonds (Clausing 1997), which comprise the bulk of the Rio Soriso suite. Thus, the diamonds may record a distinct temperature path from lower crystallization temperatures to higher temperatures necessary to fully aggregate N in diamond. The origin of diamonds in subducted oceanic crust can account for the non-ultramafic bulk composition of their protolith and the recorded thermal evolution.

Eclogitic upper mantle diamonds

Three diamonds are classified to the upper mantle eclogitic paragenesis based on the presence of eclogitic, non-majoritic garnet and low-Ni pyrrhotite. One diamond (No. 4–10) containing garnet also hosts CaSi-Prv, which cannot be in equilibrium in the eclogitic assemblage. A fourth grain is tentatively included based on similarities in diamond type, FL (strong blue), CL (turquoise to blue) and crystal form. The eclogitic diamonds tend to be less resorbed than lower mantle diamonds, but more resorbed than peridotitic diamonds of Subgroup F.

There is excellent agreement between mineral inclusion chemistry and diamond Type (IaA and IaAB) as both lines of evidence suggest an upper mantle origin. All four diamonds contain some nitrogen in the form of A centres, which are unlikely to be preserved in diamonds from depths >410 km. As well, diamonds from lithospheric sources with only B centres are relatively rare (Kaminsky and Khachatryan 2001).

Upper mantle xenoliths recovered from Juina kimberlites (Costa et al. 2003) are a possible source rock for the eclogitic diamonds in this paragenetic group. Our calculations show that the aggregation state and nitrogen concentration of the individual diamonds are consistent with temperatures (712–941°C and 1,182–1,287°C) and mantle residence times (1,648 and 1,593 Ma) constrained by two types of eclogite xenoliths (Costa et al. 2003).

Peridotitic upper mantle diamonds

Two diamonds are assigned to the upper mantle peridotitic paragenesis based on the presence of ‘olivine’ in the absence of fPer. One diamond also contains (Mg,Fe)SiO₃ that we interpret as orthopyroxene. The diamonds (Types IaAB and IaB) have many shared characteristics and are different in several respects from the majority of the population, the most striking difference being the bright green CL colour. Based on the green CL colour and lower aggregation state (~75% B

centres), a third diamond is tentatively assigned to this paragenesis, although it contains no inclusions. Diamonds are generally intact and crystals tend not to be very resorbed. Peridotitic xenoliths provide temperature (856–1,361°C) and time (1,114–1,242 Ma) constraints (Costa et al. 2003) that are consistent with the nitrogen contents and aggregation states for two diamonds.

Plume origin of Rio Soriso diamonds

The discovery of several subpopulations in a diamond suite is typical for most studies. Most diamond suites, however, sample diamond populations sourced from only within the cratonic root (~150–250 km), whereas the diamonds in this study are interpreted as having origins spanning depths from ~150 km to >1,700 km. Certainly an explanation is required on how material from such markedly different depths could be brought to the surface.

The simplest explanation invokes entrainment in a mantle plume as it rises from depths within the lower mantle to the base of the craton. This model has been proposed by several authors to explain the occurrence of fPer as an inclusion in diamond (e.g. Hutchison 1997; Griffin et al. 1999; Kaminsky et al. 2001). Plumes that originated at the core–mantle boundary and affect large areas on the surface are called “superplumes” (Larson 1991; Haggerty 1994). The main evidence for a link between the outer core and the generation and eruption of magma is the restriction of magmatic events to time intervals where no reversals of Earth’s polarity are observed. The age of Juina kimberlites places them in the middle of the 80–120 Ma no-reversal period (Haggerty 1994). It is suggested that the Rio Soriso diamonds were brought up into the upper mantle in an ascending plume in the mid-Cretaceous and were subsequently entrained in a kimberlitic magma generated from this plume and brought to shallow crustal levels. The global restriction of Fe-rich ferropericlasite to Juina indicates that this plume and the ascending melts generated from this plume were unique in sampling lower mantle materials from depths >1,700 km. Moreover, a possible equilibration of Fe-rich fPer with post-perovskite at the core–mantle boundary (Murakami et al. 2004b) may further support an ultra-deep origin for plumes and kimberlites. Recent studies of Nd–Hf isotopic compositions of kimberlites indicate that they may have origins in the transition zone or at the core–mantle boundary (Nowell et al. 2004).

