Mineral inclusions in diamonds track the evolution of a Mesozoic subducted slab beneath West Gondwanaland

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ABSTRACT

Three major suites of silicate inclusions in sublithospheric diamonds show evidence of formation at depths >250 km, and for each suite there is evidence of their formation from subducted material. Two of these are the well known basic (majoritic garnet) and ultrabasic (MgSi-perovskite + ferropericlase) suites. The third, the recently recognised Ca-rich suite, is characterised by carbonate, Ca–Si–Ti minerals and some aluminous material. Carbon isotope ratios in the host diamonds and geochemical–petrological features of the inclusions themselves provide evidence for their derivation from subducted lithosphere materials. The diamonds hosting the basic and ultrabasic suites are suggested to form in fluids/melts resulting from the release of water caused by dehydration reactions affecting both the crustal and mantle portions of a subducting slab of ocean lithosphere. Conversely, the diamonds containing the Ca-rich suite are linked with the formation of carbonatitic melts. In the Juina kimberlite province of Brazil, all three suites have been found in close proximity. A model is presented whereby the formation of the suites occurs progressively during the subduction and stagnation of a single lithospheric slab, with all three suites being transported to the lithosphere by a plume with which the carbonatitic melts of the Ca-rich suite are associated. Nd–Sr isotopic data are presented for the Juina majoritic-garnet inclusions, which supports their formation from oceanic crust of Mesozoic age. In conjunction with published age data for a Ca–Si–Ti inclusion, the Juina (Brazil) sublithospheric inclusions document a series of events involving diamond formation during and following the emplacement of a subducted slab between ca 190 and 90 Ma beneath west Gondwanaland. This slab and related subducted slabs dating from the Palaeozoic at the Gondwanan margin may be the source of the widespread DUPAL geochemical anomaly in the South Atlantic and Indian Oceans. The kimberlites bringing the diamonds to the Earth's surface may have arisen from a superplume, developed from a graveyard of former Gondwanan stagnant slabs, at the Core–Mantle-Boundary.

1. Introduction

The majority of the mineral inclusions found in kimberlitic diamonds indicate their formation in thick continental lithosphere at depths less than 200 km. The potential occurrence of deep diamonds, deriving from much greater depths, was first recognised with the discovery of separate inclusions of $(Mg,Fe)SiO_3$ and $(Mg,Fe)O$ in the same diamond from the Koffiefontein kimberlite, South Africa. Scott-Smith et al. (1984) pointed out that this mineral association potentially represented a mineral assemblage of Mg(Fe)Si-perovskite and ferropericlase, predicted to occur in ultrabasic (peridotitic) rocks in the Lower Mantle in place of minerals of essentially olivine composition, $(Mg,Fe)_2SiO_4$, found in the Upper Mantle. This discovery was closely followed by the report of inclusions in diamonds from the Monastery kimberlite, South Africa, with the composition of majoritic garnet believed to have formed at depths from around 250 to 450 km (Moore and Gurney, 1985, 1989; Moore et al., 1991). The majoritic garnet compositions point to derivation from protoliths of basic igneous (or eclogitic) bulk rock composition; thus the two types of deep inclusions found at this time, represented the ultrabasic and basic compositions generally expected for the Earth's mantle, though the two groups appeared to have restricted and different depths of formation.

During the last 20 years, the recognition of diamonds with inclusions of the $(Mg,Fe)Si$-perovskite + ferropericlase (mPv + fPer) suite and the majoritic garnet suite has extended throughout the world with discoveries particularly seen in the: Juina area, Brazil (Wilding, 1990; Harte and Harris, 1994; Harte et al., 1999; Hutchison et al., 2001; Kaminsky et al., 2001; Hayman et al., 2005); Northwest Territories, Canada (Davies et al., 1999, 2004); Kankan, west Africa

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(Stachel et al., 2000a, 2000b, 2002); Jagersfontein, South Africa (Stachel, 2001; Tappert et al., 2005) and Orroroo, Australia (Tappert et al., 2009). In addition, inclusions of Fe–Mg–(Ti,Cr) oxide minerals from Juina have been attributed to a deep origin (Kaminsky et al., 2001, 2009); as have sets of Ca-rich inclusions, involving both carbonates and Ca–Si–Ti minerals, recently recognised at Kankan (Brenker et al., 2005) and most particularly at Juina (Brenker et al., 2007; Walter et al., 2008; Bulanova et al., 2010). But despite this progressive expansion in the recorded occurrence of deep inclusions, the mineral assemblages indicated have maintained a strong bias to derivation of basic and especially ultrabasic inclusions from particular depth zones, and thus by no means suggestive of random sampling through a section of the Earth's mantle.

Geochemical evidence of the involvement of subducted crustal components in the protoliths of the deep inclusions first arose in the finding of positive and negative Eu anomalies in the REE patterns of some inclusions and the carbon isotope (^{13}C/^{12}C) ratios of some host diamonds (e.g. Harte et al., 1999; Stachel et al., 2000b, 2002, 2005; Tappert et al., 2005). This evidence has been strongly augmented by recent data from the Ca-rich inclusions (Brenker et al., 2007; Bulanova et al., 2010). Harte (2010) also argued that the formation of many deep diamonds was probably triggered by the dehydration of deeply subducted material.

The purpose of this paper is to propose a model whereby the various suites of deep diamonds and inclusions may be formed during the evolution of a slab of oceanic lithosphere subducted to the region of the upper–lower mantle boundary. The evidence provided by the inclusions will be summarised using data from southern hemisphere kimberlite localities, and in particular including the Juina area of Brazil from which the most extensive record of deep diamonds and their inclusions is available. Emphasis will be placed upon the dominant inclusion suites involving silicate minerals because estimates of their depths of formation are available by reference to extensive high P–T experimental data.

The preferred subduction model will then be constrained for the particular case of the Juina inclusions to a time of evolution in the Mesozoic era using existing radiometric dates and previously unpublished Nd–Sr isotopic data presented here for the majoritic garnet inclusions. We believe the Juina model provides an example of a series of subducted slabs that developed along the entire southern (Pacific) margin of Gondwanaland during the Palaeozoic and Mesozoic (Maruyama et al., 2007; Tappert et al., 2009); and it is suggested that this extensive zone of subducted lithosphere may be responsible for the widely developed DUPAL[1] geochemical anomaly (Duprée and Allègre, 1983; Hart, 1984) in basalts of the South Atlantic and Indian Oceans.

2. Suites of silicate minerals in deep diamonds

The nature of the minerals belonging to three sets of inclusions in sublithospheric diamonds is summarised below. The first two have been found worldwide and form the majoritic garnet and MgSi-perovskite + ferropericlase (mPv + fPer) suites, respectively indicating dominantly basic and ultrabasic rock compositions; more detailed reviews of these two suites may also be found in Stachel et al. (2005) and Harte (2010). Recent publications (Brenker et al., 2005, 2007; Walter et al., 2008; Bulanova et al., 2010) make it clear that another complex suite must now be recognised. The third suite, dominated by Ca-rich minerals, has only been extensively documented for diamonds from the Juina province, Brazil; this suite shows evidence of the involvement of carbonatitic melts, but its ultimate source appears

to have been subducted oceanic crust containing carbonated basic and ultrabasic rocks and sediments. Pertinent data on depths of formation and the carbon isotope ratios of the host diamonds for all three suites are summarised in Table 1.

2.1. The majoritic garnet suite of inclusions

Majoritic garnet is characterised by having an excess of Si by comparison with lower-pressure lithospheric garnet; it occurs as a consequence of Si occupying the octahedral as well as the tetrahedral sites in the garnet atomic structure. This expansion in the chemical composition of the garnet means that pyroxene mineral chemical components can be taken into solid solution in garnet, and so with increasing pressure the composition of an eclogite rock (with garnet and clinopyroxene) becomes a single-phase garnet rock (garnetite) near the top of the mantle Transition Zone (e.g. Irifune, 1987; Perillat et al., 2006).

Individual inclusions of the majoritic garnet suite consist either of garnet alone or of garnet together with clinopyroxene. Where clinopyroxene occurs it commonly appears to represent an exsolution product from an original single-phase high-Si majoritic garnet — the exsolution occurring as a result of decompression associated with transport upwards to the lithosphere and Earth's surface (Harte and Cayzer, 2007). A characteristic feature of the inclusions is that their bulk compositions indicate basic (basaltic or eclogitic) bulk compositions rather than ultrabasic ones (Moore and Gurney, 1985; Moore et al., 1991; Harte and Cayzer, 2007). In the southern hemisphere, majoritic garnet is well represented in South African kimberlite locations (Monastery and Jagersfontein), and in Brazil at Juina (Table 1). An approximate assessment of the depth of formation of the inclusions may be made using the Si content of the majoritic garnet (e.g. Akaogi and Akimoto, 1979; Irifune, 1987; Moore et al., 1991; Stachel, 2001; Tappert et al., 2005; Harte, 2010), and estimated depths of 250 to 450 km are common; though at Jagersfontein two inclusions indicate depths around 500 km.

