

# Stable Isotopes and the Origin of Diamond

Pierre Cartigny<sup>1</sup>

**M**ost diamonds form in a relatively narrow depth interval of Earth's subcontinental mantle between 150 and 250 km. From carbon isotope analyses of diamond obtained in the 1970s, it was first proposed that eclogitic diamonds form from crustal carbon recycled into the mantle by subduction and that the more abundant peridotitic diamonds formed from mantle carbon. More recent stable isotope studies using nitrogen, oxygen, and sulfur, as well as carbon, combined with studies of mineral inclusions within diamonds, have strengthened arguments supporting and opposing the early proposal. The conflicting evidence is reconciled if mantle carbon is introduced via fluid into mantle eclogites and peridotites, some of which represent subducted oceanic crust.

KEYWORDS: diamond, stable isotopes, mantle, metasomatism

## INTRODUCTION

Natural diamonds crystallize only at high pressures and temperatures. These conditions occur in the upper mantle, at depths exceeding ~150 km and temperatures above 950°C (FIG. 1). Diamonds are brought from the mantle to the surface as xenocrysts (foreign crystals) within volumetrically rare volcanic rocks called kimberlites and lamproites. These magmas not only form deep enough to pick up diamond, but also ascend to the surface fast enough to prevent transformation of diamond to graphite or its dissolution in the magma. The occurrence of diamond on the Earth's surface is thus both accidental and the result of the unique resistance of diamond to dissolution. For Earth scientists, the study of diamond and its impurities not only provides important insights into the conditions prevailing in the very deep mantle, but also helps us to understand the evolution of our planet.

Over the last twenty-five years, studies of diamonds from occurrences worldwide have yielded an enormous amount of data. It is now generally accepted that most natural diamonds are old and xenocrystic, and come from ancient lithosphere. In spite of major advances, the remaining questions about their formation are profound and complex. In particular, the source of carbon from which diamonds formed is still a hotly debated subject. This article reviews available stable isotopic data on diamonds, with a focus on the potential source(s) of carbon. The current models for the origin of diamonds in Earth's mantle will be presented and discussed in the light of stable isotope data on carbon and nitrogen from diamonds and on sulfur and oxygen from mineral inclusions found in diamonds.

## CARBON ISOTOPES IN DIAMONDS

Carbon has two stable isotopes, <sup>12</sup>C and <sup>13</sup>C, with abundances of 98.9% and 1.1%, respectively. The <sup>13</sup>C/<sup>12</sup>C ratio of most terrestrial samples varies little, from ~0.010956 to

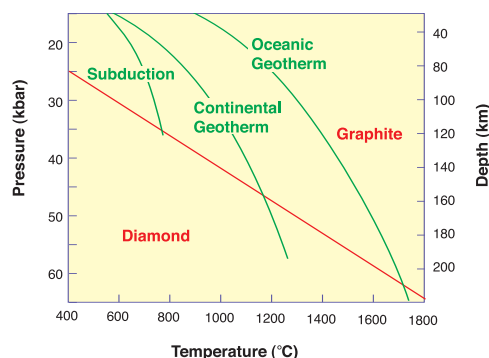
~0.011237. <sup>13</sup>C/<sup>12</sup>C ratios are expressed in terms of how they deviate in ‰ (parts per thousand) relative to the Pee Dee Belemnite, an internationally accepted standard (see glossary p. 70).

Carbon isotopic compositions are available from more than four thousand diamonds worldwide. Major sources include Siberia, Canada, Australia, Brazil, and West, East, and southern Africa (Botswana and South Africa). Data are also available from (1) impact-diamonds grown at high tempera-

tures over an extremely short time period, (2) metamorphic diamonds formed within crustal rocks buried at high pressure and temperature along subduction/collision zones (Ogasawara this issue), and (3) diamond types that are less well understood, e.g., carbonados (Heaney et al. this issue).

## Variation in Carbon Isotopes

The distribution of δ<sup>13</sup>C values in diamonds formed in Earth's mantle (FIG. 2A) can be divided into distinct populations on the basis of the mineralogy and chemistry of inclusions of silicate minerals. These are usually about 200 μm in maximum dimension and define two principal groups referred to as 'peridotitic' or P-type and 'eclogitic' or E-type. The P-type reflects the mineral assemblage of a peridotite, a four-phase assemblage of olivine, enstatite, garnet, and clinopyroxene. The E-type is related to eclogite, a rarer rock consisting principally of garnet and clinopyroxene. Sulfides are also common as inclusions and have P- or E-type affinities. Peridotitic and eclogitic diamonds can



**FIGURE 1** P-T phase diagram for elemental carbon. The different geotherms illustrate that diamond is stable in continental settings at pressures of ~45 kbar (corresponding to depths of 150 km) and in oceanic settings at ~60 kbar. In subduction zones, as illustrated here by a 'warm' subduction gradient, diamond is stable at lower pressures (~35 kbar). With a steeper geothermal gradient (not shown), diamond is stable at pressures of ~30 kbar (i.e., 100 km depth).

<sup>1</sup> Laboratoire de Géochimie des Isotopes Stables, Institut de Physique du Globe de Paris, 4 place Jussieu, Paris Cédex 75251, France  
E-mail: cartigny@ipgg.jussieu.fr

have diamond overgrowths, and these are usually referred to as fibrous, cubic, or coated diamond. Hereafter, such overgrowths will be referred to as “coated/fibrous diamonds”. They may be related to kimberlite magmatism (Boyd et al. 1994) and record the date of kimberlite emplacement (less than 350 Ma ago), making them genetically different from their cores, which vary in age from 1 to 3 Ga (Shirey et al. 2002).

