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Diamonds and the Geology of Mantle Carbon

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INTRODUCTION TO DIAMOND CHARACTERISTICS

Introduction

Earth's carbon, derived from planetesimals in the 1 AU region during accretion of the Solar System, still retains similarities to carbon found in meteorites (Marty et al. 2013) even after 4.57 billion years of geological processing. The range in isotopic composition of carbon on Earth versus meteorites is nearly identical and, for both, diamond is a common, if volumetrically minor, carbon mineral (Haggerty 1999). Diamond is one of the three native carbon minerals on Earth (the other two being graphite and lonsdaleite). It can crystallize throughout the mantle below about 150 km and can occur metastably in the crust. Diamond is a rare mineral, occurring at the part-per-billion level even within the most diamondiferous volcanic host rock although some

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rare eclogites have been known to contain 10-15% diamond. As a trace mineral it is unevenly distributed and, except for occurrences in metamorphosed crustal rocks, it is a xenocrystic phase within the series of volcanic rocks (kimberlites, lamproites, ultramafic lamprohyres), which bring it to the surface and host it. The occurrence of diamond on Earth's surface results from its unique resistance to alteration/dissolution and the sometimes accidental circumstances of its sampling by the volcanic host rock. Diamonds are usually the chief minerals left from their depth of formation, because intact diamondiferous mantle xenoliths are rare.

Diamond has been intensively studied over the last 40 years to provide extraordinary information on our planet's interior. For example, from the study of its inclusions, diamond is recognized as the only material sampling the "very deep" mantle to depths exceeding 800 km (Harte et al. 1999; McCammon 2001; Stachel and Harris 2009; Harte 2010) although most crystals (~95%) derive from shallower depths (150 to 250 km). Diamonds are less useful in determining carbon fluxes on Earth because they provide only a small, highly variably distributed sample that is usually not directly related to the host magma. One major achievement in our understanding of diamond formation both in Earth's mantle and metamorphic rocks is the increasing evidence for its formation from a mobile C-bearing phase, commonly referred to as "C-O-H-bearing fluid or melt". *These free fluids give diamond the remarkable ability to track carbon mobility in the deep mantle, as well as mantle mineralogy and mantle redox state and hence a unique ability to follow the path and history of the carbon from which diamond is composed. Thus, diamond truly occupies a unique position in any discussion of the igneous and metamorphic aspects of Earth's carbon cycle.* Beyond simply providing deep samples, diamond studies have revealed active geodynamics. These studies have pinpointed the initiation of subduction (Shirey and Richardson 2011), tracked the transfer of material through the mantle transition zone (Stachel et al. 2005; Walter et al. 2011), recorded the timing of ingress of fluids to the continental lithosphere (Richardson et al. 1984; Pearson et al. 1998; Shirey et al. 2004b), preserved carbonatitic fluids that trigger deep mantle melting (Schrauder and Navon 1994; Walter et al. 2008; Klein-BenDavid et al. 2009; Klein-BenDavid et al. 2010; Kopylova et al. 2010), captured the redox state of the mantle (McCammon et al. 2004; Stagno and Frost 2010; Rohrbach and Schmidt 2011), and provided samples of primordial noble gases (Wada and Matsuda 1998; Ozima and Igarashi 2000).

The present chapter does not attempt to review all aspects of diamond studies—for this an entire volume of *Reviews in Mineralogy and Geochemistry* would be required. For summaries on the various aspects of diamond mineralogy, geochemistry, and formation, the reader is referred to works by Harris and coworkers (1968, 1979, 1992), Sobolev and others (1977, 1990), Deines (1980), Gurney and others (2010), Pearson and coworkers (1999, 2003), Stachel et al. (2005), Cartigny (2005), Spetsius and Taylor (2008), Stachel and Harris (2008), Harte (2010), and Tappert and Tappert (2011). *Rather, this chapter will review the key observations and the current state of research on naturally occurring diamonds using modern methods of analysis as they apply to diamond formation, the source of carbon-bearing species in the mantle, the role of carbon during mantle melting, and the geologic history of the mantle with emphasis on the main difficulties to be unlocked in future studies.*

Types of diamond. For a cubic mineral of simple composition, diamond displays a remarkable range of properties. Diamond also displays a variety of shapes reflecting growth under variable conditions of supersaturation and resorption. These characteristics have been covered in recent popular books and articles on diamond (e.g., Harlow 1998; Harlow and Davies 2005; Spetsius and Taylor 2008; Tappert and Tappert 2011). For the geological purposes of tracing the history of C-bearing fluids it is important to consider the three main forms in which diamond occurs: polycrystalline, monocrystalline, and coated (Fig. 1). Polycrystalline diamond includes many subtypes of mantle-derived diamonds (e.g., framesite, bort, ballas), some of unknown origin (e.g., carbonado), and some impact diamonds (e.g., yakutite). Most

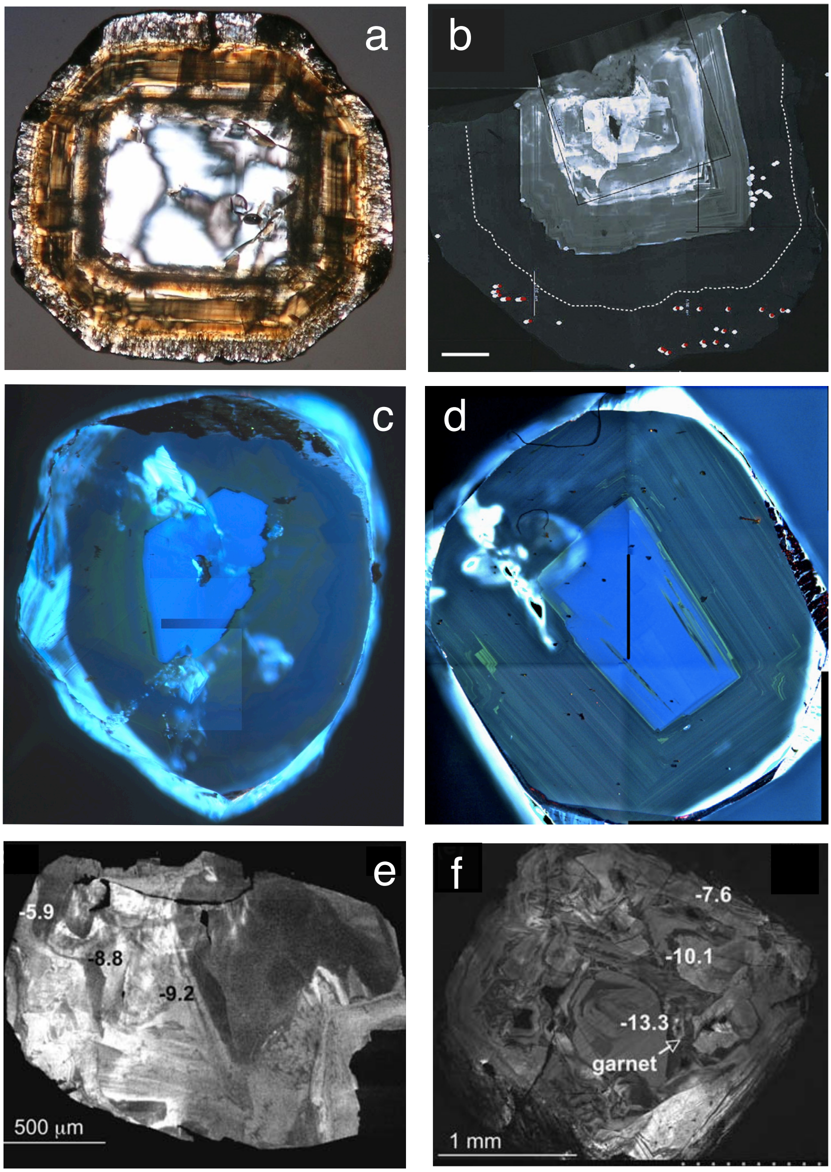

Figure 1. These diamond plates show the textural differences that can occur between coated diamonds (a,b) monocrystalline lithospheric diamonds (c,d), and monocrystalline sub-lithospheric diamonds (e,f). Coated diamond in (a) is an optical photomicrograph, plane light courtesy Ofra Klein-Bendavid. Diameter of diamond is 1 cm. Coated diamond (b) from the Congo (alluvial) is a catholuminescence (CL) image (Used by permission of Elsevier Limited, from Kopylova et al. (2010) *Earth and Planetary Science Letters*, Vol. 291, Fig. 1, p. 128). Dots indicate positions of analyzed inclusions, scale bar is 0.6 mm. Diamonds in (c) and (d) are from Orapa, Botswana. They are both about 6 mm across. The color CL images show multiple growth histories with significant resorption in (c) after a first stage of growth. Note the very thin growth rings in (d). Diamonds (e) and (f) are gray-scale CL images of sub-lithospheric diamonds from the Collier 4 kimberlite pipe, Juina field, Brazil (Used by permission of Springer, from Bulanova et al. (2010) *Contributions to Mineralogy and Petrology*, Vol. 160, Figs. 3d,e, p. 493). Diamond in (e) is about 3 mm on the long axis. Note the irregular zoning in both diamonds.

studied mantle-derived polycrystalline diamonds fall into two main categories: 1) framboids of diamond crystals sintered together without silicates (bort); and 2) diamondite, fine to medium-grained rocks composed of subequal amounts of silicate minerals (typically garnet and pyroxene but lacking olivine) and diamond. Monocrystalline diamond is micro (<0.5 mm) to macro (>0.5 mm) single-crystal diamond from which gem diamonds are cut and polished. Often these monocrystals display a complicated internal growth history with episodes of resorption and regrowth (Fig. 1) as well as simple composite forms (e.g., twin forms such as macles and intergrowths). Monocrystalline diamonds have been an important source of inclusions for study and the ages of these diamonds have been determined via geochronology on their inclusions as Proterozoic to Archean. Coated diamonds are a special case of of mixed polycrystalline-monocrystalline diamond, where monocrystals have been overgrown by a thick, cloudy, polycrystalline coat laden with microinclusions of fluid. If the coat is composed of rods or blades of diamond (Fig. 1) it will exhibit a fibrous structure and be termed a fibrous diamond. These coats are believed to grow during transport in the kimberlite and thus represent young, new diamond growth surrounding often ancient diamond (e.g., Boyd et al. 1994). More research to date has been on monocrystals because they are more available for study, are less complicated morphologically, and are the most robust hosts for mineral inclusions.

Diamond parental and host rocks. Diamonds are chiefly carried to Earth's surface in only three rare types of magmas: kimberlite, lamproite, and lamprophyre (e.g., Gurney et al. 2010). Of the three types, kimberlites are by far the most important, with several thousand known, of which some 30% are diamondiferous. A similar percentage of the several hundred known lamproites is diamondiferous and diamonds are occasionally recorded from ultramafic lamprophyres. Lamproites are next in importance to kimberlites because they host the world's largest diamond mine, Argyle (Australia), and notable diamond occurrences in the United States and India. Lamprophyres currently are only of petrological interest as hosting the oldest known diamonds, which occur in Wawa, Ontario. In general, these magma types are derived by small amounts of melting deep within the mantle, are relatively volatile (H_2O, CO_2, F, or Cl) and MgO-rich, erupt rapidly, and are not oxidizing. In nearly all cases of magmatically-hosted diamonds, Archean to Proterozoic diamonds are carried by Phanerozoic to younger (Cretaceous/Tertiary) kimberlitic volcanic rocks (Pearson and Shirey 1999; Gurney et al. 2010). The composition of kimberlitic magmas can vary widely depending on the relative proportions disaggregated mantle xenoliths, phenocryst phases such as olivine, assimilated country rock, the ratio of H_2O to CO_2 in the volatile phase, and the extent of interaction with metasomatic minerals in the subcontinental lithospheric mantle. Of great importance for diamond petrogenesis the distinction between Group I (GI) and Group II (GII) kimberlites as diamond carriers. Generally, GI kimberlites contain normal (i.e., non-metasomatic) mantle minerals and initial isotopic compositions for Sr, Nd, Hf, and Pb that are indicative of equilibration chiefly with the convecting mantle, whereas GII kimberlites contain micaceous and metasomatic minerals and extreme isotopic compositions for Sr, Nd, Hf, and Pb that are indicative of equilibration with the metasomatized subcontinental lithospheric mantle (e.g., Smith 1983).