2.2. The MgSi-perovskite + ferropericlase (mPv + fPer) suite of inclusions

The recognition of the mPv + fPer suite of inclusions particularly rests upon the identification of 'associations' of minerals; i.e. the occurrence of separate inclusions of several minerals in the same diamond (Harte et al., 1999; Harte, 2010). This is especially important in the case of the mPv + fPer suite, because the original Lower Mantle minerals have altered to lower pressure phases on decompression. Also the occurrence of ferropericlase alone within a diamond does not unequivocally imply a Lower Mantle origin (Brey et al., 2004; Stachel et al., 2005), and it is for this reason that the group as a whole is referred to as the mPv + fPer suite. Table 1 lists the associations of minerals attributed to this suite at southern hemisphere localities. The depths of formation near the Upper/Lower Mantle boundary and from the uppermost Lower Mantle have been estimated using extensive experimental data (e.g. see summaries: Fei and Bertka, 1999; Perillat et al., 2006; Stixrude and Lithgow-Bertelloni, 2007). However, it should be noted that the depths given in Table 1 are based on an average normal geotherm, with a temperature of ca 1850 K at the Upper/Lower Mantle boundary. In a subducted slab, lower temperatures will slightly depress this boundary to greater depths, whilst the upper boundary of the Transition Zone will occur at shallower depths (e.g. Fukao et al., 2001, 2009; Tagawa et al., 2007).

Nearly all the associations containing ferropericlase and/or mPv Table 1 indicate ultrabasic bulk compositions. It is the breakdown of (Mg,Fe)$_2$SiO$_4$ (ringwoodite) to (Mg,Fe)SiO$_3$ (mPv) and (Mg,Fe)O (fPer) in ultrabasic (peridotite and pyrolite) compositions that defines the boundary between the upper and lower mantle at ca 660 km depth (Fei and Bertka, 1999; Perillat et al., 2006; Stixrude and

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[1] The DUPAL anomaly is named after Duprée and Allègre (1983) who pointed out consistent differences in ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb and ^{87}Sr/^{86}Sr ratios in Indian Ocean and South Atlantic Ocean Island and Ocean Ridge basalts by comparison with values from the North Atlantic and western Pacific.

Table 1
Mineral associations included in diamonds formed at depths >250 km in the southern hemisphere.

Suites and mineral associations[a]	No.[b]	Depth[c] (km)	Diamond[d] $\delta^{13}C$ ‰	Locations[e]	Refs.[f]
Majoritic garnet suite					
Majoritic garnet	43	250–450		Monastery	a, basic
{Majoritic garnet, cpx}	3	250–450		Monastery	a, b
{Majoritic garnet, cpx}	17	250–450	−4.6 to −11.0	Juina (SL)	c, e
Majoritic garnet	12	250–500	−17.2 to −24.0	Jagersfontein	f
Ferropericlase + MgSi-perovskite suite					
fPer + mPv + Mg_2SiO_4	1	ca 660		Juina (RS)	g
fPer + mPv + TAPP + Mg_2SiO_4	1	ca 660		Juina (RS)	g
fPer + mPv + cPv + TAPP + Mg_2SiO_4	1	ca 660		Juina (RS)	g
fPer + mPv	1	660–750	−3.8	Orroroo	h, i
fPer + mPv	1			Koffiefontein	h, j
fPer + mPv	3		−4.1	Juina (SL, RS)	d, e, g
fPer + mPv + TAPP	1	660–750	−4.9	Juina (SL)	d, e
mPv + TAPP	1	660–750	−5.1	Juina (OR)	k
fPer + mPv(Al)	1	>750	−4.9	Juina (SL)	d, e,
fPer + mPv(Al) + crn	1	>750	−5.3	Juina (SL)	e, l
mPv(Al), cPv, CF, NAL	6	>750	−24.1 to −0.9	Juina (5)	p
fPer + SiO_2^3	1	?550–750		Juina(SL, RS)	d
fPer + TAPP	3	?550–750	−5.3, −5.6	Juina (SL)	d,e
fPer + TAPP + Mg_2SiO_4	1	?550–750	−5.3	Juina (SL)	e, l
fper + Mg_2SiO_4	1	?550–750		Juina (OR)	k
fPer + cPv	4	?550–750		Juina (SL, RS)	d, g
fPer + "NaAl-pyroxene"/garnet[e]	1	?550–750	−5.2	Juina (SL)	e, l
TAPP + "NaAl-pyroxene"/garnet	1	?550–750	−4.7	Juina (SL)	e, l
Ca-rich suite					
{$CaSiO_3$, $CaTiO_3$}	2			Juina (RS)	g
{$CaSiO_3$, $CaTiO_3$} + pyrrhotite	1	>300 <600	−14.4 to −13.1	Juina (C)	m
{$CaSiO_3$, $CaTiO_3$} + garnet + pyrrhotite	1	>300 <600	−14.7 to −12.7	Juina (C)	m
$CaSiO_3$ + $CaTiSiO_5$	1			Juina (RS)	g
{$CaSiO_3$, $CaTiSiO_5$}	1		−4.4	Juina (OR)	k
$CaSiO_3$ + ilm + garnet + SiMg-phase	1		−11.4	Juina (OR)	k
$CaSiO_3$ + Mg_2SiO_4	1		−4.9	Juina (OR)	k
$CaSiO_3$ + SiO_2	1	>510	−8.5 to −6.4	Juina (C)	m
$CaSiO_3$ + Ni	1		−4.3	Juina (OR)	k
$CaSiO_3$ + carbonate	1			Juina (OR)	n
{$CaSiO_3$, $CaTiO_3$} + carbonate + Mg_2SiO_4	1			Juina (OR)	n
Mg_2SiO_4 + carbonate	1		−5.6 to −6.4	Juina (C)	m
TAPP + carbonate	1		−5.8 to −6.6	Juina (C)	m
Hydrous Al-silicate ('Egg') + fluid	1			Juina (OR)	o
{CaAlSi-phase, kyanite} + KAlSi-phase + MgFeAlspinel + Mgt + Fe	1	>450	−24.6 to −14.7	Juina (C)	m
Kyanite + SiO_2	1		−23.4 to −22.9	Juina (C)	m

fPer, mPv, cPv, crn, CF and NAL are respectively the abbreviations for primary minerals: ferropericlase, MgSi-perovskite, CaSi-perovskite, corundum, calcium ferrite phase, and new aluminium silicate phase; mPv (Al) refers to an Al-rich MgSi-perovskite.

cpx, ky, are abbreviations for clinopyroxene and kyanite, which may or may not be primary phases.

TAPP is an acronym for Tetragonal Almandine-Pyrope Phase.

"NaAL-pyroxene"/garnet refers to inclusions of Na–Al pyroxenes believed to have crystallised as garnets.

$CaSiO_3$, $MgSi_2O_4$ and SiO_2 are listed as compositions because there is uncertainty about their initial structural state.

Carbonates are typically of Ca–Mg composition [$CaCO_3$, $CaMg(CO_3)_2$], but may have Fe and Na.

Mg_2SiO_4 is only listed where it occurs as separate inclusions in diamond; composite inclusions of Mg_2SiO_4 with mPv and/or fPer are ignored because they are possibly a product of retrograde reaction (Brey et al., 2004; Hayman et al., 2005).

[a] 'Associations' of minerals linked with a plus sign are separate inclusions of minerals found in the same diamond; where phases are enclosed in curly brackets they occur together within a single inclusion; where phases are separated by commas alone they occur in separate diamonds but are believed to represent an actual mineral assemblage.

[b] No. refers to the number of diamonds reported (multiple inclusions may occur in one diamond).

[c] The estimated depths of formation are based on phase equilibria along a normal mantle geotherm (with temperature at the Upper/Lower Mantle boundary approximately 1850 K), and do not take into account lowering of temperatures associated with subduction zones.

[d] Data expressed in standard ‰ deviation relative to Vienna_Pee Dee belemnite.

[e] Locations in Juina province are as follows: SL is São Luiz; RS is Rio Soriso; OR other rivers; C is Collier 4 pipe.

[f] References (Refs): a — Moore and Gurney (1985); b — Moore et al. (1991); c — Harte and Cayzer (2007); d — Harte et al. (1999); e — Hutchison et al. (1999); f — Tappert et al. (2005); g — Hayman et al. (2005); h — Scott-Smith et al. (1984); i — Tappert et al. (2009); Moore et al. (1986); k — Kaminsky et al. (2001); l — Hutchison et al. (2001); m — Bulanova et al. (2010); n — Brenker et al. (2007); o — Wirth et al. (2007); p — Walter et al. (submitted for publication).

