A Diamond Trilogy: Superplumes, Supercontinents, and Supernovae

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Diamond is a remarkable mineral and has been long recognized for its unusual physical and chemical properties: robust and widespread in industry, yet regally adorned. This diversity is even greater than formally appreciated because diamond is recognized as an extraordinary recorder of astrophysical and geodynamic events that extend from the far reaches of space to Earth's deep interior. Many diamonds are natural antiques that formed in presolar supernovae by carbon vapor deposition, in asteroidal impacts and meteorite craters by shock metamorphism, and in Earth's mantle 1 to 2 billion years after planetary accretion from fluids and melts. The carbon in diamond is primordial, but there are unexplained isotopic fractionations and uncertainties in heterogeneity.

Carbon is the fourth most abundant element in the solar system after hydrogen, helium, and oxygen (*1*). As a nucleosynthetic bridge to the heavy elements, to stellar evolution, and to biosynthesis, carbon holds an interesting position in the periodic system of elements. Diamond is pure C and is an impervious time capsule: Some diamonds are presolar and have recorded such extraordinary astrophysical events as supernovae explosions, other diamonds bear witness to solar system formation, and diamonds from our planet are a window to the geodynamic evolution of Earth's deep interior. The study of diamond and its polymorphs (lonsdaleite, fullerene, and graphite) has seen a recent burst of activity in geochemistry and astrophysics, in novel methods of synthesis, and in the development of useful applications that take advantage of its covalent bonding, clarity, extreme hardness, high thermal conductivity, and electrical resistance. Here I review the natural occurrences of diamond and the implications of diamond for Earth and solar system processes.

Diamond Synthesis

The many ways in which diamonds have been synthesized (*2*) are clues to the conditions under which diamonds form naturally. Diamond is the stable C phase at pressure (P) > 5 GPa. Industrial-scale production of diamond is from amorphous carbon or graphite in high-temperature (T) (1200° to 1400°C) and high-P (5 to 7 GPa) presses; the method typically requires both a solvent and catalyst of Fe, Co, Cr, Ti, and Al or is assisted by minute diamond seeds. Diamond morphologies vary as a function of T at constant P (for example, 6 GPa): Octahedrons form preferentially at high temperatures (1500° to 1600°C), cubo-octahedrons at 1350° to 1500°C, and cubes at <1300°C. Spherical clusters of microdiamonds (5 to 10 μm across) form in detonation experiments, and hexagonal lonsdaleite is synthesized by ballistically accelerating metal projectiles into carbon targets. The most recent industrial method is to form diamond through carbon vapor deposition (CVD). In this process, a thin (nanometer to micrometer) metastable diamond film is formed on metal substrates from methane (CH_4) or other hydrocarbons at low pressures (<1 Pa) and at high temperatures (~1000°C), in the presence of excess hydrogen. Metastable diamond synthesis on diamond seeds has also been achieved under hydrothermal conditions at 700°C and 100 to 500 mPa.

Distribution of Cratons, Kimberlites, and Diamonds

Diamonds were first recorded in India around 2000 B.C., but it was not until much later that discoveries were made in Brazil (1720 A.D.) and South Africa (1867 A.D.) (*3*). The major producers today are Africa, Australia, and Russia, with smaller operations in China, Brazil, and India (Fig. 1) (*4*). New diamond discoveries in Arctic Canada are world-class deposits, and the first mine opened in October 1998. About 500 metric tons of diamond have been mined worldwide since 1900, and forecasts for the year 2000 exceed 24 metric tons or 120 million carats [1 carat = 0.2 g (*4*, *5*)].

Diamond is transported from Earth's interior from depths of more than 180 km (equivalent to pressures of ~5 GPa) in highly explosive, rapidly injected magmas known as kimberlites (named after the famous diamond mining district in South Africa). Only a few kimberlites contain diamond, and, where present, concentrations are only 1 to 5 parts per million (ppm). High-velocity transport is inferred to inhibit the transformation of diamond to graphite or the combustion of diamond to a carbon gas species (*6*).

Diamondiferous kimberlites have only been found in old continental cratons (Fig. 1), but diamonds are also present in a closely related rock, lamproite [the suite is hereafter referred to as kimberlite-clan rocks (KCRs)

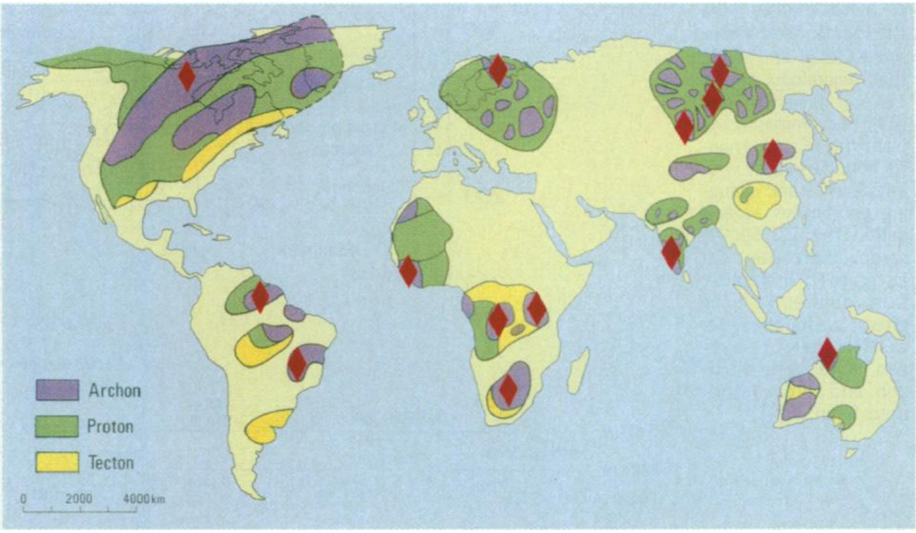

Fig. 1. Global distribution of cratons, age provinces (Archons, >2.5 Ga; Protons, 2.5 to 1.6 Ga; and Tectons, 1.6 to 0.8 Ga), and major diamond deposits (red diamonds). [Modified from (*4*, *15*)]

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(*7*)], that has a preferred setting in mobile belts adjacent to cratons (Fig. 2). A craton is an ancient tract of continental crust that has not been involved in tectonic activity for billions of years (*8*). From studies of xenoliths (accidental inclusions rocks in rock melts) in KCRs (*9*), mineral inclusions in diamonds (*10*), geophysics (*11*), field geology (*12*), and models for the lithosphere and early crustal genesis (*13*), there is a general consensus that the similarity among cratons is the result of a specific set of geological processes that operated in Earth's early history. Cratons have low-density keels that are at least 200 km thick (*14*) and >3 billion years (Ga) in age (Fig. 2); they were created by mantle melting and extraction of continental crust. Most diamondiferous intrusives are into crust that is >2.5 Ga, some lamproites intrude crust formed from 1.6 to 2.5 Ga, and no primary diamond deposits are recognized intruding crust younger than 1.6 Ga (*15*). KCRs typically have high MgO (> 25 weight %) contents, are rich in volatiles (water, carbon dioxide, and fluorine), and have atypically high concentrations of selected trace elements (K, Na, Ba, Sr, rare Earth elements, Ti, Zr, Nb, and P). These characteristics are attributed to the influx of fluids into the mantle source region from which KCRs formed later by small degrees of partial melting (*14*).

Diamonds from KCRs range from smooth-faced octahedra to hopper crystals and from fibrous diamond in cubes (and ballas) to polycrystalline aggregates in framesite (Fig. 3, A to O). Diamonds range in size up to the famous Cullinan, recovered in South Africa in 1905, at 3106 carats (*3*). Diamonds greater than 500 carats are rare, and sizes decrease exponentially as a function of frequency (*4*). Diamonds are typically clear but also vary in body color. Green transparent diamonds show radiation damage, whereas green opaque or green opaque–coated diamonds contain abundant mineral and fluid inclusions. Brown and pink diamonds usually exhibit laminations because of plastic deformation (*16*). Yellow and greenish-yellow diamonds contain nitrogen substituting for carbon, and semiconducting blue diamonds have trace amounts of boron.

Diamonds are spectroscopically classified (*16*) into type I (nitrogen-bearing) and type II (nitrogen-free). Subdivision of type I diamonds is based on the state of N site occupancy. Type Ib diamonds have N randomly replacing C (typical of rapidly quenched synthetic diamond), but this type of diamond is very rare among natural diamonds. In type Ia diamonds ($\sim$98% of cratonic macrodiamonds), N is present in aggregation, as A centers (a pair of N atoms), N3 centers (three N atoms and a vacancy), and B centers (four N atoms and a vacancy). N aggregation is time and temperature dependent (*17*), and diamond formation in type IaA is at lower temperatures (1050° to 1100°C) than in type IaB (1200° to 1400°C).