Within the mantle, eclogite and peridotite are the main parental rocks of diamonds, as the loose monocrystalline diamonds seen in kimberlite are considered to have been released from eclogitic or peridotitic hosts by alteration and mechanical disaggregation during sampling by the kimberlitic magma in the lithosphere or early transport by the kimberlite (Kirkley et al. 1991; Harlow 1998). Both diamondiferous and diamond-free eclogites often survive transport by kimberlite, whereas diamondiferous peridotite is exceptionally rare and nearly all peridotite xenoliths are diamond-free. The physical distribution of diamond in eclogite has been studied recently by CAT-scan techniques, which have revealed that diamonds are often found in between the major silicate phases in their host eclogite and often along pathways where metasomatic fluids traveled (Keller et al. 1999; Anand et al. 2004). Presumably diamond in peridotite has a similar textural relationship to its major silicates; however, the ready reaction of CO_2-rich diamond-forming fluids with abundant magnesian silicates to form friable magnesite ($MgCO_3$) along silicate grain boundaries promotes disaggregation of the xenoliths and release of the diamonds, thus destroying the textural relationship with their host.

In the crust, diamonds are found directly within their host lithologies, which have been exhumed by the orogenic process of continental collision (Ogasawara 2005; Dobrzhinetskaya 2012; Schertl and Sobolev 2012). These occurrences are typically in carbonate-bearing rocks, and/or those that have been subjected to the flow of water/carbonate-bearing metamorphic fluids as can be seen by infrared spectroscopy showing fluid inclusions with carbonates, silicates, hydroxyl groups, and water (e.g., de Corte et al. 1998). In the Kokchetav massif, northern Kazakhstan, for example (Sobolev and Shatsky 1990; Claoue-Long et al. 1991), these hosts include garnet-biotite gneisses and schists, which make up 85 vol% of the rocks with the remainder being dolomite, Mg-calcite, garnet, and clinopyroxene in different proportions. Other high-pressure terranes contain diamond as multiphase inclusions coexisting with minerals such as garnet, K-clinopyroxene, magnesite, high-Si phengite, and coesite. In many cases, these inclusions appear to be shielded from retrogression by garnet, zircon, or kyanite, showing the significance of the host minerals as containers of UHP mineral inclusions and their significance in the search for further diamondiferous metamorphic rocks. In the Erzebirge terrane, Germany, diamond occurs within all three host minerals in a muscovite-quartz-feldspar rock (Massonne 2003). In the Western Gneiss terrane, Norway, diamond is enclosed exclusively with spinel in garnet that occurs within garnet-websterite pods (Dobrzhinetskaya et al. 1995; van Roermund et al. 2002), whereas in the Dabie Shan and North Quaidem areas, China, diamond occurs with coesite and jadeite within garnet or zircon in eclogite, garnet pyroxenite, and jadeite (Shutong et al. 1992; Song et al. 2005).

Diamond formation also occurs during the high pressures and temperatures produced when an extraterrestrial body impacts Earth's surface (impact diamonds). Given the short time scales, diamond formation occurs within either C-rich targets (graphite to diamond solid-state transition) or impact melts (Hough et al. 1995; Koeberl et al. 1997). Impact diamonds can reach up to 1 cm size in the well-studied Popigai impact crater (Koeberl et al. 1997) but diamonds are typically much smaller (submicron to millimeter in size). Lonsdaleite, the hexagonal-form of *sp*3-bonded carbon (Hazen et al. 2013), is characteristic of impact diamonds. Although somewhat rare in nature, impact diamond and lonsdaleite could actually be spread over Earth's entire surface, as illustrated by their occurrence at the K/T boundary layer. Impact diamonds are comparatively little studied and have been mostly used to identify the occurrence of large impacts (Hough et al. 1997).

Diamond distribution in Earth. At depths below about 150-200 km along both continental and oceanic geothermal gradients, the entire Earth, including the base of the continental lithosphere and the convecting mantle beneath the lithosphere-asthenosphere boundary, is in the diamond stability field (e.g., Stachel et al. 2005; Fig. 2). Locally, given the typically low solubility of C in mantle silicate and oxides, there is the potential to crystallize diamond within a large volume of Earth's mantle in the presence of a free C-bearing phase such as methane or carbonate. But under the conditions of typical plume-related magmatism and relatively slow transport to the surface, diamonds will re-equilibrate, either graphitize or more likely oxidize. With few exceptions diamonds are erupted only by kimberlite and lamproite magma and such volcanism is rare. Thus, the true amount of diamond crystallizing at depth in Earth below the lithosphere is not known but could be much larger than what has erupted with kimberlite. When these diamonds are exhumed from below the continental lithosphere, they are referred to as *superdeep* or *sub-lithospheric* diamonds, whereas if they are derived from within the continental lithosphere they are referred to as lithospheric (Fig. 2). Crustal diamonds that occur in high-pressure metamorphic terranes are known as "ultra-high-pressure metamorphic" or UHPM diamonds for the amazingly high pressures that they signify for crustal conditions. Note

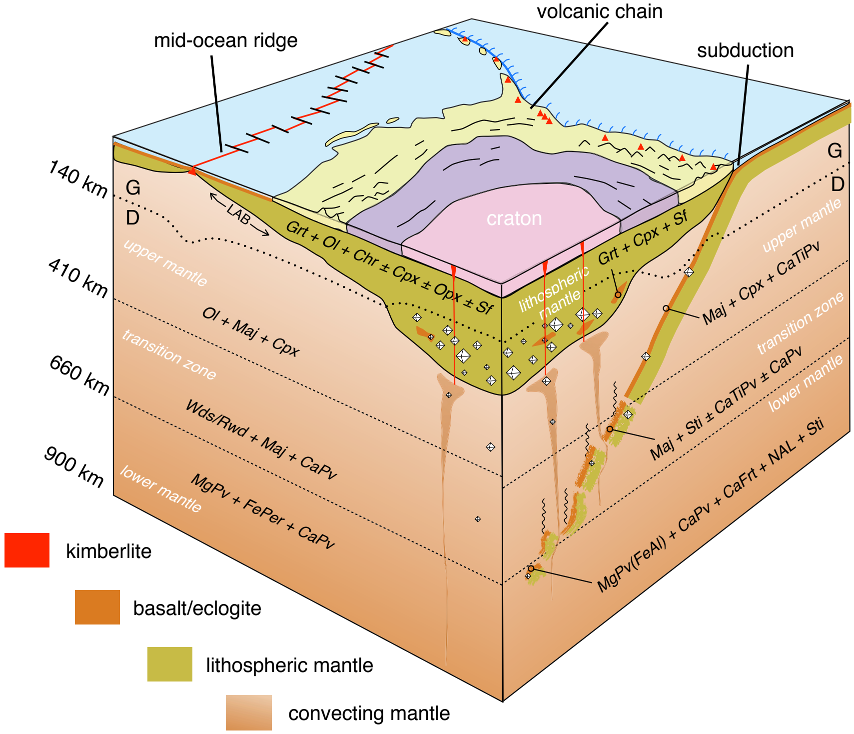

Figure 2. Block diagram showing the basic relationship between a continental craton, its lithospheric mantle keel and diamond stable regions in the keel, and the convecting mantle. Under the right f_{O_2}, diamonds can form in the convecting mantle, the subducting slab, and the mantle keel. Figure redrawn from an original by Tappert and Tappert (2011) with additions. G=graphite, D=diamond, LAB=lithosphere/asthenosphere boundary. Mineral assemblage information and abbreviations defined in Tables 1 and 2. These assemblages give the expected inclusions to be found in peridotitic or ultramafic (left) and eclogitic or basaltic (right) rock compositions.

that all mantle diamonds form at higher pressures than UHPM diamonds. The point here is that diamond is a good tracer mineral for carbon throughout the mantle and crust.

Geologic setting for diamond formation. At Earth's surface, macro-diamonds are highly unevenly distributed, being found primarily within erupted kimberlite with a direct association to stable Archean continental nuclei (e.g., Harlow and Davies 2005; Fig. 3). Beneath the seismically stable, old, interior portions of cratons, the lithospheric mantle extends from about 40 km depth down to perhaps 250-300 km, whereas under the oceans it is thinner and extends from about 40 km to only about 110 km (e.g., Jordan 1975, 1978; Ritsema et al. 2004). Because of the downward protruding shape and the long-term attachment of this mantle to the continental crust of the craton, this portion of mantle has taken the term "mantle keel" (Fig. 2). Archean lithospheric keels are more melt-depleted and deeper than Proterozoic and younger continental mantle keels and their lowermost reaches are squarely in the diamond stability field (e.g., Haggerty 1999; Fig. 2). They are the most diamond-friendly regions of Earth and their depth is thought to facilitate the production of kimberlitic magma by deepening the onset of melting of carbonated mantle. This connection produces an amazingly strong association between diamondiferous kimberlite and the oldest interior portions of continental nuclei having the most melt-depleted mantle keels—a relationship known as "Clifford's Rule" (e.g., Kennedy

1964; Clifford 1966). This association is so strong that it has proved to be the most essential consideration in diamond exploration; its corollary is the complete absence of macrocrystalline diamonds in the oceanic mantle.

Diamonds found in kimberlite provide a recent snapshot of their occurrence at depth in the mantle because most kimberlites are relatively young. Nonetheless, since the diamonds are ancient (e.g., billions of years older than the kimberlite) their compositions can record the active geological processes that initially placed the diamondiferous fluids into the lithosphere. *Thus diamonds alone can provide a record of the carbon cycle older than the oldest oceanic lithosphere (e.g., >200 Ma), especially in the Archean and Proterozic, when major changes in Earth's geodynamics, crustal growth, and atmospheric chemistry occurred.* The oldest diamonds yet dated are thought to be intimately associated with initial production of the depleted mantle keel itself either in the plume upwelling and attendant melting that is responsible for the extensive depletion (e.g., Aulbach et al. 2009b), or in some closely-associated recycling (e.g., Westerlund et al. 2006) and advective thickening (e.g., Jordan 1975, 1978). They potentially track some of the oldest carbon-bearing fluids released by Earth. Once formed, the keel is not just a passive player in diamond genesis. During continental collision the keel can capture eclogite (e.g., Shirey and Richardson 2011) and trap fluids emanating from any underthrusted oceanic lithosphere (e.g., Aulbach et al. 2009b). During the supercontinent cycle, orogenesis around ancient continental nuclei may permit marginal subduction to repeatedly add diamond-forming fluids generated from tectonic processes near the edges of cratonic blocks (e.g., Richardson et al. 2004; Aulbach et al. 2009a) or orogenesis may even rework the lithosphere beneath mobile belts, in some cases recycling the extant carbon that is part of much older mantle lithosphere (e.g., Smit et al. 2010). Diamonds formed in association with continental tectonism record geologic processes from the deepest portions of the continents and can be a key to understanding the stabilization of the continents. Persistent, sub-lithospheric magmatism can also be a source of heat and fluids to add diamonds to the interior of cratons from below. The continental keels provide the only evidence for the source, timing, and geological causes of such ancient deep carbon.

Crustal diamonds from ultra-high-pressure (UHP) metamorphic terranes record the fate of carbon trapped at much shallower levels in the lithosphere. Diamonds found in these crustal settings are often cubic and microcrystalline and occur with metamorphic mineral assemblages that can be used to trace the diamond-forming reactions. Here we have the converse of Clifford's Rule in that these diamonds are chiefly forming in Paleozoic to Cenozoic orogenic belts, where extreme conditions of continental tectonic instability have allowed the crustal section to be buried to the diamond stability field and later exhumed (e.g., Ogasawara 2005; Dobrzhinetskaya 2012; Fig. 3). Although the study of Sumino et al. (2011) highlighted the occurrence of some mantle-derived rare gases, there is no doubt that, for the vast majority of UHP diamonds, the carbon reservoir is crustal, apparently isolated from mantle carbon. The crustal source of carbon is evident from the association of the diamonds with metasedimentary protoliths, the unusual chemical composition of their fluids (e.g., Hwang et al. 2005, 2006), and their high-N content (up to 1 wt%) or heavy $\delta^{15}N$ (Cartigny 2005, 2010) that are not found among mantle-derived diamonds.

