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Formation of diamond in the Earth's mantle

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Abstract

The principal sources of natural diamonds are peridotitic (about 2/3 of diamonds) and eclogitic (1/3) domains located at 140–200 km depth in the subcratonic lithospheric mantle. There, diamonds probably form during redox reactions in the presence of melt (likely for eclogitic and lherzolititic diamonds) or under subsolidus conditions in the presence of CHO fluids (likely for harzburgitic diamonds).

Co-variations of $\delta^{13}\text{C}$ and the nitrogen content of diamonds suggest that two modes of formation may have been operational in peridotitic sources: (1) reduction of carbonates, that during closed system fractionation drives diamond compositions to higher $\delta^{13}\text{C}$ values and lower nitrogen concentrations and (2) oxidation of methane, that in a closed system leads to a trend of decreasing $\delta^{13}\text{C}$ with decreasing nitrogen. The present day redox state of subcratonic lithospheric mantle is generally too reduced to allow for methane oxidation to be a widespread process. Therefore, reduction of carbonate dissolved in melts and fluids is likely the dominant mode of diamond formation for the Phanerozoic (545 Ma–present) and Proterozoic (2.5 Ga–545 Ma). Model calculations indicate, however, that for predominantly Paleoproterozoic (3.6–3.2 Ga) to Mesoproterozoic (3.2–2.8 Ga) harzburgitic diamonds, methane reduction is the principal mode of precipitation. This suggests that the reduced present day character (oxygen fugacity below carbonate stability) of peridotitic diamond sources may be a secondary feature, possibly acquired during reducing Archean (>2.5 Ga) metasomatism. Recycling of biogenic carbonates back into the mantle through subduction only became an important process in the Paleoproterozoic (2.5–1.6 Ga) and diamonds forming during carbonate reduction, therefore, may predominantly be post-Archean in age. For eclogitic diamonds, open system fractionation processes involving separation of a CO_2 fluid appear to dominate, but in principle the same two modes of formation (methane oxidation, carbonate reduction) may have operated. Direct conversion of graphitized subducted organic matter is not considered to be an important process for the formation of eclogitic diamonds. The possible derivation of ^{12}C enriched carbon in eclogitic diamonds from remobilized former organic matter is, however, feasible in some cases and seems likely involved, for example, in the formation of sublithospheric eclogitic diamonds from the former Jagersfontein Mine (South Africa).

1. Introduction

Research on the origin of natural diamonds, mined from kimberlite and lamproite volcanoes, dramatically accelerated after the stimulus of the 1st International Kimberlite Conference (1973) and has produced a number of fundamental insights since. Most importantly, dating of mineral inclusions in diamonds (Richardson *et al* 1984) unequivocally established

their ancient formation relative to the timing of host kimberlite emplacement and thereby provided clear evidence that diamonds are xenocrysts, and not phenocrysts, in the kimberlite magma. Based on numerous studies on mineral inclusion chemistry and radiometric dating, and the stable isotope composition and nitrogen characteristics of diamonds themselves, the sources, ages and conditions of diamond formation in the Earth's mantle can now be fairly well constrained.

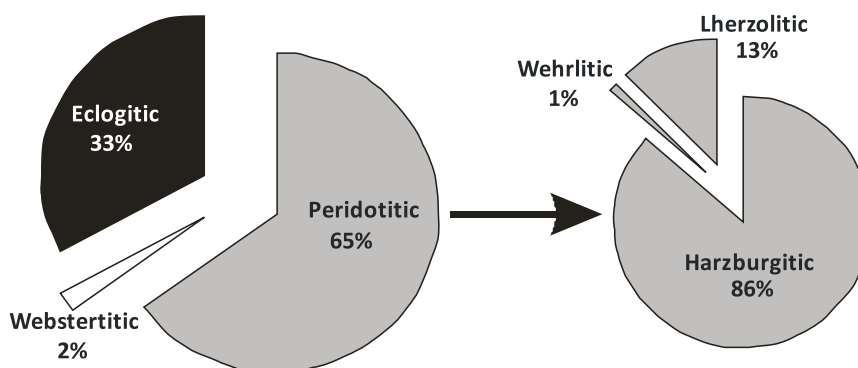


Figure 1. Left: the relative abundance of the peridotitic, eclogitic and websteritic suites based on 2844 inclusion bearing diamonds. Right: the relative proportions of the harzburgitic (-dunitic), lherzolitic and wehrlitic parageneses derived from compositional classification of 685 peridotitic garnet inclusions. Data base of Stachel and Harris (2008), corrected for an overrepresentation of inclusion bearing diamonds from DeBeers Pool mines (South Africa).

In this contribution we focus on physical conditions and possible precipitation mechanisms for the formation of diamonds in the Earth's mantle. Our discussion is based on a large number of analyses of diamonds and their mineral inclusions available in the published literature and full references for our data base are given in Stachel and Harris (2008) and Stachel *et al* (2009).

2. The environment of diamond formation

2.1. The source rocks of diamonds in the Earth's mantle

With the exception of rare super-deep diamonds—derived from the convecting upper mantle, the transition zone (410–660 km) and the lower mantle (660–2890 km)—the principal source of diamonds in the Earth's mantle is the deep subcratonic lithosphere (e.g. Boyd and Gurney 1986). Cratons, areas of continental crust that have remained stable for at least 2.5 Ga, are underlain by thick lithospheric mantle extending to depth of about 200 km. The formation of lithospheric mantle in the Archean involved very high degrees of melt extraction that left behind a buoyant residue extremely depleted in heat producing radioactive elements (such as potassium). The combination of conductive heat transport and low radiogenic heat production causes the lithospheric mantle to be distinctly cooler than convecting mantle at equivalent depth, which results in the temperature dependent graphite–diamond transition rising to shallower depth (typically about 140 km). Diamonds are sampled from these deep-reaching lithospheric ‘keels’ beneath the cratons by kimberlite or lamproite magma rapidly ascending from diamond stable conditions to the Earth's surface.