Lithgow-Bertelloni, 2007). Thus the associations where mPv and fPer occur together with a separate inclusion of Mg_2SiO_4 are placed at ca 660 km in Table 1, whilst the associations of mPv + fPer without Mg_2SiO_4 are placed in the lower mantle. In some cases composite inclusions have been found in which Mg_2SiO_4 accompanies mPv or fPer in the same inclusion (Brey et al., 2004; Hayman et al., 2005); these have not been listed in Table 1 because of the likelihood that the Mg_2SiO_4 is a result of a re-equilibration reaction between mPv and fPer during decompression. In the ferropericlase and MgSi-perovskite suite associations listed in Table 1, the associated minerals occur in

separate inclusions in the same diamond, and it is presumed that the extremely low rates of diffusion in diamond (e.g. Craven et al., 2009; Harte et al., 2009) protect the individual inclusions from interaction. The lower mantle (>660 km) associations in Table 1 are divided into those believed to have formed within the 660–750 km depth range and those formed at ca 750 km or more, according to whether the mPv is poor or rich in aluminium (Harte et al., 1999; Harte, 2010).

Table 1 shows that diamonds with the association mPv + fPer may also contain the phases CaSi-perovskite (cPv) and Tetragonal Almandine-Pyrope Phase (TAPP). Experimental studies show that

CaSi-perovskite is expected to be the principal Ca-bearing phase in both basic and ultrabasic bulk compositions in the lower Transition Zone and Lower Mantle (e.g. Perillat et al., 2006; Stixrude and Lithgow-Bertelloni, 2007). In the inclusions cPv always appears to have undergone retrogression during decompression to form lower pressure phases (e.g. Stachel et al., 2000b). The TAPP phase found as inclusions has not so far been synthesised in experimental studies. It is a FeMg-silicate phase with compositions closely similar to those of garnets with pyrope–almandine compositions, but it has a distinct tetragonal structure (Harris et al., 1997). Consideration of the inclusion associations listed in Table 1 in conjunction with experimental data shows that TAPP commonly appears in inclusion associations where garnet is found experimentally, and thus in the natural associations it appears to substitute for an Al-rich phase (Harte, 2010).

The associations in Table 1 marked as coming from ?550–750 km depth are of uncertain depth because they do not have clearcut identifiers of depth of origin. They are believed to come from this depth range because they show inclusions with similar chemical characteristics to those which occur in association with mPv and fPer. The "NaAl-pyroxene/grt" phase listed in Table 1 has a very restricted occurrence, but is believed on experimental grounds (Gasparik and Hutchison, 2000) to represent retrogressed Mg- and Na-rich majoritic garnets from the lower Transition Zone. However, Na-rich garnet compositions are also found in experimental studies of basic assemblages in the Lower Mantle (Hirose and Fei, 2002; Litasov and Ohtani, 2005). Until very recently the NaAl-pyroxene/grt inclusions have been the principal indicators of basic, rather than ultrabasic bulk compositions, in diamonds from the Upper/Lower Mantle boundary and uppermost Lower Mantle. However, Walter et al. (submitted for publication) have now found a set of inclusions involving: a calcium ferrite phase (CF-phase), and the "new aluminium silicate" phase (NAL-phase) together with MgSi-perovskite, CaSi-perovskite and possibly stishovite. The MgSi-perovskite in this set of inclusions is Al, Ti and Fe rich compared with those found in association with ferropericlase, and likewise the CaSi-perovskite is Ti-rich. Thus this rare set of inclusions shows distinctions in compositions to the ultrabasic inclusions, and is listed as a mineral association in Table 1 because it also shows good correspondence with experimental data for Lower Mantle basic rock compositions (Walter et al., submitted for publication).

2.3. The Ca-rich suite of inclusions

This suite is most particularly marked by the occurrence of inclusions of $CaSiO_3$ composition in conjunction with $CaTiO_3$ (normal perovskite) and $CaTiSiO_5$ (titanite) inclusions, with or without carbonates. The $CaSiO_3$ phase found is typically the lower pressure phase wahlstromite, but this is probably usually a product of inversion from higher pressure CaSi-perovskite (cPv). It is possible that some of the cPv associations listed under the mPv + fPer suite in Table 1 should be placed in the Ca-rich suite, because all appear to involve cPv enriched in REE and other trace elements (Stachel et al., 2005; Walter et al., 2008). In the Ca-rich suite, $CaSiO_3$ and $CaTiO_3$ often occur together within single inclusions, and are inferred to represent exsolution products of an original $Ca(Si,Ti)O_3$ solid solution (Hayman et al., 2005; Brenker et al., 2007; Bulanova et al., 2010). The carbonate inclusions found are usually extremely small (<20 μm), but morphological evidence (Brenker et al., 2007) indicates their crystallisation at the same time as the host diamonds. The carbonate species identified are mainly $CaCO_3$ and/or $CaMg(CO_3)_2$ but they may be Na-rich (Bulanova et al., 2010).

Table 1 lists the mineral species belonging to the Ca-rich suite, placing emphasis on diamonds containing an association of two or more inclusions of different minerals in the same diamond. In the Juina area, samples have been obtained from alluvial deposits and from the specific Collier 4 kimberlite pipe. Diamonds from Collier 4

also yield unusual inclusion associations with aluminous phases (e.g. kyanite, garnet, K feldspar) and since they are associated with the Ca-rich inclusion suite (Bulanova et al., 2010) they are also listed in Table 1. An exceptional inclusion of the high pressure phase Egg, $AlSiO_3(OH)$, found in an alluvial diamond (Wirth et al., 2007) may also be of related origin.

Brenker et al. (2007) suggested that the Ca-rich lithologies with carbonates were formed from subducted oceanic lithosphere that potentially included carbonated basic and ultrabasic rocks and calcareous oozes. Bulanova et al. (2010) also argue for the origin of the Collier 4 inclusions from carbonated subducted materials, and in this case the evidence for subducted materials is strongly supported by the Al-rich inclusions that indicate a sedimentary origin. Highly enriched trace element compositions in $Ca(Si,Ti)O_3$ and majorite inclusions suggest that the diamonds and inclusions have crystallised from carbonatitic melts formed by melting of the carbonated subducted materials (Walter et al., 2008; Bulanova et al., 2010).

Evidence for the depths of origin of the Ca-rich inclusion associations largely rests on the relatively abundant CaSi- and CaTi-phases, which undergo phase changes in the range of P–T conditions of the Transition Zone and asthenosphere. Estimates for the depths of crystallisation of the commonly $CaSiO_3$-bearing associations are generally considered to be at depths greater than ca 300 km (Brenker et al., 2007) and often in the Transition Zone (Walter et al., 2008; Bulanova et al., 2010); overall depths of 300 to 600 km are dominantly implied for the primary crystallisation of the inclusions, but there is evidence of diamond crystallisation and re-equilibration of inclusions to shallower depths.

3. Protoliths and host diamond compositions

In the characterisation of natural diamonds their carbon isotope ($^{13}C/^{12}C$) ratios have been widely determined, and these are given for the diamonds hosting the above inclusion suites using the standard $\delta^{13}C$ notation (Cartigny, 2005) in Table 1. There are marked distinctions in the ranges of composition shown by the host diamonds of the three inclusion suites. The diamonds of deepest origin with ultrabasic inclusions of the ferropericlase + MgSi-perovskite, have 'normal' mantle $\delta^{13}C$ values, largely in the range −4 to −5.5‰. These values are the expected range for carbon of mantle origin. On the other hand, majoritic garnet suite diamonds and those of the Ca-rich suite show marked departures from the expected mantle norm. The majoritic suite diamonds have a marked bias to light carbon with negative $\delta^{13}C$ values largely in the range −10 to −24‰, and a similar range (−11 to −25‰) is seen for many of the Ca-rich suite diamonds though some have values of −4 to −6‰ (Table 1). The particularly high negative values are potentially indicative of derivation from living tissues (including microbes) and have been the subject of much debate concerning identification of original crustal material in the mantle (Kirkley et al., 1991; Cartigny, 2005). In the case of the deep diamonds with distinctly negative $\delta^{13}C$, the evidence of crustal protoliths is supported by other evidence. For the specimens from Jagersfontein with exceptionally $\delta^{13}C$ negative values of −17 to −24‰ (Table 1), Tappert et al. (2005) note the occurrence of negative Eu anomalies whose origin is attributed to plagioclase fractionation in crustal basaltic protoliths. Likewise an initial crustal origin for the Ca-rich suite inclusions is shown by the occurrence of carbonates and Al-rich minerals indicating sedimentary protoliths (see above). The intermediate $\delta^{13}C$ compositions of −9 to −10‰ found in the majorite and Ca-rich suite diamonds (Table 1) could imply a mixing of crustal and mantle sources in the formation of these diamonds, and this is supported by zoning of the diamond compositions to less negative values in the rims (Bulanova et al., 2010).

Despite the dominant lack of $\delta^{13}C$ evidence for formation of the mPv + fPer suite inclusions from subducted protoliths, some indications of a lithospheric origin have been noted. The slightly high value of −3.8‰ for an Ororoo diamond (Table 1) may indicate the

influence of carbonate compositions (Tappert et al., 2009). Eu anomalies indicating high-level plagioclase fractionation occur in the REE patterns of some $CaSiO_3$ associated with fPer (Stachel et al., 2000b, 2005) inclusions. In addition, the rare diamonds with Lower Mantle minerals indicating basic (potential crustal protolith) compositions (with CF and NAL in Table 1) show $\delta^{13}C$ ‰ values down to −24.1.