Microscale components in diamonds

The advent of microanalytical techniques, such as secondary ion mass spectrometry (SIMS), laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS), focused ion beam (FIB) lift out, high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and high-intensity light sources (synchrotron), have revolutionized the ability to look at the diamond itself even beyond the way that the electron microprobe (EPMA) revolutionized mineral analysis in the 1960's. Not only can ever smaller inclusions be found and imaged, but their chemical and isotopic compositions can be determined in some instances.

Elemental substitution. The substitution of elements into the diamond structure has long been an area of study because of its effect on the gem qualities, and hence value, of natural diamond and its effect on the physio-chemical properties of diamond. The first quantitative measurements of trace elements in diamonds were published by Fesq et al (1975). More than 60% of elements in the periodic table can be found in diamond but chiefly it is only nitrogen, boron, hydrogen, silicon, and nickel that substitute into the diamond structure (e.g., Field 1992; Gaillou et al. 2012) in routinely measurable quantities. Nitrogen is the main substitutional diamond impurity (Kaiser and Bond 1959) and, for historical reasons (Robertson et al. 1934), it forms the basis of diamond classification into so-called Type I (nitrogen-bearing) and Type II (nitrogen so low as to be thought of as essentially nitrogen-free) diamond. With modern instrumentation it proves possible to detect traces of N in diamonds that previously would have been termed Type II. Pearson et al. (2003) suggest defining type II as <20 ppm N, but this value may decrease in the future. In diamond, nitrogen occurs as different N-bearing centers, the most abundant (A, B, C defects) being the basis of the diamond classification into IaA, IaB, and Ib diamond respectively (e.g., Harlow 1998; Breeding and Shigley 2009). A second-order diffusion process (Chrenko et al. 1977; Evans and Qi 1982) leads C-centers (single substitution N-defect) originally present in the diamond matrix to migrate to form A-defects (N-pairs) and subsequently B-defect (cluster of 4 N-atoms around a vacancy). This difference can best be ascertained by infrared (IR) spectroscopy (e.g., Breeding and Shigley 2009). The abundance of N-bearing diamonds vary from one locality to the other. From published data, about 70% of diamonds contain > 20 ppm nitrogen and are classified as Type Ia, most (99.9%) being mixtures of IaA and IaB. Early studies investigated the potential of N-aggregation to date mantle residence time of diamond, but appeared to be so sensitive to temperature (Evans and Harris 1989) to make N-aggregation is actually a better thermometer (Taylor et al. 1990). Consistency in diamond N-aggregation state occurs, however. Metamorphic diamonds have short residence times in the crust (typically a few Ma; Finnie et al. 1994) at rather low temperatures (<1000 °C) and therefore display low-aggregation states (Ib-IaA diamonds). Fibrous diamonds and the coats of coated diamonds, being related to the kimberlite magmatism, also have short residence times (close to 1 Ma; Boyd et al. 1987; Navon et al. 1988), but at higher (i.e., mantle) temperatures and consistently display higher N-aggregation states (99% are IaA diamonds, plus some rare Ib-IaA diamonds; for review see Cartigny 2010 and references therein). Finally, having spent

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Figure 3 (*on facing page*). Diamond localities of the world in relation to Archean cratons and classified as to whether they are kimberlite-hosted and from mantle keels (lithospheric), kimberlite-hosted and from the convecting mantle (superdeep), of surface origin (i.e., weathered out of original host; alluvial), from ultra-high pressure crustal terranes (UHP), or formed by the shock of meteorite impact (impact). The crustal age/craton basemap is modified from Pearson and Wittig (2008). Diamond locality information from Tappert et al. (2009), Harte (2010), Harte and Richardson (2011), Tappert and Tappert (2011), Dobrzhinetskaya (2012), and information from the authors. Localities as follows: (1) Diavik, Ekati, Snap Lake, Jericho, Gahcho Kue, DO-27; (2) Fort a la Corne; (3) Buffalo Hills; (4) State Line; (5) Prairie Creek; (6) Wawa; (7) Victor; (8) Renard; (9) Guaniamo; (10) Juina/Sao Luis; (11) Arenapolis; (12) Coromandel, Abaete, Canasta; (13) Chapad Daimantina; (14) Boa Vista; (15) Koidu; (16) Kankan; (17) Akwatia; (18) Tortiya; (19) Aredor; (20) Bangui; (21) Mbuji-Mayi; (22) Camafuca, Cuango, Catoca; (23) Mavinga; (24) Mwadui; (25) Luderitz, Oranjemund, Namaqualand; (26) Orapa/Damtshaa, Lhetlakane, Jwaneng, Finsch; (27) Murowa, Venetia, The Oaks, Marsfontein, Premier, Dokolwayo, Roberts Victor, Letseng-la-Terae, Jagersfontein, Koffiefontein, Monastery, Kimberley (Bultfontein, Kimberley, DeBeers, Dutoitspan, Kamfersdam, Wesselton); (28) Kollur; (29) Majhgawan/Panna; (30) Momeik; (31) Theindaw; (32) Phuket; (33) West Kalimantan; (34) South Kalimantan; (35) Springfield Basin, Eurelia/Orroro, Echunga; (36) Argyle, Ellendale, Bow River; (37) Merlin; (38) Copetown/Bingara; (39) Mengyin; (40) Fuxian; (41) Mir, 23rd Party Congress, Dachnaya, Internationalskaya, Nyurbinskaya; (42) Aykhal, Yubileynaya, Udachnaya, Zarnitsa, Sytykanskaya, Komsomolskaya; (43) Ural Mts.; (44) Arkhangelsk; (45) Kaavi-Kuopio; (46) W Alps; (47) Moldanubian; (48) Norway; (49) Rhodope; (50) Urals; (51) Kokchetav; (52) Qinling; (53) Dabie; (54) Sulu; (55) Kontum; (56) Java; (57) New England Fold Belt; (58) Canadian Cordillera; (59) Lappajarvi; (60); Reis; (61) Zapadnaya; (62) Popigai; (63) Sudbury; and (64) Chixculub.

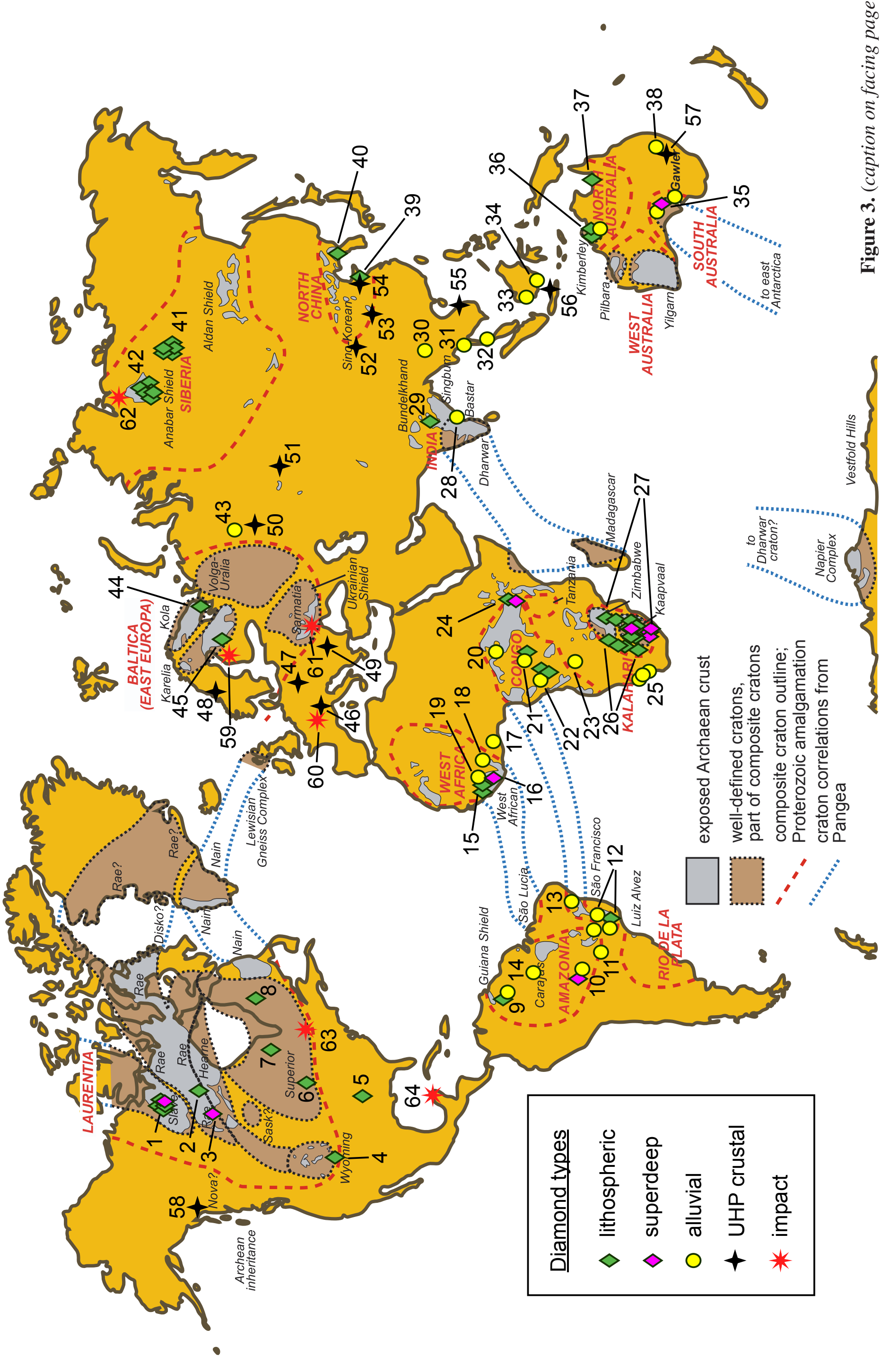


Figure 3. (*caption on facing page*)

billions of years at mantle temperatures, xenocrystal eclogitic and peridotitic diamonds show higher aggregation states (>99.9% are IaA-IaB diamonds). Transition zone and lower mantle are usually deprived in nitrogen (Type II) but the few type I deep diamonds are characterized by highly aggregated nitrogen (IaB diamond), reflecting their high-temperature environment (Stachel et al. 2002 and references therein).

For determining the source of the carbon in the fluids/melts that have crystallized diamond, —an essential aspect of carbon cycle research—the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ isotopic compositions, and N abundance have emerged as the most important measurements (Cartigny 2005; and see section on "*Stable isotopic compositions and formation of diamonds*"). These measurements can be done in bulk by gas source, isotope ratio mass spectrometry (IRMS) at high precision and accuracy or on individual spots by SIMS in spatial relationship to diamond growth zones at lower levels of precision and accuracy. Fractionation of both the C and N isotopic compositions occurs with diamond growth and active debate centers on the extent to which fractionation versus source reservoir composition controls the isotopic composition of a diamond (Cartigny et al. 2003; Stachel and Harris 2009).

Trace element analysis by LA-ICPMS recently has emerged as a powerful new tool for relating diamonds to the fluids/melts from which they have grown (see below). But at current sensitivity and blank levels the trace elements analyzed by LA-ICPMS are in the micro-inclusions of cloudy and fibrous diamonds and are not direct constituents of the clear, gem-quality diamond lattice.