Based on the study of inclusions in diamonds (e.g. Meyer 1987, Gurney 1989, Stachel and Harris 2008), three suites of rocks have been identified that may act as a substrate for diamond formation in the lithospheric mantle: peridotite, eclogite and websterite. Peridotite constitutes the bulk of the upper mantle. Compared to convecting mantle, lithospheric peridotites have lost their easily fusible components, reflected in low Na and Ca, and high Cr/Al and Mg/Fe. Moderately depleted peridotite in the deep lithospheric mantle is a

four phase assemblage with olivine (usually >66 vol%), orthopyroxene, clinopyroxene and garnet, and is termed lherzolite. With increasing depletion clinopyroxene may disappear entirely and such peridotites are called harzburgites. Even more extreme melt extraction (>50% melt removed) results in dunites, consisting to over 90 vol% of olivine. For the subsequent discussion of diamond source rocks, the term ‘harzburgitic paragenesis’ encompasses the entire harzburgite–dunite continuum. Rare wehrlites represent a type of peridotite with clinopyroxene but without orthopyroxene and likely relate to overprint by infiltrating melts. Eclogite is the high pressure equivalent of basalt, a volcanic rock that covers ~2/3 of the Earth's surface beneath the oceans. Eclogite in the lithospheric mantle is considered to relate largely to the subduction and subcretion of former oceanic crust (e.g. Jacob 2004). From inclusion studies, the websteritic suite is only loosely defined as being compositionally intermediate between peridotite and eclogite (e.g. in their Mg/Fe and Cr/Al ratios). The genesis of websteritic diamond sources may involve multiple origins, such as crystallization directly from mafic magmas or mixing of peridotite with silica-rich partial melts from descending oceanic slabs (see Aulbach *et al* 2002).

Paragenetic studies based on silicate and oxide inclusions in diamonds indicate that peridotite is the most important source rock of diamonds (65% of inclusion bearing diamonds, see figure 1), followed by eclogite (33%). On a worldwide scale, websterite (2%) has so far not been recognized as an important diamond source. In contrast to a strong predominance of lherzolite over harzburgite in the subcratonic lithospheric mantle sampled by kimberlites, for diamonds with peridotitic inclusions the harzburgitic paragenesis strongly dominates (Gurney 1984; see figure 1).

2.2. Pressure–temperature constraints and solidus temperature of peridotite

The occurrence of inclusions of different minerals in single diamonds allows the determination of both the conditions of diamond formation (from non-touching inclusions) and of diamond residence in the Earth's mantle (from touching inclusion pairs). Comparison of temperature estimates for

touching and non-touching inclusion pairs on the level of individual localities indicates that diamond formation occurred at temperatures ca 100–150 °C hotter than the ambient conditions of the host mantle directly preceding kimberlite eruption (e.g. Stachel *et al* 2003, Phillips *et al* 2004). Using a data base of inclusion analyses from worldwide occurrences (touching and non-touching inclusion not separated, since commonly not recorded), thermal conditions for formation/storage of peridotitic and eclogitic diamonds may be compared. Calculated for an assumed pressure of 5 GPa, both suites yield temperature conditions that are indistinguishable within error (modes in class 1150–1200 °C, means of ~1160–1170 °C; see figure 2). This suggests that irrespective of their source rocks, lithospheric diamonds form under similar temperature conditions. For peridotitic diamonds, the pressure of formation/storage may be derived along with temperature (garnet–orthopyroxene geothermobarometry; Harley 1984, Brey and Köhler 1990) and such data show that lithospheric diamonds crystallize between 140 and 200 km depth (equivalent to 4.5–6.5 GPa) along model geothermal gradients (Pollack and Chapman 1977) consistent with 38–42 mW m⁻² surface heat flow. In the likely presence of hydrous volatiles during diamond formation, these pressure–temperature conditions indicate that formation of lherzolitic and eclogitic diamonds will generally occur above the solidus temperature (beginning of melting) of their respective source rocks (figure 2). A higher solidus temperature for more magnesian and clinopyroxene-free harzburgitic sources (figure 2) implies that formation of harzburgitic diamonds straddles the beginning of melting but more commonly occurs under subsolidus conditions. For mixed fluids (CH₄–H₂O or CO₂–H₂O) the solidus temperature increases with decreasing water activity; the ‘dry’ solidus temperature of diamond stable peridotite (>1600 °C at depth >150 km; Takahashi 1986) far exceeds realistic geothermal gradients.

2.3. Trace elements (Zr–Y) and mantle metasomatism

To constrain the formation of peridotitic diamonds, further insights into the chemical environment and a possible relationship to infiltration of fluids (subsolidus) or melts (supersolidus) into their sources may be derived from the trace element composition of inclusions. Trace elements, based on their behavior during partial melting, may be compatible (remain in the solid residue) or incompatible (partition into the melt phase). Consequently, during the massive melt extraction events invariably associated with the early evolution of cratonic peridotites, incompatible elements were quantitatively removed from the lherzolitic and harzburgitic diamond sources. Garnet inclusions in diamonds, therefore, should contain only very low concentrations (up to a few ppm) of trace elements such as Zr (highly incompatible) and Y (moderately incompatible). Studies on garnet inclusions in diamonds show, however, that there are two trends, both originating from the expected depleted composition but extending to higher incompatible trace element contents: one trend is associated with re-enrichment of both Zr and Y, and a second trend with re-enrichment of Zr but without

