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# 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 Carich 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.

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#### 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<sub>3</sub> 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)<sub>2</sub>SiO<sub>4</sub>, 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<sup>1</sup> 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 MgSiperovskite + 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)<sub>2</sub>SiO<sub>4</sub> (ringwoodite) to (Mg,Fe)SiO<sub>3</sub> (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

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

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