



Evidence of subduction and crust–mantle mixing from a single diamond

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Abstract

Cathodoluminescence (CL) imaging of polished sections of a diamond from the Guaniamo region of Venezuela suggests a history of the diamond involving two periods of growth separated by a period of resorption and possibly brittle deformation. In situ electron probe analysis of multiple eclogitic garnet inclusions reveals a correlation between garnet composition and location in the stone. An early-formed garnet in the diamond core has higher Ca/(Ca + Mg) and lower Mg/(Mg + Fe) values than later garnets associated with the second period of diamond growth. This variation conforms to an extensive trend of variation in the suite of eclogitic garnets extracted from Venezuelan diamonds. The diamond is zoned in carbon isotope composition (in situ secondary ion mass spectrometry, SIMS, data). The core compositions ($\delta^{13}\text{C}$ PDB), corresponding to the first stage of growth, average -17.7% . The second period of growth is apparently in two sub-sets of CL zones with mean values of -13.0% and -7.9% . Nitrogen contents of diamond are low (30–300 atomic ppm) and do not correlate with carbon isotope composition. Oxygen isotope ratios of the garnet inclusions are elevated substantially above those expected for “common mantle”; $\delta^{18}\text{O}$ VSMOW of early garnet is approximately $+10.5\%$ and two late garnets average $+8.8\%$. The evolutionary trend of magnesium enrichment in garnet is unlikely to represent igneous fractionation. The stable isotope data are consistent with diamond formation in subducted meta-basic rocks that had interacted with sea water at low temperatures at or near the sea floor and contained a substantial biogenic carbon component. During or following subduction, diamonds continued to form in an evolving system that was progressively modified by interaction with mantle material.

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1. Introduction

The study of the minute minerals found as primary (syngenetic) inclusions in diamonds has provided

a wealth of information bearing on the origin of diamonds within Earth's interior (e.g., [Sobolev, 1976](#); [Meyer, 1987](#); [Gurney, 1989](#)). Due to technical limitations, and expediency, however, most studies to date have involved breaking or burning diamonds to liberate their inclusions. In many cases, multiple inclusions of the same mineral in a single diamond have been found to have virtually the same compo-

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sition (e.g., [Prinz et al., 1975](#)). In cases in which multiple inclusions of one mineral have been found to vary in composition within a single diamond, however, information on their position within the diamond is lost if they are extracted by breaking or burning (e.g., [Jaques et al., 1989](#); [Sobolev et al., 1998](#)). Furthermore, with the extraction method, the composition of the host diamond, typically analysed as bulk fragments in separate studies, cannot be directly correlated with compositions of specific inclusions.

Recently, investigators have begun to study diamonds and their mineral inclusions in situ, in polished sections or plates of diamonds, using a variety of microbeam methods (e.g., [Rudnick et al., 1993](#); [Bulanova, 1995](#)). This approach has provided new insights into diamond formation, as individual mineral compositions can be correlated with specific stages of diamond growth.

We have studied polished sections of inclusion-bearing diamonds of the eclogite suite from the Guaniamo region of Venezuela, on the Guyana Shield (e.g., [Meyer and McCallum, 1993](#); [Channer et al., 2001](#)), using electron microprobe, cathodoluminescence (CL) and secondary ion mass spectrometry (SIMS) techniques. In one stone, we have found a correlation between major element composition of garnet inclusions and carbon isotope composition of the diamond host that can be related using CL imaging to position in the stone, and thus with growth history of the diamond. Comparison of these data with the large existing data set for Guaniamo diamond inclusion minerals ([Sobolev et al., 1998](#); [Kaminsky et al., 2000](#)) allows us to place constraints on the source material and processes involved in formation of eclogitic diamonds.

2. Diamond #13-127-27

2.1. CL textures

Within a small suite of diamonds from the Guaniamo region of Venezuela, cut and polished to expose mineral inclusions, we identified eight stones with garnet inclusions exposed by polishing. One of these, diamond 13-127-27, cut approximately parallel to (100), has six garnet grains exposed on its polished

surfaces, three on each half of the laser-cut stone. A CL image of one half of this stone is illustrated in [Fig. 1](#), and a portion of the other half is shown in [Fig. 2](#). The major portion of the stone is relatively dark, with only faint zoning visible in CL, and contains a single large garnet (#27-1). A brighter, more complex CL response characterises much of the rim, which is only partially preserved, but also fills a “re-entrant” into the stone ([Fig. 1](#)). (The term “re-entrant”, as used here, does not refer to a physical hole or opening in the stone, but to the elongate bright CL portion of the diamond projecting into the centre from the rim. [Anand et al. \(2003\)](#) have described a somewhat similar CL feature in a diamond and attributed it to late diamond forming in a healed fracture.) Two smaller garnets (#27-2 and #27-3) occur in the late-formed diamond in the re-entrant. Three other garnets (#27-4 to -6) are exposed on the polished surface of the other half of the stone ([Fig. 2](#)), and also occur within the re-entrant portion of the late, bright complex CL zone, although the re-entrant portion in half B does not extend fully to the rim. The faint CL zoning visible in the dark, major portion of the stone appears, in half A, to be abruptly truncated on the upper right margin and overgrown by the light, complex CL diamond rim phase ([Fig. 1](#)).

2.2. Electron microprobe data

The garnet inclusions were analysed with a Cameca SX-50 electron microprobe at University of Toronto using standard WDS techniques. Compositions are given in [Table 1](#). Garnet #27-1 is more calcic (molar $\text{Ca}/(\text{Ca} + \text{Mg})$ (ca)=0.271) and less magnesian (molar $\text{Mg}/(\text{Mg} + \text{Fe})$ (mg)=0.561) than are garnets 2 and 3, which are virtually identical in composition (ca=0.218, mg=0.610). Garnets 4–6 are intermediate in composition between these two extremes, though very similar to garnets 2 and 3 (ca=0.226–0.233, mg=0.596–0.600). Garnet 1 also has lower contents of TiO_2 (0.60 wt.%) and Na_2O (0.19 wt.%) than do the later-formed garnets 2–6 (0.77–0.85 wt.% TiO_2 and 0.27–0.28 wt.% Na_2O).