A subducted origin for mPv + fPer suite inclusions has been argued on petrogenetic grounds by Harte (2010). A very limited depth distribution is shown by ultrabasic inclusions − despite the expected dominance of ultrabasic rocks in the mantle there is an apparent absence of ultrabasic inclusions originating in the asthenosphere or upper Transition Zone. Harte (2010) notes that there is a close correspondence between the depths of inclusion formation (near the UM/LM boundary region and in the uppermost Lower Mantle) and the potential depths of dehydration of hydrous meta-peridotites which may form a major part of cool subducted slabs (Ohtani, 2005; Komabayashi and Omori, 2006). These loci of dehydration will give rise to miscible fluid-melt compositions within which diamond crystallisation can occur and the inclusions captured. Although this model involves subducted hydrated meta-peridotites, these rocks will have had mantle protoliths previously incorporated into the oceanic lithosphere, and it is possible that they may be recycled back into the mantle with relatively little change in geochemistry apart from hydration; thus explaining the lack of strong crustal signatures in the diamond isotopic ratios. It is now widely accepted that major hydration of oceanic lithosphere largely occurs where the oceanic plate bends and undergoes normal faulting prior to descent into the subduction zone (Ranero et al., 2003; Grevemeyer et al., 2007; Zhao and Ohtani, 2009; Santosh et al., 2010).

Tappert et al. (2005) suggested a solid state origin for the majorite-bearing diamonds, whereby biogenic carbon in subducted crustal basic rocks is converted to diamond probably following formation of graphite at shallower levels. However, the crystallisation of the majoritic suite diamonds may also be from H–C–O-rich melts. Harte (2010) suggests that the majoritic suite diamonds may derive from organic carbon incorporated in melts generated by dehydration reactions. Thus the breakdown of metamorphic lawsonite within the metamorphosed basalts may provide a source of H_2O for the fluids crystallising diamonds and majorites at depths of ca 300 km (Kawamoto, 2006), whilst conversion of hydrous wadsleyite to less-hydrous olivine in mantle peridotite at the surface of the slab may provide another source at the top of the Transition Zone (Karato, 2006). At deeper levels, the dehydration reactions affecting the hydrous meta-peridotites (see above) may provide a source of fluids percolating into the metamorphosed crustal protoliths from below and potentially passing into the Transition Zone above a descending and stagnating subducted slab (Ichiki et al., 2006; Richard et al., 2006; Suetsugu et al., 2006; Santosh et al., 2009; Zhao and Ohtani, 2009).

For the diamonds hosting the Ca-rich suite inclusions and commonly showing highly negative $\delta^{13}C$ values, Bulanova et al. (2010) argue persuasively for crystallisation from carbonatitic melts which are generated when a rising plume intersects subducted material and causes melting.

4. A general subduction model for the formation of DEEP diamond suites

The deep diamond inclusion suites are distinct in their mineral associations and chemical compositions, and indicate the occurrence of distinctly selective processes of diamond and inclusion formation at different depths. In addition, the data presented above shows that all the three suites of diamonds may be derived from subducted materials but under different conditions and circumstances. At the same time all three suites show close associations in occurring in kimberlites of the same age in small geographic areas. To explain


Fig. 1. Showing the separation of West (orange-brown) and East (purple) Gondwanaland in the early Mesozoic at ca 160 Ma (modified from Storey, 1995), with an extensive subduction zone along the Pacific margin. Blue diamond symbols are kimberlite and diamond localities: J — Juina, K — Koffiefontein, Ja — Jagersfontein, M — Monastery; O — Orroroo. P and E are the locations of the Parana, and Etendeka continental flood basalts. T, D, G, and S, mark the estimated positions of the DUPAL hotspots (Tristan, Discovery, Gough and Shona) at the time of opening of the South Atlantic Ocean and prior to their transit into the South Atlantic (Le Roex, 1986).

these features we present a model involving diamond inclusion formation at different stages in the evolution of a single subducted slab.

The model proposed is illustrated in Fig. 2. The progressive development of the subducted slab is based upon the extensive evidence gathered from seismic tomographic studies, which show that the downward descent of a slab often stalls at the Upper/Lower Mantle boundary and a "stagnant slab" is emplaced in the Transition Zone and/or the uppermost Lower Mantle (e.g. Fukao et al., 2001, 2009; Zhao and Ohtani, 2009; Zhao et al., 2009, 2011). Variations in the detailed evolution of such slabs may be linked to factors such as variations in temperature, viscosity, trench retreat, and slab weakening in the Transition Zone due to grain-size reduction (Fukao et al., 2009). Slab weakening can lead to deformation of the slab at the 660 km phase boundary (Tagawa et al., 2007). The marked buckling of the slab shown in Fig. 2b allows the possibility of metabasites of the former ocean crust to experience uppermost Lower Mantle pressure–temperature conditions, as suggested by the rare inclusions of the CF and NAL phases in diamonds (Table 1). Alternatively, Santosh et al. (2010) and Walter et al. (submitted for publication) depict the formation of imbricate slices of subducted lithosphere at the Upper/-Lower Mantle boundary.

The sequence of sketches in Fig. 2 shows the progressive formation of the different diamond inclusion suites based on the circumstances of formation discussed in previous sections: the majoritic garnet suite forms in meta-basalts as the subducted slab descends through the upper mantle; the mPv + fPer suite forms essentially in hydrated meta-peridotites (and rarely in metabasites) as the subducted slab reaches the lower Transition Zone and uppermost Lower Mantle; whilst the Ca-rich suite derives from carbonated crustal rocks in the stagnant slab that become entrained in carbonatitic melts in a rising plume. The upward pointing arrow in Fig. 2c indicates the traverse of carbonatitic melts through the upper mantle documented by the range of depths of formation of Ca-rich suite inclusions (Bulanova et al., 2010). The upwelling plume responsible for the development of the carbonatitic melts must originate at greater depths, and is believed to entrain the previously formed diamonds with the
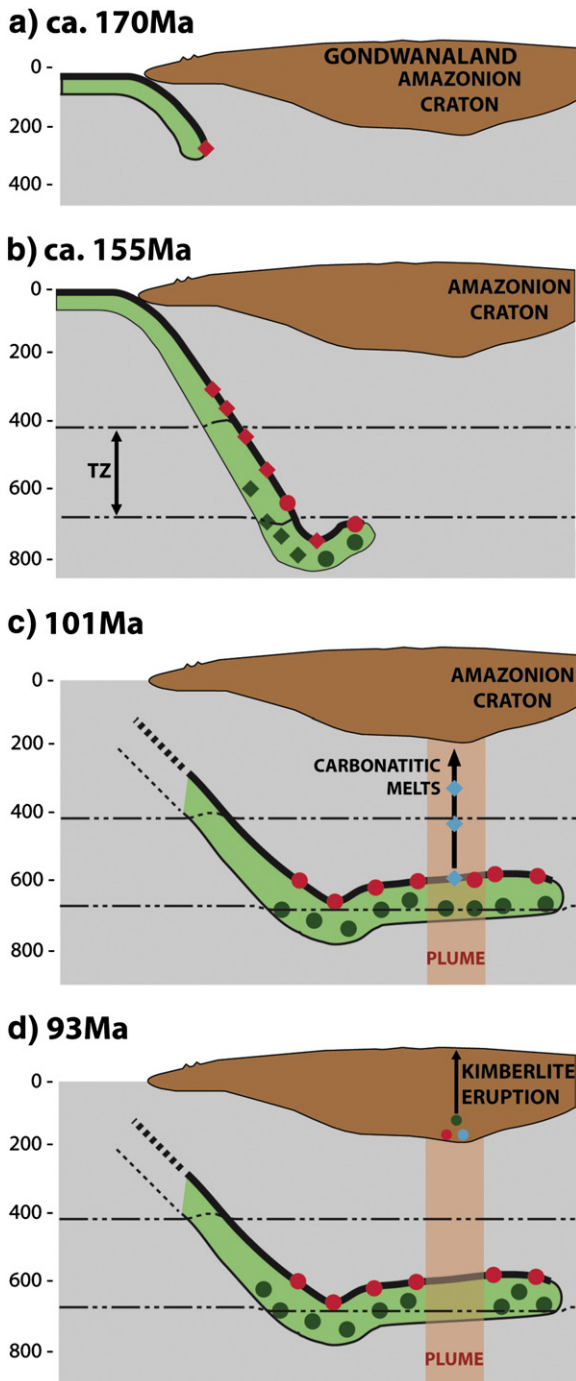
Fig. 2. Schematic history of a subducted slab and diamond formation beneath West Gondwanaland in the Mesozoic era. The dates placed on the model at ca 170, 155, 101 and 93 Ma refer specifically to the Juina area, Brazil. Red, green and blue symbols refer to diamonds of the Majoritic garnet, fPer + mPv, and Ca-rich suites respectively; solid diamond symbols are shown at places of diamond crystallisation, and solid circles represent diamonds already formed. The carbonatitic melts in (c) are associated with Ca-rich suite inclusions (Bulanova et al., 2010). Transport to the lithosphere of diamonds with all three inclusion suites and subsequent kimberlite eruption to the Earth's surface, are associated with a plume possibly originating near the Core–Mantle-Boundary (see text). TZ marks the Transition Zone.

majoritic and mPv + fPer suite inclusions, and thus brings all three suites of diamonds to the lower lithosphere (Fig. 2 and graphical abstract). The diamonds are subsequently carried to the Earth's surface by kimberlite eruptions (Fig. 2d), possibly as a continuation of

the same plume activity. The plume might arise near the Upper/Lower Mantle boundary as a consequence of gradual heating and fluid activity, or it might arise from near the Core–Mantle-Boundary as a consequence of superplume activity (Maruyama et al., 2007); and this will be further considered in Section 6.3 of this paper.