Conclusions

1. Most Rio Soriso diamonds are strongly resorbed monocrystals that are colourless, grey or yellow. The majority of diamonds show blue and turquoise fluorescence and cathodoluminescence. There is a strong correlation between diamond body colour

and FL colour in Rio Soriso diamonds. Brown and yellow diamonds are more likely to fluoresce in various shades of turquoise and green. Most diamonds are Type IaB with low concentrations of N and degraded platelets, but there is also a large proportion of stones that contain no detectable N. Nitrogen content correlates positively with IR-active hydrogen concentrations in Rio Soriso diamonds. Rio Soriso diamonds and their inclusions are similar to other Juina area diamond suites in many aspects.

2. The examined suite of Rio Soriso diamonds contains several subpopulations of diamonds that originated in the upper and lower mantle, from ~ 150 to $> 1,700$ km depths. The subpopulations show distinct mineral inclusions, N contents and aggregations, morphologies, FL, CL, and internal structures. The large depth interval sampled by the Rio Soriso diamonds is explained by their ascent in a plume formed at the core–mantle boundary.
3. Rio Soriso ferropericlasite enriched in Fe cannot be a product of a metasomatic or decarbonation reaction. An association of Fe-rich fPer with ‘olivine’-free diamonds and a lower $K_D\text{Fe}^{2+}$ between fPer and MgSi-Prv suggests an origin in the lowermost mantle, possibly from depths $> 1,700$ km. A preferential survival of diamonds with fPer over diamonds with other lower mantle inclusions may be partly controlled by the absence of fPer lattice transformation upon ascent.

Acknowledgments The authors are grateful to Diagem International Resource Corporation and personally to David Cohen for permission to publish. Mati Raudsepp is thanked for his help with the electron microprobe and Andrea De Stefano is thanked for doing SEM-CL on several diamonds and for help in interpreting the data. Reviews by R. Davies and N. Tomioka improved the manuscript immensely. Funding for this project was provided by an NSERC research grant to MGK.

References

- Araujo DP, Gaspar JC, Yingwei F, Hauri EH, Hemley R, Bulanova G (2003) Mineralogy of diamonds from the Juina province, Brazil. In: Extended abstracts, VIIIth International Kimberlite Conference, Victoria, Canada
- Badro J, Fiquet G, Guyot F, Rueff JP, Struzhkin VV, Vanko G, Monaco G (2003) Iron partitioning in Earth's mantle: toward a deep lower mantle discontinuity. *Science* 300:789–791
- Badro J, Fiquet G, Guyot F (2004) Electronic transitions in (Mg, Fe)SiO₃ perovskite and post-perovskite phases: implications for deep Earth dynamics. *Eos Trans AGU*, 85(47), Fall Meet Suppl MR22A-03
- Barron LM (2003) A simple model for the pressure preservation index of inclusions in diamond. *Am Mineral* 88:1615–1619
- Boyd SR, Kiflawi I, Woods GS (1994) The relationship between infrared absorption and the A defect concentration in diamond. *Philos Mag B* 69:1149–1153
- Boyd SR, Kiflawi I, Woods GS (1995) Infrared absorption by the B nitrogen aggregate in diamond. *Philos Mag B* 72:351–361
- Brenker F, Stachel T, Harris JW (2002) Exhumation of lower mantle inclusions in diamond: ATEM investigation of retrograde phase transitions, reactions and exsolution. *Earth Planet Sci Lett* 198:1–9
- Bulanova GP (1995) The formation of diamond. *J Geochem Explor* 53:1–23
- Bulanova GP, Griffin WL, Ryan CG, Shestakova OY, Barnes SJ (1996) Trace elements in sulfide inclusions from Yakutia diamonds. *Contrib Mineral Petrol* 124:111–125
- Bulanova GP, Griffin WL, Ryan CG (1998) Nucleation environment of diamonds from Yakutian kimberlites. *Mineral Mag* 62:409–419
- Canil D (1994) Stability of clinopyroxene at pressure-temperature conditions of the transition zone. *Phys Earth Planet Int* 86:25–34
- Chopelas A (1999) Estimates of mantle relevant Clapeyron slopes in the MgSiO₃ system from high-pressure spectroscopic data. *Am Mineral* 84:233–244
- Clark CD, Davey ST (1984) One-phonon absorption in diamond. *J Phys C Solid State* 17:1127–1140
- Clausing RE (1997) Diamond morphology. In: Prelas MA, Popovici G, Bigelow LK (eds) *Handbook of industrial diamonds and diamond films*, Marcel Dekker, New York, pp 19–48
- Collins AT, Mohammed K (1982) Optical studies of vibronic bands in yellow luminescing natural diamonds. *J Phys C Solid State* 15:147–158
- Costa VS, Gaspar JC, Pimentel MM (2003) Peridotite and eclogite xenoliths from the Juina kimberlite province, Brazil. In: Extended abstracts, Proceedings of the VIIIth International Kimberlite Conference, Victoria, Canada
- Davies RM (1998) The characteristics and origins of alluvial diamonds from Eastern Australia. PhD thesis, Macquarie University
- Davies RM, Griffin WL, Pearson NJ, Andrew AS, Doyle BJ, O'Reilly SY (1999a) Diamonds from the deep: pipe DO-27, Slave craton, Canada. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) *The JB Dawson volume*, Proceedings of the VIIth international kimberlite conference, Red Rood Design, Cape Town, pp 148–155
- Davies RM, O'Reilly SY, Griffin WL (1999b) Diamonds from Wellington, NSW, insights into the origin of eastern Australian diamonds. *Mineral Mag* 63:447–471
- DeVries RC (1975) Plastic deformation and “work-hardening” of diamond. *Mater Res Bull* 10:1193–1200
- Evans T (1992) Aggregation of nitrogen in diamond. In: Field JE (ed) *The properties of natural and synthetic diamond*. Academic, London, pp 259–290
- Fei Y, Bertka CM (1999) Phase transitions in the Earth's mantle and mantle mineralogy. In: Fei Y, Bertka CM, Mysen BO (eds) *Mantle petrology: field observations and high-pressure experimentation: a tribute to Francis R (Joe) Boyd*. *Geochem Soc Spec Publ* 6, USA, pp 189–207
- Griffin WL, Doyle BJ, Ryan CG, Pearson NJ, O'Reilly SY, Natapov L, Kivi K, Kretschmar U, Ward J (1999) Lithospheric structure and mantle terranes: Slave craton, Canada. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) *The JB Dawson volume*, Proceedings of the VIIth International Kimberlite Conference, Red Rood Design, Cape Town, pp 299–360
- Haggerty SE (1994) Superkimberlites: a geodynamic diamond window to the Earth's core. *Earth Planet Sci Lett* 122:57–69
- Harris JW, Hutchison MT, Hursthouse M, Light M, Harte B (1997) A new tetragonal silicate mineral occurring as inclusions in lower-mantle diamonds. *Nature* 387:486–488
- Harte B, Harris JW (1994) Lower mantle mineral associations preserved in diamonds. *Mineral Mag* 58A:384–385
- Harte B, Harris JW, Hutchison MT, Watt GR, Wilding MC (1999) Lower mantle mineral associations in diamonds from Sao Luiz, Brazil. In: Fei Y, Bertka CM, Mysen BO (eds) *Mantle petrology: field observations and high-pressure experimentation: a tribute to Francis R (Joe) Boyd*. *Geochem Soc Spec Publ* 6, USA, pp 125–153