While most macrocryst diamonds sampled by kimberlites and related rocks originate from the base of ancient lithosphere known as cratons (~100–250 km depth), they can also form at much greater depths including Earth’s lower mantle ( $\geq 660$  km depth) (see Stachel et al. this issue). Over the depth range of 330 to 660 km, macrocryst diamonds belong mostly to the eclogitic growth environment, as indicated by the present eclogite/peridotite abundance ratio of about 8 to 1 (Stachel et al. this issue).

Worldwide diamonds have a carbon isotopic composition ( $\delta^{13}\text{C}$ ) ranging from  $-38.5$  to  $+5.0$ ‰ (FIG. 2A). Of these, approximately 72% are contained within a narrow interval between  $-8$  and  $-2$ ‰, which is within the range of mantle values. The distribution is continuous, with a clear decrease in frequency on either side of a peak  $\delta^{13}\text{C}$  value of about  $-5 \pm 1$ ‰.

The  $\delta^{13}\text{C}$  distributions of the two principal diamond types are significantly different (Sobolev et al. 1979). P-type diamonds (FIG. 2B) exhibit a narrower range of  $\delta^{13}\text{C}$  values (from  $-26.4$  to  $+0.2$ ‰) than E-type (FIG. 2C) (from  $-38.5$  to  $+2.7$ ‰), while both fibrous/coated (FIG. 2D) and lower-mantle diamonds (FIG. 2E) show narrow ranges of values:  $-8.1$  to  $-4.9$ ‰ and  $-8.5$  to  $-0.5$ ‰, respectively. A much greater proportion of E-type diamonds than P-type diamonds (34 and 2%, respectively) have very negative  $\delta^{13}\text{C}$  values (defined here as  $< -10$ ‰).  $\delta^{13}\text{C}$  values for diamond formed in crustal rocks—represented by microdiamonds formed in subducted metamorphic rocks—range from  $-30$  to  $-3$ ‰ (FIG. 2F). See Fig. 1 in Heaney et al., this issue, for  $\delta^{13}\text{C}$  data from impact-related diamonds ( $\delta^{13}\text{C}$  from  $-22$  to  $-8$ ‰) and carbonados ( $\delta^{13}\text{C}$  from  $-32$  to  $-25$ ‰). Sedimentary carbon is divided between a concentration near 0‰ and a scatter of light values between about  $-40$  and  $-15$ ‰ (average about  $-25$ ‰, FIG. 2G).

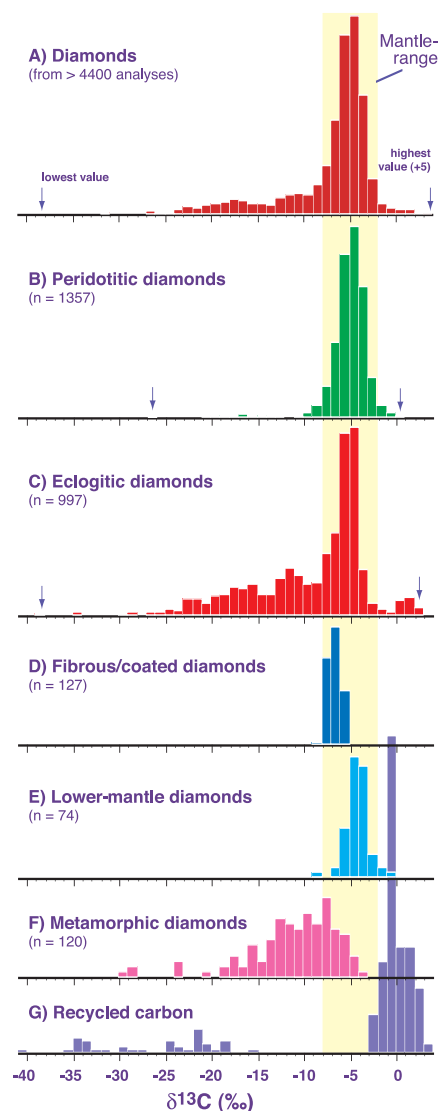
The distributions shown in figures 2a to 2d are based on diamond analyses from worldwide kimberlites, lamproites, and their placer deposits. A comparison of the carbon isotope values from individual localities, using the example of Venetia, South Africa (FIG. 3A) shows that more than 90% of individual locations have a similar range and distribution of values. However, there are several striking exceptions. Diamonds from the Guaniamo kimberlites (Venezuela, FIG. 3B), from the Argyle lamproite (western Australia, FIG. 3C), and from the New South Wales placer deposits (eastern Australia, FIG. 3D) show  $\delta^{13}\text{C}$  distributions for eclogitic diamonds centered at approximately  $-15$ ‰,  $-11$ ‰, and  $+2$ ‰, respectively. Rare peridotitic diamonds analyzed so far from these sources show typical mantle  $\delta^{13}\text{C}$  values of about  $-5$ ‰. In addition, locations such as Orapa (Botswana) and Jagersfontein (South Africa) (FIG. 3E) show a strong E-type, bimodal  $\delta^{13}\text{C}$  distribution with a peak at about  $-5$ ‰ and another at about  $-20$ ‰. For both sources, the  $\delta^{13}\text{C}$  range for P- and E-type diamonds is nearly identical.