5. Dating the evolution of the Juina deep subduction diamonds

A general model of tectonic evolution of the type illustrated in Fig. 2 potentially applies to several worldwide localities where more than one suite of deep diamonds occurs. But in the case of Juina (Brazil), where all three suites are well represented, the model may be particularly well constrained by knowledge of Gondwanan tectonic evolution in conjunction with isotopic dating evidence from the inclusions themselves. These time constraints, specific to Juina, are summarised below and provide the basis for the ages in Fig. 2.

Although many of the Juina diamonds have been recovered from alluvial deposits, kimberlite pipes occur in the same region and it appears most probable that all the diamonds are derived from a set of diamondiferous kimberlite eruptions in the Cretaceous period at ca 93 Ma (Kaminsky et al., 2010). An age for the formation of the Ca-rich suite diamonds is based on the U–Pb dating of a CaTiSi-pvk inclusion at ca 101 Ma, and this age also constrains the time of carbonatitic melt formation and upward plume transport (Fig. 2c) to the base of the lithosphere (Bulanova et al., 2010). A time gap between transport to the base of the lithosphere and subsequent kimberlite eruption is also suggested on the basis of the extensive re-equilibration of the majoritic garnet inclusions towards normal garnet and clinopyroxene (eclogite assemblage) inclusions (Harte and Cayzer, 2007).

In order to constrain the age of establishment of the subduction and penetration of the subducted slab into the mantle we present here previously unpublished isotopic data for the São Luiz (Juina) majoritic garnet suite. A precise date is not available, but a significant control is given by Rb–Sr and Sm–Nd isotopic data for these majoritic inclusions (Table 2). The data is based upon some 40 separate garnet inclusions, which were divided into two groups of deep orange (high Fe) and pale orange (low Fe) colour, to obtain enough material for sufficiently precise isotopic analysis. The Rb content of all these two garnet composites is very low and $^{87}Rb/^{86}Sr$ ratios are negligible, so that age corrections are small and $^{87}Sr/^{86}Sr$ ratios can be directly compared with those of possible depleted mantle (DM) derived precursors like MORB or OIB. Furthermore, the $^{147}Sm/^{144}Nd$ ratios of the garnets are mildly superchondritic suggesting that $^{143}Nd/^{144}Nd$ ratios should also be comparable to those of MORB sources. In fact, the $^{87}Sr/^{86}Sr$ (0.7024) and $^{143}Nd/^{144}Nd$ (0.5130) ratios of the pale orange (low Fe) garnet are remarkably similar to those of depleted MORB whilst the deep orange (high Fe) garnet values (0.7032; 0.5129) are reminiscent of enriched MORB or OIB. Thus, the isotopic signatures of the majoritic garnets are consistent with a modern MORB/OIB origin and the complete opposite of the radiogenic Sr and unradiogenic Nd isotopic signature of typical octahedral macrodiamonds from old enriched subcontinental lithospheric mantle (SCLM) as illustrated in Fig. 3.

The isotopic evidence suggests formation of the protoliths of the São Luiz majoritic garnet suite from asthenosphere [convecting mantle] in the Mesozoic era. Thus, the ocean floor basalt protoliths of the majoritic garnets have a maximum age in the early Mesozoic of ca 200–180 Ma. This coincides with the beginning of break-up of the Pangaea supercontinent, and in particular with the separation of west and east Gondwanaland continental blocks (Fig. 1). Palaeogeographic reconstructions for this time (e.g. Storey, 1995) show that a major zone of subduction for the palaeo-Pacific Ocean lay at the border of South America near the line of the present day Andean orogenic belt. The dates given on Fig. 2a,b assume average subduction velocities of ca 30 mm yr^{-1}, but the subduction rates could be closer to 100 mm yr^{-1} (e.g. Doglioni et al., 2007; Maruyama et al., 2007).

Table 2
Rb–Sr and Sm–Nd isotopic composition of garnet inclusions[a] in São Luiz diamonds.

	Wt (mg)	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$
d.o.g	0.18	0.032	13.9	0.0067	0.70319(4)	6.363	15.19	0.2533	0.51285(6)
p.o.g	0.38	0.036	20.7	0.0050	0.70244(3)	1.378	3.409	0.2444	0.51300(6)

Isotope dilution analysis was completed in 1987 at MIT in parallel with work on garnet inclusions in Orapa and Finsch diamonds reported in Richardson et al. (1990). Concentrations are in ppm after correction for minimum applicable blanks: Rb, 3 pg; Sr, 4 pg; Sm, 0.6 pg; Nd, 1.5 pg. Estimated uncertainties in concentrations (ignoring small-sample weighing errors) are indicated by the number of significant digits. Present-day $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios are normalised to 0.70800 for E & A $SrCO_3$ and 0.51264 for BCR-1, as per Richardson et al. (1990). In-run precision is indicated by the errors ($2\sigma_{mean}$) in the least significant digits given in parentheses.

[a] Inclusions were liberated from a suite of 424 "orange garnet" inclusion-bearing diamonds by breaking the stones in a steel cracker but only ~10% of 'inclusions' proved to be syngenetic silicates. These were then divided on the basis of colour into two composites of deep orange garnet (d.o.g.) and pale orange garnet (p.o.g.) with average inclusion weight 10–15 μg.

The time of ending of the period of active subduction of the Juina slab is uncertain, but it is likely that some adjustment of convergent plate boundary positions accompanied the opening of the South Atlantic Ocean at 130–120 Ma. By this time a substantial stagnant slab could have been emplaced in the Transition Zone and uppermost lower Mantle, and have underlain the estimated positions of the Parana and Etendeka flood basalts (e.g. Hawkesworth et al., 1986) before their time of eruption at ca 130 Ma (Fig. 1). Likewise, the stagnant slab may well have underlain the estimated positions of South Atlantic hotspots (Fig. 1) prior to the opening of the South Atlantic.

6. Summary, discussion and conclusions

6.1. The contrasting deep inclusion suites

Three suites of inclusions involving silicate minerals may now be recognised in diamonds deriving from depths >250 km.

1. A majoritic garnet suite with depths dominantly of 250 to 450 km and evidence of crustal protoliths of basic composition on the basis of Eu anomalies in some inclusions and low $\delta^{13}C$ of host diamonds.
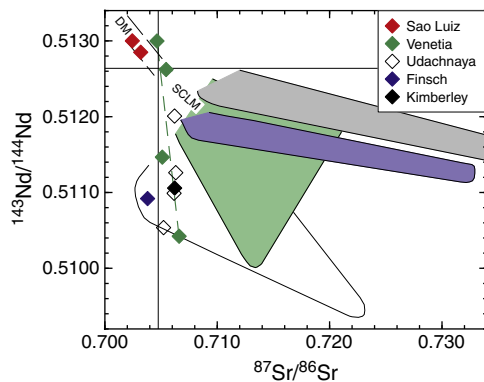
Fig. 3. Present-day Nd–Sr isotope correlation diagram for majoritic garnet inclusions in deep diamonds from São Luiz (Juina) compared to harzburgitic garnet inclusions in lithospheric diamonds from Kimberley and Finsch (Richardson et al., 1984), Udachnaya (Richardson and Harris, 1997) and Venetia (Richardson et al., 2009). Also shown for reference are the oceanic mantle array (DM in depleted quadrant) and a range of subcontinental lithospheric mantle arrays (colour-coded SCLM fields in enriched quadrant) defined by subcalcic garnet macrocrysts from disaggregated diamond host rocks at Kimberley, Finsch, Udachnaya and Venetia (Richardson et al., 1984; Richardson, 1986; Pearson et al., 1995; Richardson et al., 2009). In all cases, the garnet macrocrysts show much higher $^{87}Sr/^{86}Sr$ values at low $^{143}Nd/^{144}Nd$ than the encapsulated garnet inclusions, reflecting long-term residence in old enriched SCLM. Conversely, the São Luiz garnet inclusions show the lowest present-day $^{87}Sr/^{86}Sr$ values at high $^{143}Nd/^{144}Nd$ comparable to depleted MORB/OIB, reflecting derivation from relatively young (i.e. Mesozoic) convecting mantle. Premier (not shown), Udachnaya and Venetia garnet inclusions show intermediate $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ values on mixing arrays (green dashed line) resulting from the interaction of Bushveld-type magmas with Archean harzburgitic diamond precursors prior to diamond (re) crystallisation at ca. 2.0 Ga (Richardson et al., 1993; Richardson and Harris, 1997; Richardson and Shirey, 2008; Richardson et al., 2009).