Diamonds cannot be directly dated, but the ages of mineral inclusions in diamond can be determined with the decay systematics of radiogenic isotopes: Sm-Nd for garnet, Ar-Ar in Ca pyroxene inclusions, and U-Pb, ^{207}Pb, and Re-Os in sulfide inclusions (*18*). These data imply that diamonds from KCRs range in age from 1.5 to >3 Ga. In contrast, most of the KCRs that brought diamonds to the surface are 50 million years old (Ma) to 1 Ga (*19*). Thus, the age and compositions of mineral inclusions imply that most diamonds were formed in an early event in the keel of a craton and then stored there for long periods of time. Cathodoluminescence observations show that many diamonds are complexly zoned and have reentrant angles (Fig. 3J) resulting from corrosion and multiple overgrowths (*20*). These textures imply that diamonds grew over long periods of time in the mantle. In addition, the kinetic transformation of type Ib to type Ia diamonds is slow, and the segregation of nitrogen under mantle conditions is considered to take a billion or more years (*17*, *21*).

The preferred distribution of diamonds, although related to the minimum pressures required to form diamond, must also be related to carbon speciation (CH_4, CO_2, or carbonate) and oxidation state (*22*). Diamond host rocks can be determined from the presence of diamond in mantle xenoliths and from the mineral compositions of inclusions in diamond. Two types of rocks are seen

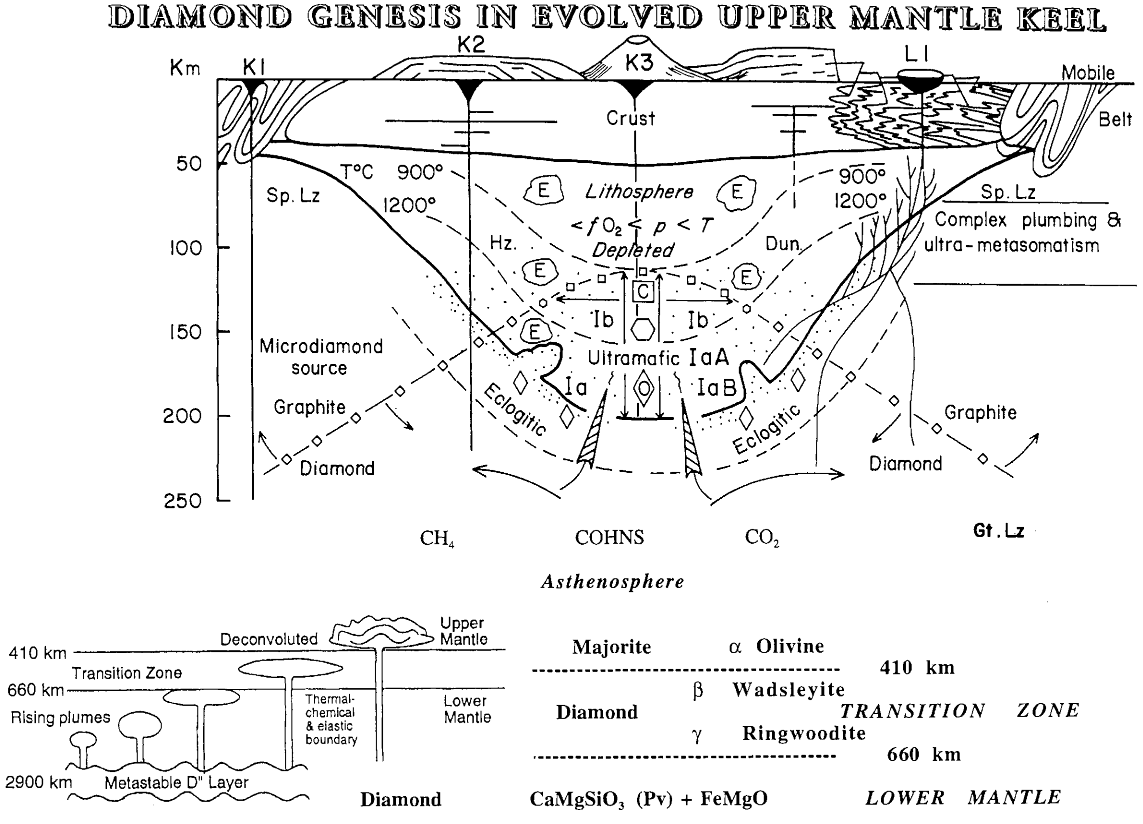

Fig. 2. Schematic cross section of a subcontinental, subcratonic lithospheric keel showing the distribution of dominant rock types (*14*), the diamond-graphite inversion curve, diamond types and morphologies, zones of metasomatism (*14*), the locations of intrusive KCRs (K and L) (*7*), the mineralogy of the TZ and lower mantle (*23*), and plumes rising from the D″ core-mantle boundary layer with interference and changing geometries at and within the TZ. Sp. Lz, spinel lherzolite; Gt. Lz, garnet lherzolite; Dun, dunite; E, eclogite; Hz., harzburgite; COHNS, carbon, oxygen, hydrogen, nitrogen, and sulfur. [Modified from (*22*)]

(*14*): One, known as peridotite (P type), is rich in Mg-olivine, Mg-pyroxene, Mg-Cr garnet, and chromian spinel. It is thought to represent the principal rock of subcratonic keels and is strongly depleted in crustal elements. The second is eclogite (E type), a bimineralic rock of Ca-Fe–rich garnet and Ca-Na–rich pyroxene, which by contrast is rich in crustal elements, is geochemically more primitive than the keel, and implies later injection of eclogite into the keel.

The compositions of mineral inclusions in diamond correspond to the principal host rocks of diamond. Fe- and Ni-rich sulfide minerals, however, are overwhelmingly dominant, which suggests that S may act as a catalyst in forming some diamond (*22*). P-type diamonds have sulfides rich in Ni (16 to 34 weight %), whereas E-type diamonds have high-Fe sulfides (0.5 to 8 weight % Ni), and these differences are geochemically in accord with depleted peridotites and undepleted eclogites. Mineral inclusions in P-type diamonds are typically older (>3 Ga) than E-type (1.5 Ga) diamonds (*18*), which supports the inferred age relation between keels and eclogites. Some mineral inclusions in diamond are from the mantle transition zone (TZ) at depths of 410 to 660 km, and others are from the lower mantle at depths >660 km (*23*). A small number of diamonds contain Fe, FeC, and SiC inclusions that imply extremely low oxidation states, substantially more reduced than rocks and minerals from the upper mantle and more compatible with Earth's metallic Fe core (*19*). At the other extreme are diamonds with cores of high-T octahedra that are coated by fluid-rich, lower T diamond cubes. This implies that some diamonds may have formed by hydrothermal growth at high P and T (*24*).

The Source of Carbon in Cratonic Diamond

From the vast reservoir of C in the solar system and from the old ages of diamond, it would seem quite natural to assume that most diamonds formed from primordial C initially present during accretion of Earth. It is estimated, on the basis of geochemical and cosmochemical arguments, that the upper mantle contains $\sim$100 ppm C but that the undegassed lower mantle has $\sim$1000 to 3700 ppm C, making it a substantial C reservoir (*25*). However, eclogites may form from subducted oceanic crust, and some C could be recycled biological matter. Two factors are relevant in evaluating this model for the source of C in diamond: The first is the antiquity of diamond (1.5 to >3.5 Ga) in relation to the fossil record, and the second is that in the Archean, because of high heat flow, subducted oceanic plates may have melted at shallow depths and never reached the stability field of diamond in the mantle (*26*).