Fluid and micro-mineral inclusions. For purposes of discussion, a distinction is being made here between discrete micro-inclusions located usually in the interior of gem-quality monocrystalline diamonds and suited for individualized X-ray, thermobarometric, chemical, and isotopic study (discussions in the "*Inclusions Hosted in Diamonds*" section) and dispersed clusters and clouds of nano- to micro-inclusions that have been included during coated diamond growth or exsolved from melt after diamond crystallization. Fibrous and coated diamonds can occur as single-crystal cubes (fibrous cuboids) or as the thick outer rim or coat on clear octahedral cores. Some diamonds oscillate between fluid-poor (gem-quality, layer-by-layer growth) and fluid-rich, fibrous growth (e.g., Fig 1, top), whereas other have a center of fluid-rich fibrous growth that transforms into fluid-poor, gem diamond outwards (so-called "cloudy diamonds"). The first published report of fluids in fibrous diamonds was made by Chrenko et al. (1967) and early studies of their growth structures were made by Custers (1950) and Kamiya and Lang (1964).

Fibrous diamonds generally make up less than 1% of mine production but can comprise as much as 8% at some mines such as Jwaneng, Botswana (Harris 1992), 90% in Mbuji Mayi Zaire, and 50% in Sierra Leone (see Boyd et al. 1994 for review). Typically, the compositions within any one diamond are uniform but significant variations exist between individual diamonds. Fibrous diamonds have been the active research focus of Navon and coworkers for many years (e.g., Navon et al. 1988; Weiss et al. 2008, 2011), as summarized by Pearson et al. (2003). The fluid compositions are typically measured for major elements by electron microprobe (Navon et al. 1988; totals are typically <5% and are normalized to 100%) or FTIR (Weiss et al. 2008), whereas INAA (Schrauder et al. 1996) and ICPMS (Resano et al. 2003; Tomlinson et al. 2005, 2006; Zedgenizov et al. 2007; Rege et al. 2008, 2010; McNeill et al. 2009; Tomlinson and Mueller 2009; Klein-BenDavid et al. 2010) are the preferred methods for trace element determinations. In addition, radiogenic isotope characteristics can now be measured by novel applications (e.g., combustion, off-line laser ablation) of standard analytical techniques (Akagi and Masuda 1988; Klein-BenDavid et al. 2010). The fluids range in composition from carbonatitic to hydrous and silicic end-members, with intermediate compositions (Schrauder and Navon 1994; Fig. 4). The carbonatitic fluid is rich in carbonate, CaO, FeO, MgO, and P_2O_5 with a magnesio-carbonatitic end-member (Klein-BenDavid et al. 2009; Kopylova et al. 2010)

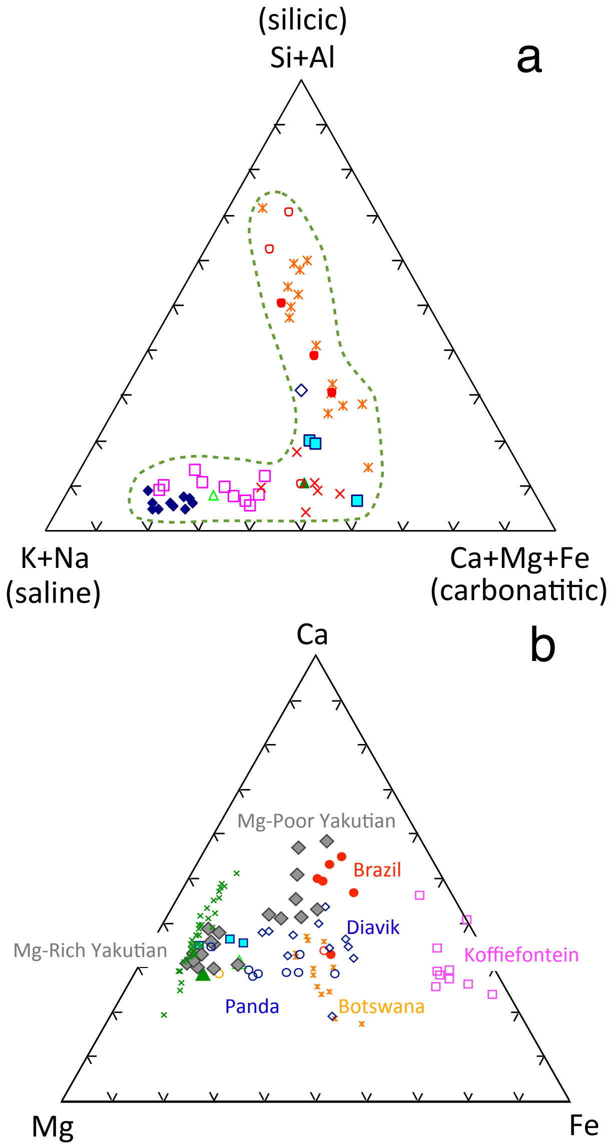


Figure 4. Composition of fluids in diamonds from worldwide locations. Data from the work of Klein-BenDavid (2004, 2007a, 2009), Izraeli (2001), and Tomlinson (2006, 2009). Note the clear delineation of three end-members (a), the large compositional variability (b), and that some localities have specific differences in their Fe/Mg (b).

whereas the hydrous fluid is rich in SiO_2, Al_2O_3 (Schrauder and Navon 1994). K_2O contents are high in both fluid types. In contrast, fluid inclusions from cloudy diamonds contain much higher Cl contents and are classified as brines, being distinct from the other fluid types found in fibrous diamonds (Izraeli et al. 2001). The brines carry very little SiO_2 (3-4 wt%), possibly because of the low water content restricting the solvating capacity of the fluid. Recent work over the last decade has discovered fluids in diamonds (Fig. 4) from some localities (Diavik, Udachnaya, Kankan) that are carbonatitic and with high-Mg content (10 to 15 wt%; Klein-BenDavid et al. 2009; Kopylova et al. 2010; Weiss et al. 2011). These fluids are capable of being in equilibrium with carbonated peridotite and thus represent a more primitive end-member perhaps existing deeper in the lithosphere and associated with the fluids in proto-kimberlitic magmas (Klein-BenDavid et al. 2009). Their high alkali (K_2O > 10 wt%) and Cl contents are thought to be too elevated to be completely primary and may suggest assimilation of these components (Klein-BenDavid et al. 2009). Recent experimental work (e.g., Bureau et al. 2012) has confirmed these studies of natural diamond by showing that hydrous silicate melt and aqueous fluid can coexist in regions of active diamond growth, though at higher pressures and temperatures these fluids become one supercritical fluid. These fluids crystallize cloudy and fibrous diamond with complex mixed-phase inclusions (Bureau et al. 2012).

The concentration of incompatible elements of varying geochemical affinity (K, Na, Br, Rb, Sr, Zr, Cs, Ba, Hf, Ta, Th, U, and the light rare earth elements) in the fluid inclusions from fibrous diamonds is much higher than in typical mantle-derived magmas and phenocryst-hosted melt inclusions (Schrauder et al. 1996; Weiss et al. 2008, 2011; Tomlinson and Mueller 2009; Klein-BenDavid et al. 2010). Recent advancements in LA-ICPMS techniques (e.g., Klein-BenDavid et al. 2010) have permitted enough improvements in trace element measurements so that even Sr, Nd, and Pb isotopic compositions can now be determined (Fig. 5). The concentrations of

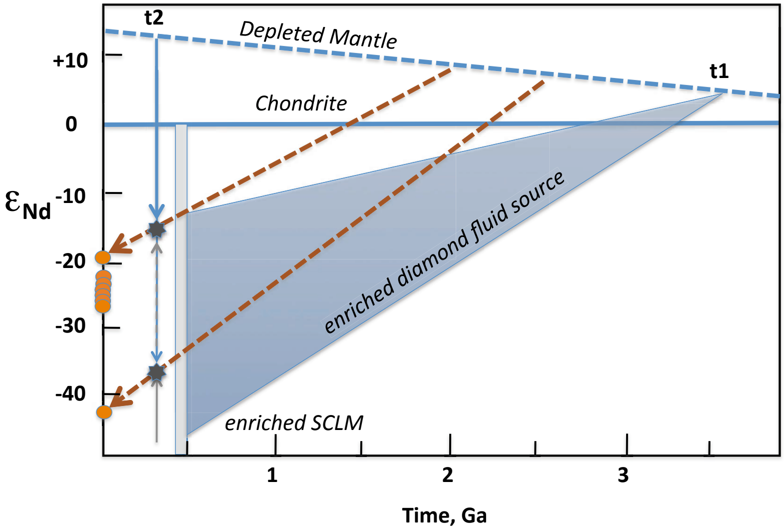


Figure 5. Nd isotope evolution diagram based on data in Klein-BenDavid et al. (2010; and unpublished) on fibrous diamonds from Botswana obtained by closed-system laser ablation ICP-MS (McNeill et al. 2009). Nd evolution illustrated is meant to be typical of the multi-stage history required explain not only the Nd data but the concurrently obtained Pb and Sr isotopic compositions and trace element data (not shown, but see Klein-BenDavid et al. 2010) on the same mass of diamond. Initial development of the enriched reservoir, at t1, requires early separation of the enriched source from either a chondritic or depleted mantle reservoir sometime in the Archean (as required by elevated $^{207}Pb/^{204}Pb$ at modest $^{206}Pb/^{204}Pb$). A spectrum of incompatible element enrichment was generated at this time, leading to a wide range in Nd isotope compositions over 2 to 3 Ga. A second event (t2), in the Phanerozoic, may coincide with diamond formation and involved mixing (as depicted by arrows) between a fluid derived from a more depleted mantle composition (the convecting mantle) and the highly-enriched mantle source generated between t1 and t2. This process created diamond-fluids with mixed compositions (circles) whose model ages (dashed lines) give ages younger than t1 and do not have direct age significance. The timing of stage t2 is constrained to be in the Phanerozoic by Pb isotope systematics and the un-aggregated nitrogen present in all fluid-rich fibrous diamonds.

most trace elements decrease by a factor of two from the carbonate-rich fluids to the hydrous fluids, with the high-Mg carbonatitic fluids among the highest trace element content (e.g., Weiss et al. 2011). Rare earth element (REE) contents of the fluid inclusions are higher than those of kimberlites and lamproites but the fluids show very similar levels of extreme light REE enrichment over the heavy REE typical of these rock types. Negative anomalies in Nb, Sr, Zr, Hf, and Ti are typical (e.g., McNeill et al. 2009; Tomlinson and Mueller 2009; Weiss et al. 2009, 2011; Klein-BenDavid et al. 2010). These features suggest that the fluids may be related to carbonatite- or kimberlite-like magmas in displaying a dominant metasomatic component in their source and fractionation of carbonate plus other phases such as rutile, and zircon. The amount of fractionation of these latter minerals must be small; otherwise middle REE and heavy REE systematics of the fluids would show distinctive fractionation effects. Early Sr isotope studies (Akagi and Masuda 1988) and carbon isotope measurements (Boyd et al. 1987, 1992) supported a link between the fluids in fibrous diamonds and kimberlite-like magmas. But recent, more complete isotopic work (Klein-BenDavid et al. 2010) has shown that fluids in fibrous diamonds have Sr isotopic compositions too radiogenic and Nd isotopic compositions too unradiogenic to be related just to the kimberlite hosting the diamonds. Generation of these fluids must also involve lithospheric components. These fluids are thought to have been derived from mixing between an ancient component derived from the breakdown of micaceous phases in the lithosphere and carbonatitic-kimberlitic fluids from beneath the lithosphere (Klein-BenDavid et al. 2010). Nonetheless, the incompatible-element-rich nature of the fluids in fibrous diamonds illustrate that carbonate-rich and hydrous deep mantle fluids are efficient carriers of incompatible elements. Despite the wide range of Sr and Nd isotopic compositions (Klein-BenDavid et al. 2010; Fig. 5), the C and N isotopic compositions of all fibrous diamonds measured so far (summarized in Cartigny 2005; additional data in Klein-BenDavid et al. 2010) is very restricted and falls close to the canonical mantle values of −5‰, indicating a dominant source within the convecting mantle.