2. A MgSi-perovskite + ferropericlase (mPv + fPer) suite with depths of formation near the UM/LM boundary and in the uppermost Lower Mantle. These inclusions indicate dominantly ultrabasic (meta-peridotite) rock compositions. The formation of the diamonds may be linked to melts formed as a result of dehydration of DHMS minerals in subducted ultrabasic lithosphere near the depths of UM/LM boundary.

3. A Ca-rich suite, with carbonates, Ca–Si–Ti silicates and some aluminous minerals, formed at depths of ca 300 to 600 km. This suite is derived from oceanic crust containing carbonated basic–ultrabasic rocks and sediments, and probably crystallised in carbonatitic melts. A subduction origin is supported by inclusion compositions and the low $\delta^{13}C$ of host diamonds.

6.2. A subduction model for Juina, Brazil, and the extended period of Gondwanan subduction

In the most comprehensively characterised locality of Juina, Brazil, the occurrence of all three suites in diamonds in a small area suggests a close linkage in the circumstances of their derivation and formation. A model has therefore been presented for the formation of all three suites during the evolution of a single subducted slab of oceanic lithosphere: (i) the majoritic garnet inclusions form from oceanic crust basaltic rocks during descent of the slab; (ii) the mPv + fPer suite inclusions form predominantly from the ultrabasic rocks of the slab near the UM/LM boundary; (iii) the Ca-rich suite diamonds form during transport in carbonatitic melts associated with a plume transecting the stagnant slab and carrying inclusions of all three types up to the base of the lithosphere (Fig. 2). In the specific case of the Juina inclusions the slab is constrained to be of Mesozoic age by: Nd–Sr isotope data on the majoritic inclusions, and Cretaceous ages for a Ca–Si–Ti-rich inclusion and the eruption age of diamondiferous Juina kimberlites.

Given the close proximity of South America and southern Africa before the opening of the South Atlantic ocean, it appears possible that the same subducted slab was responsible for the majoritic-garnet and mPv + fPer suites found in Cretaceous kimberlites in southern Africa. However, by analogy with the modern Pacific Ocean there may have been a series of subducting segments with varying times of initiation and termination. For the south Australian deep diamonds, whose kimberlites give an age of ca 170 Ma (Scott-Smith et al., 1984) an earlier subduction zone at the palaeo-Pacific margin may be postulated (Tappert et al., 2009). An orogenic zone of subduction and accretion, the Terra Australis Orogen of Cawood (2005), existed near the outline of the zone of subduction in Fig. 1 from the Neoproterozoic until late Palaeozoic, culminating in the Gondwanide Orogeny of 320–280 Ma and the final assembly of Pangaea (see also Boger, 2011). Using seismic tomographic evidence, Maruyama et al. (2007) have similarly postulated the existence of a whole series of Neoproterozoic and Palaeozoic Gondwanan subducted stagnant slabs, which eventually collapsed through the Lower Mantle and accumulated in a "slab graveyard" at the CMB (Core–Mantle-Boundary).

6.3. Slab graveyards, superplumes, and kimberlite eruptions

The Gondwanan CMB slab graveyard provides a potential location for the formation and the development of the plume and accompanying carbonatitic and kimberlitic melts which transport the Juina diamonds to the lithosphere and eventually to the Earth's surface (Fig. 2c,d). Following the model of Maruyama et al. (2007) the cold CMB graveyard is initially a locus for formation of the post-perovskite-phase, but with time and the reconversion of post-perovskite to perovskite, the graveyard heats up and becomes the site of an ultra-low velocity zone (ULVZ) characterised by reduced shear wave velocity and the development of a superplume. Once formed the superplume gives rise to kimberlitic and carbonatitic volcanism at the surface and the eruption of flood basalts. Maruyama et al. (2007) envisage melt formation to move progressively towards the margins of the superplume.

Support for the formation of the Juina kimberlites as a consequence of a superplume initiated near the CMB has come from Torsvik et al. (2010). Using plate reconstructions and tomographic images Torsvik et al. (2010) show that the margin of a sub-African LLSVP (large low-shear-wave-velocity province) was underlying the Juina kimberlite region at ca 90 Ma, and therefore in the ideal position to promote kimberlite formation. These authors also note a general tendency for kimberlites and large igneous provinces to be associated in space and time in plume generation zones at the margins of LLSVP. The probable connection between large igneous provinces and kimberlites has been previously argued on geological grounds (Helmstaedt and Gurney, 1997; Tappert et al., 2009).

One further piece of evidence supporting the existence of a superplume near the CMB at the time of the Juina kimberlites, is the occurrence of some exceptional (Fe,Mg)O inclusions in diamonds from Juina. These rare inclusions, unlike the common fPer inclusions described previously, are Fe-rich magnesio-wustites. Harte et al. (1999), Hayman et al. (2005) and Wirth et al. (submitted for publication) have all suggested the formation of these Fe-rich inclusions in the D″ layer next to the CMB.

6.4. Subducted slabs and the DUPAL geochemical anomaly

The stagnant subducted slab postulated for the Juina diamonds and potentially extending beneath South America to southern Africa prior to the opening of the South Atlantic Ocean, provides a potential explanation for the origin of the South Atlantic DUPAL trace element and isotope anomalies. This anomaly (Duprée and Allègre, 1983; Hart, 1984), which is particularly well defined by hotspot basalts in the S Atlantic between about 25° and 55° S latitude, is largely based upon the occurrence of anomalous lead and strontium isotope signatures whose nature indicates an origin from enriched continental lithosphere or subducted and recycled sediments (Hofmann, 1997). In the southern Atlantic Ocean the region covered by this anomaly coincides closely with the area expected to be underlain by the subducted slab evidenced above by the Juina diamond inclusions. Thus the slab would underlie the positions of the hotspots yielding basalts with DUPAL signatures as they tracked into the opening South Atlantic Ocean (Fig. 1). The slab would also underlie the positions of the Parana and Etendeka continental flood basalts, whose eruption ages are 130–120 Ma and which also show geochemical features similar to the DUPAL anomaly (Hawkesworth et al., 1986).

Bearing in mind the broad inferences noted above of a potential series of late Palaeozoic and Mesozoic subduction slabs forming all along the southern margins of both west and east Gondwanaland (see also Tappert et al., 2009), it is possible that the DUPAL geochemical signatures in the Indian Ocean may have a similar origin in subducted sedimentary material. Similar isotope geochemical characteristics of the Group II kimberlites (age 114 to 200 Ma) of southern Africa (Le Roex, 1986; Helmstaedt and Gurney, 1997), may owe their origin to

the same series of subducted lithospheric slabs. Recent determinations of Sr, Nd and Hf isotope ratios in Group II kimberlites (Coe et al., 2008) also correspond closely with those of ancient sediments.

6.5. The age contrast between 'deep' and 'normal' diamonds

Diamondiferous kimberlites of Mesozoic age in the southern hemisphere yield diamonds with deep (>250 km depth) inclusions as discussed above, but more commonly they yield diamonds with inclusions of eclogite and garnet–peridotite mineralogy and probably of lithospheric origin. Despite the similarity in age of the kimberlites in both cases, the diamonds and their inclusions contrast hugely in age as well as in depths of formation. We have shown that the formation of the deep diamonds and their inclusions is closely connected with Phanerozoic subduction events in the southern hemisphere. In contrast, the common macrodiamonds retrieved from many southern African kimberlite pipes characteristically show Archaean to Proterozoic ages (Richardson et al., 1984; Shirey et al., 2004; Richardson and Shirey, 2008; Stachel and Harris, 2008; Gurney et al., 2010).

References

Akaogi, M., Akimoto, S., 1979. High pressure phase equilibria in a garnet lherzolite, with special reference to Mg²⁺–Fe²⁺ partitioning among constituent minerals. Physics of the Earth and Planetary Interiors 19, 31–51.

Boger, S.D., 2011. Antarctica — before and after Gondwana. Gondwana Research 19, 335–371.

Brenker, F.E., Vincze, C., Vekemans, B., Nasdala, L., Stachel, T., Vollmer, C., Kersten, M., Somogyi, A., Adams, F., Joswig, W., Harris, J.W., 2005. Detection of a Ca-rich lithology in the Earth's deep (>300 km) convecting mantle. Earth and Planetary Science Letters 236, 579–587.

Brenker, F.E., Vollmer, C., Vincze, C., Vekemans, B., Szmanski, A., Janssens, K., Szaloki, I., Nasdala, L., Joswig, W., Kaminsky, F., 2007. Carbonates from the lower part of the transition zone or even the lower mantle. Earth and Planetary Science Letters 260, 1–9.

Brey, G.P., Bulatov, V., Girnis, A., Harris, J.W., Stachel, T., 2004. Ferropericlase — a lower mantle phase in the upper mantle. Lithos 77, 655–663.