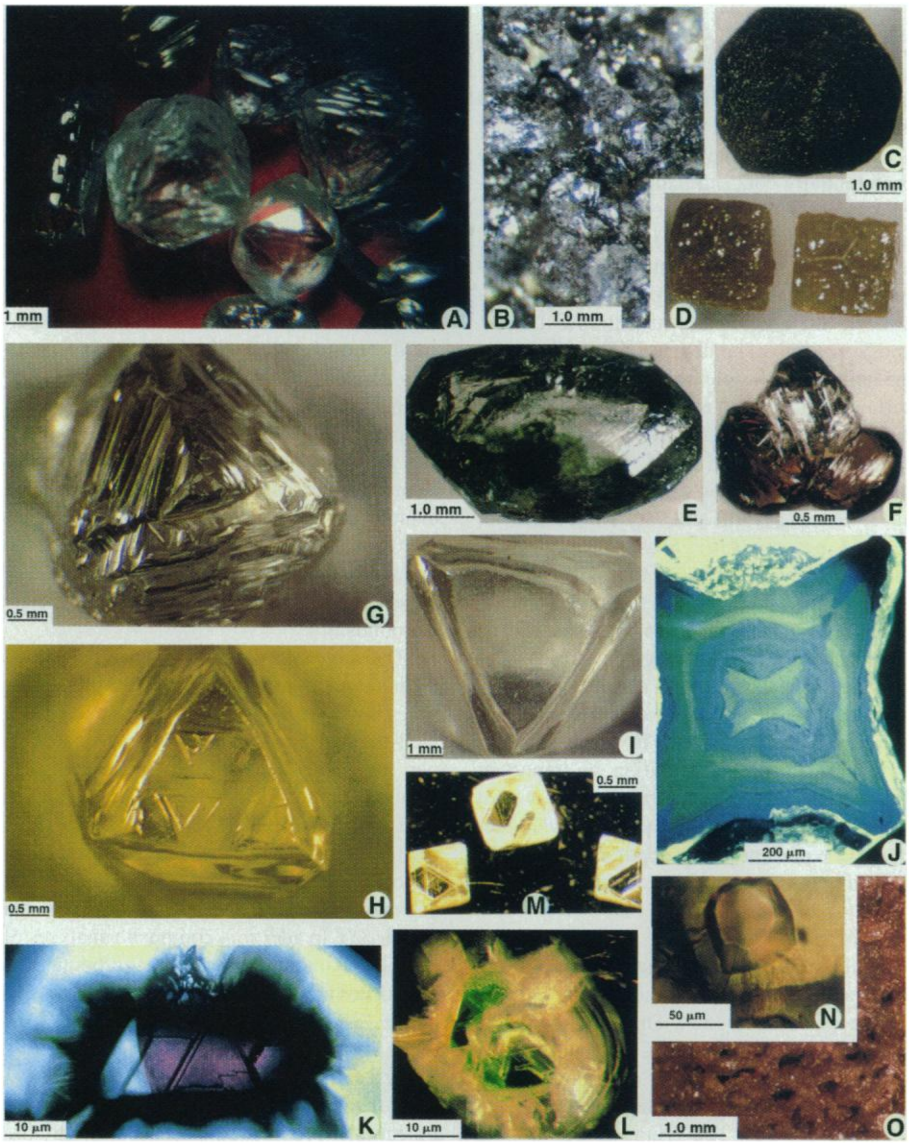

Fig. 3. Photomicrographic examples of terrestrial diamonds; all are cratonic with mantle protoliths except for (N), which has a crustal protolith from Kazakhstan, and (O), which has an unknown protolith from Brazil. Diamonds (A), (B), and (D) to (L) are from various cratons in Africa, (C) is from Brazil, and (M) is from Siberia. **(A)** A variety of clear gem quality octahedra with smooth surfaces and growth lines typical of the subcratonic lithosphere (Fig. 2) and an unusual elongate diamond. **(B)** Framesite, an aggregate of loosely bonded irregularly shaped clear diamonds, locally common and of controversial origin. **(C)** Ballas (literally ball) with fibrous diamonds in thin laminated shells. **(D)** High N, yellow cubes with fibrous habit that grew rapidly in the mantle. **(E)** A highly resorbed green irradiated diamond, typical of diamonds affected by radioactive sources in the crust. **(F)** Contact growth of two brown, highly strained diamonds in association with an irregular octahedron that point to changing environments in the mantle. **(G)** An octahedron with inverted hopper, crystal face growth in triangular patterns. **(H)** The triangular pattern on an octahedral face in this diamond differs from (G) and is the result of etching in the mantle; the geometry, apex down from the coign, is a negative trigon that formed under different redox conditions from positive trigons that have the etch apex pointing toward the octahedral coign. **(I)** Selective corrosion along the edges and at the coigns, producing characteristic spherical triangles on octahedral faces. **(J)** Cross section of a complexly zoned diamond viewed in cathodoluminescence (color variations are vacancies or dislocations) and showing in exquisite detail episodes of repeated resorption and renewed slow growth over protracted periods of time in the mantle. **(K)** A purple Cr-pyrope garnet inclusion in diamond, characteristic of depleted P-type (peridotitic) paragenesis. **(L)** A green omphacitic (*12*) pyroxene typical of E-type eclogitic (*14*) paragenesis. **(M)** Unetched, sharp-edged octahedral microdiamonds typical of all KCRs with formation in the mantle shortly before eruption. **(N)** A modified octahedron of microdiamond enclosed in garnet, which is a substantial difference from cratonic diamonds and indicates the possible presence of $-C-H-$ bonds on diamond surfaces. **(O)** An example of porous, coke-like carbonado, the most enigmatic in origin of all diamonds, which is possibly related to meteorites (*78*, *79*). (J to L) Courtesy of H. O. A. Meyer. [(K) originally appeared in H. O. A. Meyer, in *Mantle Xenoliths*, P. H. Nixon, Ed. (Wiley, New York, 1987), pp. 501–522. Copyright John Wiley and Sons Limited. Reproduced with permission.]

The compositions of the stable isotopes of C (as a major element) and N (as a trace constituent) in diamond and of S in sulfide inclusions in diamond have been used in efforts to understand the source of C, N, and S in the mantle. The light isotopes (*27*) are preferentially concentrated in biotically driven processes, whereas there are only small (generally 1 to 2 per mil) isotopic fractionations at the high temperatures at which diamond is stable. Meteorites offer important clues to the abundances of primordial C, N, and S in Earth. The degree of isotopic heterogeneity of these elements, however, is uncertain (*28*), and the effects of mass-independent processes are unknown (*29*).

Carbon isotopes. The C isotopes of diamonds (Fig. 4A) show a prominent $\delta^{13}C$ peak at −4 to −7 per mil and vary from 0 per mil to −35 per mil (*30*). Most P- and E-type diamonds have $\delta^{13}C = -5$ to -8 per mil, but ~10% of E-type diamonds, and a few P-type diamonds, have lighter isotopic values that have been ascribed to biogenic C (*31*). The skewness of the C isotope distribution, however, may be due to redox effects in reactions that crystallize diamonds from mixtures of CH_4 and CO_2 (*32*). In addition, an important but poorly understood observation is that some diamonds become increasingly lighter in $\delta^{13}C$ with increasing depth, and these diamonds may reach values of up to −20 per mil at 450 km (*33*).

Biological C was likely restricted to prokaryotic bacteria and archaea lineages in the Archean and to primitive eukaryotic cells in the Neoproterozoic (*34*). The ratio of carbonate C (C_{carb}) to organic C (C_{org}) (but not always demonstrated to be of biological origin) on Earth's surface was ~80:20 in the Precambrian (*35*). The average $\delta^{13}C$ of C_{carb} is +2 per mil, and the average for C_{org} is −27 per mil, which by simple mixing yields a value of $\delta^{13}C = -3.8$ per mil, a value that is different from the ~10% of E-type diamonds in the range of −10 to −35 per mil (Fig. 4A). Present-day, but taxonomically primitive, cyanobacteria (modern and ancient stromatolites) and methanogenic bacteria yield gas compositions of $\delta^{13}C$ between −40 and −60 per mil (*36*). These gases alone cannot account for the eclogitic diamond $\delta^{13}C$ mean of −17 per mil, and if mixing with $C_{carb} + C_{org}$ is invoked, and taking −50 per mil as the mean gas composition, the result is a gas: solid ratio of 30:70, which seems unreasonably large for bacterial production at 2 Ga. Because KCRs are substantially younger than diamonds and because KCRs contain carbonate, they provide an opportunity to identify chemical and biogenetic carbonate in the mantle, possibly subducted since the Archean. Carbonates in KCRs, however, are in the mantle $\delta^{13}C$ range of −5 to −7 per mil (*37*); hence, marine C is most unlikely in E-type diamonds.

The most compelling evidence that the C in diamond is primordial is from the C isotopes in stony and iron meteorites that have a well-defined $\delta^{13}C$ mantle peak at −5 to −7 per mil, with other lesser maxima and a smaller number of light values decreasing to −31 per mil (Fig. 4B) (*38*). An unexplained relation in iron meteorites is that nodular C is isotopically lighter (−5 to −7 per mil) than coexisting C (−18 to −21 per mil) in the metal (*38*). In addition, composite analyses of presolar diamonds in primitive carbonaceous chondrites have a range of $\delta^{13}C$ between −32 and −38 per mil (Fig. 4B). Thus, the C isotopes are consistent with material that likely formed Earth.