Most fibrous/fluid-rich diamonds and diamond coats are thought to have formed near the age of kimberlite eruption and hence have not experienced protracted mantle residence times on the basis of their unaggregated nitrogen (IaA diamonds) and the similarity of fluids to kimberlitic fluids. Smith et al. (2012) have recently analyzed fluids within fibrous diamonds from Wawa, Ontario, where the diamonds are thought to have been emplaced at Earth's surface a minimum of 2.7 Ga ago. These authors find trace element systematics that are very similar to the fluids in "modern" fibrous diamonds. This study is strong evidence for a similar parentage for these late Archean diamonds and those fibrous diamonds of today, and provides supporting evidence for a dominant style/source of diamond formation from the late Archean onwards as proposed by Shirey and Richardson (2011).

Transmission electron microscopy coupled with sample removal by focused ion beam lift-out (TEM, FIB; Wirth 2004, 2009) is increasingly being applied to the study of fluid- and inclusion-rich diamonds (e.g., Dobrzhinetskaya et al. 2005, 2006, 2007; Klein-BenDavid et al. 2006, 2007b; Logvinova et al. 2008; Jacob et al. 2011). Klein-BenDavid et al. (2006) found abundant solid inclusions of carbonates, halides, apatite, and high-Si mica. The TEM results, together with the narrow range of compositions measured by EPMA, along with the volatiles evident from infrared (IR) spectroscopy, suggest that the micro-inclusions trapped a uniform, dense, supercritical fluid and that the included nano-phases grew as secondary phases during cooling. Kvasnytsya and Wirth (2009) found nano-inclusions of typical lherzolitic silicates in micro-diamonds from the Ukraine, plus a number of likely epigenetic phases, such as graphite and K-richterite. Fe-Sn oxides were also reported, whose primary origin is unclear. The same study also revealed abundant nano-inclusions of carbonate, ilmenite, rutile, apatite, sylvite, and low-Si mica in fibrous microdiamonds. This assemblage is consistent with formation of these diamonds from a carbonatitic to a slightly silicic melt, rich in alkali and volatile components, as proposed for other fibrous diamonds. A single polycrystalline diamond aggregate from Orapa was studied by Jacob et al. (2011), who found a syngenetic micro- and nano-inclusion suite of magnetite, pyrrhotite, omphacite, garnet, rutile, and C-O-H fluid. This assemblage led the authors to propose a novel redox reaction between carbonatitic melt and the sulfide-bearing eclogite during diamond crystallization.

While fibrous and cloudy diamonds with their characteristically high abundances of a variety of inclusions were studied first, these techniques are being increasingly applied to clearer, monocrystalline stones as the only way to look at rare, exceedingly tiny inclusions in superdeep diamonds (e.g., Brenker et al. 2002, 2007; Wirth et al. 2007, 2009; Kaminsky et al. 2009; Kaminsky and Wirth 2011). Certain suites of superdeep diamonds have yielded a dazzling array of nano-inclusions although whether they are syngenetic remains to be proven. Some inclusions, such as halides, anhydrite, phlogopite, or hydrous aluminosilicate (Wirth et al. 2007, 2009) are unexpected in the mantle unless they have been introduced by deep recycling of volatile-enriched slabs. Other superdeep inclusions, such as iron carbide and nitrocarbide (Kaminsky and Wirth 2011), are providing primary evidence for the redox shifts due to the disproportionation of Fe^{3+} into perovskite, whereas nyerereite and nahcolite (Kaminsky et al. 2009) suggest the existence of primary carbonatite associated with diamond formation (e.g., Walter et al. 2008). One expects that these techniques will be applied with more frequency to typical lithospheric monocrystalline diamonds of low inclusion abundance. In the end, it seems clear that such TEM and microanalytical studies will provide the answers to the questions of the speciation of diamond-forming fluids and the oxygen fugacity of the mantle regions in which diamond forms.

Internal textures in diamonds

Diamonds show no growth zonation in visible light but display it in polarized light, photoluminescence, and cathodoluminesce (CL). The best technique for observations is CL, which has been widely applied to diamonds. In CL a beam of electrons generated in either an electron probe or a Luminoscope™ (a microscope-mounted CL instrument) can excite photons through electron transfer. In diamonds this technique is best accomplished on polished plates, which must be oriented perpendicular to one of the {110} axes (e.g., not parallel to {100} or {111}; Bulanova et al. 2005) to cut across growth faces. Nitrogen, the major diamond impurity, is the chief activator of CL in diamond. The technique has been widely applied to diamonds and dramatic images displaying a variety of growth textures (e.g., see Fig. 1) have been presented by Bulanova (1996), Kaminsky and Khachatryan (2004), Spetsius and Taylor (2008), and Tappert and Tappert (2011).

Lithospheric diamond textures. Despite the irregular forms that exist (macles, bort, etc.) most monocrystalline lithospheric diamonds have an internal structure that is roughly concentric. The zoning patterns are characterized by two chief features: 1) extremely thin oscillations between stronger and weaker luminescence (Fig. 1c); and, 2) alternating episodes of resorption and overgrowth on top of the resorption (Fig. 1d). Both features strongly support the idea that diamond grows from an aqueous fluid and/or low-viscosity melt with an aqueous component (Bureau et al. 2012) rather than a solid medium such as graphite. Growth from graphite is not only energetically unfavorable for monocrystalline diamonds (Stachel and Harris 2009), but growth from graphite would likely not produce the internal diamond textures observed such as the fine oscillations (e.g., rapid change in N content) or periods of resorption between periods of growth. Growth of polycrystalline diamonds directly from graphite is feasible, however (Irifune et al. 2004). The growth history revealed by CL is extremely important to the interpretation of individual mineral inclusions (e.g., Pearson et al. 1999a,b; Westerlund et al. 2006) and C and N isotopic composition changes during diamond growth (e.g., Boyd et al. 1987; Cartigny et al. 2001; Stachel and Harris 2009; Smart et al. 2011). In combination with electron backscatter diffraction (EBSD) and the FIB-SEM, CL can even be used to study the 3-dimensional growth zonation around inclusions in diamond. In general, the ability to analyze individual inclusions and analyze C and N isotopes *in situ* by SIMS has made it essential to use such techniques to guide the placement of *in situ* analyses.

Superdeep diamond textures. The textures revealed in sub-lithospheric diamonds are strikingly different than those seen in lithospheric diamonds (Hayman et al. 2005; Bulanova et al. 2010; Araujo et al. 2013). External morphologies of such diamonds are not polycrystalline in the same way that lithospheric diamonds can be, yet they rarely form euhedral monocrystals either. In CL, regular concentric zonation is rare. Instead, these diamonds (Figs. 1e,f) are characterized by multiple growth centers, non-concentric zonation of a blocky nature, and even what appears to be deformation texture; in short they display almost polycrystalline internal structures. The major difference between sub-lithospheric diamonds compared to lithospheric diamonds is that they grow at much higher pressure and temperature and in a mantle that is actively convecting, whereas lithospheric diamonds grow in a mantle host that is not convecting. At present, it remains speculation as to whether these textural differences are caused by the dramatic differences in the nature of the host mantle or by the possibility that some growth from solid graphite (e.g., Irifune et al. 2004) is favored by the much higher *P-T* conditions and deformation.

DIAMOND FORMATION

Diamond formation in the mantle is generally considered to be a metasomatic process (e.g., Haggerty 1999; Stachel et al. 2005). The agents of metasomatism, most likely supercritical fluids or melts, react with the mantle rocks in which they infiltrate, and diamond crystallizes as a consequence of the reduction of carbon via redox reactions, simple examples of which are:

$$CO_2 = C + O_2 \tag{1}$$

$$CH_4 + O_2 = C + 2H_2O \tag{2}$$

As such, the speciation of carbon and the formation of diamond will be intimately associated with the oxidation state of mantle rocks, which is likely controlled by Fe^0-Fe^{2+}-Fe^{3+} components in silicate minerals, metals, and melts (e.g., Rohrbach et al. 2007, 2011; Frost and McCammon 2008; Rohrbach and Schmidt 2011). A synthesis of diamond formation includes a modern view of mantle oxidation state, carbon speciation in peridotitic and eclogitic mantle rocks, diamond growth within a framework provided by experimental and thermodynamic observations, as well as by the stable isotopic compositions of diamonds. Discussion is arranged separately for lithospheric versus sub-lithospheric diamonds because of their different and unique nature.

Experimental and thermodynamic constraints of growth in the lithospheric mantle

Oxygen fugacity in the cratonic mantle. The majority of diamonds sampled at the surface originated in cratonic lithosphere at depths less than 250 km and so the prevailing oxygen fugacity in cratonic mantle peridotite is important to consider. At the pressures of diamond stability, garnet is stable in peridotite. The oxygen fugacity at which garnet peridotite xenoliths from cratonic mantle equilibrated can be determined using the oxy-thermobarometer calibrated by Gudmundsson and Wood (1995) that employs the garnet-olivine-orthopyroxene (GOO) equilibrium,

$$\text{GOO} \qquad \underset{garnet}{2Fe_3Fe_2^{3+}Si_3O_{12}} = \underset{olivine}{4Fe_2SiO_4} + \underset{opx}{2FeSiO_3} + O_2 \tag{3}$$

(see also Woodland and Peltonen 1999). Figures 6a and 6c show f_{O_2} determinations made using this oxy-thermobarometer for garnet-bearing xenoliths from the Kaapvaal craton (see also Frost and McCammon 2008) from equilibration pressures and temperatures corresponding to the diamond stability field, determined from further thermometry and barometry equilibria (Luth et al. 1990; Woodland and Koch 2003; Creighton et al. 2009; Lazarov et al. 2009). We note here

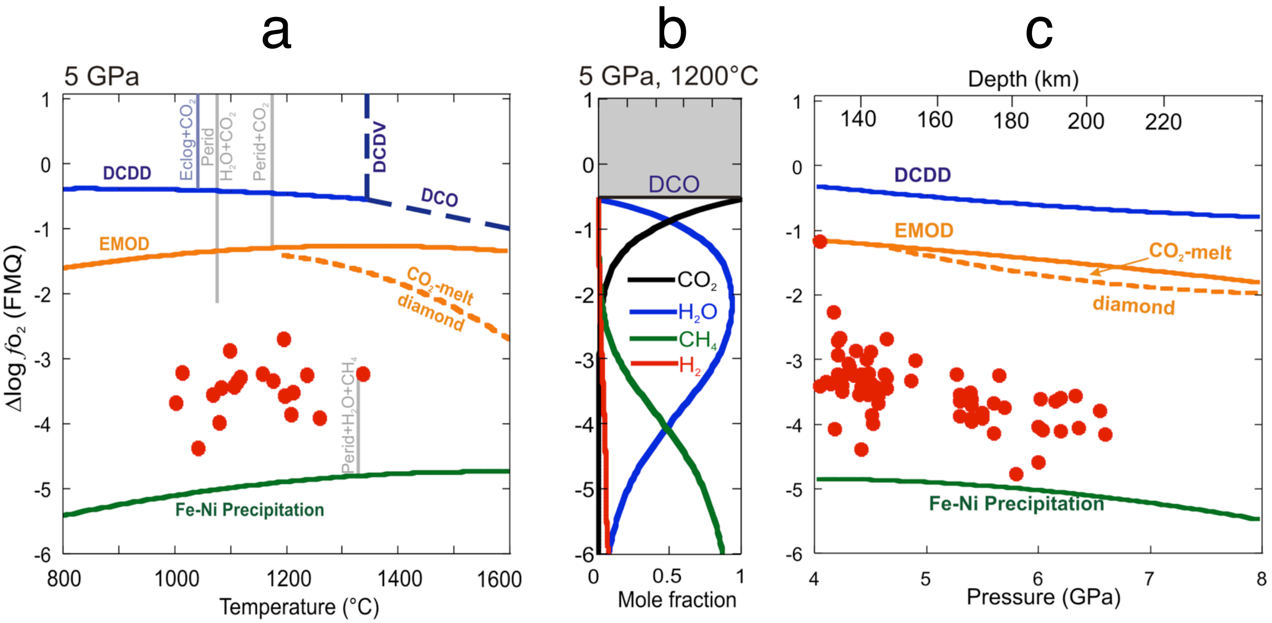


Figure 6. The oxygen fugacity relative to FMQ estimated for garnet peridotite xenoliths (red circles) compared with reactions that determine the speciation of carbon over the pressure and temperature range of cratonic diamond formation. (a) The oxygen fugacity of mantle xenoliths with equilibration pressures of 5 ± 0.5 GPa as a function of temperature. The curve for the EMOD buffer (solid orange) describes the f_{O_2} of the equilibrium between diamond and magnesite in peridotitic rocks, while the diamond CO_2-melt curve (dashed orange) describes the same equilibrium for molten carbonate. Curves describing the stability of carbonate with respect to diamond and CO_2 in eclogite rocks are shown in blue as defined in the text. The Fe-Ni precipitation curve marks the f_{O_2} where Ni-rich Fe metal will start to exsolve from peridotite minerals, as calculated using the procedure described by O'Neill and Wall (1987). Vertical lines in grey show melting temperatures for peridotite saturated with H_2O and CO_2 (perid+H_2O+CO_2; Foley et al. 2009), carbonated peridotite (perid+CO_2; Dasgupta and Hirschmann 2006), and reduced peridotite saturated with H_2O and CH_4 (perid+H_2O+CH_4; Taylor and Green 1988). The blue vertical line shows the carbonated eclogite solidus (Eclog+CO_2) of Dasgupta et al. (2004). The vertical extent of these curves is an approximation of the f_{O_2} range over which such melts are stable. (b) The speciation of a C-O-H fluid in equilibrium with diamond calculated at 5 GPa and 1200 °C using the equation of states from Belonoshko and Saxena (1992) following the procedure of Holloway (1987). Diamond is unstable above the horizontal DCO buffer line. (c) The f_{O_2} of mantle xenoliths as a function of pressure or depth. Carbon speciation curves are the same as in A) but are calculated along the average geothermal gradient recorded by the xenoliths.