### Intradiamond Variability

Intradiamond carbon isotope variability is studied by comparing results of the combustion of several fragments from a single stone. Such a method detects  $\delta^{13}\text{C}$  zonation only on a scale of up to 1 mm and will not detect any oscillato-

ry zonation on a scale of 10–100  $\mu\text{m}$ . Although large  $\delta^{13}\text{C}$  variations of up to 15‰ have been measured within a single diamond, most stones show little  $\delta^{13}\text{C}$  variability across growth zones, more than 95% of analyses varying by less than 3‰. When large variations are found, they usually correspond to distinct growth episodes such as the formation of a coat over a pre-existing diamond core.

Within the small range of internal  $\delta^{13}\text{C}$  variations, no systematic trend of increasing or decreasing  $\delta^{13}\text{C}$  values from core to rim is recorded for either E- or P-type diamonds. Within the coats of fibrous/coated diamonds, a systematic trend of increasing  $\delta^{13}\text{C}$  values (from  $-8$  to  $-5$ ‰) from core to rim has been detected (Boyd et al. 1994). Sufficiently detailed data are not available from which to determine the scale of  $\delta^{13}\text{C}$  variability in diamonds formed in the lower mantle or other environments (see above).

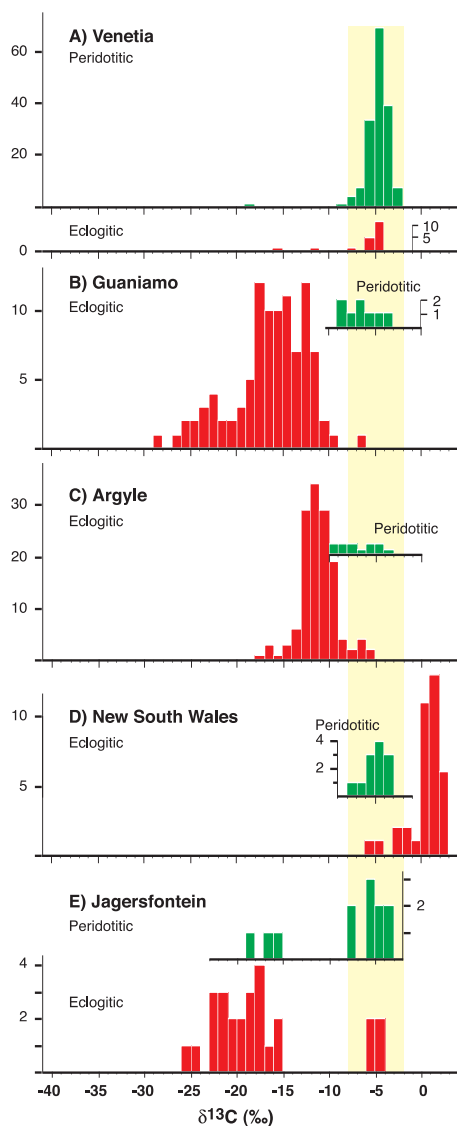


**FIGURE 2** Comparative histograms of  $\delta^{13}\text{C}$  values for (A) worldwide diamonds of known and unknown paragenesis, (B) peridotitic diamonds, (C) eclogitic diamonds, (D) fibrous/coated diamonds, (E) diamonds from the lower mantle, (F) metamorphic diamonds, and (G) sedimentary carbon represented by carbonates and organic matter. The mantle range (vertical yellow band) defined by the study of mid-ocean ridge basalts, carbonatites, and kimberlites is also indicated. For A to C, each diamond locality has been weighted, because more than 10% of all published data on eclogitic diamonds are from Argyle, and without weighting these data would cause a false second peak at about 11‰ in B.

### Origin of Carbon Variability

Carbon isotope data combined with the study of inclusions in diamonds have led to the emergence of three main models to explain the variability of carbon isotope compositions.

**Model 1 – Distinct carbon sources:** Low  $\delta^{13}\text{C}$  values within some eclogitic diamonds led many scientists to suggest that such diamonds formed from distinct carbon sources, unlike their peridotitic counterparts (Kirkley et al. 1991). This model suggests that eclogitic diamonds are derived from sedimentary carbon recycled into the mantle via subduction zones, whereas peridotitic diamonds formed from mantle-derived carbon. Metasedimentary carbon consists of mixtures of organic matter and carbonates with end member  $\delta^{13}\text{C}$  values averaging  $-25$ ‰ and 0‰, respectively



**FIGURE 3** Comparative histograms of  $\delta^{13}\text{C}$  values for diamonds from individual localities. (A) Venetia (South Africa) represents a typical locality, while (B) Guaniamo (Venezuela), (C) Argyle (Australia), (D) New South Wales (Australia), and (E) Jagersfontein (South Africa) are atypical localities. Vertical axis is number of diamonds.

During subduction, the carbon isotope compositions of organic matter and carbonates re-equilibrate as temperature increases, the fractionation factor for  $\delta^{13}\text{C}_{\text{carbonate}} - \delta^{13}\text{C}_{\text{graphite}}$  being  $4.5 \pm 1.5\text{‰}$  at  $700^\circ\text{C}$  (Satish-Kumar et al. 2002). Thus the isotopic compositions of metasediments will be homogenized if they maintain chemical connectivity, and extreme variability should not be present within the diamond stability field. A comparison of true metamorphic diamonds (formed in crustal rocks) with eclogitic diamonds (cf. Figs. 2c and 2f) shows some general similarities in their  $\delta^{13}\text{C}$  range, but the  $\delta^{13}\text{C}$  distributions differ principally because there is a near-complete absence of  $\delta^{13}\text{C}$  values around  $-5\text{‰}$  for metamorphic diamonds.