Nitrogen isotopes. N isotopes in diamonds potentially provide additional data on diamond origins. One problem though is that the source regions for N in cratonic diamonds are uncertain in part because primary heterogeneity in the mantle is unknown and because of possible isotopic fractionation of N and C at high pressures. Another factor that may have substantial isotopic effects is the separation of C and N in marine sediments: C combines with H or O, whereas N is fixed in clays and subsequently in feldspar and mica as ammonia (HNO_3). The mantle value of $\delta^{15}N$ is −5 per mil, organic nitrogen in modern marine sediments is 2 to 12 per mil, and ammonia in subduction zone sediments is 0 to 7 per mil. Diamonds have a range from −25 to +15 per mil but form two general groups in which diamonds with heavy isotopic C have light N values and vice versa. The two groups are bridged by diamonds from select KCRs and by fibrous diamonds (*28*). This relation could argue for two populations of C in diamond, one mantle-derived and the other from recycling. There are, however, substantial and poorly understood differences in the isotopic behavior of C and N even in single crystals of diamond: C is typically isotopically homogenous, whereas N isotopes may show extreme variations from core to rim, and $\delta^{15}N$ values between octahedral and cube faces may differ by as much as 40 per mil. In addition, $\delta^{15}N$ values increase with decreasing N abundance (*39*). These patterns are compounded by the isotopic distribution of N in meteorites. For example, C1, C2, and ordinary chondrites are enriched in $\delta^{15}N$ (0 to 170 per mil), relative to C3 and enstatite chondrites (−10 to −40 per mil), indicating that there may also be substantial heterogeneities in primordial N in Earth (*40*).

Sulfur isotopes. S isotopes for sulfide inclusions (pyrite, pyrrhotite, and monosulfide solid solutions) in diamond are also interpreted as having either a primordial (*41*) or a subduction origin (*42*). In the recycled interpretation, the source of S may be from oce-

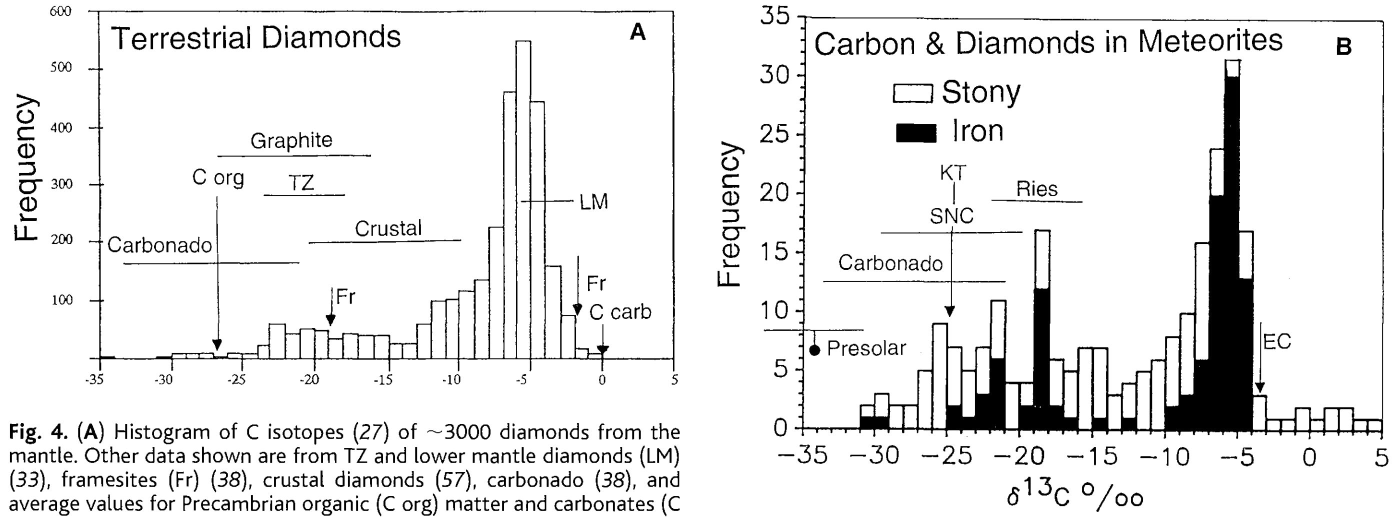

Fig. 4. (**A**) Histogram of C isotopes (*27*) of ~3000 diamonds from the mantle. Other data shown are from TZ and lower mantle diamonds (LM) (*33*), framesites (Fr) (*38*), crustal diamonds (*57*), carbonado (*38*), and average values for Precambrian organic (C org) matter and carbonates (C carb) (*35*). (**B**) Histogram of ~1200 measurements of C-bearing species in meteorites (*38*). Other data are for impact diamonds at Ries (*74*), the Cretaceous-Tertiary boundary (*75*), an enstatite chondrite (EC) (*89*), the presolar range (*89*), and carbonado (*38*). SNC, Martian meteorites (*38*).

anic basalt, from sulfides in marine hydrothermal vent systems, from S in sediments, or from sulfate reduction of seawater (*43*). $\delta^{34}S$ values in these sources are extreme and vary from light (−5 to −20 per mil) in biologically mediated S in shales to +21 per mil for seawater sulfate. Oceanic basaltic glasses have a $\delta^{34}S$ range of +0.5 to −0.1 per mil (which is close to the meteoritic value of 0 per mil), and hydrothermal vent systems range from 1 to 10 per mil. This spectrum represents a range in redox conditions. In magmatic systems, loss of H_2S leads to an increase in $\delta^{34}S$, and degassing of SO_4 results in a decrease in $\delta^{34}S$ values. Oxidation of sulfides in basalt results in relative depletion of ^{34}S in the residue and enrichment in the sulfate by-product. Seawater-altered oceanic crust may increase $\delta^{34}S$ by 3 to 5 per mil, but this increase is typically offset by $\delta^{34}S$ depletions, so that unless there has been a substantial influx of highly fractionated S, altered and unaltered ocean floor basalts differ very little in $\delta^{34}S$. From the relatively few S isotopic studies of mantle samples, the $\delta^{34}S$ range for most KCRs, xenoliths, and sulfide inclusions in diamond is −5 to +5 per mil, with a peak close to 0 per mil, equivalent to meteorites. $\delta^{34}S$ values for sulfides (−10 to +10 per mil) and sulfates (+10 to +30 per mil) in oceanic environments extending back to 1.6 Ga (*43*) have varied greatly, and it is likely, given the antiquity of diamond, that such variations existed in the Paleoproterozoic and Archean. Ocean floor smokers contain abundant Cu, Pb, and Zn sulfides and Ba, Ca, and Pb sulfates (*43*), but neither base metal sulfides nor sulfates have been reported as mineral inclusions in diamond, and metasedimentary host rocks are absent among KCR xenoliths.

Models for the Formation of Cratonic Diamond

Diamond is possibly nucleated in the mantle from supercritical primordial gases or fluids dissolved in melts. The abundance of water in the upper mantle is ~200 ppm and 550 to 1900 ppm in the lower mantle (*25*). The oxidation state of the asthenosphere approximates the reaction $3Fe_2SiO_4$ fayalite + O_2 = $2Fe_3O_4$ magnetite + $3SiO_2$ quartz (FMQ). Keels (*22*) and the TZ (*25*) are inferred to be one to two orders of magnitude more reduced than FMQ, which is consistent with the redox state of chromite mineral inclusions in diamond (*44*). The lower mantle, however, is plausibly more oxidized than FMQ (*25*). Thus, the stable phase of C in keels is graphite at low P and diamond at high P, whereas C in the lower mantle is predictably in magnesite ($MgCO_3$), CO_2, or CCO (*25*). There are two contrasting views on the effect of oxidation and diamond formation in keels. In the first, diamonds condense when oxidized fluids interact with reduced keels (*22*), and in the second, reduced gas species precipitate diamond by melting of oxidized subcontinental lithosphere (*45*). Both of these models are applicable to P-type diamonds, and both imply that C was introduced, possibly by lower mantle plumes, into developing keels or keels that were already in place. E-type diamonds are considered to have crystallized directly from a magma (*22*), intruded into or ponded at the base of keels (Fig. 2). In the magmatic model, oxidation states were low and S was present. Many E-type diamonds have fibrous diamond coats that grew rapidly and entrapped mineral and fluid inclusions (*24*, *46*). On the other hand, oscillatory zoning in many diamonds and the pervasive etching of diamond surfaces (Fig. 3, H and I) point to slow growth in a changing environment. Microdiamonds (millimeters in size) are ubiquitous in KCRs; the diamonds are unetched, unzoned, and typically high-T octahedra (Fig. 3M). These diamonds are thought to be condensates of young age related to KCR volcanism (*21*, *22*, *32*, *47*). Diamonds that seem to have been derived from Earth's TZ (410 to 660 km) (*18*) may have formed by similar mechanisms to those modeled for E-type diamonds, namely, crystallization from a melt. The upper part of the TZ at 410 km may be an important repository for diamond, given that diamond is less dense than mafic melts at 16 to 20 GPa (*48*). Although small in number, lower mantle diamond-inclusion assemblages are moderately enriched (*14*, *23*), and diamonds are most likely to have formed from the reduction of CCO or the dissociation or magnesite in plumes.