that the oxy-thermobarometer of Gudmundsson and Wood (1995) has not been tested experimentally at pressures above 3 GPa, so some unquantified uncertainty exists in garnet peridotite oxygen fugacity estimates due to extrapolation of thermodynamic data beyond the tested range. In Figure 6a and 6c oxygen fugacity is reported relative to the fayalite-magnetite-quartz (FMQ) buffer reaction,

$$\text{FMQ} \qquad \underset{\textit{fayalite}}{3\text{Fe}_2\text{SiO}_4} + \text{O}_2 = \underset{\textit{magnetite}}{2\text{Fe}_3\text{O}_4} + \underset{\textit{quartz}}{3\text{SiO}_2} \tag{4}$$

i.e., $\Delta\log f_{O_2}$ (FMQ), which removes some of the temperature and pressure dependence inherent in all f_{O_2} dependent equilibria (e.g., Frost et al. 1988). The majority of xenolith samples plot in the range between −2.5 and −4.5 $\Delta\log f_{O_2}$ (FMQ). There is a slight f_{O_2} pressure dependence to the xenolith samples, which mainly arises from the volume change of Equation (3) that has the tendency to drive the determined oxygen fugacities to lower levels at high pressures (e.g., Frost and McCammon 2008). Consequently, some of the highest-pressure xenolith samples shown in Figure 1c, which record the lowest oxygen fugacities, are relatively fertile peridotites with garnet $Fe^{3+}/\Sigma Fe$ ratios that are among the highest for these samples. Many xenolith samples in fact record oxygen fugacities close to the Fe-Ni precipitation curve. This curve marks the f_{O_2} where Ni-rich Fe alloy will start to precipitate out of mantle silicates as a consequence of reduction of iron oxide, which can be calculated following procedures described in O'Neill and Wall (1987). The curve has a f_{O_2} close to the iron-wüstite buffer (IW),

$$\text{IW} \qquad \underset{\textit{iron}}{2\text{Fe}} + \text{O}_2 = \underset{\textit{wüstite}}{2\text{FeO}} \tag{5}$$

and marks an effective lower bound in mantle f_{O_2} because significant amounts of FeO would be required to reduce from the silicates before the f_{O_2} could pass substantially below this curve. The important point here is that at pressures where diamond is stable, cratonic lithosphere is likely to have a prevailing f_{O_2} that is reducing enough that carbon can exist as diamond.

Carbon speciation in peridotite. The highest oxygen fugacity at which diamond could form within carbonated peridotite assemblages can be described in simplified terms by the reaction,

$$\text{EMOD} \qquad \underset{\textit{enstatite}}{\text{MgSiO}_3} + \underset{\textit{magnesite}}{\text{MgCO}_3} = \underset{\textit{olivine}}{\text{Mg}_2\text{SiO}_4} + \underset{\textit{diamond}}{\text{C}} + \text{O}_2 \tag{6}$$

which is referred to by the mineral acronym EMOD (enstatite-magnesite-olivine-diamond) (Eggler and Baker 1982; Luth 1993). The f_{O_2} buffered by this equilibrium is shown in Figures 6a and 6c. Curves plotted in Figure 6c are calculated along the average geothermal gradient for the Archean lithosphere recorded by the xenolith samples, and EMOD falls between −2 and −0.5 $\Delta\log f_{O_2}$ (FMQ). At oxygen fugacities above EMOD diamonds are unstable in peridotite rocks with respect to magnesite, and below EMOD carbonate minerals are unstable. As shown, the vast majority of mantle xenoliths plot firmly in the diamond stability field with respect to EMOD. The EMOD buffer can be calculated using thermodynamic data as in Figure 6 (Holland and Powell 2011) and recent experiments that have measured the f_{O_2} of this buffer using independent redox sensitive equilibria are reasonably consistent with such calculations (Stagno and Frost 2010).

Stagno and Frost (2010) measured the f_{O_2} of the equilibrium between diamond and carbonate melt for a peridotite assemblage as a function of pressure and temperature. The f_{O_2} of this diamond and CO_2-bearing melt equilibria was found to evolve to lower values compared to the extrapolated EMOD buffer as temperatures increase, as shown in Figure 6a. This lowering of the f_{O_2} arises not only from the difference in thermodynamic properties between the mineral and melt phases, but also results from the dilution of the carbonate melt by silicate components at high temperature. Experiments confirm that the dilution of the carbonate melt component by solutes other than silicates can also drive the f_{O_2} of the diamond melt equilibria to lower levels (Stagno and Frost 2010). H_2O is likely important in this role, as can be seen from the following calculations of C-O-H fluid speciation, but other solutes such as brines and phosphates would also act in a similar way.

Figure 6b shows the speciation of a C-O-H fluid calculated at 5 GPa and 1200 °C as a function of f_{O_2}, assuming an ideal mixing model (Holloway 1987; Belonoshko and Saxena 1992). This speciation calculation considers only the fluid phase and ignores the potential reaction of fluid species with silicate minerals to produce carbonates or volatile-rich melts for example. However, it provides a framework to examine likely volatile speciation as a function of f_{O_2}, even if the predicted volatile species would in reality be components in other phases. At oxygen fugacities compatible with the grey region in Figure 6b, diamond is unstable with respect to CO_2 fluid. Diamond can only form below the f_{O_2} defined by the DCO (diamond-carbon-oxygen) buffer equilibrium,

$$\text{DCO} \qquad C + O_2 = CO_2 \qquad (7)$$

The DCO buffer, as shown in Figure 6b, is generally above but within 1 log unit of EMOD at lithosphere conditions. At oxygen fugacities below the DCO buffer diamond remains stable but the equilibrium C-O-H fluid phase evolves to become more H_2O-rich. At approximately 2 log units below DCO the so-called “water maximum” occurs, where almost pure H_2O fluid is in equilibrium with diamond. At oxygen fugacities below the water maximum, concentrations of CH_4 in the fluid phase, and to a lesser extent H_2, start to increase. As shown in Figure 6a by the grey vertical melting curves, carbonate melts are likely to form at temperatures in the region of 1200 °C, but pure carbonates are incompatible with the f_{O_2} of mantle xenoliths as described above. As also shown in Figure 6a, the H_2O-CO_2 peridotite solidus is depressed to low temperatures (Foley et al. 2009) but H_2O-rich carbonate melts are also unlikely to be stable at the f_{O_2} recorded by most xenoliths. The majority of samples in fact record oxygen fugacities compatible with the existence of H_2O-CH_4 fluids, which are likely to form fluids rather than melts in the mantle due to the smaller melting point depression associated with these species (Jakobsson and Holloway 1986; Taylor and Green 1988). In a recent experimental study where the fluid in quenched experimental samples was analyzed using gas chromatography to quantify fluid speciation, however, much higher concentrations of H_2 compared to CH_4 were identified in reduced gas mixtures produced at 6.3 GPa and 1400-1600 °C (Sokol et al. 2009).

The majority of peridotite samples record an f_{O_2} consistent with the stability of H_2O-CH_4 fluids if the calculations are informative (Fig. 6), or possibly H_2O-H_2 fluids if the experiments are a better guide. In either case, these results do not mean that diamonds necessarily formed from such fluids. Instead, diamond crystallization can occur as a consequence of redox gradients that exist when metasomatic melts or fluids infiltrate mantle peridotite. Fluids that are either more oxidizing or more reducing than the fluid that would be stable at the oxygen fugacity of mantle peridotite would be expected to crystallize diamond. For example, oxidized carbonate-rich melts or high-density fluids could crystallize diamond by reduction of CO_2 component (as in Eqn. 1), whereas diamond growth from reducing fluids could occur by oxidation of CH_4 (e.g., Eqn. 2). In these cases oxygen is absorbed or supplied by local re-adjustment of Fe^{2+}-Fe^{3+} equilibria in mantle minerals. Evidence for such reactions were reported by McCammon et al. (2001), who noted significant zonation in the $Fe^{3+}/\Sigma Fe$ ratios determined for garnets in mantle xenoliths from the Wesselton kimberlite, consistent with the passage of liquids that have metasomatized and oxidized only the outer rim of garnet grains.

Carbon speciation in eclogite. A large proportion of cratonic diamonds and diamond inclusions are associated with eclogitic rocks and minerals. Currently, however, there is no calibrated oxythermobarometer that can be used to determine the f_{O_2} of eclogitic rocks. Luth (1993) performed experiments on model carbonated eclogite and concluded that the equilibrium,

$$\text{DCDD} \qquad \underset{\textit{dolomite}}{CaMg(CO_3)_2} + \underset{\textit{coesite}}{2SiO_2} = \underset{\textit{diopside}}{CaMgSi_2O_6} + \underset{\textit{diamond}}{2C} + 2O_2 \qquad (9)$$

which has the mineral acronym DCDD (dolomite-coesite-diopside-diamond), would control the stability of carbonate minerals and diamond in eclogitic rocks (see also Luth 1999). As shown in Figure 6, DCDD is approximately 1 log unit above EMOD, implying that the diamond stability field is larger with respect to f_{O_2} in eclogitic rocks. The larger stability field would imply that carbonate-bearing melts or fluids stable within peridotite rocks could be reduced to diamond on entering eclogites, even if the f_{O_2} remained essentially constant. This change in controlling equilibria may be a factor in the close association between diamonds and eclogitic xenoliths, and the prevalence of eclogitic inclusions in certain suites of lithospheric diamonds.

Diamond formation in the lithospheric mantle (experimental results). The oxygen fugacity structure of the lithospheric mantle discussed above indicates that diamond is the likely form of carbon within deep lithospheric mantle. Fluids and melts have long been favored as potential growth media for diamonds, but it is a challenge to deduce the exact conditions of growth from diamonds themselves due to their elemental purity. However, mineral and fluid inclusions, trace impurity chemistry (e.g., N, H, and other trace elements) and growth morphology, can provide important information for interpreting growth history. Diamond nucleation and growth experiments have a long and glorious history, having been motivated by the importance of diamonds in both industry and academia, and provide an important context for observations from natural diamonds (Hazen 1999). A brief synopsis of relevant experiments will contribute to understanding diamond growth in the mantle.