**Model 2 – Primordial isotopic variability:** A statistical analysis of carbon isotopes in diamond with respect to diamond shape, size, color, nitrogen content and speciation, type and chemical composition of the mineral inclusions, and the occurrence of plastic deformation led to the unambiguous conclusion that a single kimberlite can sample sev-

(FIG. 2G), values which have remained fairly constant through geological time. From the present data, about 54% of E-type diamonds have  $\delta^{13}\text{C}$  values of about  $-5 \pm 3\text{‰}$ . If these diamonds were the product of recycled carbon, mass-balance considerations indicate the need to recycle a mixture composed of 20% organic matter (average  $\delta^{13}\text{C}$  value of about  $-25\text{‰}$ ) and 80% of carbonates (average  $\delta^{13}\text{C}$  value of about  $0\text{‰}$ ) (FIG. 2G). One would accordingly expect a majority of E-type diamonds with  $\delta^{13}\text{C}$  values between  $-5$  and  $0\text{‰}$ , in contrast to the observation that most eclogitic diamonds have a  $\delta^{13}\text{C}$  range between  $-5$  and  $-25\text{‰}$  (FIG. 2C). Thus the  $\delta^{13}\text{C}$  distribution produced by mixing carbonate and organic matter does not match that of eclogitic diamond. High  $\delta^{13}\text{C}$  values (i.e.,  $1 \pm 2\text{‰}$ ) are actually extremely rare among macrodiamonds and are largely restricted to the alluvial diamonds from New South Wales.

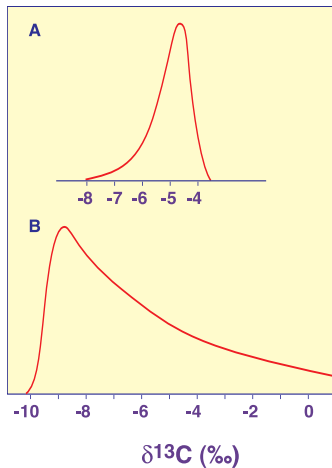
eral diamond subpopulations (Deines et al. 1993). As these distinct diamond subpopulations are not related by any of the above criteria, the authors suggested that the observed isotopic heterogeneity was primordial, acquired during Earth's accretion and not homogenized by mantle convection. This model would be supported, for instance, by the  $\delta^{13}\text{C}$  range defined by carbon in meteorites, which is indeed broadly similar to that of eclogitic diamonds (Deines 1980).

The preservation of primordial carbon isotope heterogeneity in Earth's mantle, however, is not supported by data from other fields of mantle isotope geochemistry, which show almost no evidence for preservation of primitive mantle compositions. In addition, methods used to identify diamond subpopulations are not robust. Identification by morphological features such as shape, color, size, and plastic deformation often associates primary and postgrowth diamond formation features (Harris 1992). Defining diamond subpopulations according to the chemical composition (or nature) of mineral inclusion(s) implicitly assumes fixed chemical compositions but fails to account for multiple inclusions from a single diamond spanning almost the entire known range of chemical compositions (e.g., Sobolev et al. 1998). Nitrogen contents have been assumed to reflect the diamond growth environment (high/low nitrogen contents within the diamond being derived from nitrogen rich/poor parts of the mantle), although other processes, such as growth rate, may control the incorporation of nitrogen into the crystal structure.

**Model 3 – Fractionation of stable isotopes at mantle temperatures:**

A unique property of stable isotopes is that coexisting compounds in equilibrium will display distinct stable isotopic compositions. This fractionation depends chiefly on temperature and the phases involved. For temperatures of  $1000^\circ\text{C}$ , the carbon isotope fractionation between coexisting C-bearing species is small—less than  $4\text{‰}$  (Bottinga 1969). However, the formation of carbon-bearing species in an open system, where minute amounts of material are removed continuously under conditions of a constant fractionation factor, can lead to very significant  $\delta^{13}\text{C}$  ranges, in some cases in excess of  $40\text{‰}$ . For example, the  $\delta^{13}\text{C}$  compositions of carbonates from a peridotite xenolith spanned a range from  $-5\text{‰}$  to  $+24\text{‰}$  (Deines 1968). As the most positive  $\delta^{13}\text{C}$  values are higher than metasedimentary carbon in this example, mixing involving metasedimentary carbon can be ruled out to explain the isotopically heavy end-member. Such  $\delta^{13}\text{C}$  variations are best explained by the precipitation of carbonates from  $\text{CO}_2$ .

Although the range of  $\delta^{13}\text{C}$  produced by isotopic fractionation in an open system can be large, the mode(s) and the shape(s) of the resulting distribution(s) are not random. A step towards identifying the composition of the C-bearing phase(s) (e.g.,  $\text{CO}_2$ , carbonate, methane, carbide) in the diamond growth medium/media is to examine the  $\delta^{13}\text{C}$  distribution(s) for diamond (Deines 1980). As an example, FIGURE 4 shows the model  $\delta^{13}\text{C}$  frequency distributions produced by fractionally precipitating diamond from  $\text{CO}_2$  and methane. The worldwide diamond  $\delta^{13}\text{C}$  compositions (FIG. 2a) are actually compatible with such an open-system fractionation process in which diamonds grow from different gaseous species. It has therefore been suggested that both eclogitic and peridotitic diamonds precipitated from mantle-derived carbon with an initial  $\delta^{13}\text{C}$  value of about  $-5\text{‰}$  (Javoy et al. 1986; Galimov 1991). The main strength of this model is that it accounts for the strong overlap of both eclogitic and peridotitic diamonds in the  $\delta^{13}\text{C}$  range of  $-8$  to  $-2\text{‰}$ .