- Heaman L, Teixeira NA, Gobbo L, Gaspar JC (1998) U-Pb mantle zircon ages for kimberlites from the Juina and Paranatinga provinces, Brazil. In: VIIth International Kimberlite Conference, Extended abstracts, Cape Town, pp 322–324
- Hutchison MT (1997) Constitution of the deep transition zone and lower mantle shown by diamonds and their inclusions. PhD Thesis, University of Edinburgh
- Hutchison MT, Cartigny P, Harris JW (1999) Carbon and nitrogen compositions and physical characteristics of transition zone and lower mantle diamonds from Sao Luiz, Brazil. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) The JB Dawson volume, Proceedings of the VIIth International Kimberlite Conference, Red Rood Design, Cape Town, pp 372–382
- Hutchison MT, Hursthouse MB, Light ME (2001) Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity. *Contrib Mineral Petrol* 142: 119–126
- Irifune T (1994) Absence of an aluminous phase in the upper part of the Earth's lower mantle. *Nature* 370:131–133
- Irifune T, Koizumi T, Ando JI (1996) An experimental study on the garnet-perovskite transformation in the system $\text{MgSiO}_3\text{--Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. *Phys Earth Planet Int* 96:147–157
- Isshiki M, Irifune T, Hirose K, Ono S, Ohishi Y, Watanuki T, Nishibori E, Takata M, Sakata M (2004) Stability of magnesite and its high-pressure form in the lowermost mantle. *Nature* 427: 60–63
- Joswig W, Stachel T, Harris JW, Baur WH, Brey GP (1999) New Ca-silicate inclusions in diamonds—tracers from the lower mantle. *Earth Planet Sci Lett* 173:1–6
- Kaminsky FV, Khachatryan GK (2001) Characteristics of nitrogen and other impurities in diamond, as revealed by infrared absorption data. *Can Mineral* 29:1733–1745
- Kaminsky FV, Zakharchenko OD, Griffin WL, Channer DM, DeR, Khachatryan-Bilnova GK (2000) Diamond from the Guaniamo area, Venezuela. *Can Mineral* 38:1347–1370
- Kaminsky FV, Zakharchenko OD, Davies R, Griffin WL, Khachatryan-Bilnova GK, Shiryayev AA (2001) Superdeep diamonds from the Juina area, Mato Grosso State, Brazil. *Contrib Mineral Petrol* 140:734–753
- Kesson SE, Fitz Gerald JD (1991) Partitioning of MgO, FeO, NiO, MnO and Cr_2O_3 between magnesian silicate perovskite and magnesiowustite: implications for the origin of inclusions in diamond and the composition of the lower mantle. *Earth Planet Sci Lett* 111:229–240
- Kesson SE, Fitz Gerald JD, Shelley JMG, Withers RL (1995) Phase relations, structure and crystal chemistry of some aluminous silicate perovskites. *Earth Planet Sci Lett* 134:187–201
- Kopylova MG, Gurney JJ, Daniels LRM (1997) Mineral inclusions in diamonds from the River Ranch kimberlite, Zimbabwe. *Contrib Mineral Petrol* 129:366–384
- Kubo A, Suzuki T, Akaogi M (1997) High pressure phase equilibria in the system $\text{CaTiO}_3\text{--CaSiO}_3$: stability of perovskite solid solutions. *Phys Chem Mineral* 24:488–494
- Larson RL (1991) Geological consequences of superplumes. *Geology* 19:963–966
- Liu LG (2002) An alternative interpretation of lower mantle mineral associations in diamonds. *Contrib Mineral Petrol* 144:16–21
- Liu LG, Ringwood AE (1975) Synthesis of a perovskite-type polymorph of CaSiO_3 . *Earth Planet Sci Lett* 28:209–211
- Luth RW (1999) Carbon and carbonates in the mantle. In: Fei Y, Bertka CM, Mysen BO (eds) Mantle petrology: field observations and high-pressure experimentation: a tribute to Francis R (Joe) Boyd. *Geochem Soc Spec Publ* 6, USA, pp 297–316
- McCallum ME, Huntley PM, Falk RW, Otter ML (1994) Morphological, resorption and etch feature trends of diamonds from kimberlite populations within Colorado-Wyoming State Line District, USA. In: Meyer HOA, Leonardos OH (eds) Diamonds: characterisation, genesis and exploration. *GPRM Spec. Publ. No 1/B, CPRM, Brasilia*, pp 32–50