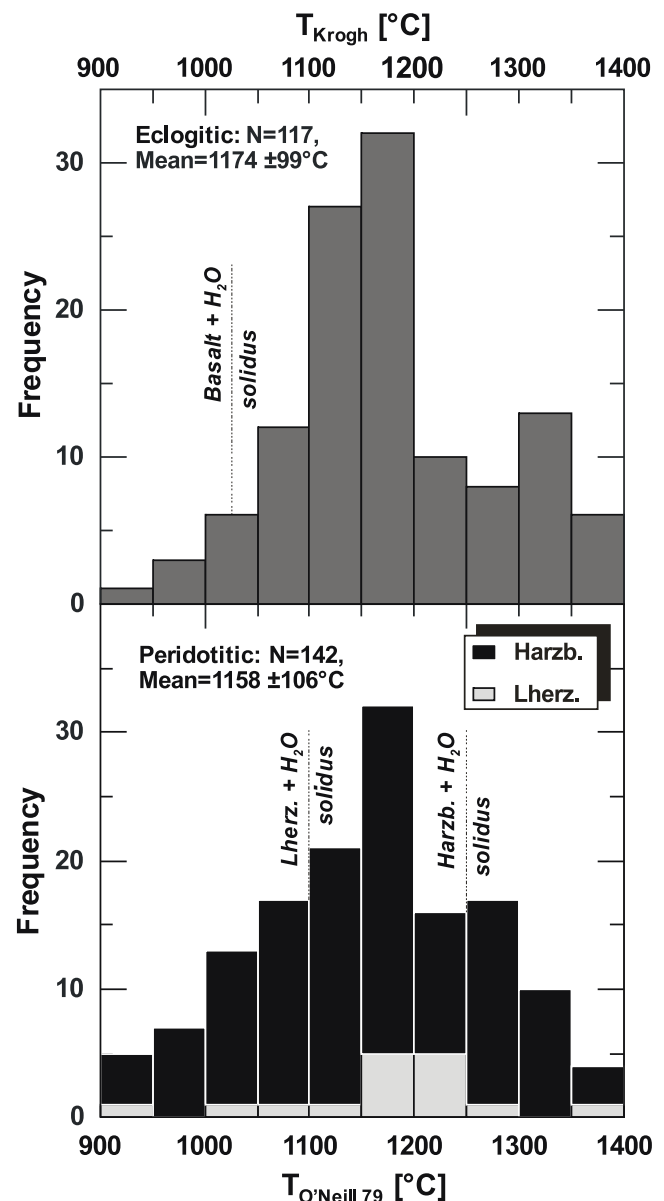


Figure 2. Equilibration temperatures (at an assumed pressure of 5 GPa) derived from Mg–Fe exchange between garnet–olivine (thermometer of O’Neill and Wood (1979); bottom) and garnet–clinopyroxene (Krogh 1988; top) inclusion pairs in diamonds. Data outside the range 900–1400 °C were excluded since such thermal conditions cannot occur along realistic geothermal gradients within diamond stable lithospheric mantle. For the eclogitic suite (top) inclusions in diamonds from Argyle are unusually high in their equilibration temperatures and, therefore, are excluded as well; otherwise, a slightly higher average of 1194 ± 95 °C would have been obtained. Wet solidi (beginning of melting in the presence of a hydrous fluid) for harzburgite, lherzolite and eclogite (‘basalt’) are shown for a pressure of 5 GPa and are taken from Inoue (1994) and Kessel *et al* (2005 and references therein). Addition of CO₂ or CH₄ to the fluid phase would increase the solidus temperature.

significant increase in Y (figure 3). The former trend was shown to be typically related to melt infiltration whereas the latter is characteristic of the passage of fluids, enriched in highly incompatible elements only, through peridotite (Griffin and Ryan 1995). Such percolation of melts or

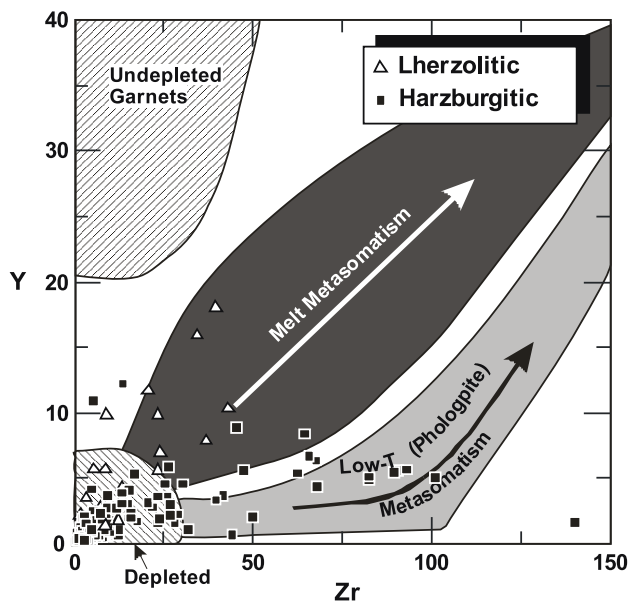


Figure 3. Variations in Y and Zr (wt. ppm) content of peridotitic garnet inclusion. Compositional fields and trends were defined by Griffin and Ryan (1995). Fluid metasomatism is characterized by re-enrichment in Zr without concomitant addition of significant quantities of Y and is restricted to garnet inclusions of harzburgitic paragenesis. Simultaneous addition of Zr and Y, attributed to melt metasomatism, is observed mainly for lherzolitic garnets. Data base of Stachel and Harris (2008) with additional analyses from Banas *et al* (2009).

fluids through peridotite and the associated re-enrichment in incompatible elements constitutes the process of mantle metasomatism. From the available data it appears that melt metasomatism is typically associated with lherzolitic diamonds whereas subsolidus fluid metasomatism is documented for harzburgitic diamonds only (figure 3). This observation is consistent with the earlier conclusion that lherzolitic diamonds mainly form at temperatures above the wet lherzolite solidus (presence of melt) whereas harzburgitic diamonds largely form under subsolidus conditions (presence of fluid only). For garnet inclusions plotting into the depleted field (figure 3), metasomatic overprint is, however, too subtle to distinguish between melt and fluid metasomatism based on Zr–Y covariations. Using extremely mantle incompatible elements—such as the light rare earth—as indicators, the source rocks of these ‘depleted’ garnets can nevertheless be shown to have been affected by some degree of fluid style metasomatic re-enrichment.