**FIGURE 4** The  $\delta^{13}\text{C}$  distribution produced by the precipitation of diamond from (A)  $\text{CO}_2$  and (B) methane (modified from Deines 1980). In both cases, the initial  $\delta^{13}\text{C}$  value was  $-5\text{‰}$ .

### ADDITIONAL TRACERS

Because the isotopic compositions of mantle-derived and metasedimentary carbon overlap, carbon isotopes alone will not resolve the origin of diamond. An alternative approach consists of analyzing major and trace elements (Stachel et al. 2004) and radiogenic and stable isotopes of inclusions in diamond. Radiogenic isotopes have been used to decipher the history of diamond formation in the mantle, in particular to demonstrate the Archean to Proterozoic formation age of most peridotitic and eclogitic diamonds (Shirey et al. 2002). The oxygen and sulfur isotopes of silicate and sulfide inclusions are described in the present article.

A second approach consists of analyzing the elements trapped within the diamond matrix. More than 80 elements have been detected in the crystal structure of diamonds, of which nitrogen, boron, oxygen, and hydrogen (ppm levels) are the most abundant. Nitrogen, the main impurity in diamond (Kaiser and Bond 1959), is the only element that has been systematically studied.

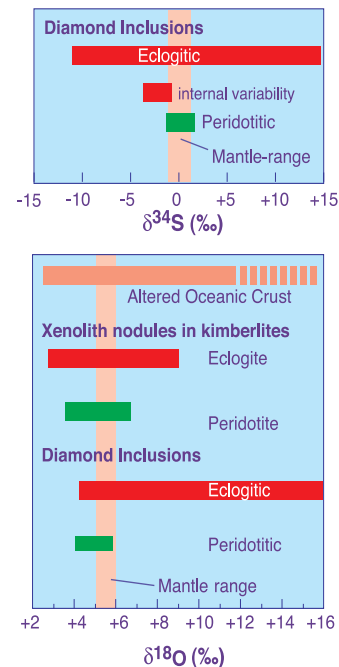
### Oxygen and Sulfur Isotopes

For both oxygen and sulfur isotopes, Earth's mantle is assumed to be homogeneous with  $\delta^{18}\text{O}$  values from  $+5$  to  $+6\text{‰}$  relative to SMOW and  $\delta^{34}\text{S}$  from  $-1$  to  $+1\text{‰}$  relative to CDT (see glossary p. 70). In contrast, the igneous oceanic crust, altered by seawater and including accompanying sediments, shows values deviating greatly from the mantle range. Fairly limited oxygen and sulfur isotope data are currently available from silicate (less than 20 analyses) and sulfide (less than 50 analyses) inclusions in diamond. The  $\delta^{18}\text{O}$  values (from  $+4$  to  $+16\text{‰}$ ) and  $\delta^{34}\text{S}$  (from  $-11$  to  $+14\text{‰}$ ) (Fig. 5) obtained respectively from silicate and sulfide eclogitic inclusions clearly fall outside the mantle range, and such evidence has been taken to support a subduction-related origin (Chaussidon et al. 1987; Lowry et al. 1999; Taylor and Anand 2004). In addition, the identification of mass-independent fractionation of sulfur isotopes ( $\delta^{33}\text{S} \neq 0.5 \times \delta^{34}\text{S}$ ) within eclogitic sulfide inclusions in diamonds (Farquhar et al. 2002) is key evidence that eclogite and eclogitic inclusions in diamonds are fragments of subducted Archean oceanic crust. This is because, on Earth, mass-independent fractionations were produced only in the anoxic Archean atmosphere. Thus, oxygen and sulfur isotopes data from inclusions in diamonds link them to subducted oceanic crust. Whether oxygen and sulfur iso-

tope data can be used to constrain the source of the carbon from which the diamonds formed relies heavily on the assumption that the carbon in diamond came from the same source as the hosting eclogite.

### Nitrogen Content and Isotopic Composition

In diamonds, nitrogen present within the crystal structure substitutes for, and is strongly bonded to, carbon atoms. Nitrogen concentrations in diamonds range widely, from traces up to 3500 ppm, and average  $\sim 200$  ppm and  $\sim 300$  ppm in peridotitic and eclogitic diamonds, respectively (FIGS. 6A AND 6B, Deines et al. 1993). In contrast to an early suggestion from Dyer et al. (1965) that 98% of all diamonds would be nitrogen bearing (i.e., Type I), a survey of recent publications