Models for Diamond-Bearing Intrusions

The increasing recognition that some xenoliths and mineral inclusions in diamonds from KCRs worldwide have an origin close to or in the TZ requires that magmas (*49*) transporting these samples must originate either in the TZ or in the lower mantle (660 to 2900 km).

Three models have been proposed. The first model is that thick cratonic crust and lithosphere insulate the mantle and heat builds up over time, in part through radioactive decay. The implied depth of KCR genesis is 200 to 250 km (*50*). The second is that mantle diapirs separate from subducted oceanic slabs on reaching the TZ (*51*). The third is that KCRs are related to plumes (*52*) that sample the lower and upper mantles and are synchronously intruded on a global scale (*19*). In the first model, it is likely that diamonds might be destroyed in the lithospheric keel over time, and it is unlikely to yield deep mantle melting, melt assimilation at a variety of mantle depths, or the transport of ultradeep xenoliths (including diamond) from the TZ and the lower mantle. In the second model, oceanic KCRs should form but are not found, and a convincing case has yet to be made for either KCR genesis in the TZ or a mechanism to forcefully inject KCRs by any process related to localized subduction. There is simply a lack of sustained thermal energy in the TZ to produce large clusters of KCRs. Moreover, the source of C in diamonds is incompatible with subduction. In the third model, noncontinental analogs of KCR intrusives may be ocean island basalts that lack the subcontinental contribution of metasomatism (*14*), and TZ and lower mantle diamonds are absent in these rocks because of high thermal gradients and high states of oxidation. The weight of evidence thus favors the involvement of mantle plumes from at least the lower mantle and possibly as deep as the core-mantle boundary layer (D″) at 2900 km (*19*, *53*).

Pumping pristine C from the lower mantle that is unfettered by recycled contaminants is intuitively more appealing in a global framework and over geological time scales than having the source of C be either fortuitously isolated or specifically located in keels. Plumes may transgress the entire vertical extent (2900 km) of the mantle (*54*), and the opportunity, therefore, to sequester substantial concentrations of incompatible elements, including C, is greatly enhanced by the enormous volume of material encountered along the conduit path.

Plumes have been correlated with long periods of persistent, unidirectional behavior (superchron) of Earth's geomagnetic field (*55*), and both are considered to be related to KCR intrusives (*19*). Seven major diamondiferous KCR eruptive events occurred between ~1 Ga and ~50 Ma, and five of these globally synchronous episodes correlate with superchron events of Earth's magnetic field (*19*). At 1 Ga, KCRs were intruded into the supercontinent of Rodinia (1200 to 750 Ma), and although the geomagnetic data are ill-defined for this event, this period is predicted to be a superchron. Theory holds that on disruption of D″, heat is released to the mantle and creates more vigorous convection in the liquid outer core; this results in instabilities and lower intensities of the geomagnetic field, with constant directions rather than high frequencies in reversal rates (*55*). The Tertiary, Cretaceous, Jurassic, and Permo-Triassic KCR events were preceded by, or are directly related to, large igneous provinces of voluminous (1 million to 40 million km^3) basalt that erupted over short periods of time (5 to 10 Ma) and are ascribed to extensive melting of the mantle by plumes (*56*). The mid-Cretaceous KCR episode is the most widespread and well documented of all diamondiferous intrusions. This global event is related to the breakup of the supercontinent Pangea: Rifting was initiated at ~200 Ma. This rifting was followed by the intrusion of flood basalts along major fracture zones between 180 and 130 Ma, and hundreds of diamondiferous KCRs erupted between 80 and 120 Ma (*19*).

Crustal Diamonds

Some diamonds are not in KCRs but are found in crustal rather than mantle rocks. Diamonds in metasedimentary rocks coexist with coesite (the high-*P* polymorph of quartz) and preserved high-*P* metamorphic assemblages that attest to subduction of crustal rock to depths of at least 120 km (*57*). Diamond host rocks vary from calc-silicate assemblages to amphibolites and pyroxenites. Although enclaves of eclogite of higher metamorphic grade than the diamond host rocks are intimately associated in these terranes, the eclogites typically do not contain diamond. Crustal diamonds have been identified in Kazakhstan (*58*), Norway (*59*), and China (*60*) (Fig. 5). Kazakhstan has the largest proven reserves, with an impressive 3 billion carats, whereas reports of diamonds in the other localities are restricted to a few stones.

Crustal diamonds are typically a few tens of micrometers across, and the largest find is 100 μm. Octahedra, cubes, and cubo-octahedral combinations are present, but most have an irregular morphology (Fig. 3N). Clear diamonds are prevalent with uncommon pale yellow and light green varieties. Most of the diamonds are enclosed in garnet and zircon, but some are in other minerals such as mica that grew under retrograde metamorphic conditions. Although the crustal host rocks were originally sediments, the stable isotopic composition of diamonds in Kazakhstan has a distinctly mantle signature of $\delta^{13}C = -5$ to -15 per mil (Fig. 4A); N concentrations are up to 4500 ppm, but N aggregation is low and the diamonds are Type Ib and IaB (*61*).

The crustal diamonds have not been dated, but the ages of the metamorphic host rocks are 520 to 530 Ma (Kazkhakstan), 400 to 500 Ma (Norway), and 210 to 230 Ma (China) (*57*, *62*). These mark periods of major continent-continent collisions that produced the Eurasian supercontinent (*63*). The metamorphic rocks formed when crust was subducted to depths of at least 120 km (*57*), to stabilize coesite, and ~160 to 180 km, depending on the continental geotherm, for the formation of diamond. After this deep burial, packages of rocks were subsequently exhumed. The exhumation of rocks may have been accomplished during the same tectonic event that initially led to subduction (*57*, *64*). The process is not clear, and the length of time is uncertain (*61*), but the low density (~2.6 g/cm^3) of some of the deeply buried crust, compared with the surrounding mantle (~3.5 g/cm^3), may have aided buoyancy and exhumation (Fig. 6).

There are major and as yet unresolved problems that allow for the preservation of diamond in these settings. Slow uncovering over millions of years and heating would promote the transition to graphite. Although some protection is provided by encapsulation in garnet and zircon, coexisting coesite in most of these rocks is either partially or completely transformed to quartz (*57*). Some of the crustal diamonds may have formed at pressures less than the true diamond stability field and structurally may not be purely covalent. Dangling C−O and COOH bonds (as in CVD diamonds) might account for the preferred inclusion of crustal diamonds in silicate minerals, rather than the other way around, which is typical of diamonds in KCRs. This is supported by spectroscopic data on diamonds from Norway that show prominent peaks for hydrogen and implied C−H bonds (*59*).