2.4. Diamond forming reactions

The simplest mode of diamond formation is the isochemical conversion of graphite to diamond and this process has been invoked for the formation of diamond from subducted former organic matter (e.g. Kirkley *et al* 1991). Very high activation energies for the graphite to diamond transition require overstepping of the phase boundary by >3 GPa in a static compression process (Sung 2000). In nature, the required overstepping of the graphite–diamond

transition could be reduced through shearing which may aid the martensitic transition from hexagonal to rhombohedral graphite. Likely, the high activation energy and associated overstepping will cause the graphite–diamond conversion to occur catastrophically resulting in polycrystalline aggregates of microscopic crystallites (Sung 2000, Irifune *et al* 2004). The direct conversion of graphite to diamond, therefore, is not considered a relevant process for the formation of macroscopic octahedral diamonds in nature.

As alternative to direct conversion from graphite, Deines (1980) considered seven possible redox reactions involving CH₄, CO and CO₂ for the formation of natural diamonds. Eliminating all reactions involving CO, which is not a significant fluid species at high pressures (Woermann and Rosenhauer 1985), and considering that CO₂ is buffered by carbonation reactions in olivine bearing rocks at high pressure (Wyllie and Huang 1976), two principal types of redox reactions are relevant for natural diamond formation:

- (1) *Reduction of carbonate*, present as a solid or dissolved in a melt/fluid. The redox equilibria governing carbonate reduction for eclogite, harzburgite and lherzolite are respectively: dolomite + coesite = cpx + diamond (DCDD; Luth 1993), enstatite + magnesite = olivine + diamond (EMOD; Rosenhauer *et al* 1977, Eggler and Baker 1982) and enstatite + magnesite = olivine + cpx + diamond (EMFDD; Luth 1993). The diamond forming reaction in eclogites occurs at oxygen fugacities (a measure of how oxidizing a chemical system is) about 1 log unit higher (i.e. more oxidizing) than for the two peridotitic sources. At high temperatures (>1300 °C), which may be lowered through the presence of H₂O, diamond formation in eclogites (no olivine present) may additionally occur through reduction of CO₂ (CCO: CO₂ = C + O₂; e.g. Luth 1993). Studies on the paleo oxygen fugacity state (time of kimberlite eruption) of the subcratonic lithospheric mantle (e.g. Luth *et al* 1990, McCammon and Kopylova 2004, Creighton *et al* 2009) suggest that elemental carbon rather than carbonate is usually stable in subcratonic peridotitic mantle at pressure exceeding ~3 GPa (Frost and McCammon 2008), implying that only reduction of carbonate dissolved in upward migrating fluids/melts has to be considered.
- (2) *Oxidation of a reduced carbon species (methane)*: CH₄ + O₂ = C + 2H₂O. This reaction is thought to reflect the influx of reduced fluids from the convecting upper mantle into a more oxidized lithospheric mantle and, because it produces free water, will be associated with a reduction in solidus temperature (‘redox melting’; Taylor and Green 1989). Although present day subcratonic lithospheric mantle is generally too reduced for this process to occur, its operation has been demonstrated for a set of ~1.9 Ga old lherzolitic diamonds (Richardson *et al* 1993) from the Premier (Cullinan) Mine in South Africa by Thomassot *et al* (2007) and hence methane reduction must be considered, at least locally, as a diamond forming process.

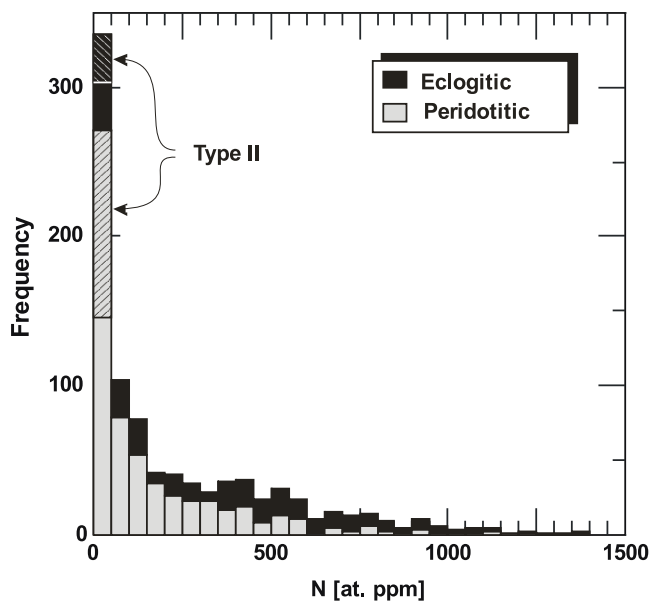


Figure 4. Nitrogen content in diamonds with peridotitic and eclogitic inclusions. Samples for inclusion studies typically are in the size range $-9 + 5$ (DTC sieve classes, corresponding to diamonds <2.88 mm and >1.83 mm in two dimensions). Analyses of the 916 samples shown were generally conducted via micro-FTIR. Type II diamonds (nitrogen below the limit of detection: ≤ 10 at. ppm) are included in class 0–50 at. ppm and shown with hatched patterns. 24% of diamonds with peridotitic inclusions and 10% with eclogitic inclusions classify as Type II. The histogram is cut off at 1500 at. ppm, excluding three peridotitic and three eclogitic diamonds with nitrogen concentrations up to 3830 at. ppm.

3. Nitrogen in diamond

In inclusion bearing diamonds, nitrogen concentrations range from 0 to 3830 at. ppm (median value of 91 at. ppm) and thus N is the most abundant molecular impurity in diamond. Type II diamonds (in micro-FTIR studies defined as having $N \leq 10$ at. ppm) constitute 10% of eclogitic and 24% of peridotitic samples (figure 4). Nitrogen contents tend to be higher in eclogitic (median value of 378 at. ppm) than in peridotitic (median of 72 at. ppm) diamonds. Overall, nitrogen is generally strongly enriched in diamonds relative to primitive mantle concentrations (only ~ 2 wt. ppm N; e.g. Palme and O'Neill 2004).