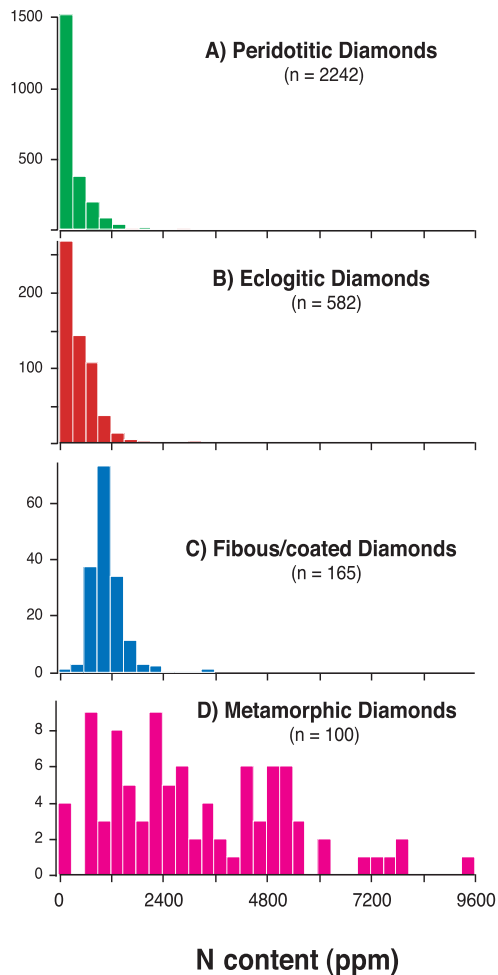


**FIGURE 5** Ranges of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values measured from sulfide and silicate inclusions in diamonds. The mantle ranges, as defined by mid-ocean ridge basalts, are indicated for comparison. The range of  $\delta^{18}\text{O}$  values for eclogite and peridotite xenolith nodules from kimberlites are also shown.

shows that, in the investigated size of crystals ( $\sim 2$  to  $\sim 4$  mm, i.e.  $<0.02$  carat), a value of  $\sim 70\%$  is more appropriate. Diamonds of different types show distinctly different N contents. Fibrous/coated diamonds have, on average, high N contents, while those from the lower mantle (not shown in Fig. 6) include a high proportion of diamonds with low N contents (Type II;  $<20$  ppm). Metamorphic diamonds (Fig. 6b) are unique in their range of very high N contents. The distributions of nitrogen contents shown in Figures 6a and 6c are representative of diamonds from most kimberlite occurrences, with only subtle differences in the abundance of Type II diamonds and average N contents.

Within a single diamond growth zone, sharp variations or oscillations of more than several hundred ppm of nitrogen are readily identified between layers using Fourier-transform infrared or cathodoluminescence mapping (Mendelsohn and Milledge 1995; Harte et al. 1999). Such abrupt changes or oscillations probably reflect changing growth conditions. Their preservation over billions of years of storage in the mantle demonstrates that nitrogen cannot diffuse out of the crystal structure—the observed distance of diffusion is about  $30 \mu\text{m}$ . Recent experiments by Koga et al. (2003) further support this premise.

Nitrogen has two stable isotopes,  $^{14}\text{N}$  and  $^{15}\text{N}$  ( $\sim 99.6\%$  and  $\sim 0.4\%$ , respectively). Unlike C isotopes, upper mantle-derived samples and (meta)sediments show distinct isotopic signatures for nitrogen. Nitrogen in sediments is present as ammonium ions. Because of similarities in charge and ionic radius, nitrogen follows potassium and enters potassic minerals such as illite, smectite, and phengite (the first two minerals being clays, the last a mica). Most sediments show positive  $\delta^{15}\text{N}$  values, with an average of about  $+6\text{‰}$  relative to air. With increasing metamorphism, devolatilization leads to a decrease in N content and relative enrichment in  $^{15}\text{N}$  (Haendel et al. 1986). Accordingly,



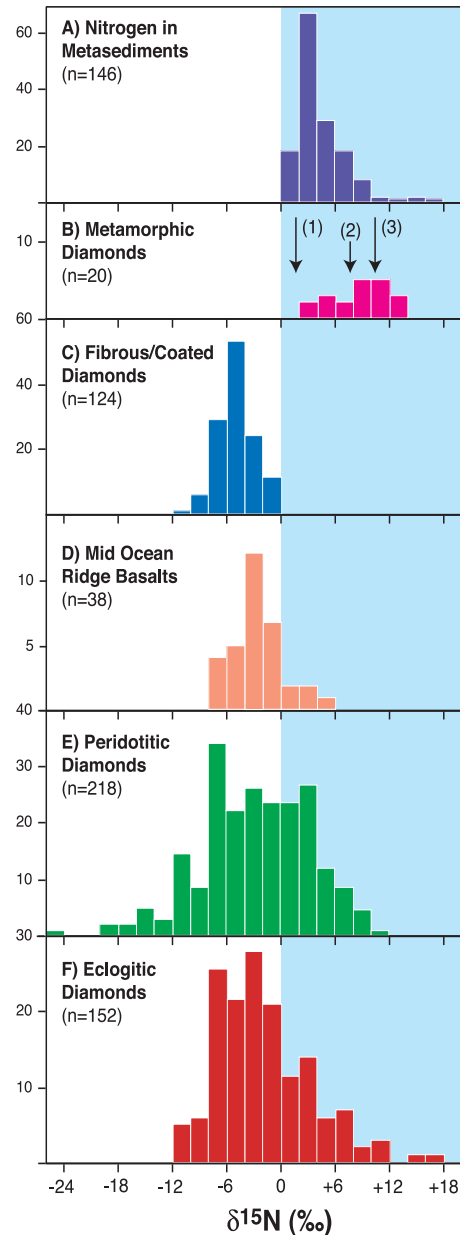
**FIGURE 6** Comparative histograms of nitrogen contents of diamonds. Lower-mantle diamonds, usually with N contents less than 50 ppm, are not shown here.

metasedimentary nitrogen is characterized by  $\delta^{15}\text{N}$  values that are invariably positive (Fig. 7A), from the Archean to recent geological periods.