Bulanova, G.P., Walter, M.J., Smith, C.B., Kohn, S.C., Armstrong, L.S., Blundy, J., Gobbo, L., 2010. Mineral inclusions in sublithospheric diamonds from Collier 4 kimberlite pipe, Juina, Brazil: subducted protoliths, carbonated melts and primary kimberlite magmatism. Contributions to Mineralogy and Petrology 160, 489–510.

Cartigny, P., 2005. Stable isotopes and the origin of diamond. Elements 1, 79–84.

Cawood, P.A., 2005. Terra Australis Orogen: Rodinia breakup and development of the Pacific and Iapetus margins of Gondwana during the Neoproterozoic and Palaeozoic. Earth-Science Reviews 69, 249–279.

Coe, N., le Roux, A., Gurney, J., Pearson, D.G., Nowell, G., 2008. Petrogenesis of the Swartruggens and star Group II kimberlite dyke swarms, South Africa: constraints from whole rock geochemistry. Contributions to Mineralogy and Petrology 156, 627–652.

Craven, J.A., Harte, B., Fisher, D., Schulze, D.J., 2009. Diffusion in diamond: I Carbon isotope mapping of natural diamond. Mineralogical Magazine 73, 193–200.

Davies, R.M., Griffin, W.L., Pearson, N.J., Andrew, A.S., Doyle, B.J., O'Reilly, S.Y., 1999. Diamonds from the deep: pipe DO-27, Slave craton, Canada. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the VIIth International kimberlite Conference, J.B. Dawson volume. Red Roof Design, CapeTown, pp. 148–155.

Davies, R.M., Griffin, W.L., O'Reilly, S.Y., Doyle, B.J., 2004. Mineral inclusions and geochemical characteristics of microdiamonds from the DO27, A154, A21, A418, DO18, DD17 and Ranch Lake kimberlites at Lac de Gras, Slave craton, Canada. Lithos 77, 39–55.

Doglioni, C., Carminati, E., Cuffaro, M., Scrocca, D., 2007. Subduction kinematics and dynamic constraints. Earth-Science Reviews 83, 125–175.

Duprée, B., Allègre, C.J., 1983. Pb–Sr isotope variation in Indian Ocean basalts and mixing phenomena. Nature 303, 142–146.

Fei, Y., Bertka, C.M., 1999. Phase transitions in the Earth's mantle and mantle mineralogy. In: Fei, Y., Bertka, C.M., Mysen, B.O. (Eds.), Mantle Petrology: Field Observations and High Pressure Experimentation; a Tribute to Francis R. (Joe) Boyd: Geochemical Society Special Publication, No 6, pp. 189–207.

Fukao, Y., Widiyantoro, S., Obayashi, M., 2001. Stagnant slabs in the upper and lower mantle transition region. Reviews of Geophysics 39, 291–323.

Fukao, Y., Obayashi, M., Nakakuki, T., 2009. Stagnant Slab: a review. Annual Review of Earth and Planetary Sciences 37, 19–46.

Gasparik, T., Hutchison, M.T., 2000. Experimental evidence for the origin of two kinds of inclusions in diamonds from the deep mantle. Earth and Planetary Science Letters 181, 103–114.

Grevemeyer, I., Ranero, C.R., Flueh, E.R., Klaschen, D., Bialas, J., 2007. Passive and active seismological study of bending-related faulting and mantle serpentinisation at the Middle America trench. Earth and Planetary Science Letters 258, 528–542.

Gurney, J.J., Helmstaedt, H.H., Richardson, S.H., 2010. Diamonds through time. Economic Geology 105, 689–712.

Harris, J.W., Hutchison, M.T., Hursthouse, M., Light, M., Harte, B., 1997. A new tetragonal silicate mineral occurring as inclusions in lower mantle diamonds. Nature 387, 486–488.

Hart, S.R., 1984. A large-scale isotope anomaly in the southern hemisphere mantle. Nature 309, 753.

Harte, B., 2010. Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones. Mineralogical Magazine 74, 189.

Harte, B., Cayzer, N., 2007. Decompression and unmixing of crystals included in diamonds from the mantle transition zone. Physics and Chemistry of Minerals 34, 647–656.

Harte, B., Harris, J.W., 1994. Lower mantle mineral associations preserved in diamonds. Mineralogical Magazine 58A, 384–385.

Harte, B., Harris, J.W., Hutchison, M.T., Watt, G.R., Wilding, M.C., 1999. Lower mantle mineral associations in diamonds from Sao Luiz, Brazil. In: Fei, Y., Bertka, C.M., Mysen, B.O. (Eds.), Mantle Petrology: Field observations and High Pressure Experimentation; a Tribute to Francis R. (Joe) Boyd: Geochemical Society Special Publication, No 6, pp. 125–153.

Harte, B., Taniguchi, T., Chakraborty, S., 2009. Diffusion in diamond: high-pressure–temperature experiments. Mineralogical Magazine 73, 201–204.

Hawkesworth, C.J., Mantovani, M.S.M., Taylor, P.N., Palacz, Z., 1986. Evidence from the Parana of south Brazil for a continental contribution to Dupal basalts. Nature 322, 356–359.

Hayman, P.C., Kopylova, M.G., Kaminsky, F.V., 2005. Lower mantle diamonds from Rio Soriso (Juina area, Mato Grosso, Brazil). Contributions to Mineralogy and Petrology 149, 430–445.

Helmstaedt, H.H., Gurney, J.J., 1997. Geodynamic controls of kimberlites — what are the roles of hotspot and plate tectonics. Russian Geology and Geophysics 38, 492–508.

Hirose, K., Fei, Y., 2002. Subsolidus and melting relations of basaltic composition in the uppermost lower mantle. Geochimica et Cosmochiica Acta 66, 2099–2108.

Hofmann, A.W., 1997. Mantle geochemistry: the message from oceanic volcanism. Nature 385, 219–229.

Hutchison, M.T., Cartigny, P., Harris, J.W., 1999. Carbon and nitrogen compositions and physical characteristics of transition zone and lower mantle diamonds from São Luiz, Brazil. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the VIIth International Kimberlite Conference, J.B. Dawson Volume. Red Roof Design, CapeTown, pp. 372–382.

Hutchison, M.T., Hursthouse, M.B., Light, M.E., 2001. Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity. Contributions to Mineralogy and Petrology 142, 119–126.

Ichiki, M., Baba, K., Obayashi, M., Utada, H., 2006. Water content and geotherm in the upper mantle above the stagnant slab: interpretation of electrical conductivity and seismic P-wave velocity models. Physics of the Earth and Planetary Interiors 155, 1–15.

Irifune, T., 1987. An experimental investigation of the pyroxene–garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle. Physics of the Earth and Planetary Interiors 45, 324–336.

Kaminsky, F.V., Zakharchenko, O.D., Davies, R., Griffin, W.L., Khacatryan-Blinova, G.K., Shiryaev, A.A., 2001. Superdeep diamonds from the Juina area, Mato Grosso State, Brazil. Contributions to Mineralogy and Petrology 140, 734–753.

Kaminsky, F.V., Khachatryan, G.K., Andreazza, P., Araujo, D., Griffin, W.L., 2009. Super-deep diamonds from kimberlites in the Juina area, Mato Grosso State, Brazil. Lithos 112 (Supplement 2), 833_842.

Kaminsky, F.V., Sablukov, S.M., Belousova, E.A., Andreazza, P., Tremblay, M., Griffin, W.L., 2010. Kimberlitic sources of super-deep diamonds in the Juina area, Mato Grosso State, Brazil. Lithos 114, 16–29.

Karato, S., 2006. Remote sensing of hydrogen in Earth's mantle. In: Keppler, H., Smyth, J.R. (Eds.), Water in Nominally Anhydrous Minerals. Reviews in Mineralogy & Geochemistry, Vol. 62. Mineralogical Society of America, USA, pp. 343–375.

Kawamoto, T., 2006. Hydrous phases and water transport in the subducting slab. In: Keppler, H., Smyth, J.R. (Eds.), Water in Nominally Anhydrous Minerals. Reviews in Mineralogy & Geochemistry, Vol. 62. Mineralogical Society of America, USA, pp. 273–289.

Kirkley, M.B., Gurney, J.J., Otter, M.L., Hill, S.J., Daniels, L.R., 1991. The application of C isotope measurements to the identification of the sources of C in diamonds: a review. Applied Geochemistry 6, 477–494.

Komabayashi, T., Omori, S., 2006. Internally consistent thermodynamic data set for dense hydrous magnesium silicates up to 35 GPa, 1600 °C: implications for water circulation in the Earth's deep mantle. Physics of the Earth and Planetary Interiors 156, 89–107.

Le Roex, A.P., 1986. Geochemical correlation between southern African kimberlites and South Atlantic hotspots. Nature 34, 243.

Litasov, K.D., Ohtani, E., 2005. Phase relations in hydrous MORB at 18–28 GPa: implications for heterogeneity of the lower mantle. Physics of the Earth and Planetary Interiors 150, 239–263.

Maruyama, S., Santosh, M., Zhao, D., 2007. Superplume, supercontinent, and post-perovskite: mantle dynamics and anti-plate tectonics on the Core–Mantle boundary. Gondwana Research 11, 7–37.