Diamond synthesis directly from C-O or C-O-H fluids has been studied experimentally at pressures generally appropriate for the lithosphere (e.g., ~5-8 GPa), although experimental temperatures tend to be higher than lithospheric because of the chemically simple systems. In general, results show that diamonds can grow from a wide range of fluid compositions at oxygen fugacities at or below the DCO buffer (Hong et al. 1999; Akaishi et al. 2000, 2001; Kumar et al. 2000; Pal'yanov et al. 2000; Sokol et al. 2001b, 2009; Sun et al. 2001; Yamaoka et al. 2002). These studies attest to the fecundity of CO_2-rich fluids, CO_2-H_2O fluids, graphite-H_2O fluid, and CH_4-rich fluids as media for nucleation and growth of diamond. Nucleation and growth is apparently enhanced in H_2O-rich fluids but inhibited in H_2-rich fluids (Sokol et al. 2009).

Diamond growth can occur directly by reduction of carbonate components in minerals and melts, and numerous experiments show that carbonated fluids and melts provide productive diamond-forming media (e.g., Pal'yanov et al. 1998; Sato et al. 1999; Sokol et al. 2000, 2001a, 2004; Arima et al. 2002; Sokol and Pal'yanov 2004; Spivak and Litvin 2004). For example, at 7.7 GPa diamonds can form readily either from molten Ca- and Mg-carbonate (Sato et al. 1999; Arima et al. 2002) or from solid carbonate in equilibrium with a reduced, CH_4-H_2O fluid (Yamaoka et al. 2002). Experiments also indicate enhanced diamond growth from dolomitic melts in the presence of fluids enriched in H_2O and CO_2 (Sokol et al. 2000), although Bataleva et al. (2012) found that CO_2-rich ferrous carbonate-silicate melt can be an effective waterless medium for diamond crystallization at 6.3 GPa. The addition of alkalies to carbonate-rich fluids and melts also yields fertile diamond growth media (Litvin et al. 1997, 1998a,b; Litvin and Zharikov 1999).

Although experiments in simplified C-O-H fluid and carbonated systems are essential and insightful, fluids and melts in the lithospheric mantle will react with silicate minerals in peridotite or eclogite, which can lead to a wide range of chemically diverse compositions as seen, for example, in fibrous diamonds. Experimental data show that an array of complex fluid and melt compositions involving C-O-H fluids, carbonates, chlorides, and silicates, reminiscent of those trapped in natural diamonds, can provide suitable diamond growth media. Pal'yanov et al (2002, 2005) show that reaction of carbonated fluids or melts with silicates can lead to diamond nucleation and growth. Alkaline-carbonate-silicate melts can be highly efficient for diamond formation, but nucleation and growth is apparently limited to specific compositional ranges (Shatsky et al. 2002). Litvin (2009) discusses how in the system Na_2O-K_2O-MgO-CaO-Al_2O_3-SiO_2-C at 8.5 GPa that, as silicate components dissolve into melts, a concentration exists beyond which diamond nucleation and growth is inhibited. According to experiments from model peridotitic-carbonate systems, the barrier may occur at ~30% dissolved silicate (Litvin et al. 2008), whereas in model eclogitic-carbonate a value closer to 50% dissolved silicate is indicated (Litvin and Bobrov 2008). As in simple systems, H_2O apparently enhances diamond crystallization in more complex alkali-chloride-carbonate-silicate-water systems. Diamonds can grow readily in volatile-rich kimberlitic magma (Arima et al. 1993), and a number of studies have verified diamond nucleation and growth in a range of alkali- and chloride-rich C-bearing systems (Pal'yanov et al. 2007b; Safonov et al. 2007, 2011; Pal'yanov and Sokol 2009). A common theme amongst these studies is the importance of fluid/melt composition in facilitating or inhibiting diamond nucleation and in determining growth mechanism and crystal form.

Sulfide inclusions, such as pyrrhotite, are common amongst inclusions in lithospheric diamonds. Bulanova et al (1998) identified the potential importance of sulfide melts, possibly immiscible with a volatile-rich silicate melt, in the nucleation and growth of diamond. Simple system experiments verified that carbon-saturated sulfide melts nucleate and crystallize cubo-octahedral diamond (Pal'yanov et al. 2001, 2006, 2009; Litvin et al. 2002), even if low carbon solubility indicates a limited role for sulfide as an agent of C dissolution and transport. Gunn and Luth (2006) suggest that FeS melt may dissolve sufficient oxygen such that carbonate in a coexisting melt could be reduced by a reaction such as:

$$MgCO_3 + MgSiO_3 = Mg_2SiO_4 + C + O_2 \tag{10}$$

where the oxygen is dissolved in the Fe-S-O melt. Whereas Palyanov et al (2007a) showed that when a carbonate component is involved, the role of sulfur may increase due to its important role as a reducing agent, as in the simplified reaction:

$$2FeS + CO_2 = 2FeO + S_2 + C \tag{11}$$

where CO_2 would be a component in a fluid or melt. Shushkanova and Litvin (2006) showed that at 6 GPa sulfide-carbonic melts are highly efficient diamond-forming media, and that formation of diamond polycrystals, reminiscent of natural diamondite and carbonado, can occur from highly C-oversaturated sulfide melts. In experiments in silicate-carbonate-sulfide systems, immiscible carbonate-silicate and sulfide melts form, and diamonds can nucleate and grow from either media (Shushkanova and Litvin 2008), although again the overall low solubility of C in sulfide would make it a less efficient diamond producer than coexisting carbonate.

Although rare, metallic iron, sometimes accompanied by wüstite, has been reported as inclusions in natural diamonds (e.g., Bulanova et al. 1998, 2010; Stachel et al. 1998a). Molten transition metals (e.g., Fe, Ni, Co) have long been noted for their utility as solvents for diamond growth (Bundy et al. 1955; Strong and Hanneman 1967; Sumiya et al. 2000). Given that the oxygen fugacity of the mantle may reach the metal saturation curve as described above, the potential for Fe-rich metallic melts as diamond-forming agents in the mantle is clear. Fedorov et al (2002) studied diamond crystallization from Fe-Ni-C melts and found diamond nucleation and growth at P-T conditions appropriate for the lithosphere. These authors found that either iron (iron-nickel) or wüstite can crystallize together with diamond, depending on the redox conditions, and that iron-carbon melts are stable over a range of f_{O_2} ranging from the stability field of iron to that of wüstite. Siebert et al. (2005) produced diamonds in experiments by reaction between carbonates and highly reducing Si-bearing iron metal phases. Thus, it is clear that metallic melts are excellent catalytic solvents for diamond growth, and if they occur in the mantle could be agents of diamond formation. What is not clear is why metallic iron inclusions would precipitate from liquids in equilibrium with diamond. According to calculated and experimental phase relations in the Fe-C system, there is no stability field for diamond +

Fe metal, as the intermediate carbide phases Fe_3C and Fe_7C_3 are stable throughout the pressure-temperature range of diamond stability in the mantle (Wood 1993; Lord et al. 2009; Nakajima et al. 2009; Oganov et al. 2013; Wood et al. 2013).

Experimental and thermodynamic constraints of growth in the sub-lithospheric mantle

Oxygen fugacity in the sub-lithospheric mantle. A number of studies have proposed that in a vertically isochemical mantle the oxygen fugacity will decrease with increasing pressure as a result of the stabilization of Fe_2O_3 over FeO components in modally abundant mantle minerals (O'Neill et al. 1993b; Ballhaus 1995; Frost et al. 2004; Rohrbach et al. 2007; Frost and McCammon 2008). Experiments that support this stabilization demonstrate high $Fe^{3+}/\Sigma Fe$ ratios in mineral phases from the deep upper mantle, transition zone and lower mantle, even when these minerals are equilibrated with iron metal. Rohrbach et al. (2007), for example, showed that at pressures above 10 GPa majoritic garnet contains over 20% of total Fe in the Fe^{3+} state in equilibrium with Fe metal. Wadsleyite, the main mineral in the transition zone, has been shown to contain about 2% Fe^{3+} at the same f_{O_2} (O'Neill et al. 1993a).

As can be seen in Figure 6a, many of the deepest lithospheric samples are not far displaced from the Fe-Ni precipitation curve where equilibrium with metal would start to occur. Therefore the f_{O_2} of the base of the upper mantle and transition zone are likely to be on average close to the IW oxygen buffer. Frost and McCammon (2008), for example, estimate that for an upper mantle Fe/O content, mantle oxygen fugacity would decrease with depth such that an FeNi-metal alloy would precipitate beginning at depths of about 250 km. Estimates for the bulk $Fe^{3+}/\Sigma Fe$ ratio of the upper mantle are less than 2% (Canil and O'Neill 1996; O'Neill et al. 1993a). In the transition zone where the dominant minerals are wadsleyite and majoritic garnet, the upper mantle Fe^{3+} content would be below that required for these minerals to be in equilibrium with Fe metal. Thus, for a mantle with constant Fe/O, the implication is that another source must produce the additional Fe^{3+} required for these iron-bearing minerals to be in equilibrium with iron metal (O'Neill et al. 1993b; Ballhaus 1995; Rohrbach et al. 2007). The additional source of Fe^{3+} is predicted to be disproportionation of FeO in mineral phases through the reaction:

$$3FeO = Fe_2O_3 + Fe \qquad (12)$$

In the lower mantle the modally predominant mineral is aluminous silicate perovskite, which has an $Fe^{3+}/\Sigma Fe$ content of over 50% when coexisting with metallic Fe (Frost et al. 2004). As in the case of the transition zone, if whole mantle convection occurs and the total oxygen content of the upper mantle is similar to the lower mantle (e.g., constant Fe/O), then metallic Fe-Ni alloy must precipitate in the lower mantle to provide sufficient Fe^{3+} for perovskite (Frost et al. 2004; Frost and McCammon 2008). The f_{O_2} of the lower mantle is therefore also likely to be at or below IW and anomalously large concentrations of Fe_2O_3 would have to arise from somewhere to raise the f_{O_2} above IW. Thus, the deep upper mantle and the entirety of the transition zone and lower mantle are expected to be reducing and metal-saturated.

Carbon speciation in the sub-lithospheric mantle. Several recent experimental studies have indicated that the f_{O_2} of buffering reactions between diamond and magnesite, which are analogs to EMOD in the transition zone and lower mantle rocks, are at approximately the same oxygen fugacity relative to IW as EMOD in the upper mantle (Rohrbach and Schmidt 2011; Stagno et al. 2011). For example, the reaction,

$$MgO + C + O_2 = MgCO_3 \qquad (13)$$

is the analog buffering reaction to EMOD throughout the lower mantle and lies between two and three log units above IW. Therefore, given no large perturbation in the bulk oxygen content, the deeper mantle should be in the diamond stability field.

On the basis of calculations of carbon speciation in the C-O-H system like those shown in Figure 6, the deep upper mantle, transition zone, and possibly the uppermost lower mantle could be in equilibrium with a CH_4-H_2O fluid, whereas in the deeper lower mantle equilibrium fluids may become H_2O-dominated (Frost and McCammon 2008). We stress again that such a fluid is calculated without consideration of equilibrium with silicate minerals, and with gross extrapolation of thermodynamic data. Experiments and first-principles calculations are needed to identify and quantify carbon species in more realistic deep mantle fluids and melts (e.g., Dasgupta 2013; Manning et al. 2013).

Diamond formation in the sub-lithospheric mantle. As described in the preceding sections, over much of its depth range, sub-lithospheric mantle is metal-saturated. If a free fluid phase were present in this reducing primitive mantle peridotite, calculations suggest it will be CH_4 and H_2O-rich. However, given the high-storage capacity of the deep upper mantle and transition zone for hydrogen (e.g., Hirschmann et al. 2009), a free fluid phase likely is not present, and carbon may be locked up in solid Fe(Ni) carbides and diamond. Given the low estimates for the C content of the primitive mantle (~50 to 200 ppm), carbides such as Fe_3C and Fe_7C_3 that are stable along a mantle adiabat (Wood 1993; Lord et al. 2009; Nakajima et al. 2009; Wood et al. 2013) can accommodate the entire primitive mantle carbon budget. Thus, in ambient primitive sub-lithospheric mantle, diamond may not be present.