- McCammon CA, Lauerbach S, Seifert F, Langenhorst F, van Aken PA (2004a) Iron oxidation state in lower mantle mineral assemblages I. Empirical relations derived from high pressure experiments. *Earth Planet Sci Lett* 222:423–434
- McCammon CA, Stachel T, Harris JW (2004b) Iron oxidation state in lower mantle mineral assemblages II. Inclusions in diamonds from Kankan, Guinea. *Earth Planet Sci Lett* 222:435–449
- McDade P, Harris JW (1999) Synthetic inclusion bearing diamonds from Letseng-la-Terai, Lesotho. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) The PH Nixon volume, Proceedings of the VIIth International Kimberlite Conference, Red Rood Design, Cape Town, pp 557–565
- Meyer HOA (1987) Inclusions in diamonds. In: Nixon PH (ed) Mantle xenoliths, Wiley, Chichester, pp 501–522
- Meyer HOA, McCallum ME (1986) Mineral inclusions in diamonds from the Sloan kimberlites, Colorado. *Geology* 94:600–612
- Mitchell RH, Reed SJ (1988) Ion microprobe determination of rare earth elements in perovskite from kimberlites and alnoites. *Mineral Mag* 52:331–339
- Murakami M, Hirose K, Kawamura K, Sata N, Ohishi Y (2004a) Post-perovskite phase transition in MgSiO_3 . *Science* 304:855–858
- Murakami M, Hirose K, Sata N, Ohishi Y (2004b) Mineralogy of the Earth's lowermost mantle. *Eos Trans AGU*, 85(47), Fall Meet Suppl MR22A-01
- Nowell GW, Pearson DG, Dell DR, Carlson RW, Smith CB, Kempton PD, Noble SR (2004). Hf isotopic systematics of kimberlites and their megacrysts: new constraints on their source regions. *J Petrol* 45:1–29
- Orlov YL (1977) Mineralogy of the diamonds. Wiley, New York
- Otter ML, Gurney JJ (1989) Mineral inclusions in diamonds from the Sloan diatremes of Colorado-Wyoming State line kimberlite district, North America. Kimberlite and related rocks, vol 2. Geological Society of Australia Special Publication No. 14:1042–1053
- Pearson DG, Canil D, Shirey SB (2003) Mantle samples included in volcanic rocks: xenoliths and diamonds. In: Carlson R (ed) Treatise of geochemistry, vol 2. Elsevier, Amsterdam
- Pouchou JL, Pichoir F (1985) “PAP” $\phi(\rho z)$ procedure for improved quantitative microanalysis. In: Armstrong JT (ed) Microbeam analysis 1985, San Francisco Press, USA, pp 104–106
- Pratesi G, Lo Giudice A, Vishnevsky S, Manfredotti C, Cipriani C (2003) Cathodoluminescence investigations on the Popigai, Ries, and Lappajärvi impact diamonds. *Am Mineral* 88:1778–1787
- Ringwood AE (1991) Inaugural ingerson lecture. *Geochim Cosmochim Acta* 55:2083–2110
- Robinson DN (1979) Surface textures and other features of diamonds. PhD thesis, University of Cape Town
- Rondeau B, Fritsch E, Guiraud M, Chalain JP, Notari F (2004) The historical ‘asteriated’ hydrogen-rich diamonds: growth history and sector-dependence impurity incorporation. *Diamond Relat Mater* 13:1658–1673
- Scott-Smith BH, Danchin RV, Harris JW, Stracke KJ (1984) Kimberlites near Orreroo, South Australia. In: Kornprobst J (ed) Kimberlites I: kimberlites and related rocks. Elsevier, Amsterdam, pp 121–142
- Sellschop JPF (1992) Nuclear probes in the study of diamond. In: Field JE (ed) The properties of natural and synthetic diamond, Academic, London, pp 81–179
- Sobolev NV (1984) Kimberlites of the Siberian platform: their geological and mineralogical features. In: Glover JE, Harris PG (eds) Kimberlite occurrence and origin: a basis for conceptual models in exploration, vol 8. Geology Department and University Extension, University of Western Australia, pp 275–287
- Sobolev NV, Yefimova ES, Pospelova LN (1981) Native iron in Yakutian diamonds and its paragenesis. *Geologiya I Geofizika* 12:25–29