The problem of exhumation of large (>100 km by 180 km) continental terranes extends to Alpine-type peridotites, which are large tracts of mantle rocks, some of which contained diamond, that were also evidently emplaced into or onto crust during collisions. In Spain and Morocco, the paradox is somewhat eased because the C polymorph in peridotites is octahedral graphite ($\delta^{13}C = -16$ to -27 per mil) pseudomorphed after diamond (*65*). It is also eased in the most spectacular of modern continental collisions in the Hima-

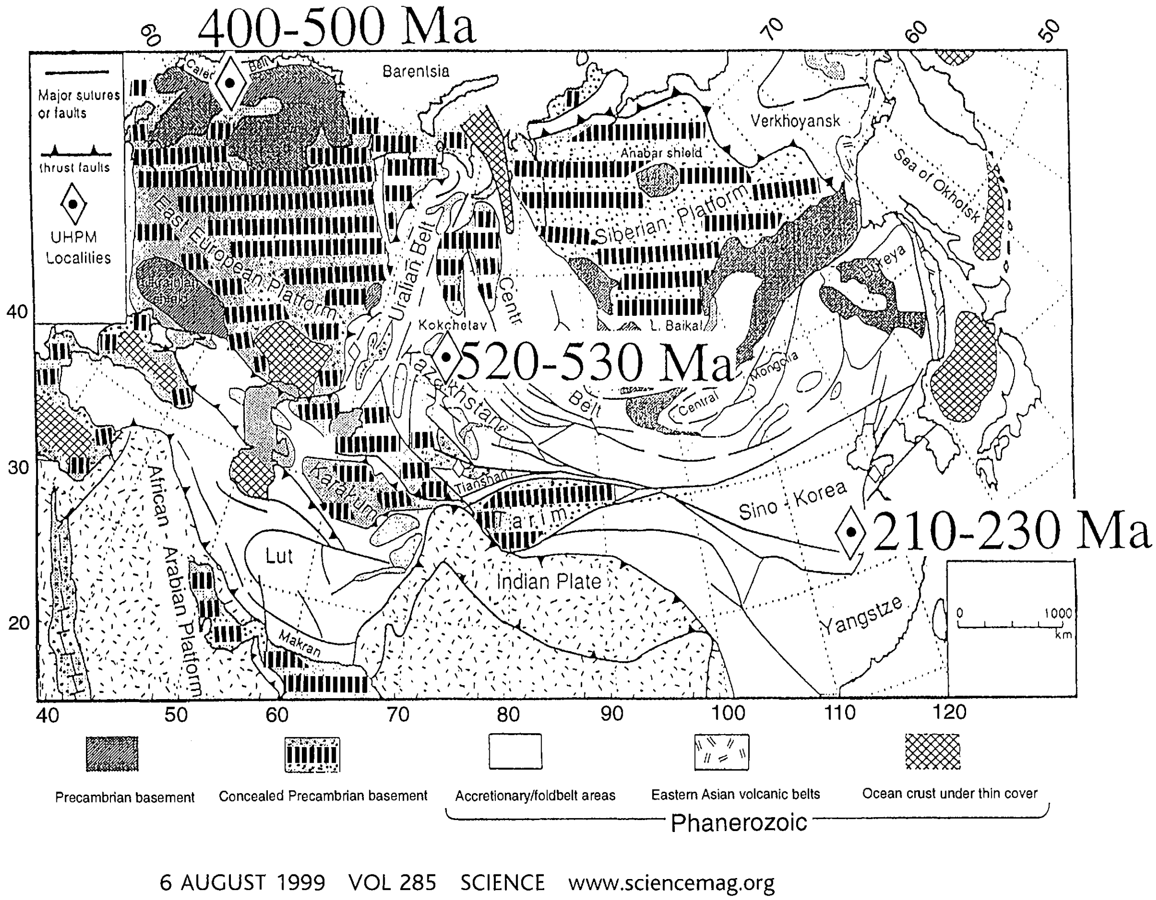

Fig. 5. The locations of diamonds in crustal protoliths and the ages of the protoliths in Norway, Kazakhstan, and China. These continental collisional zones were created during supercontinent assembly of the Eurasian Plate. [Modified from (*62*)]

layas because some microdiamonds reported earlier in Tibet (*66*) are now known to be synthetic contaminants (*67*).

Meteoritic Diamonds

Diamond was first reported in a meteorite in 1888 from two fireballs seen to land near Novo-Urei in Siberia (*68*). One piece of the meteorite (~8 kg) was sent to St. Petersburg for mineralogical study, where the presence of diamond was established; the other, a much smaller piece, was eaten by the farmers who recovered the stones! Other reports of diamond in meteorites surfaced in 1889 and 1890, but it was only much later that the Siberian meteorite was shown to be similar to other meteorites that typically contain graphite and, if severely shocked, to contain diamond in veins (*69*). Ureilites, as this class of stony meteorites is now known, are mafic achrondrites (lacking spherical chondrules) with major olivine and pyroxene, elemental C, and minor metals and sulfides (*70*). Intercrystalline textures are interpreted either as magmatic cumulates or residues from the partial melting of primitive asteroidal material. Diamond and lonsdaleite grains are unevenly distributed, irregularly shaped, and a few micrometers in size. Aggregate isotopic compositions are $\delta^{13}C = -2$ to -6 per mil. The origin of diamond and lonsdaleite is by shock-induced, meteorite impact metamorphism on the parent body (*70*). Diamond in an iron meteorite ($\delta^{13}C = -5$ to -6 per mil) recovered from Antarctica is possibly from ultradeep (core) shock wave penetration during asteroidal collision and parent body disruption (*71*).

Meteorite impacts on Earth have transformed carbon and graphite into diamond and lonsdaleite, and shocked quartz in sediments is locally converted to the high-*P* polymorphs coesite and stishovite. Microdiamonds in meteorite impact craters at Canyon Diablo, Arizona (*72*), and Popogai, Siberia (*73*), have carbon isotopic compositions of $\delta\ ^{13}C = -5$ to -7 per mil and -8 to -20 per mil, respectively, indicating that diamonds at both localities were likely formed from primordial carbon (Fig. 4B). At the Ries (Germany) meteorite impact crater, diamond, lonsdaleite, and SiC are in nanometer- to micrometer-sized crystals in rapidly cooled, glass-rich melt ejecta (*74*). The C-based mineral assemblage has an isotopic range of $\delta^{13}C = -16$ to -32 per mil (Fig. 4B). Mineral condensation and isotope fractionation are considered to have occurred in the plasma created on impact in a process similar to diamond synthesis by passive CVD (*2*, *75*). Strata at the Cretaceous-Tertiary boundary (65 Ma) have yielded nanodiamonds ($\delta^{13}C = -11$ to -19 per mil) at locations coincident with large iridium anomalies (*75*). Diamond, but also fullerene (*76*), and the iridium signature are ascribed to a large meteorite impact in the Gulf of Mexico (*77*).

Carbonado (Fig. 3O) is the most enigmatic of all diamonds. These coke-like objects lack mantle mineral inclusions and any affinity to KCRs (*78*, *79*). Carbonados are in 1.5-Ga metasedimentary rocks that are localized in Brazil (Bahia) and the Central African Republic (Bangui). The two locations lie on the West Congo–Salvador craton and are ~1500 km apart in a plate tectonic reconstruction of Gondwanaland. The sintered, polycrystalline microdiamond aggregates have a porous ceramic texture and a melt-like surface patina. Carbonados range up to 3167 carats, which is 61 carats heavier than Cullinan, the largest diamond from a KCR. Crystals in carbonado are 30 to 100 μm across; some are much finer, others reach a millimeter in size, and all are embedded in a strongly bonded matrix of microdiamond to nanodiamond. Some of the coarser diamonds have defect lamellae and dislocation tangles and mineral inclusions of Fe, Ti, Si, SiC, and Fe-Cr alloys (*80*). The microstructural textures are consistent with shock metamorphism, and the highly reduced metals and alloys preclude a mantle or crustal origin. In addition, $\delta^{13}C$ ranges from -21 to -34 per mil, and nitrogen concentrations are low with $\delta^{15}N = 2.3$ to 3.4 per mil. This places carbonado in a C-N field that is isotopically unlike crustal diamonds and diamonds from KCRs (Fig. 4B). Mantle and crustal origins and formation by radioactive ion implantation into coal deposits have been suggested [reviewed in (*79*)]. None of these suggestions are compatible with porosity, patina, mineral inclusions, and defect structures, and there was no coal in the Proterozoic. Carbonado has been posited as a product of a large meteorite impact into a terrestrial C target (*78*), and it has also been suggested to be a meteorite, possibly from a fragmented carbon-type asteroid (*79*).

Presolar Diamonds

The extreme isotopic anomalies in the rare gases (Ne, Ar, Kr, and Xe) of primitive carbonaceous chondrites have been recognized for some time, but the carriers remained elusive (*81*). Diamond, graphite, and moissanite (SiC) were finally identified as the host minerals to the exotic anomalies in 1987 (*82*). The result was startling and the implications staggering because it was concluded, on the basis of theoretical considerations and nucleosynthetic predictions (*83*, *84*), that these grains were presolar in origin. Some corundum (Al_2O_3), spinel ($MgAl_2O_4$), nierite (Si_3N_4), and other exotic carbides of Ti, Mo, W, and Zr in a few chondritic meteorites are also of presolar origin (*85*, *86*).