The isotopic composition of nitrogen in the upper mantle has been estimated from the study of fibrous/coated diamonds, mid-ocean ridge basalts, and diamonds associated with peridotite (Figs. 7C to 7E). The  $\delta^{15}\text{N}$  values for these samples are spread over a large range, from  $-25\text{‰}$  to  $+15\text{‰}$ , with most values being negative ( $\sim 65\text{‰}$ ) and centered around  $-5 \pm 3\text{‰}$ . Because of the relative  $^{15}\text{N}$  enrichment during subduction, we would expect to find positive  $\delta^{15}\text{N}$  values in eclogitic diamonds if they were formed solely from crustal carbon and nitrogen. In support of this statement, metamorphic diamonds show  $\delta^{15}\text{N}$  values from  $-1.8$  to  $+12.4\text{‰}$  (Fig. 7B). However,  $\delta^{15}\text{N}$  values for eclogitic diamonds are mostly ( $\sim 70\%$ ) negative (Fig. 7F). Furthermore, about half of the eclogitic diamonds with low  $\delta^{13}\text{C}$  values also show negative  $\delta^{15}\text{N}$  values. While Figure 7 is a compilation of worldwide nitrogen isotope data, eclogitic and peridotitic diamonds from a single kimberlite often show striking similarities in range and distribution of  $\delta^{15}\text{N}$  values. Distinct carbon sources for eclogitic and peridotitic diamonds are therefore not supported by nitrogen isotope systematics. On the basis of the average negative  $\delta^{15}\text{N}$  values (Fig. 7F), the carbon comprising most eclogitic and

peridotitic diamonds is mantle-derived rather than subduction-related.

In light of the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  data, a variation to Model 1, above, would involve mixing of mantle-derived carbon with subduction-related organic carbon (Navon 1999). Subducted organic carbon should produce diamond with low  $\delta^{13}\text{C}$  values, whereas mantle carbon should grow diamond (separate, overgrowth, or via mixing) with higher  $\delta^{13}\text{C}$  values, approaching  $-5\text{‰}$ . Given the high nitrogen contents of metamorphic diamonds, an enrichment in nitrogen with decreasing  $\delta^{13}\text{C}$  might be expected. However, both eclogitic and peridotitic diamonds show the opposite trend of decreasing N contents with decreasing  $\delta^{13}\text{C}$  values (not shown). Also, metamorphic diamonds are not as depleted in  $^{13}\text{C}$  as some eclogitic diamonds, and this model would predict some overlap. Thus, C and N isotopes data do not provide evidence of a connection between subduction-related carbon and E-type diamonds.



**FIGURE 7** Comparative histograms of  $\delta^{15}\text{N}$  values for (A) metasedimentary nitrogen; (B) metamorphic diamonds from Akluilak (Canada); the three arrows represent the mean values for metamorphic diamonds from three different areas in the Kokchetav massif (Kazakhstan) (see Ogasawara this issue); (C) fibrous/coated diamonds; (D) mid-ocean ridge basalts (E) peridotitic diamonds; and (F) eclogitic diamonds.

## METASOMATIC DIAMOND FORMATION IN EARTH'S MANTLE

The evidence provided by S and O isotopes, on the one hand, and by C and N isotopes, on the other, can be reconciled if diamonds grew from external carbon and nitrogen introduced into eclogites and peridotites through a metasomatic process—that is, one in which a new mineral grows from or by reacting with a fluid permeating a mineral aggregate.

Evidence supporting a metasomatic process includes (1) 3D X-ray tomographic imaging of eclogite nodules (Schulze et al. 1996), showing that diamonds are confined to metasomatic veins; (2) trace-element analysis of inclusions in diamonds (Stachel et al. 2004); (3) fluid(s) trapped during

fibrous/coated diamond growth (Navon 1999); and (4) the presence of metasomatic inclusions within diamonds (Loest et al. 2003). These studies demonstrate that carbonate-bearing melt/fluid(s) are involved in diamond crystallization.

With metasomatic growth of diamond, both eclogitic and peridotitic types can be derived from the same carbon source, which was initially homogenous isotopically (i.e., no need to call for multiple, isotopically distinct sources) and mantle derived (with  $\delta^{13}\text{C}$  values of about  $-5\%$ ). In the simplest scenario, isotopic fractionation associated with diamond crystallization is not significant because it cannot be the main process responsible for the distinct distributions shown in Figures 2b and 2c. The distinct distributions are produced before diamond formation, diamond being a *passive recorder* of the event(s). The carbon precursors are likely to have been carbonates, and as decarbonation reactions are known to be restricted to eclogitic mineral assemblages (Luth 1993), the escape of  $\text{CO}_2$  enriched in  $^{13}\text{C}$

would leave a  $^{13}\text{C}$ -depleted residue from which eclogitic diamonds can subsequently crystallize (Cartigny et al. 1998). In conclusion, the varied isotopic compositions of carbon in mantle-derived diamonds may reflect, in part, distinct carbon sources, but mineral-fluid reactions controlled by the mineral assemblages of the rocks in which the diamonds formed are probably the most important factor involved in producing the observed isotopic variations.