- Sobolev NV, Yefimova ES, Channer DMD, Anderson PFN, Barron KM (1998) Unusual upper mantle beneath Guianamo, Guyana Shield, Venezuela; evidence from diamond inclusions. *Geology* 26:971–974
- Stachel T (2001) Diamonds from the asthenosphere and the transition zone. *Eur J Mineral* 13:883–892
- Stachel T, Harris JW, Brey GP (1998) Rare and unusual mineral inclusions in diamonds from Mwadui, Tanzania. *Contrib Mineral Petrol* 132:34–47
- Stachel T, Harris JH, Brey GP, Joswig W (2000) Kankan diamonds (Guinea) II: lower mantle inclusion parageneses. *Contrib Mineral Petrol* 140:16–27
- Stachel T, Harris JH, Aulbauch S, Deines P (2002) Kankan diamonds (Guinea) III: $\delta^{13}\text{C}$ and nitrogen characteristics of deep diamonds. *Contrib Mineral Petrol* 142:465–475
- Tassinari CCG, Macambira MJB (1999) Geochronological provinces of the Amazonian craton. *Episodes* 22:174–182
- Taylor WR, Jacques AL, Ridd M (1990) Nitrogen-defect aggregation characteristics of some Australian diamonds: time-temperature constraints on the source regions of pipe and alluvial diamonds. *Am Mineral* 75:1290–1320
- Titkov SV, Zubin NG, Gorshkov AI, Sivtsov AV, Magazina LO (2003) An investigation into the cause of color in natural black diamonds from Siberia. *Gems Gemol* 39:200–209
- Varghese S, Dubrovinsky LS (1997) Thermodynamic data for the phases in the CaSiO_3 system. *Geochim Cosmochim Acta* 61:1181–1191
- Wilding MC (1991) A study of diamonds with syngenetic inclusions. PhD Thesis, University of Edinburgh
- Woods GS (1986) Platelets and the infrared absorption of type Ia diamonds. *Proc R Soc Lond A* 407:219–238
- Zaitsev AM (2000) Vibronic spectra of impurity-related optical centres in diamond. *Phys Rev B* 61:12909–12922