Despite the similar charge and ionic radius of nitrogen and carbon, Boyd *et al* (1994) and Cartigny *et al* (2001) proposed that nitrogen is incompatible in the diamond structure and that incorporation of nitrogen is controlled by a kinetic process rather than by equilibrium distribution. In this model, high nitrogen in diamond occurs as a consequence of rapid disequilibrium growth where the carbon–nitrogen ratio of diamond approaches that of the precipitating fluid or melt. For slow equilibrium growth, the formation of Type II diamonds is predicted, irrespective of the nitrogen content of the growth medium (Cartigny *et al* 2001).

During high pressure diamond synthesis in metal melts (e.g. Reutsky *et al* 2008), decreasing nitrogen contents from core to rim indicated compatibility of nitrogen in diamond

relative to the growth medium and, as a consequence, great care is usually taken (outgassing of starting materials, addition of nitrogen getters) to achieve synthesis of low nitrogen diamonds. In addition, high nitrogen in diamond has been observed not only during experiments using transition metal catalysts (i.e. very reducing conditions) but also during diamond growth involving de-carbonation reactions (i.e. more oxidizing conditions) in the presence of silicates (Pal'yanov *et al* 2002). Experimental evidence, therefore, is not consistent with a strong control of oxygen fugacity (cf Deines *et al* 1989) on the incorporation of N into diamond. Experimental growth of diamonds occurs at temperatures significantly above the conditions of natural diamond formation—the high temperatures speeding up diffusion and hence permitting better equilibration between diamond and its growth medium—and formation proceeds via a smooth growth process resulting in flat octahedral and cubic faces. Compatibility of nitrogen in synthetically grown diamonds is higher for octahedral than for cubic faces by a factor of 2–10 (Boyd *et al* 1988, 1994). It, therefore, appears implausible that synthetic diamonds should generally grow and incorporate nitrogen under disequilibrium conditions whereas commonly octahedral natural diamonds are supposed to generally form much closer to equilibrium conditions. Consequently, we interpret the common strong enrichment of nitrogen in natural diamond relative to the Earth's mantle as reflecting compatibility of nitrogen in the diamond lattice, similar to observations in experimental studies.

4. Stable isotope composition

4.1. Carbon isotopes

The carbon isotopic composition ($^{13}\text{C}/^{12}\text{C}$ ratio) of diamond is conventionally reported in the $\delta^{13}\text{C}$ notation representing the normalized difference, expressed in ‰, to the international VPDP standard (Vienna-Pee Dee Belemnite).

The distributions in carbon isotopic composition of peridotitic and eclogitic diamonds (figure 5) both show prominent modes at about $-5\text{‰} \pm 1\text{‰}$, a value that is generally assumed to represent the composition of mantle derived carbon (e.g. Deines 1980, Cartigny 2005). Whereas $>95\%$ of all peridotitic diamonds fall within the range -9 to -1‰ , eclogitic diamonds show a distribution skewed to ^{12}C enriched compositions (figure 5) with a poorly defined second mode, or several overlapping modes, between about -19 and -8‰ , combined with an overall much wider compositional range (-38.5 to $+2.9\text{‰}$). For eclogitic diamonds the prominent mode at -5‰ is only typical for diamonds from some cratons: it is present, for example, at the Kalahari Craton in southern Africa, but absent at the Kimberley Craton in Australia and the Amazon Craton in Brazil and Venezuela (Stachel *et al* 2009).

Examining the prominent mode at -5‰ for peridotitic diamonds on a detailed level (figure 6) shows that the normal distribution seen in figure 5 actually is polymodal. For the harzburgitic paragenesis two modes exist, a larger mode at about -5.5‰ and a smaller mode around -4‰ ; for lherzolitic diamonds the main mode is slightly shifted to -5‰ , the

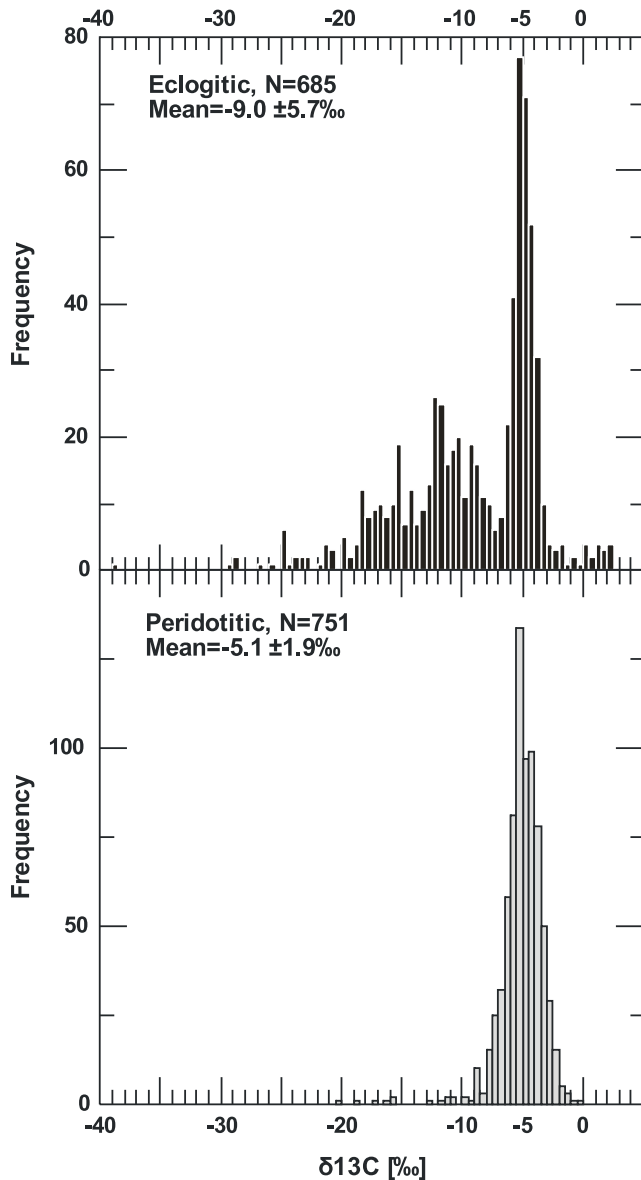


Figure 5. Carbon isotopic composition of diamonds with peridotitic (bottom) and eclogitic (top) inclusions. Bin (class) size is 0.5‰ . For references of data sources, see Stachel *et al* (2009).

second mode seen for harzburgitic diamonds near -4‰ is present as well and either represents a population skewed to ^{13}C enriched compositions or overlaps with a third population peaking at around -3‰ (the current data base of only 92 lherzolithic samples is too small to distinguish between these two possibilities).

