

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

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Introduction

Diamonds from the São Luiz alluvial deposit have yielded syngenetic mineral inclusions whose mutual associations and compositional characteristics are evidence for many stones having an origin within the Earth's deep transition zone (TZ) and lower mantle (LM) (Harte and Harris, 1994 and Hutchison, 1997). Variations in diamond characteristics and composition have been investigated for both bulk stones (in terms of mineral inclusion association) and within individual diamonds, by optical microscopy (fracturing, plastic deformation, colour and morphology), SEM (fracturing), cathodoluminescence spectroscopy, combustion mass spectrometry (bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ composition and nitrogen concentration), SIMS (micron scale $\delta^{13}\text{C}$ composition and nitrogen concentration) and FTIR (micron scale nitrogen concentration and aggregation state).

Diamond characteristics

Of the bulk sample of deep mantle diamonds, octahedral forms are in the minority with most LM stones being irregular (54%) and most stones of TZ origin being dodecahedra or macles (each type comprising 38%). Brown diamonds dominate the sample suite and are particularly prevalent amongst LM stones (65%). This colour is invariably associated with diamonds which have undergone plastic deformation, (see Harris 1992), with over 70% deformed for both associations. Internal brittle fracturing is common, with 39% of LM and 38% of TZ stones showing this feature, usually associated with some kind of inclusion, or other internal blemish. Very few fractures extend to the surface of the diamond. SEM analysis of four polished LM diamonds show evidence for multiple events of fracturing. For example, many fractures are sinuous and display 'augen' features characteristic of rehealing after initial deformation, but before subsequent plastic deformation. Furthermore, straight sharply terminated fractures in the same stones suggest a final deformation within a brittle régime (probably as a result of final inclusion-related fracturing on eruption, Hutchison, 1997).

Cathodoluminescence

Cathodoluminescence (CL) characteristics have been determined for six diamonds of LM origin in addition to a further two stones of unknown depth of origin. All stones show a low overall intensity in blues with one diamond (of unknown depth) showing a slight purplish tinge. All CL patterns are complex, exhibiting a number of different styles. For example, concentric zonation with areas of differing CL colours with sharp boundaries, apparently random areas showing diffuse CL boundaries, and sharply bound zones of CL in random orientations. Boundaries between each style often show significant embayments and are rarely linear. Concentric zonation is often centred on a point not coincident with the centre of the stone in its present form. CL characteristics are interpreted as being indicative of complex histories of growth, resorption and re-precipitation within régimes of stable equilibrium growth and more chaotic precipitation.

Carbon isotopic composition

LM stones cluster strongly around $\delta^{13}\text{C}$ values of -5 ‰ (with the possible exception of a single ruby-occluding stone with a value of -11.56 ‰). $\delta^{13}\text{C}$ compositions around -5 ‰ are characteristic of diamonds of LM origin in general, having been recorded for Koffiefontein diamonds (Deines et al., 1991), a single Letseng-la-terai stone (McDade and Harris, 1996) and a single Guinean stone (Hutchison, 1997). Variations within single diamonds range between -1.30 and -10.24 \pm 2 ‰ 2σ (using SIMS), although mean values for individual stones still all lie around -4 ‰. Bulk carbon isotopic content of TZ stones, also cluster around $\delta^{13}\text{C}$ of -5 ‰, but in some cases, are significantly depleted (down to -12.42 ‰). Such a negatively skewed distribution has previously been observed for TZ diamonds from Jagersfontein (Deines et al., 1991), however these diamonds are even more depleted (-19 to -24 ‰).

Nitrogen composition

Amongst the LM stones, nitrogen bulk contents are generally low, <100 ppm; most stones (26 of 28) being classified as Type II (<20 ppm N). In the two diamonds for which nitrogen could be determined by FTIR, both are highly aggregated (> 90% IaB). Using SIMS, these two highly aggregated stones contain a range in nitrogen concentration between <0.1 and 200 ppm, with most N concentrations being below 50 ppm. Individual stones, therefore, occasionally show a more marked variation in N than the population as a whole. SIMS analysis of a further two Type II diamonds yielded values of <10 ppm throughout. There is a close positive correlation between CL intensity and nitrogen concentration. A single analysis of $\delta^{15}\text{N}$ for a LM diamond gave a depleted value, -6 \pm 0.6 ‰.

TZ stones show relatively higher concentrations of nitrogen (two stones are Type II and the others contain up to ~300 ppm), compared to diamonds of the LM suite. Those with measurable nitrogen absorption, have significant IaB aggregation (>70 %) and $\delta^{15}\text{N}$ compositions from two stones are similar and positive at \sim +1.3 \pm 1.0 ‰.

Environment of formation

The striking homogeneity of $\delta^{13}\text{C}$ for LM stones indicates that the lower mantle is strongly homogeneous in $\delta^{13}\text{C}$ composition and may indicate that the lower mantle is physically well mixed. Localised heterogeneities within individual diamonds, probably reflect varying mechanisms and conditions of diamond precipitation. Following the work of Deines (1980), the distribution of $\delta^{13}\text{C}$ within individual LM stones is consistent with crystallisation via the reduction of CO_2 .

A similar fluid composition is proposed for the TZ sourced diamonds although here, variation in $\delta^{13}\text{C}$ compositions both within São Luiz and worldwide localities, is indicative of a number of separate diamond precipitating reservoirs. It is unlikely that the range of 20‰ can be inferred from fluid fractionation, especially at transition zone temperatures (Deines, 1980).

The variation of $\delta^{13}\text{C}$ composition and nitrogen concentration within single stones and from each population, has been used to investigate precipitation mechanisms: whether by equilibrium or fractional crystallisation or by mixing. Because nitrogen is a compatible element in diamond, nitrogen concentration can be used as an indicator of the degree of fluid remaining on crystallisation. During a single growth event the different mechanisms of diamond precipitation should show different behaviour of $\delta^{13}\text{C}$ composition in terms of nitrogen concentration. No clear trend in $\delta^{13}\text{C}$ composition with N content was observed, either within individual diamonds, or amongst the two diamond populations. This result suggests multiple diamond growth events where

each reservoir has a different initial nitrogen concentration and is consistent with the observations of cathodoluminescence.

Plotting $\delta^{13}\text{C}$ against $\delta^{15}\text{N}$ provides a useful means to compare the bulk composition of diamond with models proposed for the bulk composition of mantle regions. The TZ stones plot in a region consistent with the composition of C1 chondrites whereas the single LM data point plots in a distinct region, consistent with an enstatite chondrite composition. The LM diamond is not so depleted in $\delta^{15}\text{N}$ as to be entirely consistent with Javoy's (1995) proposal that the bulk mantle is composed of enstatite chondrite. However, this composition does not contradict his model if the depth of C1 chondrite veneer extends deeper into the mantle than he proposes.

Significant differences are observed between LM diamonds and stones of TZ origin in terms of carbon and nitrogen isotopic composition and nitrogen concentration and aggregation state. These observations suggest that up to the genesis of the São Luiz diamonds, little mixing has occurred between the Earth's lower mantle and the deep transition zone within the region sampled. In this instance, the deep transition zone appears to act as a graveyard for a variety of recycled upper mantle material. Such a conclusion is consistent with the significant bulk compositional differences indicated by inclusion associations recovered from São Luiz diamonds (Hutchison, 1997). Diamond deformation, on the other hand, is independent of this boundary.

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