In [Fig. 3](#), compositions of the garnets in diamond 13-127-27 are compared with those from other eclogitic diamonds from the Guaniamo region. The suite, as a whole, has a very distinct negative correlation between $\text{Ca}/(\text{Ca} + \text{Mg})$ and $\text{Mg}/(\text{Mg} + \text{Fe})$, and the

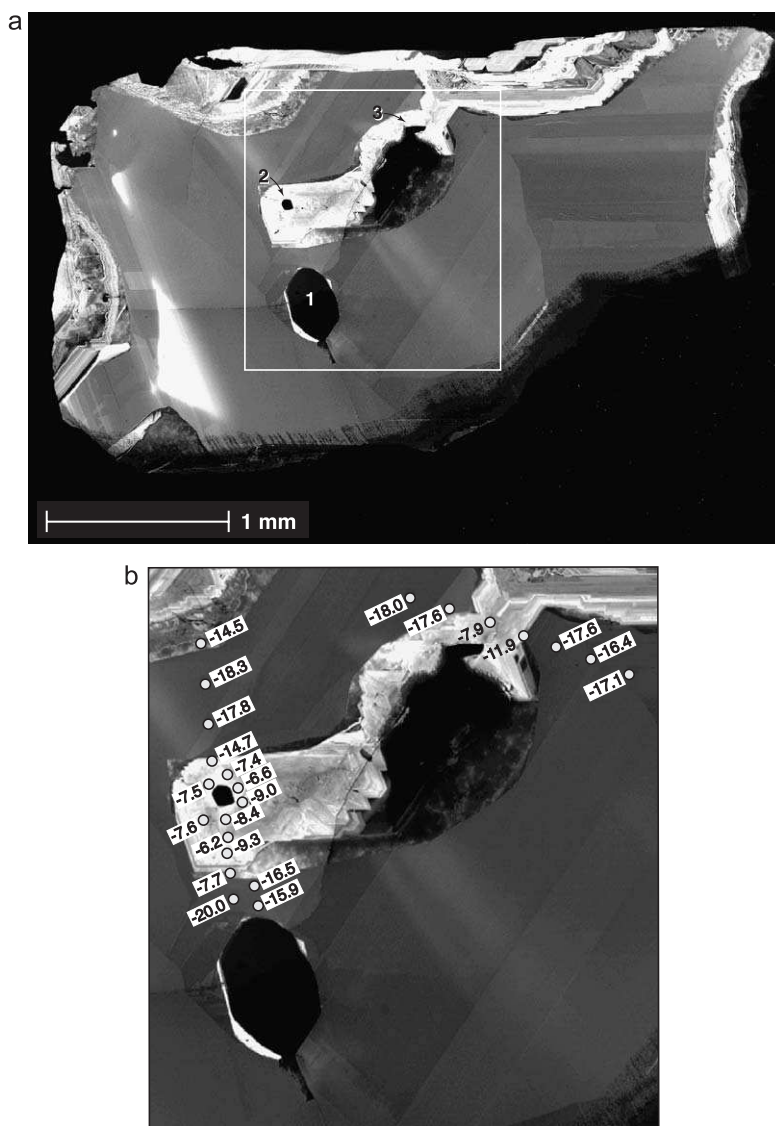


Fig. 1. (a) Cathodoluminescence image of polished section of half A of diamond #13-127-27. Three non-luminescent garnet inclusions are labelled (1, 2, 3). Adjacent to garnet #27-3 is a large, irregular hole with a poor to absent CL response due to the presence of epoxy. The saw-tooth pattern and general darkness on the bottom margin of the stone is due to incomplete removal during polishing of amorphous carbon build-up remaining after laser cutting of the stone, which partly obscures the CL response in the region. The area outlined in white is enlarged in (b). (b) Enlargement of region indicated in (a) showing positions of the ion probe points where carbon isotope ratios were measured. Values of $\delta^{13}\text{C}$ are indicated for each point.

garnets included in diamond #13-127-27 form part of this trend and typify it.

Fig. 4 illustrates the co-variation of $\text{Mg}/(\text{Mg} + \text{Fe})$ and Cr content of the Guaniamo diamond inclusion garnets. There is a subtle, though distinct, positive correlation between $\text{Mg}/(\text{Mg} + \text{Fe})$ and Cr.

2.3. SIMS data

Using secondary ion mass spectrometry (SIMS), we have determined the carbon isotope composition and nitrogen abundance of the diamond in both of the distinct CL zones, and the oxygen isotope composi-

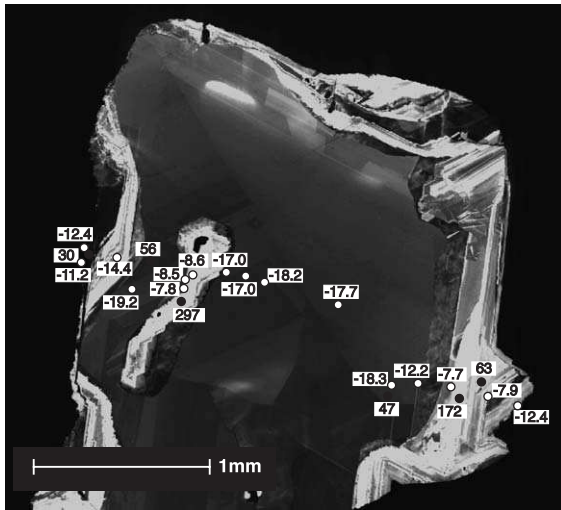


Fig. 2. Cathodoluminescence image of a portion of half B of diamond 13-127-27. Positions of points analysed for carbon isotope values ($\delta^{13}\text{C}$) are indicated in light circles and those for nitrogen abundance (ppm, atomic) in dark circles.

tion of three of the garnet inclusions. SIMS data were acquired using a Cameca ims-4f ion microprobe at the University of Edinburgh using a primary beam of $^{133}\text{Cs}^+$ defocused to a spot approximately $30\ \mu\text{m}$ in diameter and with an impact potential of 14,150 eV. An energy offset of 350 V was used for oxygen and carbon analysis. Detailed descriptions of the analytical techniques in use at the Edinburgh Ion Microprobe Facility can be found in the works of [Eiler et al. \(1997\)](#), [Valley et al. \(1998\)](#), [Harte et al. \(1999\)](#) and [Fitzsimmons et al. \(2000\)](#).