4.2. Co-variations between carbon isotopes and nitrogen content

For diamonds with eclogitic (and fairly rare websteritic) inclusions there is a relationship of decreasing maximum nitrogen content with decreasing $\delta^{13}\text{C}$ (figure 7, top; Stachel and Harris 1997). Cartigny *et al* (2001) modeled this relationship as resulting from the escape of CO_2 —enriched in $^{13}\text{C}/^{12}\text{C}$ —together with some nitrogen, from melts in an

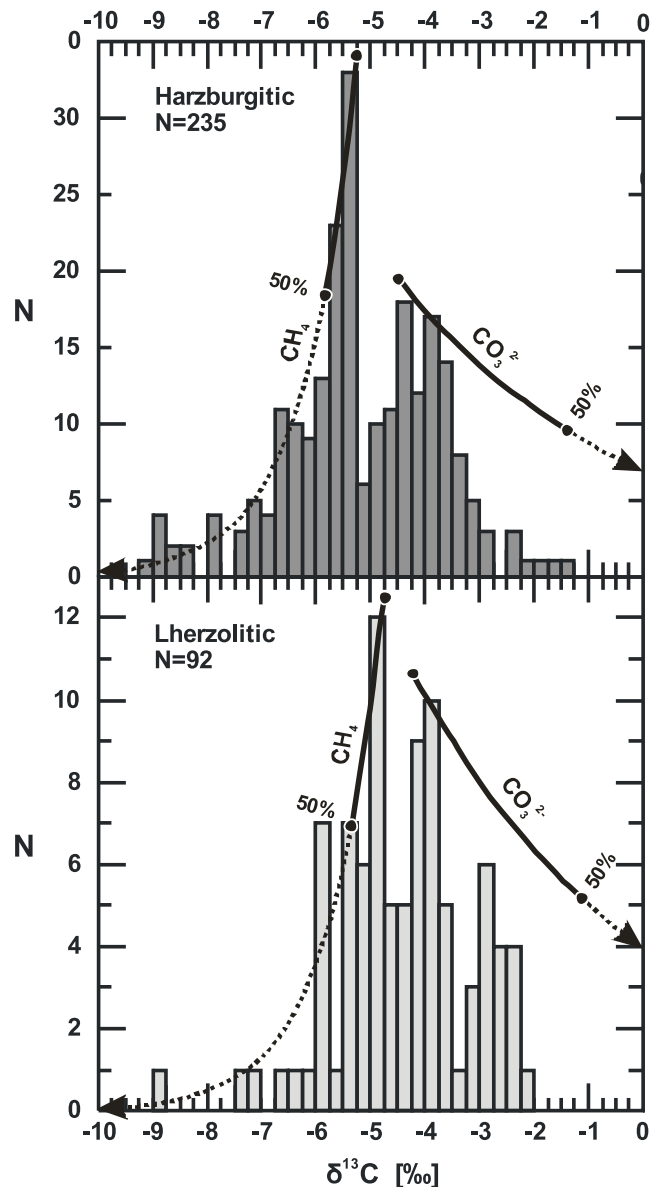


Figure 6. Carbon isotopic composition of diamonds with peridotitic inclusions: harzburgitic paragenesis (top) and lherzolithic paragenesis (bottom). Bin size is 0.25‰ , which still exceeds analytical uncertainty ($\pm 0.1\text{‰}$, 2 sigma). Curves reflect modeled relative diamond abundances based on closed system Rayleigh fractionation for precipitation of diamond from methane- and carbonate bearing melts/fluids. Diamond is depleted in ^{12}C relative to methane (ΔC of about $+1\text{‰}$) but enriched relative to carbonatitic melt (ΔC of about -3.5‰) (see Deines 1980, Thomassot *et al* 2007 and references therein). The initial fluid composition ($\delta^{13}\text{C}_0$) for the model curves is about -6‰ for precipitation from methane and about -1‰ for precipitation from a carbonatitic fluid/melt. Precipitation of the first 50% of diamond in the models is shown as solid lines, the remaining 50% as dashed lines. The models only represent first order approximations, there likely is variability in $\delta^{13}\text{C}_0$ (especially for subduction initiated carbonatitic fluids/melts) and crystallization may never proceed to 100%.

open system and introduced the term ‘limit sector curve’ (arrow labeled ‘melt evolution’ in figure 7, top). Diamonds plotting at variable nitrogen contents below the limit sector are