Moore, R.O., Gurney, J.J., 1985. Pyroxene solid solution in garnets included in diamond. Nature 318, 553–555.

Moore, R.O., Gurney, J.J., 1989. Mineral inclusions in diamonds from the Monastery kimberlite, South Africa. In: Ross, J. (Ed.), Kimberlites and Related Rocks Vol.2: Their Mantle/Crustal Setting, Diamonds and Diamond Exploration: Geological Society of Australia Special Publication, No. 14, pp. 1027–1041.

Moore, R.O., Otter, M.L., Rickard, R.S., Harris, J.W., Gurney, J.J., 1986. The occurrence of moisannite and ferro-periclase as inclusions in diamond. In: Smith, C.B. (Ed.), Fourth International Kimberlite Conference, Extended Abstracts: Geological Society of Australia Abstracts, No. 16, pp. 409–411.

Moore, R.O., Gurney, J.J., Griffin, W.L., Shimizu, N., 1991. Ultra-high pressure inclusions in Monastery diamonds: trace element abundance patterns and conditions of origin. European Journal of Mineralogy 3, 213–230.

Ohtani, E., 2005. Water in the mantle. Elements 1, 25–30.

Pearson, D.G., Shirey, S.B., Carlson, R.W., Boyd, F.R., Pokhilenko, N.P., Shimizu, N., 1995. Re–Os, Sm–Nd, and Rb–Sr isotope evidence for thick Archaean lithospheric mantle beneath the Siberian craton modified by multistage metasomatism. Geochimica et Cosmochimica Acta 59, 959–977.

Perillat, J.-P., Ricolleau, A., Daniel, I., Fiquet, G., Mezouar, M., Guignot, N., Cardon, H., 2006. Phase transformations of subducted basaltic crust in the upmost lower mantle. Physics of the Earth and Planetary Interiors 157, 139–149.

Ranero, C.R., Phipps Morgan, J., McIntosh, K., Reichert, C., 2003. Bending, faulting, and mantle serpentinization at the Middle America Trench. Nature 425, 367–373.

Richard, G., Bercovici, D., Karato, S., 2006. Slab dehydration in the Earth's mantle transition zone. Earth and Planetary Science Letters 251, 156–167.

Richardson, S.H., 1986. Latter-day origin of diamonds of eclogitic paragenesis. Nature 322, 623–626.

Richardson, S.H., Harris, J.W., 1997. Antiquity of peridotitic diamonds from the Siberian craton. Earth and Planetary Science Letters 151, 271–277.

Richardson, S.H., Shirey, S.B., 2008. Continental mantle signature of Bushveld magmas and coeval diamonds. Nature 453, 910–913.

Richardson, S.H., Gurney, J.J., Erlank, A.J., Harris, J.W., 1984. Origin of diamonds in old enriched mantle. Nature 310, 198–202.

Richardson, S.H., Erlank, A.J., Harris, J.W., Hart, S.R., 1990. Eclogitic diamonds of Proterozoic age from cretaceous kimberlites. Nature 346, 54–56.

Richardson, S.H., Harris, J.W., Gurney, J.J., 1993. Three generations of diamonds from old continental mantle. Nature 366, 256–258.

Richardson, S.H., Poml, P.F., Shirey, S.B., Harris, J.W., 2009. Age and origin of peridotitic diamonds from Venetia. Limpopo Belt, Kaapvaal-Zimbabwe craton. Lithos 112, 785–792.

Santosh, M., Maruyama, S., Omori, S., 2009. A fluid factory in solid Earth. Lithosphere 1, 29–33.

Santosh, M., Maruyama, S., Komiya, T., Yamamoto, S., 2010. Orogens in the evolving Earth: from surface continents to lost continents at the core mantle boundary. In: Kusky, T.M., Zhai, M.-G., Xiao, W. (Eds.), The Evolving Continents: Understanding Processes of Continental Growth, 338. Geological Society, London, pp. 77–116. Special Publications.

Scott-Smith, B.H., Danchin, R.V., Harris, J.W., Stracke, K.J., 1984. Kimberlites near Orroroo, South Australia. In: Kornprobst, J. (Ed.), Kimberlites I: Kimberlites and Related Rocks. Elsevier, Amsterdam, pp. 221–242.

Shirey, S.B., Richardson, S.H., Harris, J.W., 2004. Integrated models of diamond formation and craton evolution. Lithos 77, 923–944.

Stachel, T., 2001. Diamonds from the asthenosphere and the transition zone. European Journal of Mineralogy 13, 883–892.

Stachel, T., Harris, J.W., 2008. The origin of cratonic diamonds — constraints from mineral inclusions. Ore Geology Reviews 34, 5–32.

Stachel, T., Brey, G.P., Harris, J.W., 2000a. Kankan diamonds (Guinea) I: from lithosphere down to the Transition Zone. Contributions to Mineralogy and Petrology 140, 1–15.

Stachel, T., Harris, J.W., Brey, G.P., Joswig, W., 2000b. Kankan diamonds (Guinea) II: lower mantle inclusion parageneses. Contributions to Mineralogy and Petrology 140, 16–27.

Stachel, T., Harris, J.W., Aulbach, S., Deines, P., 2002. Kankan diamonds (Guinea) III: δ^{13}C and nitrogen characteristics of deep diamonds. Contributions to Mineralogy and Petrology 142, 465–475.

Stachel, T., Brey, G.P., Harris, J.W., 2005. Inclusions in sublithospheric diamonds: glimpses of deep Earth. Elements 1, 73–78.

Stixrude, L., Lithgow-Bertelloni, C., 2007. Influence of phase transformations on lateral heterogeneity and dynamics in the Earth's mantle. Earth and Planetary Science Letters 263, 45–55.

Storey, B.C., 1995. The role of mantle plumes in continental breakup — case histories from Gondwanaland. Nature 377, 301–308.

Suetsugu, D., Inoue, T., Yamada, A., Zhao, D., Obayashi, M., 2006. Towards mapping the three dimensional distribution of water in the transition zone from P-velocity tomography and 660-km discontinuity depths. In: Jacobsen, S.D., van der Lee, S. (Eds.), Earth's Deep Water Cycle: AGU Geophysical Monograph, 168, pp. 237–249.

Tagawa, M., Nakakuki, T., Tajima, F., 2007. Dynamical modelling of trench retreat driven by the slab interaction with the mantle transition zone. Earth Planet Space 59, 65–74.

Tappert, R., Stachel, T., Harris, J.W., Muelenbachs, K., Ludwig, T., Brey, G.P., 2005. Diamonds from Jagersfontein (South Africa): messengers from the sublithospheric mantle. Contributions to Mineralogy and Petrology 150, 505–522.

Tappert, R., Foden, J., Stachel, T., Muelenbachs, K., Tappert, M., Wills, K., 2009. Deep mantle diamonds from South Australia: a record of Pacific subduction at the Gondwanan margin. Geology 37, 43–46.

Torsvik, T.H., Burke, K., Steinberger, B., Webb, S.J., Ashwal, L.D., 2010. Diamonds sampled by plumes from the core–mantle boundary. Nature 466, 352–355.

Walter, M.J., Bulanova, G.P., Armstrong, L.S., Keshav, S., Blundy, J.D., Gudfinnson, G., Lord, O.T., Lennie, A.R., Clark, S.M., Smith, C.B., Gobbo, L., 2008. Primary carbonatite melt from deeply subducted oceanic crust. Nature 454, 622–626.

Walter, M.J., Kohn, S.C., Araujo, D., Bulanova, G.P., Smith, C.B., Wang, J., Shirey, S.B., submitted for publication. Lower mantle diamonds with inclusions from subducted basaltic crust. Science.

Wilding, M.C., 1990. A study of diamonds with syngenetic inclusions. Ph.D. thesis, University of Edinburgh, Scotland.

Wirth, R., Dobrzhinetskaya, L., Harte, B., Schreiber, A., H.W. Green, H.W., submitted for publication. A sample of the lowermost Mantle suggesting very low fO$_2$ and low-spin Fe^{3+}. Nature.

Wirth, R., Vollmer, C., Brenker, F., Matsyuk, S., Kaminsky, F., 2007. Inclusions of nanocrystalline aluminium silicate "Phase Egg" in superdeep diamonds from Juina (Mato Grosso State, Brazil). Earth and Planetary Science Letters 259, 384–399.

Zhao, D., Ohtani, E., 2009. Deep slab subduction and dehydration and their geodynamic consequences: evidence from seismology and mineral physics. Gondwana Research 16, 401–413.

Zhao, D., Tian, Y., Lei, J., Liu, L., Zheng, S., 2009. Siesmic image and origin of the Changbai intraplate volcano in East Asia: role of big mantle wedge above the stagnant Pacific slab. Physics of the Earth and Planetary Interiors 173, 197–206.

Zhao, D., Zheng, Y., Ohtani, E., 2011. East Asia: seismotectonics, magmatism and mantle dynamics. Journal of Asian Earth Sciences 40, 689–709.