The carbon and nitrogen measurements of diamond 13-127-27 were standardized against synthetic diamond “SYNA” ($\delta^{13}\text{C}$ PDB = -23.93% , N = 230.4 ppm by weight; [Harte et al., 1999](#)). In a given analytical session, typical reproducibility on the standards is approximately $\pm 0.7\%$ to 1.0% (1 S.D.) for carbon isotope measurements and $\pm 7\%$ (1 S.D.) for N abundance.

In the absence of standards close in chemical composition to the unknowns (not a difficulty encountered in diamond work, as a diamond standard is used to analyse unknown diamonds), corrections for instrumental mass fractionation due to composition are required (e.g., [Eiler et al., 1997](#)). An instrumental mass fractionation correction procedure applicable to determination of the oxygen isotope composition of

eclogitic garnets has been developed at the University of Edinburgh (J. Craven, personal communication, 2003) and applied to the garnets in diamond 27. The garnet oxygen isotope standards used to develop the instrumental mass fractionation correction include the garnet end-members almandine, spessartine, grossular and pyrope and nine additional garnets close in composition to, and surrounding, the range of Guaniamo diamond inclusion garnets. These garnet standards were determined to be homogeneous by the ion probe, and their $\delta^{18}\text{O}$ values were calibrated by laser fluorination at the University of Wisconsin. The details of this method will be presented elsewhere (Schulze et al., manuscript in preparation). The instrumental mass fractionation corrections are very sensitive to compositional variation, and reproducibility on the unknowns is on the order of 1% to 2% .

Two ion probe traverses were made in the diamond in the vicinity of garnets 1, 2 and 3. The locations of the analysed points are shown in [Fig. 1b](#).

Table 1

Compositions of garnets included in diamond #13-127-27 (weight percent oxide)

Garnet #	27-1	27-2	27-3	27-4	27-5	27-6
SiO ₂	40.09	40.73	40.60	40.44	39.97	40.56
TiO ₂	0.60	0.85	0.84	0.81	0.79	0.77
Al ₂ O ₃	22.54	22.09	21.96	21.91	21.89	22.07
Cr ₂ O ₃	0.05	0.06	0.03	0.04	0.06	0.06
FeO ^a	17.56	16.26	16.19	16.51	16.21	16.63
MnO	0.35	0.36	0.35	0.33	0.27	0.37
MgO	12.60	14.31	14.23	13.94	13.47	13.74
CaO	6.52	5.54	5.54	5.67	5.66	5.80
Na ₂ O	0.19	0.28	0.27	0.27	0.28	0.27
Total	100.51	100.48	100.02	99.92	98.61	100.26

Cations normalised to 12 oxygens

Si	2.971	2.993	2.997	2.994	2.996	2.994
Ti	0.034	0.047	0.047	0.045	0.045	0.043
Al	1.969	1.913	1.911	1.912	1.934	1.920
Cr	0.003	0.003	0.002	0.003	0.004	0.003
Fe	1.088	0.999	1.000	1.022	1.016	1.027
Mn	0.022	0.022	0.022	0.021	0.017	0.023
Mg	1.392	1.567	1.565	1.538	1.505	1.512
Ca	0.518	0.436	0.438	0.449	0.455	0.459
Na	0.027	0.040	0.039	0.039	0.041	0.039
Total	8.023	8.021	8.020	8.023	8.012	8.020
Mg/(Mg + Fe)	0.561	0.611	0.610	0.601	0.597	0.596
Ca/(Ca + Mg)	0.271	0.218	0.219	0.226	0.232	0.233

^a Total Fe reported as FeO.

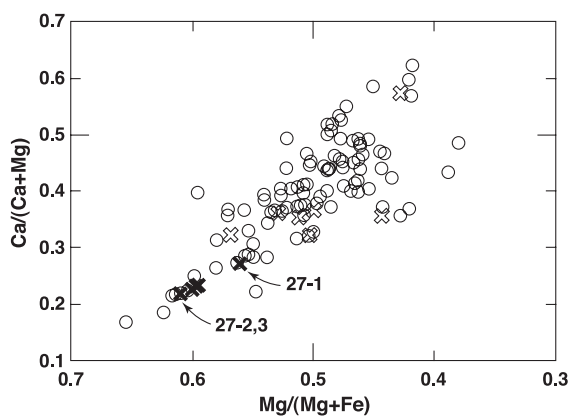


Fig. 3. Compositions of garnets included in Guaniamo diamonds in terms of molar $\text{Ca}/(\text{Ca}+\text{Mg})$ and $\text{Mg}/(\text{Mg}+\text{Fe})$ values. The six garnet inclusions in diamond #13-127-27 analysed in this study are indicated as black “x” symbols, and inclusions 27-1, -2 and -3 (27-2 and 27-3 plots at the same point) are labelled. Inclusions 27-4, -5 and -6 have compositions intermediate between 1 and 2/3. The other new data in this study (open “x” symbols) confirm the early data of Sobolev et al. (1998) and Kaminsky et al. (2000), indicated by open circles.

One traverse (16 points in the left portion of Fig. 1b) extends from the dark, early CL zone beside garnet #27-1, across the re-entrant characterised by bright and complicated CL response and containing garnet #27-2, continues back into the dark CL region, and finishes just inside the bright rim CL zone near the top of the stone. The second traverse (seven spots in the upper right of Fig. 1b) starts and finishes in the dark CL zone and includes data in the bright re-entrant near garnet 3.