## ACKNOWLEDGMENTS

The author would like to acknowledge the numerous uncited contributions and data of Eric Galimov, Nikolai Sobolev, Peter Deines, and their co-workers published during the last twenty-five years. Jeff Harris is greatly thanked for his unlimited support to the author and for a thorough review, and therefore clarification, of the present article. Steve Shirey is thanked for his very constructive review, and Rondi Davies and George Harlow for their editorial handling of the manuscript. IPGC contribution 2031. ■

## REFERENCES

- Bottinga Y (1969) Carbon isotope fractionation between graphite, diamond and carbon dioxide. *Earth and Planetary Science Letters* 5: 301-307
- Boyd SR, Pineau F, Javoy M (1994) Modelling the growth of natural diamonds. *Chemical Geology* 116: 29-42
- Cartigny P, Harris JW, Javoy M (1998) Eclogitic diamond formation at Jwaneng: no room for a recycled component. *Science* 280: 1421-1423
- Chaussidon M, Albarède F, Sheppard, SMF (1987) Sulfur isotope heterogeneity in the mantle from ion microprobe measurements of sulphide inclusions in diamonds. *Nature* 330: 242-244
- Deines P (1968) The carbon and oxygen isotopic composition of carbonates from a mica peridotite dike near Dixonville, Pennsylvania. *Geochimica et Cosmochimica Acta* 32: 613-625
- Deines P (1980) The carbon isotopic compositions of diamonds: relationship to diamond shape, color, occurrence and vapor composition. *Geochimica et Cosmochimica Acta* 44: 943-961
- Deines P, Harris JW, Gurney JJ (1993) Depth-related carbon isotope and nitrogen concentration variability in the mantle below the Orapa kimberlite, Botswana, Africa. *Geochimica et Cosmochimica Acta* 57: 2781-2796
- Dyer HB, Raal FA, Du Preez L, Loubser JHN (1965) Optical absorption features associated with paramagnetic nitrogen in diamond. *Philosophical Magazine* 11: 763-774
- Farquhar J, Wing BA, McKeegan KD, Harris JW, Cartigny P, Thiemens MH (2002) Mass-independent sulfur of inclusions in diamond and sulfur recycling on early Earth. *Science* 298: 2369-2372
- Galimov EM (1991) Isotope fractionation related to kimberlite magmatism and diamond formation. *Geochimica et Cosmochimica Acta* 55: 1697-1708
- Haendel D, Mühle K, Nitzsche H-M, Stiehl G, Wand U (1986) Isotopic variations of the fixed nitrogen in metamorphic rocks. *Geochimica et Cosmochimica Acta* 50: 749-758
- Harris JW (1992) Diamond geology. In: Field JE (ed) *The properties of diamond*. Academic Press, London, pp 345-393
- Harte B, Fitzsimons ICW, Harris JW, Otter ML (1999) Carbon isotope ratios and nitrogen abundances in relation to cathodoluminescence characteristics for some diamonds from the Kaapvaal Province, South Africa. *Mineralogical Magazine* 63: 829-856
- Javoy M, Pineau F, Delorme H (1986) Carbon and nitrogen isotopes in the mantle. *Chemical Geology* 57: 41-62
- Kaiser W, Bond L (1959) Nitrogen, a major impurity in common type I diamond. *Physical Review* 115: 857-863
- Kirkley MB, Gurney JJ, Otter ML, Hill SJ, Daniels LR (1991) The application of C isotope measurements to the identification of the sources of C in diamonds: a review. *Applied Geochemistry* 6: 477-494
- Koga KT, Van Orman JA, Walter MJ (2003) Diffusive relaxation of carbon and nitrogen isotope heterogeneity in diamond: a new thermochronometer. *Physics of the Earth and Planetary Interiors* 139: 35-43
- Loest I, Stachel T., Brey GP, Harris JW, Ryabchikov ID (2003) Diamond formation and source carbonation: mineral associations in diamonds from Namibia. *Contributions to Mineralogy and Petrology* 145: 15-24
- Lowry D, Matthey DP, Harris JW (1999) Oxygen isotope composition of syngenetic inclusions in diamond from the Finsch Mine, RSA. *Geochimica et Cosmochimica Acta* 63: 1825-1836
- Luth RW (1993) Diamonds, eclogites, and the oxidation state of the Earth's mantle. *Science* 261: 66-68
- Mendelssohn MJ, Milledge HJ (1995) Geologically significant information from routine analysis of the mid-infrared spectra of diamonds. *International Geology Review* 37: 95-110
- Navon O (1999) Diamond formation in the Earth's mantle. In: Gurney JJ, Gurney, JL, Pascoe MD, Richardson SH (eds), *Proceedings of the 7th International Kimberlite Conference, Red Roof Design, Cape Town, Vol 2*, pp 584-604
- Satish-Kumar M, Wada H, Santosh M (2002) Constraints on the application of carbon isotope thermometry in high- to ultrahigh-temperature metamorphic terranes. *Journal of Metamorphic Geology* 20: 335-350
- Schulze DJ, Wiese D, Steude J (1996) Abundance and distribution of diamonds in eclogite revealed by volume visualization of CT X-Ray scans. *Journal of Geology* 104: 109-113
- Shirey SB, Harris JW, Richardson SH, Fouch MJ, James DE, Cartigny P, Deines P, Viljoen F (2002) Diamond genesis, seismic structure, and evolution of the Kaapvaal-Zimbabwe craton. *Science* 297: 1683-1686
- Sobolev NV, Galimov EM, Ivanovskaya IN, Yefimova ES (1979) Isotope composition of carbon in diamonds containing crystalline inclusions. *Doklady Akademii Nauk SSSR* 249: 1217-1220
- Sobolev NV et al. (1998) Extreme chemical diversity in the mantle during eclogitic diamond formation: evidence from 35 garnet and 5 pyroxene inclusions in a single diamond. *International Geology Review* 40: 567-578
- Stachel T, Aulbach S, Brey GP, Harris JW, Loest I, Tappert R, Viljoen KS (2004) The trace element composition of silicate inclusions in diamonds: a review. *Lithos* 77: 1-19
- Taylor LA, Anand M (2004) Diamonds: time capsules from the Siberian mantle. *Chemie der Erde* 61: 1-74 ■