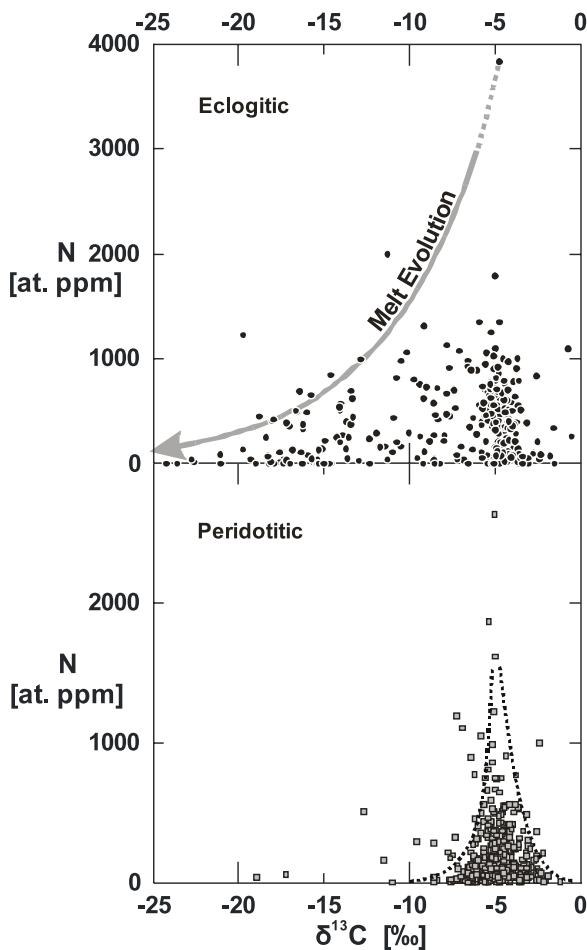


Figure 7. Co-variations between nitrogen content and carbon isotopic composition for diamonds containing eclogitic (top) and peridotitic (bottom) inclusions. The melt evolution trend for eclogitic diamonds is taken from Cartigny *et al* (2001) and represents a bounding ('limit sector') curve for the data. Diamond falling below the trend may reflect slow growth fractionation (Cartigny *et al* 2001), or a combination of (1) variation in initial nitrogen and $\delta^{13}\text{C}_0$ for the melt evolution curve and (2) nitrogen depletion during subsequent closed system fractionation. The bottom graph shows hypothetical bounding curves that include the bulk (>95%) of peridotitic diamonds. Such bounding curves can be modeled as relating to diamond precipitation from methane and carbonate bearing fluids/melts (see figure 6), assuming compatibility of nitrogen in the diamond lattice (see Stachel *et al* 2009).

considered by Cartigny *et al* (2001) to reflect altering growth speed, with rapidly growing diamonds falling on or near the limit sector and slowly growing diamonds being nitrogen poor (see section 3). If compatibility of nitrogen in diamond is accepted (see above), then deviations from the limit sector towards lower nitrogen contents may instead reflect closed system processes, possibly coupled with variations in initial melt compositions (both nitrogen content and $\delta^{13}\text{C}$). The Cartigny *et al* (2001) CO_2 escape model satisfactorily explains the observation that strongly ^{13}C depleted diamonds are almost exclusively restricted to olivine free parageneses (eclogite and websterite), consistent with the fact that separation of a free CO_2 fluid cannot occur in peridotitic diamond sources (see section 2.4). The alternative model for the origin of

^{13}C depleted eclogitic diamonds (e.g. Sobolev and Sobolev 1980, McCandless and Gurney 1997), the remobilization of graphitized subducted organic matter ($\delta^{13}\text{C} \leq 20\text{‰}$), cannot, however, be ruled out as being a second operational process. In particular, the origin of ^{13}C depleted eclogitic diamonds of super-deep origin (e.g. Tappert *et al* 2005) cannot be explained through separation of a ^{13}C enriched CO_2 fluid, since at sublithospheric pressures CO_2 is buffered through carbonation reactions with both clinopyroxene and garnet (see Luth 2003 and references therein).

For peridotitic diamonds (figure 7, bottom), the highest nitrogen contents coincide with the mode in $\delta^{13}\text{C}$ around -5‰ and away from this mode, towards both lower and higher $\delta^{13}\text{C}$, nitrogen contents rapidly drop off. The data distribution may be fitted by two bounding curves (figure 7, bottom) that include over 95% of the samples. In analogy to the limit sector curve for eclogitic diamonds (which covers a much wider $\delta^{13}\text{C}$ range), for the formation of peridotitic diamonds two processes must operate leading to depletion in nitrogen coinciding with fractionation of carbon isotopes towards both lower and higher $\delta^{13}\text{C}$. Stachel *et al* (2009) modeled the $\delta^{13}\text{C}$ -N distribution of peridotitic diamonds based on precipitation from methane and carbonate bearing fluids/melts. During closed system Rayleigh fractionation and under the premise that nitrogen is compatible in diamond, precipitation from methane drives diamond compositions towards lower $\delta^{13}\text{C}$ and N contents (Thomassot *et al* 2007) whereas crystallization from carbonatitic fluids/melts leads to a trend of increasing $\delta^{13}\text{C}$ and decreasing N contents (Stachel *et al* 2009). Diamonds falling below the bounding curves relate to variations in initial fluid composition (both nitrogen content and $\delta^{13}\text{C}$). This model provides testable predictions with respect to the distribution of $\delta^{13}\text{C}$ for peridotitic diamonds. For example, equilibrium isotope fractionation between diamond and methane ($\Delta C = \delta^{13}\text{C}_{\text{diamond}} - \delta^{13}\text{C}_{\text{methane}} = 1\text{‰}$) is much weaker than between diamond and carbonate ($\Delta C = -3.5\text{‰}$) (see Deines 1980, Thomassot *et al* 2007 and references therein). Thus, for a constant initial carbon isotopic composition, diamond precipitation from methane should produce a narrow left skewed distribution, with the first 50% of diamonds forming over an interval of only -0.6‰ in $\delta^{13}\text{C}$. By contrast, the precipitation of the first 50% of diamonds from carbonate spans $+3.6\text{‰}$, resulting in a strongly right skewed $\delta^{13}\text{C}$ distribution. Whilst precipitation from methane provides a very good match for the observed data distribution (figure 6), the calculated precipitation from carbonates predicts the occurrence of peridotitic diamonds with positive $\delta^{13}\text{C}$ (which have not been observed). This may indicate that isotope fractionation during diamond precipitation from carbonates is less severe than the assumed ΔC of -3.5‰ or that closed system diamond precipitation during reduction of carbonate dissolved in fluids/melts never exceeds 50%. The existence of closed systems during metasomatic events likely is short lived and confined to the immediate vicinity of growing diamonds. The model also implies that the similar modes (1‰ difference) for methane and carbonate related diamonds arise from initial fluids that are quite distinct (5‰ difference for the curves shown in figure 6; see figure