The diamond in the dark CL region of diamond 13-127-27 ranges in $\delta^{13}\text{C}$ from -20.0‰ to -15.9‰ , with a mean of $-17.6 \pm 1.2\text{‰}$ (9 analyses). $\delta^{13}\text{C}$ of the diamond in the bright, complex CL re-entrant ranges from -9.3‰ to -6.2‰ , with a mean value of $-7.8 \pm 1.0\text{‰}$ (10 analyses). Data for points that overlap the two zones (-16.5‰ and -14.7‰ from top and bottom of the bright CL zone in the left traverse and -11.9‰ from the right traverse) are not included in the mean values summarized above. The single point in the bright CL rim at the top of the left traverse, which is completely within the rim zone, has a $\delta^{13}\text{C}$ value of -14.5‰ .

Carbon isotope data were also acquired for the other half (27B) of the stone (Fig. 2). The $\delta^{13}\text{C}$ values of six spots in the dark core range from -19.2‰ to

-17.0‰ and average $-18.2\text{‰} \pm 0.8$. Three points within the re-entrant are in the range -8.6‰ to -7.8‰ (average = $-8.3 \pm 0.5\text{‰}$). Within the rim zone, some points have carbon isotope values similar to those of the re-entrant (two have values of $\delta^{13}\text{C}$ of -7.7‰ and -7.9‰) and others are similar to the single rim point analysed in the other half of the stone (five points are in the range $\delta^{13}\text{C} = -14.4\text{‰}$ to -11.2‰ and average $-12.5 \pm 1.2\text{‰}$).

Considering the entire stone, the three different carbon isotope populations are summarized as follows: Nineteen analyses in the dark region yield an average $\delta^{13}\text{C}$ value of $-17.7 \pm 1.0\text{‰}$; thirteen analyses in the re-entrant together with the two anomalously high rim values (-7.7‰ and -7.9‰) yield an average $\delta^{13}\text{C}$ value of $-7.9 \pm 0.8\text{‰}$; five analyses of the rim yield an average $\delta^{13}\text{C}$ value of $-13.0 \pm 1.4\text{‰}$.

Nitrogen abundance was measured at six points in half 13-127-27B (Fig. 2). Two points in the dark core (56 and 47 ppm) average 53 ppm. One point in the re-entrant has 297 ppm N, and three points in the bright rim (30, 63 and 172 ppm) have an average of 88 ppm.

Oxygen isotope data were obtained at five spots on the three garnets in 13-127-27A. Two values of $\delta^{18}\text{O}$ in garnet 27-1 in the early dark portion of the stone ($+9.7\text{‰}$ and $+11.3\text{‰}$) average $+10.5\text{‰}$. Three $\delta^{18}\text{O}$ values in garnets 27-2 ($+10.6\text{‰}$ and $+8.0\text{‰}$) and 27-3 ($+7.9\text{‰}$) yield an average of $+8.8\text{‰}$.

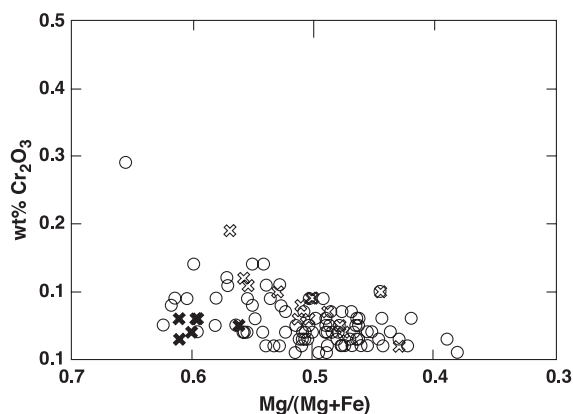


Fig. 4. Compositions of garnets included in Guaniamo diamonds in terms of molar $\text{Mg}/(\text{Mg}+\text{Fe})$ values and wt.% Cr_2O_3 . Symbols as in Fig. 3.

3. Discussion

3.1. Diamond structure

The re-entrant into the interior of diamond 13-127-27 is a rather unusual feature for diamonds studied to date using CL imaging, most of which display reasonably concentric zoning patterns (e.g., [Bulanova, 1995](#); [Harte et al., 1999](#); [Hauri et al., 1999](#)). As the diamond within the re-entrant has CL characteristics similar to those of the physical rim on the stone, and is connected to it, we interpret the re-entrant to be a late feature. Truncation of the faint CL zonation visible in the dark portion of the stone suggests that at one time, the stone may have been substantially larger and concentrically zoned. The brittle deformation event that appears to have broken the stone may also have caused incipient {111} cleavage planes now occupied by the diamond in the re-entrant. A diamond resorption event, following diamond breakage, is suggested by the convex inward regions occupied by the late-formed diamond, well-developed along the left and top sides in [Fig. 1a](#). A second generation of diamond growth, post-dating resorption, appears as the bright and complex CL region around much of the present rim of the stone, and occupying the re-entrant.

3.2. Garnet compositions

The positions of the garnets, in the context of the CL variations in diamond 13-127-27, suggest that garnet 27-1 in the dark CL portion formed before garnets 27-2 to 27-6, which occur in the late-formed, bright CL diamond in the re-entrant. The differences in $Mg/(Mg+Fe)$ and $Ca/(Ca+Mg)$ values of the two generations of garnet indicate a changing geochemical environment over the course of diamond formation, evolving from relatively iron-rich and calcic compositions, to a more magnesian and calcium-poor crystallization medium. This trend, which has a relative age significance in diamond 27, is within and parallel to that of the larger suite of garnet inclusions extracted from Guaniamo diamonds ([Sobolev et al., 1998](#); [Kaminsky et al., 2000](#)), for which there is no relative age information ([Fig. 3](#)). If the spatial–compositional relationships of the garnets in diamond 13-127-27 can be applied to the suite as a whole, it implies that the Guaniamo eclogitic diamonds have formed in an

evolving chemical system in which the mg value of coexisting silicates increased over time. The evolution of the eclogite parent bodies of the diamonds to more magnesian (and less calcic for garnet) compositions was accompanied by the subtle, though distinct, increase in Cr of their garnets ([Fig. 4](#)).