Presolar diamonds have now been isolated from ordinary, carbonaceous, and enstatite chondrites, and the proportion of C present as diamond is between 3 and 4% (*85*). The diamonds are small and average ~2 nm in size, but diamond is in extraordinarily high concentrations (120 to 1600 ppm) in some meteorites (*86*, *87*). Such diamond is more abundant than presolar SiC (~10 ppm), graphite (~2 ppm), and other minerals. Because of the extremely fine grain sizes, analytical measurements on chondritic nanodiamond, unlike graphite and SiC, can only be obtained on aggregates and not single crystals.

Three distinct noble gas components, designated as HL, P3, and P6, are identified in presolar diamonds (*86*, *88*). HL is the most distinctive and refers to anomalous enrichments of the two heavy (H) and the two light (L) isotopes of the nine isotopes of xenon. It is estimated, however, that about only one diamond in a million contains a Xe atom (*86*). N concentrations in presolar diamonds range from 2000 to 12,000 ppm (*89*). N abundances vary as a function of meteorite metamorphic grade and oxidation state, and N-rich diamonds are evidently more susceptible to modification (*89*). The $\delta^{15}N$ of $+340$ per mil differs from the estimate of $+80$ per mil for the early solar nebula (*88*), and both are substantially different from the solar value and Earth's air ($\delta^{15}N = 0$ per mil), in strong support of an exotic source for N in presolar diamonds. The $\delta^{13}C$ range of presolar diamonds (-32 to -38 per mil) is isotopically lighter than cratonic, crustal, or impact diamonds (Fig. 4B), but the average $^{12}C/^{13}C$ ratio of 93 is close to the solar ratio of 89 (*89*). Thus, N and C are evidently decoupled, but the isotopes have also been affected by other fractionating processes. For example, C and N, and the noble gas isotopes in the Efremovka meteorite, vary as a function of diamond grain size: The $^{12}C/^{13}C$ ratio

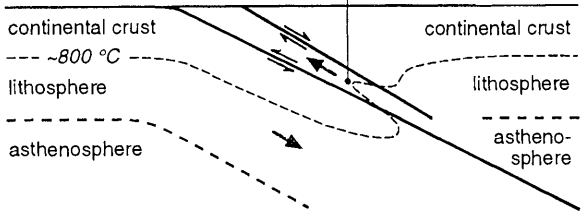

Fig. 6. A schematic model for the subduction of continental crust into the mantle and exhumation of ultrahigh pressure (UHP) metamorphic rocks by reverse buoyancy tectonics (*64*).

is greatest in the relatively coarse fraction, noble gas abundances decrease with decreasing grain size, and N is anomalous, with little variation (*90*).

There is a debate on whether the exotic noble gases formed with the diamond and were trapped, or if the gases were later implanted (*84–90*). It is generally agreed that the heavy Xe isotopes (mass number = 134 and 136) were produced by the nucleosynthetic "r-process" (neutron capture on a rapid scale) and that the lighter isotopes of Xe (mass number = 124 and 126) formed by the "p-process" of proton capture (*84*, *86*). Some data show that heavy Xe and enriched N are preferentially paired in presolar diamonds, and this may help resolve the C-N isotopic paradox (*91*).

The prevailing theory for the origin of presolar diamond is that it condenses by a CVD-like process in stellar atmospheres or in atmospheric outflows from red giant stars [with solar masses ($M_\odot$) = 8 to 12] in the evolutionary sequence of becoming type II supernovae (SN) (*92*) (Fig. 7). The process is appealing because laboratory conditions in which CVD diamonds are produced (*2*) are considered to be broadly similar to stellar atmospheres in H/C and C/O ratios and temperature (*86*). From spectroscopic data on presolar diamonds (*93*) and observations of dense molecular clouds (*94*), it is estimated that 10 to 20% of cosmic C is nanodiamond in the dense interstellar media (*94*). If C/O > 1, which is attained in the helium shell of massive stars (Fig. 7), diamond is expected to condense (*84*). The CVD model is consistent with hydrogen bonding on the surfaces of presolar diamonds (*95*, *96*) and with the prediction, from remote spectroscopy, that grain surfaces in C-rich circumstellar envelopes are saturated in $-\mathrm{C}-\mathrm{H}-$ (*97*). Thermonuclear reactions in SN take place at several million kelvin and are far in excess of temperatures of C condensation as diamond. Hence, diamond nucleation is governed by expansion and cooling of SN envelopes (*98*), which may only reach critical diamond condensation temperatures a year or so after an SN event (*99*). C availability may also increase by ionization and dissociation of inert CO into C and O (*100*).

Type I SN have also been suggested as sources of diamond and SiC (*101*). This model involves binary stars, one of which is a dense white dwarf that gravitationally accretes material from a companion, 1 to 8 $M_\odot$ C star (C/O > 2) and ultimately incinerates (Fig. 7). As C stars evolve along the Asymptotic Giant Branch (AGB), the C/O ratio increases by thermal pulsations (dredge-ups) from the burning of H and He and the creation of C in the 3α process (*102*). Sequential dredge-ups increase the ^{12}C/^{13}C and the C/O ratios, and this predictably enhances diamond nucleation near the end of the AGB C star evolutionary sequence. He burning, however, destroys N, which adds to the difficulty of a unified interpretation for the origin of presolar diamonds on the basis of N and C isotopes alone. The ^{12}C/^{13}C ratio of interstellar graphite has an extraordinarily broad spectrum of 5 to 5000 but with a prominent peak at 90; this value is similar to presolar diamonds and the solar system, and this has led to the suggestion that a ratio of around 90 may have been common in interstellar settings before 4.6 Ga (*103*). The ^{12}C/^{13}C ratio of presolar SiC is 38, which points to a different series of stellar processes. Stars in our galaxy have ^{12}C/^{13}C ratios that are either >65 or <65 (*101*).

A different model for presolar diamonds is grain-grain collision of graphite or amorphous C in the interstellar media (*104*). SN shock waves reach velocities (>600 km s^{-1}) well above the threshold of 6.8 km s^{-1} needed to form diamond. The process is predictably ineffective as only ~5% of the available C is likely to be transformed to diamond, and grain destruction is an inevitable consequence of intense shock environments (*104*). A comparative study of the microstructures of presolar nanodiamonds, with diamonds formed in experimental detonations and with diamonds condensed in the CVD process, implies that most are consistent with CVD in relatively "passive" circumstellar atmospheres, but some textures may reflect turbulent superwinds of explosive SN (*96*).

Presolar minerals in the assemblage of diamond, graphite, SiC, Si_3N_4, corundum, spinel, and other carbides are from multiple stellar sources that were assembled as solids into the early solar nebula. Although modified in the interstellar media and by metamorphic processes on asteroidal bodies, this "star dust" has retained a remarkably well preserved and informative but incomplete record to the astrophysics of our cosmic heritage (*105*). Early Earth must have been bathed in presolar diamonds, and this record may still exist in seeds that add to the glitter of cratonic macrodiamonds.

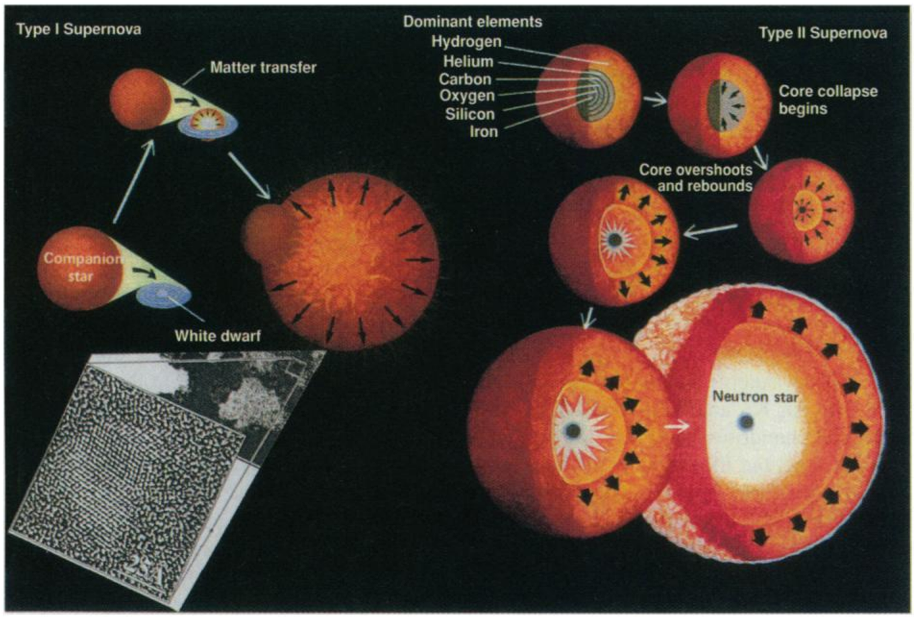

Fig. 7. A comparison of SN invoked for the formation of presolar diamonds. In the type I SN, the disruptive explosion results from the sequestering of matter from a companion star by a dense white dwarf. In a type II SN, a single star, usually a supergiant in the evolutionary sequence, undergoes a gradual and then a catastrophic collapse as core fuels in sequential layers are expended. On final implosion and rebounding, the outermost envelopes are blasted into the interstellar media. It is in these outermost expanding and cooling envelopes of type I and type II SN that nanodiamonds nucleate, perhaps a month or so after a SN event. This is shown schematically by the inset, which is an electron image of a presolar diamond from the Murchison meteorite (96). [Adapted by courtesy of Encyclopaedia Brittanica, Inc. Copyright Encyclopaedia Brittanica Yearbook of Science and the Future 1989.]