caption for details). Such a large difference is geologically reasonable as methane derived fluids may be expected to have a $\delta^{13}\text{C}_0$ corresponding to the mantle value of about $-5 \pm 1\%$ whereas carbonatitic fluids/melts may well derive from subducted oceanic lithosphere and hence will have a more variable $\delta^{13}\text{C}_0$ likely covering the entire range between the mantle value and 0% . Marine carbonates (initial $\delta^{13}\text{C}$ of $0 \pm 5\%$, Schidlowski *et al* 1983), which may be the source of carbonatitic fluids/melts, undergo progressive devolatilization during subduction and associated thermal equilibration with hot surrounding mantle, driving their isotopic composition towards lower $\delta^{13}\text{C}$ values, consistent with a range in $\delta^{13}\text{C}_0$ for diamond precipitating CO_3^{2-} .

Comparing the $\delta^{13}\text{C}$ distributions for harzburgitic and lherzolitic diamonds (figure 6), the proportion of diamonds with $\delta^{13}\text{C} > 5\%$ is significantly higher for the lherzolitic paragenesis. In the model presented here, that implies increased precipitation from carbonatitic melts/fluids for lherzolitic diamonds. This observation may relate to a broad subdivision into ancient (Paleoarchean to Mesoarchean) formation of harzburgitic diamonds followed by an addition of younger lherzolitic diamonds during the Proterozoic (established for the Kalahari Craton, Shirey *et al* 2003), the latter coinciding temporarily with a dramatic increase in the precipitation and subsequent subduction of marine carbonates. The overall shift of lherzolitic diamonds towards isotopically heavier compositions, therefore, may reflect a secular trend towards more oxidized metasomatic fluids/melts reflecting increasing subduction of biogenic carbonates subsequent to the Mesoarchean. Incidentally, the formation of harzburgitic diamonds predominantly below the solidus temperature of their source (see section 2.2) agrees well with a preferred precipitation from methane bearing fluids.

4.3. Nitrogen isotopes

Nitrogen has two stable isotopes, ^{14}N and ^{15}N , and the nitrogen isotopic composition is expressed as normalized difference to atmospheric nitrogen (which consequently has a $\delta^{15}\text{N}$ of 0%). The application of nitrogen isotopic analyses to diamond studies is difficult because of generally low nitrogen contents but has been pioneered by Javoy (e.g. Javoy *et al* 1984), Boyd (e.g. Boyd *et al* 1987) and Cartigny (e.g. Cartigny *et al* 1998b).

Nitrogen isotopes are particularly useful as tracer of a potential derivation of diamond carbon from subducted organic matter. Ammonium in oceanic sediments has a positive nitrogen isotopic signature (average $\delta^{15}\text{N}$ of about $+6\%$) and metamorphic overprint during subduction may only further increase this value (Cartigny *et al* 1998a). By comparison, the Earth's mantle is significantly depleted in ^{15}N ($\delta^{15}\text{N}$ of $-5 \pm 3\%$, Cartigny 2005) and, therefore, the proposed formation of diamonds with light carbon isotopic composition ($\delta^{13}\text{C}$ below -10%) through conversion or re-precipitation of graphitized subducted organic matter should be accompanied by positive $\delta^{15}\text{N}$ values. This is, however, not the case and about 70% of eclogitic diamonds have negative $\delta^{15}\text{N}$ values (Cartigny 2005). This absence of an association between ^{13}C depletion and ^{15}N enrichment may possibly relate to decoupling of carbon and

nitrogen during subduction (preferential loss of nitrogen from slabs) or during subsequent diamond formation. Currently available data suggest, however, that at least during subduction such a decoupling is not likely to occur (Philippot *et al* 2007) and hence, formation of diamonds directly from graphitized organic matter cannot be reconciled with the $\delta^{15}\text{N}$ data.

5. Conclusions

Formation of diamonds in the Earth's mantle occurs during redox reactions involving upward percolating fluids and melts. For eclogitic diamonds these fluids/melts may be more frequently carbonatitic in character (as opposed to methane bearing), allowing for carbon isotopic fractionation in the course of CO_2 escape and the associated occurrence of strongly ^{13}C depleted diamonds (Cartigny *et al* 2001). For peridotitic diamonds, co-variations of $\delta^{13}\text{C}$ and nitrogen content suggest involvement of both, carbonate bearing and methane bearing fluids/melts, that during closed system Rayleigh fractionation drive the carbon isotopic composition of precipitated diamonds to ^{13}C enriched and ^{13}C depleted compositions, respectively. Present day subcratonic lithospheric mantle generally is too reduced to allow for diamond precipitation from methane bearing fluids. A preferential association of diamonds fitting the methane precipitation model with the harzburgitic paragenesis may, however, indicate that during Paleoarchean to Mesoarchean formation of harzburgitic diamonds, this was not yet the case. Strongly increased production and subduction of oceanic carbonates in the Proterozoic may have given rise to more oxidized slab derived fluids and consequently, promoted a shift towards diamond precipitation through carbonate reduction as modeled here for generally younger lherzolitic diamonds. Methane oxidation may still have operated as a diamond forming process subsequent to the Mesoarchean in sections of deep lithospheric mantle that were affected by severe metasomatic events and, as a consequence, acquired a somewhat more oxidized character. Considering the Proterozoic age of lherzolitic diamonds at Premier (Cullinan) Mine (1.93 Ga, Richardson *et al* 1993), a lherzolite xenolith from there containing multiple diamonds falling on a coherent methane precipitation trend (Thomassot *et al* 2007) may serve as an example for such an 'unusual' local environment, with the lithospheric mantle beneath Premier being strongly affected by the massive ~ 2.05 Ga Bushveld magmatic event.

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