A similar compositional change in garnets, and coexisting clinopyroxenes (those from diamond interior enriched in Ca and Fe relative to those from the diamond periphery), was documented in an eclogitic diamond from Yakutia ([Bulanova, 1995](#)). The same trend was also noted in clinopyroxenes in two other zoned eclogitic diamonds, though they lacked garnet ([Bulanova, 1995](#)), and [Taylor et al. \(1996\)](#) documented similar variations between diamond inclusion minerals and those in the eclogite xenoliths hosting the diamonds in three of the four Yakutian diamond eclogites that they studied. [Bulanova \(1995\)](#) interpreted this spatial–composition variation as due to “differentiation of eclogitic melts”. Igneous differentiation during diamond formation in the mantle has also been proposed to account for geochemical trends in suites of eclogitic mineral inclusions extracted from diamonds at Orapa ([Gurney et al., 1984](#)), Sloan ([Otter and Gurney, 1989](#)) and Argyle ([Jaques et al., 1989](#)), for example, but there is no relative age information for the trends of any of these suites other than the Yakutian diamonds. In magmatic silicate systems, however, Mg partitions into the crystallizing silicates in preference to Fe (e.g., [Bowen and Schairer, 1935](#)). Precipitation of sub-equal amounts of garnet and clinopyroxene, therefore, would result in an iron-enrichment trend in cumulates and evolving liquids, which is the opposite of the evolutionary trends documented by [Bulanova \(1995\)](#) and in this study. The apparent rise in Cr (a compatible element in garnet) as the system evolves is also inconsistent with an igneous fractionation model.

It is possible that the garnets in the re-entrant formed entirely during the second diamond growth event, and thus are younger than the bulk of the diamond, which contains garnet 27-1. Alternatively, they may have existed prior to the brittle deformation event, their presence perhaps focussing the stresses that caused the {111} cleavage, and their present compositions reflect re-equilibration from a composition like that of garnet 27-1 towards the garnets in equilibrium with the second stage diamond-forming

medium. This latter scenario, termed “open system behaviour” by Anand et al. (2003), could also provide an explanation for the apparently young trace element zoning patterns of peridotite-suite diamond inclusion garnets from Yakutia (Shimizu and Sobolev, 1995), although peridotitic diamonds are considered by most workers to have ancient (i.e., Archean) origins (e.g., Richardson et al., 1984). Note that although within our suite of polished diamonds from Guaniamo, we have found only a single example of a diamond with such a complex history of breakage, resorption and renewed diamond growth revealed by CL imaging, Anand et al. (2003) cite many examples of Yakutian diamond inclusion minerals associated with similar “healed fractures” from their CL studies.

3.3. Oxygen isotope composition of garnets

Many mantle eclogite xenoliths have $\delta^{18}\text{O}$ values that are significantly outside of the range accepted as normal for mantle materials. In contrast to garnets from most mantle peridotites, which have $\delta^{18}\text{O}$ values in the very small range $+5.36 \pm 0.18$ (Lowry et al., 1999), the $\delta^{18}\text{O}$ of garnets in mantle eclogites have been shown to be approximately $+2.3\%$ to $+9.2\%$ (e.g., Garlick et al., 1971; Deines et al., 1991; Matthey et al., 1994). By analogy with basaltic rocks from ophiolite sequences (e.g., Gregory and Taylor, 1981), eclogites (or their constituent garnets and clinopyroxenes) with $\delta^{18}\text{O}$ values above those of “common mantle” are thought to represent subducted ocean-floor basalts that have been altered by interaction with sea water at temperatures below about $350\text{ }^\circ\text{C}$, whereas eclogites with lower $\delta^{18}\text{O}$ values represent basic rocks that have interacted with higher temperature hydrothermal fluids (e.g., MacGregor and Manton, 1989).

In a previous ion probe study of diamond inclusion minerals in Guaniamo eclogitic diamonds, Schulze et al. (2003) found $\delta^{18}\text{O}$ values of coesite inclusions to be in the range $+10.2\%$ to $+16.9\%$, higher than documented previously for mantle eclogite minerals or diamond inclusion minerals (Lowry et al., 1999). The oxygen isotope ratios of the garnets in diamond 27 ($\delta^{18}\text{O}=+7.9\%$ to $+11.3\%$) overlap the upper end of those from mantle eclogites and the lower end of Guaniamo coesite inclusions. The overlap of the $\delta^{18}\text{O}$ values of the Guaniamo garnet inclusions (a common

diamond inclusion mineral) with the oxygen isotope values of the included coesites (a less common diamond inclusion mineral) confirms the earlier findings for the coesites. The isotope data for both minerals are clearly highly anomalous relative to typical upper mantle values and consistent with the subducted basalt hypothesis for certain mantle eclogites and their diamonds.

3.4. Carbon isotope ratios of host diamond

The two main diamond regions in stone 13-127-27 are characterised by distinctly different carbon isotope ratios. Diamond in the early (dark CL) portion of the stone is homogeneous and has a mean $\delta^{13}\text{C}$ value near -17.7% . The late, bright CL diamond in the re-entrant has a mean $\delta^{13}\text{C}$ value near -7.9% , and within the physical rim of the stone, the diamond seems to have two distinct carbon isotope populations, one similar to that of the re-entrant material, and the other with $\delta^{13}\text{C}$ near -13.0% .