References and Notes

1. The C/H ratio in the solar system is 237 × 10^{-6} and in the interstellar media is (225 ± 50) × 10^{-6}. It is estimated that 215 C atoms per 10^6 H atoms are available for C dust formation in the solar system and 85 C atoms per 10^6 H atoms in the interstellar media. [T. Henning and F. Salama, *Science* **282**, 2204 (1999)].
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5. Carat is derived from *qirat* (Arabic), the carob bean, which has been used since antiquity and recognized as a remarkably constant measure of weight.
6. J. B. Dawson, *Kimberlites and Their Xenoliths* (Springer-Verlag, Heidelberg, 1980).
7. Kimberlites are fully discussed in (*6*) and by R. H. Mitchell [*Kimberlites: Mineralogy, Geochemistry, and Petrology* (Plenum, New York, 1986)]. Lamproites are reviewed by R. H. Mitchell and S. C. Bergman [*Petrology of Lamproites* (Plenum, New York, 1991)] and N. M. S. Rock [*Lamprophyres* (Blackie, Glasgow, Scotland, 1991)]. The nomenclature of kimberlites, lamproites, and closely related alkali rocks was discussed over a period of 6 years by a subcommission of the International Union of Geological Sciences. Among the final recommendations [A. R. Woolley *et al.*, *Can. Mineral.* **34**, 175 (1996)] were the following statements: "It must be stressed that the hierarchical system presented here is not definitive and has minimal genetic content. Any classification of a rock as a lamprophyre, kimberlite, or lamproite using this system should be considered provisional . . ." (p. 176). Hence, KCRs, as justified by J. B. Dawson [in *Alkaline Igneous Rocks*, J. G. Fitton and B. G. J. Upton, Eds. (Blackwell Scientific, London, 1987), pp. 95–101], is adopted here. The taxonomy of KCRs, with 50 to 90% olivine and variable contents of mica, amphibole, calcite, mineral oxides, and diamond (*14*), will continue to evolve but is unlikely to affect the conclusions of this review.
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14. Geochemical depletion refers to the melt extraction of basaltic (basalt is pyroxene plus feldspar, with or without olivine) components (Si, Fe, and Ca) from geochemically fertile mantle lherzolite (garnet or spinel plus olivine and Ca- and Mg-pyroxene). The residue that remains in the mantle has low Si and high Mg/Fe ratios; the rocks are dunite (largely olivine) and harzburgite (olivine and Mg-pyroxene). Melt extraction in early Earth also included olivine- and pyroxene-rich komatiite (volcanic peridotites). Basaltic compositions that are trapped in the mantle crystallize garnet and Ca-Na pyroxene (omphacite), and this bimineralic rock is known as eclogite; subducted ocean floor basalts are transformed to amplibolite and at higher pressures to eclogite. Another important rock in the mantle is metasomite; these rocks have enriched chemistries in large-ion lithophile (typical of the crust) elements (K, Na, Sr, and Ba) and in high–field-strength elements (Ti, Zr, Nb, and P) and unusual mineralogies of ferriphlogopite (mica), K-richterite (amphibole), and exotic alkali titanites in substrates of previously depleted harzburgite [M. A. Menzies and C. G. Hawkesworth, Eds., *Mantle Metasomatism* (Academic Press, London, 1987)]. Metasomites are considered essential to the bulk chemistries of KCRs, and the melting and assimilation of two mantle horizons, shown in Fig. 2, by rising proto-KCR melts from the asthenosphere and the lower mantle have been proposed [S. E. Haggerty, in *Carbonatites: Genesis and Evolution*, K. Bell, Ed. (Unwin Hyman, London, 1989), pp. 546–560; P. J. Wyllie, *Geol. Soc. Austr. Spec. Publ.* **14**, 603 (1989)]. Because of the hybrid nature of KCRs, experimental studies have contributed little to the identification of primary melts [S. F. Foley, *Proc. Indian Acad. Sci. Earth Planet. Sci. Sect.* **99**, 57 (1990)].
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19. KCR intrusives are dated at $\sim$1 Ga (Africa, Brazil, Australia, Siberia, India, and Greenland), $\sim$450 to 500 Ma (Archangel on the White Sea, China, Canada, South Africa, and Zimbabwe), 370 and 410 Ma (Siberia and United States), $\sim$200 Ma (Botswana, Canada, Swaziland, and Tanzania), 80 to 120 Ma (south, central, and west Africa, Brazil, Canada, India, Siberia, and United States), and $\sim$50 Ma (Canada and Tanzania), with minor fields in Ellendale in northwest Australia at 22 Ma [S. E. Haggerty, *Earth Planet. Sci. Lett.* **122**, 57 (1994)].
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23. The most widespread mineral inclusion in diamond from the TZ is majoritic garnet [R. O. Moore and J. J. Gurney, *ibid.* **318**, 553 (1985)]. Majorite is the high-*P* ($>$8 GPa) polymorph of pyroxene, and because majorite has the garnet structure, it forms a solid solution with discrete garnet. Majoritic garnet is recognized by having $>$3 Si atoms per 12 O atoms, and the excess Si, beyond that accomodated in the low-*P* garnet structure, is in octahedral rather than tetrahedral coordination. Octahedrally coordinated Si is favored at high pressures [L. W. Finger and R. M. Hazen, *Acta Crystallogr. Sect. B* **47**, 561 (1991)]. Unmixed majoritic garnet (garnet with crystallographically controlled lamellae of pyroxene) is present in mantle xenoliths and is indicative of depths of origin $>$300 km but with equilibration at lower (2 to 3 GPa) pressures [S. E. Haggerty and V. Sautter, *Science* **248**, 993 (1990); V. Sautter, S. E. Haggerty, S. Field, *ibid.* **252**, 827 (1991)]. Another TZ mineral inclusion in diamond is a garnet-structured Na pyroxene–Mg pyroxene solid solution that is stabilized at a minimum of 16.5 GPa ($\sim$475 km) [W. Wang and S. Sueno, *Mineral. J.* **18**, 9 (1997)]. The lower mantle mineral assemblage in diamond is ferropericlase (Fe,Mg)O plus $MgSiO_3$ [see review by S. E. Haggerty, *J. Geodyn.* **20**, 331 (1995)], which is shown experimentally to result from the breakdown of ringwoodite (high-*P* pressure olivine; Fig. 2), that is, $(Mg,Fe)_2\,SiO_4 = MgSiO_3 + (Fe,Mg)O$ [C. B. Agee, *Annu Rev. Earth Planet. Sci.* **21**, 19 (1993)]. The mineral $CaSiO_3$ is also recorded as an inclusion in diamond [B. Harte and J. W. Harris, *Mineral. Mag.* **58A**, 384 (1994)], and this phase and $(Mg,Fe)SiO_3$ are predicted to have the dense high-*P* cubic or pseudocubic structure of perovskite ($CaTiO_3$). This structure has not been confirmed, and it may require in situ verification because of structural inversion once the inclusion is broken out of the diamond for analysis. Green tetragonal garnet is a new mineral and is also of lower mantle origin [J. W. Harris *et al.*, *Nature* **387**, 486 (1997)].
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$$\delta^{H}E = \left[\frac{{}^{H}E_{samp}/{}^{L}E_{samp}}{{}^{H}E_{std}/{}^{L}E_{std}} - 1 \right] \times 1000$$

    where samp is sample and std is standard. These equations were developed to reduce the ratios to small numbers and are expressed as per mil. The astrophysical convention uses either simple ratios of ${}^{L}E/{}^{H}E$ or the δ notation.
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