An increase in the $\delta^{13}\text{C}$ value (i.e., to less negative values) of precipitating diamond over time is the opposite of the carbon isotope evolution trend predicted by the “differentiation of mantle melts” model of Cartigny et al. (2001). Such a change is, however, consistent with the blending of subducted biogenic crustal carbon (suggested by its low $\delta^{13}\text{C}$ values—e.g., Sobolev et al., 1979; Kirkley et al., 1991) with “common” mantle carbon, such as that in peridotite-suite diamonds, which typically have $\delta^{13}\text{C}$ values near -5% to -6% (e.g., Kirkley et al., 1991). This model for carbon isotope evolution in eclogite-suite diamonds is in complete agreement with the geochemical evolution of the garnets in diamond 13-127-27 and the Guaniamo diamond inclusion garnet suite as a whole, in which the progressive increase in Mg/(Mg+Fe) (and Cr) suggests an increasing mantle contribution over time. Taylor et al. (2003) have suggested that similar mixing of subducted oceanic crust with more refractory mantle material was an important process in the evolution of the non-diamondiferous Obnazhennaya (Siberia) eclogite suite.

Although it has been suggested that mantle fractionation models might be able to explain derivation of low $\delta^{13}\text{C}$ values from “normal” mantle carbon reservoirs with initial $\delta^{13}\text{C}$ near -5% (e.g., Cartigny et al., 2001), this type of model does not account for

the anomalously high oxygen isotope values of coexisting silicates. Oxygen isotope crystal–liquid fractionation is minimal at mantle temperatures, and differences in pressure do not cause a measurable change (Clayton et al., 1975). Igneous processes in the upper mantle thus cannot account for the wide range of $\delta^{18}\text{O}$ values of mantle eclogites. As discussed above, most workers interpret the anomalously high and low oxygen isotope ratios of mantle eclogite xenoliths as the result of subduction and prograde metamorphism of oceanic lithosphere that has undergone oxygen isotope exchange with sea water on or near the sea floor (e.g., Jagoutz et al., 1984; MacGregor and Manton, 1989). This explanation clearly applies to the elevated $\delta^{18}\text{O}$ values of the garnet inclusions in diamond 13-127-27 ($\delta^{18}\text{O} = +7.9\text{‰}$ to $+11.3\text{‰}$) and thus, the simplest explanation for the origin of the low $\delta^{13}\text{C}$ diamond host (as low as -20‰ in the core) is that biogenic (i.e., crustal) carbon was present in the package of altered oceanic basaltic crust that was subducted to form the parent eclogite bodies hosting the diamonds (Fig. 5).

3.5. Nitrogen abundance

The overall nitrogen content of diamond 13-127-27 is fairly low (<300 ppm). It is lowest in the dark $\delta^{13}\text{C}$ -depleted core (47 and 56 ppm) but it is high in the late-formed diamond in the re-entrant (297 ppm) and the rim diamond has N values above and below that of the core (30 to 172 ppm). There is not a regular correlation between nitrogen content and carbon isotope values (Fig. 2). The variability of both carbon isotope ratio and nitrogen content in the second generation of diamond (re-entrant and rim) suggests that both of these parameters were controlled by variations in the fluid composition from which the diamond crystallized. In part, the fluid composition will be a reflection of the extent of mixing of crust and mantle sources.

3.6. Origin and evolution of diamond #13-127-27

The geologic history of this diamond is summarized as follows. Subduction of ocean-floor basalt that had experienced low-temperature alteration by sea water (imposing elevated oxygen isotope ratios on the rock) resulted in prograde metamorphism of the

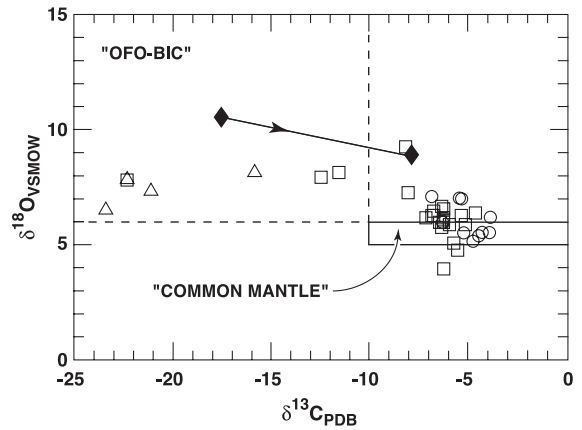


Fig. 5. Correlation between carbon isotope composition of diamond and oxygen isotope composition of silicates (garnet or clinopyroxene) from Guaniamo diamond #13-127-27 and samples of diamond eclogites from the published literature. The solid diamond symbols represent garnet 27-1 and the average value of early (dark CL) diamond, connected to the average value of the late diamond in the re-entrant and its coexisting garnets (garnets 27-2 and 27-3). Open squares represent diamond eclogites from Orapa (Deines et al., 1991), open circles represent diamond eclogites from Udachnaya (Snyder et al., 1995) and open triangles represent coexisting garnet and diamond in polycrystalline diamond aggregates from Venetia (Jacob et al., 2000). Note that all of the samples with $\delta^{13}\text{C}$ values below those typical of the “common mantle” (i.e., $\delta^{13}\text{C} < -10\text{‰}$) also have $\delta^{18}\text{O}$ values higher than “common mantle” (i.e., $\delta^{18}\text{O} > +6\text{‰}$), corresponding to values in the “OFO-BIC” (ocean-floor oxygen-biogenic carbon) quadrant.

basalt to the eclogite-facies, with the resultant silicate minerals (e.g., garnet) retaining the elevated $\delta^{18}\text{O}$ of the altered oceanic protolith. Growth of a low nitrogen octahedral diamond from a reservoir of subducted biogenic carbon ($\delta^{13}\text{C}$ in the range -16‰ to -20‰) within this eclogite body occurred following emplacement of the eclogite into the diamond stability field. A brittle deformation event (such as a deep-seated earthquake) broke the diamond, truncating some of the concentric CL zonation pattern and leaving smaller fragments that contained $\{111\}$ cleavage fractures parallel to the octahedral outline of the original stone. A diamond-resorbing event occurred, possibly due to an influx of oxidizing fluids, dissolving diamond from portions of the outer edge of the broken stone and from along the cleavage crack. A second period of diamond growth then occurred, overgrowing the rim and filling in the re-entrant, with the new diamond having substantially lower, and

more variable, $\delta^{13}\text{C}$ values and variable nitrogen contents. The new diamond-precipitating medium, which was also in equilibrium with eclogitic garnet, appears to have been a blend of crustal and mantle components, as it was more magnesian (reflected in the second generation garnet composition) and had higher $\delta^{13}\text{C}$ values than the original diamond-precipitating medium.

4. Concluding remarks

It is unclear how applicable the genesis of this stone is to the origin of eclogitic diamonds in general. A similar chemical evolution of included silicates has been documented for diamonds from Yakutia (Bulanova, 1995; Taylor et al., 1996), however, and many other suites of garnets extracted from eclogitic diamonds exhibit similar trends of $\text{Mg}/(\text{Mg}+\text{Fe})$, $\text{Ca}/(\text{Ca}+\text{Mg})$ and Cr values (e.g., Jwaneng—Gurney et al., 1995; Richardson et al., 1999 and Sloan—Otter and Gurney, 1989; Orapa—Gurney et al., 1984). The Orapa and Jwaneng diamond inclusion suites contain a “websteritic” paragenesis of diamond that is intermediate in composition (especially in mg and Cr_2O_3 content) between typical eclogitic minerals and those of the peridotite-suite. Mixing of a subducted eclogitic component with the ambient mantle, as we suggest for the Guaniamo suite, and Taylor et al. (2003) suggested for the non-diamondiferous Obnazhennaya eclogites, could explain the genesis of the websteritic diamond suite. Furthermore, the radiogenic isotope composition of eclogitic minerals in Jwaneng diamonds also suggests a mixing of subducted components with mantle lithosphere or asthenosphere (Richardson et al., 1999), and so our conclusions may indeed have a wider applicability to the genesis of eclogitic diamonds.

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References

- Anand, M., Taylor, L.A., Misra, K.C., Carlson, W.D., Sobolev, N.V., 2003. Diamondiferous eclogite dissections: anomalous diamond genesis? Ext. Abstr. 8th Int. Kimb. Conf., Victoria, BC.
- Bowen, N.L., Schairer, J.F., 1935. The system $\text{MgO}-\text{FeO}-\text{SiO}_2$. *Am. J. Sci.* 26, 151–217.
- Bulanova, G.P., 1995. The formation of diamond. *J. Geochem. Explor.* 53, 1–24.
- Cartigny, P., Harris, J.W., Javoy, M., 2001. Diamond genesis, mantle fractionations and mantle nitrogen content: a study of $\delta^{13}\text{C}-\text{N}$ concentrations in diamonds. *Earth Planet. Sci. Lett.* 185, 85–98.
- Channer, D.M.DeR., Egorov, E., Kaminsky, F., 2001. Geology and structure of the Guaniamo diamondiferous kimberlite sheets, south–west Venezuela. *Rev. Bras. Geocienc.* 31, 615–630.
- Clayton, R.N., Goldsmith, J.R., Karel, K.J., Mayeda, T.K., Newton, R.P., 1975. Limits on the effect of pressure in isotopic fractionation. *Geochim. Cosmochim. Acta* 39, 1197–1201.
- Deines, P., Harris, J.W., Robinson, D.N., Gurney, J.J., Shee, S.R., 1991. Carbon and oxygen isotope variations in diamond and graphite eclogites from Orapa, Botswana, and the nitrogen content of their diamonds. *Geochim. Cosmochim. Acta* 55, 515–524.
- Eiler, J.M., Graham, C., Valley, J.W., 1997. SIMS analysis of oxygen isotopes: matrix effects in complex minerals and glasses. *Chem. Geol.* 138, 221–244.
- Fitzsimmons, I.C.W., Harte, B., Clark, R.M., 2000. SIMS stable isotope measurement: counting statistics and analytical precision. *Min. Mag.* 64, 59–83.
- Garlick, G.D., MacGregor, I.D., Vogel, D.E., 1971. Oxygen isotope ratios in eclogites from kimberlites. *Science* 172, 1025–1027.
- Gregory, R.T., Taylor Jr., H.P. 1981. An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail Ophiolite, Oman: evidence for $\delta^{18}\text{O}$ buffering of the oceans by deep (5 km) seawater-hydrothermal circulation at mid-ocean ridges. *J. Geophys. Res.* 86, 2737–2755.
- Gurney, J.J., 1989. Diamonds. In: Ross, J. (Ed.), *Kimberlites and Related Rocks. Their Mantle/Crust Setting, Diamonds and Diamond Exploration*, vol. 2. Blackwell, Carlton, Australia, pp. 935–965.
- Gurney, J.J., Harris, J.W., Rickard, R.S., 1984. Silicate and oxide inclusions in diamonds from the Orapa Mine, Botswana. In: Kornprobst, J. (Ed.), *Kimberlites II: Their Mantle and Crust–Mantle Relationships*. Amsterdam, Elsevier, pp. 3–9.

- Gurney, J.J., Harris, J.W., Otter, M.L., Rickard, R.S., 1995. Jwaneng diamond inclusions. Ext. Abstr. 6th Int. Kimb. Conf. Novosibirsk. Siberian Branch, Russian Academy of Sciences, Novosibirsk, pp. 208–210.
- Harte, B., Fitzsimmons, I.C.W., Harris, J.W., Otter, M.L., 1999. Carbon isotope ratios and nitrogen abundances in relation to cathodoluminescence characteristics for some diamonds from the Kaapvaal Province. *S. Africa Min. Mag.* 63, 829–856.
- Hauri, E.H., Pearson, D.G., Bulanova, G.P., Milledge, H.J., 1999. Microscale variations in C and N isotopes within mantle diamonds revealed by SIMS. In: Gurney, J.J., Gurney, J.L., Pascoe, S.H., Richardson, S.H. (Eds.), Proc. 7th Int. Kimb. Conf., vol. 1. Red Roof Design, Cape Town, South Africa, pp. 341–347.
- Jacob, D.E., Viljoen, K.S., Grassineau, N., Jagoutz, E., 2000. Remobilization in the cratonic lithosphere recorded in polycrystalline diamond. *Science* 289, 1182–1185.
- Jagoutz, E., Dawson, J.B., Hoernes, S., Spettel, B., Wanke, H., 1984. Anorthositic oceanic crust in the Archean. *Lunar Planet. Sci.* 15, 395–396.
- Jaques, A.L., Hall, A.E., Sheraton, J.W., Smith, C.B., Sun, S.-S., Drew, R.M., Foudoulis, C., Ellingsen, K., 1989. Composition of crystalline inclusions and C-isotopic composition of Argyle and Ellendale diamonds. In: Ross, J. (Ed.), *Kimberlites and Related Rocks. Their Mantle/Crust Setting, Diamonds and Diamond Exploration*, vol. 2. Blackwell, Carlton, Australia, pp. 966–989.
- Kaminsky, F.V., Zakharchenko, O.D., Griffin, W.L., Channer, D.M.DeR., Khachatryan-Blinova, G.K., 2000. Diamond from the Guaniamo area, Venezuela. *Can. Mineral.* 38, 1347–1370.
- 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. *Appl. Geochim.* 6, 477–494.
- Lowry, D., Matthey, D.P., Harris, J.W., 1999. Oxygen isotope composition of syngenetic inclusions in diamond from the Finsch Mine, RSA. *Geochim. Cosmochim. Acta* 63, 1825–1836.
- MacGregor, I.D., Manton, W.I., 1989. Roberts Victor eclogites: ancient oceanic crust. *J. Geophys. Res.* 91, 14063–14079.
- Matthey, D.P., Lowry, D., Macpherson, C.G., Chazot, G., 1994. Oxygen isotope composition of mantle minerals by laser fluorination analysis: homogeneity in peridotites, heterogeneity in eclogite. *Min. Mag.* 58A, 573–574.
- Meyer, H.O.A., 1987. Inclusions in diamond. In: Nixon, P.H. (Ed.), *Mantle Xenoliths*. Wylie, London, pp. 501–522.
- Meyer, H.O.A., McCallum, M.E., 1993. Diamonds and their sources in the Venezuelan portion of the Guyana shield. *Econ. Geol.* 88, 989–998.
- Otter, M.L., Gurney, J.J., 1989. Mineral inclusions in diamonds from the Sloan diatremes, Colorado–Wyoming State Line kimberlite district, North America. In: Ross, J. (Ed.), *Kimberlites and Related Rocks. Their Mantle/Crust Setting, Diamonds and Diamond Exploration*, vol. 2. Blackwell, Carlton, Australia, pp. 1042–1053.
- Prinz, M., Manson, D.V., Hlava, P.F., Keil, K., 1975. Inclusions in diamonds. Garnet lherzolite and eclogite assemblages. *Phys. Chem. Earth* 9, 797–815.
- 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., Chinn, I.L., Harris, J.W., 1999. Age and origin of diamonds from Jwaneng kimberlite, Botswana. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proc. 7th Int. Kimb. Conf., vol. 2. Red Roof Design, Cape Town, South Africa, pp. 709–713.
- Rudnick, R.L., Eldridge, C.S., Bulanova, G.P., 1993. Diamond growth history from in situ measurements of Pb and S isotopic compositions of sulfide inclusions. *Geology* 21, 13–16.
- Schulze, D.J., Harte, B., Valley, J.W., Brenan, J.M., Channer, D.M.DeR., 2003. Extreme crustal oxygen isotope values preserved in coesite in diamond. *Nature* 423, 68–70.
- Shimizu, N., Sobolev, N.V., 1995. Young peridotitic diamonds from the Mir kimberlite pipe. *Nature* 375, 394–397.
- Snyder, G.A., Taylor, L.A., Jerde, E.A., Clayton, R.N., Mayeda, T.K., Deines, P., Rossman, G.R., Sobolev, N.V., 1995. Archean mantle heterogeneity and the origin of diamondiferous eclogites, Siberia: evidence from stable isotopes and hydroxyl in garnet. *Am. Mineral.* 80, 799–809.
- Sobolev, N.V., 1976. Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle. American Geophysical Union, Washington, DC.
- Sobolev, N.V., Galimov, E.M., Ivanovskaya, N.N., Yefimova, E.S., 1979. Isotopic composition of the carbon from diamonds containing inclusions. *Dokl. Akad. Nauk Ukr. SSR* 249, 1217–1220 (in Russian).
- Sobolev, N.V., Efimova, E.S., Channer, D.M.DeR., Anderson, P.F.N., Barron, K.M., 1998. Unusual upper mantle beneath Guaniamo, Guyana Shield, Venezuela: evidence from diamond inclusions. *Geology* 26, 971–974.
- Taylor, L.A., Snyder, G.A., Crozaz, G., Sobolev, N.V., Yefimova, E.S., Sobolev, N.V., 1996. Eclogitic inclusions in diamonds: evidence of complex processes over time. *Earth Planet. Sci. Lett.* 142, 535–551.
- Taylor, L.A., Snyder, G.A., Keller, R., Remley, D., Anand, M., Wiesli, R., Valley, J., Sobolev, N.V., 2003. Petrogenesis of group A eclogites and websterites: evidence from the Obnazhennaya kimberlite, Yakutia. *Contrib. Mineral. Petrol.* 145, 424–443.
- Valley, J.W., Graham, C.M., Harte, B., Eiler, J.M., Kinny, P.D., 1998. Ion microprobe analysis of oxygen, carbon, and hydrogen isotope ratios. *SEG Rev. Econ. Geol.* 7, 73–98.