We expect that, in general, sub-lithospheric diamonds likely formed by metasomatic processes involving reducing ambient mantle with C-bearing fluids or melts. In common with the lithospheric mantle, diamond crystallization may occur predominantly as a result of redox equilibria between a metasomatic melt and solid mantle phases. Mineral inclusions in sub-lithospheric diamonds, such as majorite, Ca-rich perovskite, and Mg-rich perovskite, provide evidence for diamond formation at depths throughout the deep upper mantle, transition, and the upper part of the lower mantle (see Stachel 2005; Harte 2010). An important goal of future research will be to link sub-lithospheric inclusion mineralogy and trace element composition to diamond fluid composition, deep mantle melt migration, and mantle redox in a way that can be related to mantle convection patterns (e.g., Walter et al. 2008).

Stable isotopic compositions and the formation of diamonds

C-isotopes of diamonds. More than four thousand carbon isotopic compositions on diamonds are available, including representative data from worldwide diamond mines including Siberia; Canada; Australia; Brazil; and West, East, and southern Africa (Botswana and South Africa), as well as diamonds formed in other usually less constrained contexts. Historically, these data stem from the combustion analyses of diamonds (e.g., Deines 1980; Galimov 1985; Cartigny et al. 2001; Cartigny 2005) but these bulk analyses are being rapidly augmented by somewhat less precise, *in situ* analyses made by SIMS (e.g., Hauri et al. 2002).

The distribution of $\delta^{13}C$-values of diamonds formed in Earth's mantle (Fig. 7) are usually divided into distinct diamond populations on the basis of several factors: (1) their eclogitic versus peridotitic paragenesis as inferred from their inclusions, (2) their relative crystallization ages as inferred by younger, often kimberlite-age fibrous coats of coated diamonds grown upon older, typically Archean and Proterozoic monocrystalline diamond cores, (3) their depth of origin in the lithosphere, transition zone or lower mantle as inferred from their inclusions, and (4) their morphology as monocrystalline versus polycrystalline aggregates (including boart, framesites), the latter whose formation age might be closely related to the kimberlite eruption age (e.g., Heaney et al. 2005). In addition, $\delta^{13}C$ values have been measured on (5) polycrystalline, sintered diamonds known as carbonado (Jeynes 1978), whose extra-terrestrial, mantle or crustal origin is unclear (see Cartigny 2010, and references therein), and (6) microdiamonds (typically < 500 microns) formed in crustal rocks subducted to pressures greater than 3.5 GPa along a cold, crustal geotherms. These latter two groups are considered petrogenetically distinct and will be discussed separately.

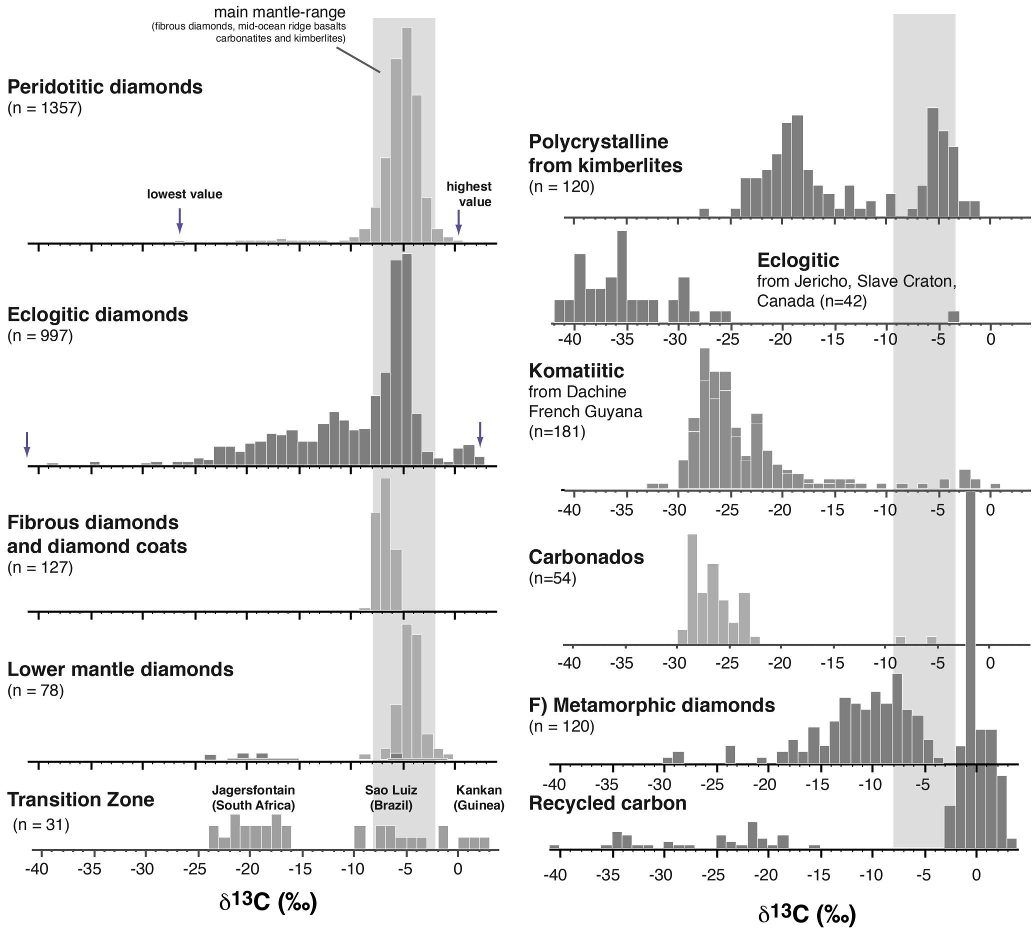


Figure 7. Carbon isotope distributions of worldwide diamonds from a different types of occurrences (e.g., see Fig. 3). Widely-studied peridotitic and eclogitic lithospheric diamonds (upper left) are compared to superdeep and coated diamonds as well as other diamond types. Monocrystalline diamonds unusual in their low $\delta^{13}C$ are represented by eclogitic diamonds from Jericho and diamonds (unknown paragenesis) from the Dachine metakomatiite or metalamprophyre. Polycrystalline diamonds, metamorphic UHP diamonds and carbonado diamonds whose origin remains unknown are also compared. The "main mantle range" defined by fibrous diamonds (i.e., kimberlite-related, see text for details), carbonatites, and carbonates from kimberlites. For references see Cartigny (2005, 2010).

Figure 7 is a summary diagram of the worldwide data set for the C isotopic composition of diamond. Several key points are clear from the distributions seen:

- Worldwide samples cover a large carbon isotopic composition ($\delta^{13}C$) ranging from −41 to +5‰, a range close to that displayed by sedimentary rocks.
- Approximately 72% are contained within a narrower interval of −8 to −2‰, centered on a value approximately −5 ± 1‰. This range is similar to the range displayed by other mantle-derived rocks such as mid-ocean ridge basalts, ocean island basalts, carbonatites, kimberlites.
- The distribution is continuous with a clear decrease in frequency on either side of a $\delta^{13}C$-value of about −5‰.
- The $\delta^{13}C$-distributions are significantly different between their respective growth environments. Peridotitic diamonds cover a narrower range of $\delta^{13}C$-values (from −26.4 to +0.2 ‰), than eclogitic diamonds (from −41.3 to +2.7‰), whilst both coated and lower mantle peridotitic diamonds show narrow ranges of values (−8.1 to −4.9‰) and (−8.5 to −0.5‰), respectively.
- Deep (from transition zone and lower mantle) eclogitic diamonds have variable abundances of negative or positive $\delta^{13}C$-values, (here defined as being below −10‰)
- Diamond formed in metamorphic rocks subducted at ultra-high pressures have $\delta^{13}C$-values ranging from −30 to −3‰, whereas carbonados are mostly from −32 to −25 ‰ and up to −5‰.

Individual mines commonly display $\delta^{13}C$-distributions similar to those illustrated by the worldwide distributions in that their peridotitic diamonds have the typical uni-modal, mantle-like C isotopic distribution and their eclogitic diamonds despite showing nearly the same mode show a strong negative skewness (Fig. 7). However there are several striking exceptions where unique uni-modal eclogitic compositions centered outside the typical mantle-like C values occur: $\delta^{13}C$ of −35‰ for the Jericho kimberlitic diamonds, Slave craton Canada (Fig. 7; De Stefano et al. 2009; Smart et al. 2011); $\delta^{13}C$ of −27‰ for the Dachine lamprophyric or komatiitic diamonds, French Guyana (Fig. 7; Cartigny 2010; Smith et al. 2012); $\delta^{13}C$ of −15‰ for the Guaniamo kimberlitic diamonds, Venezuela (Galimov et al. 1999; Kaminsky et al. 2000), $\delta^{13}C$ of −11‰ for the Argyle lamproitic diamonds, western Australia (Jaques et al. 1989) and $\delta^{13}C$ of +2‰ for placer diamonds from New South Wales, eastern Australia (Sobolev 1984). Rare peridotitic diamonds analyzed so far from these sources show typical mantle $\delta^{13}C$-values of around −5‰. Other localities such as Orapa, Botswana and Jagersfontain, South Africa (Deines et al. 1991, 1993) show a strong bimodal $\delta^{13}C$-distribution with a first peak at about −5‰ and a second at about −20‰ in both peridotitic and eclogitic diamonds. The important question of whether these carbon isotopic compositions are primordial, reflect mantle carbon, or are evidence for subducted carbon depends on the how C isotopic compositions fractionate and evolve in mantle fluids as they migrate through the mantle and diamonds crystallize.

Diamond C-isotopic variability, speciation of carbon, and carbon sources. *In-situ* analyses of single diamonds usually display a limited range ~3‰, which is more isotopically homogeneous in C-isotope composition than the range of all diamonds from the same mine. The trends in C-isotope composition with other tracers, such as N-content and N-isotopic composition, recorded either within a single diamond or within a diamond population, can help in elucidating the speciation (oxidized versus reduced) of carbon in the fluid/melt associated with diamond precipitation (Deines 1980; Thomassot et al. 2007). Carbon isotopic composition is sensitive to f_{O_2} because the reduced carbon in a diamond is depleted in ^{13}C, at isotope equilibrium, by 2-3‰ at T ~1000 °C compared to oxidized carbon (CO_2, carbonate). In comparison, diamond in equilibrium with a more reduced form of carbon such as methane is enriched in ^{13}C by about 1‰. The exact magnitude of isotope fractionation between diamond and coexisting fluid relies on theoretical calculations and experimental data (e.g., Deines 1980; Deines and Eggler 2009; Mysen et al. 2009), whose constraints on isotopic exchange are limited, at present, in temperature, pressure, and composition. Even with these uncertainties, there is no doubt that isotopic fractionation occurs as diamonds grow from fluids (see discussion in Thomassot et al. 2007; Smart et al. 2009) and must be considered in addition to C isotopic differences inherited from C sources.

Diamonds can form from reduced (methane; Eqn. 2) or oxidized (CO_2, carbonate; Eqns. 1, 9-12) carbon (e.g., Stachel and Harris 2009). A diamond or a diamond population displaying a histogram of δ^{13}C-distribution with negative skewness from the mean mantle value and a linear relationship between δ^{13}C and logarithmic values of diamond N-contents has been suggested to be formed from methane (Fig. 8; Cartigny et al. 2001; Stachel and Harris 2009). The occurrence of CO_2 inclusions (Schrauder and Navon 1993) particularly in some eclogitic diamonds (Chinn et al. 1995; Cartigny et al. 1998), the occurrence of metasomatic inclusions (Leost et al. 2003), positive skewness of some peridotitic δ^{13}C distributions (Stachel and Harris 2009), and δ^{13}C-N relationships in core-rim traverses of individual diamonds (Bulanova et al. 2002; Smart et al. 2011) provide evidence for diamond precipitation from oxidized carbon. Further evidence for formation from oxidized carbon is found in the fibrous coats of coated diamonds, which trap mantle fluids bearing carbonate nano-inclusions (Navon et al. 1988; see also Klein-BenDavid et al. 2010 and references therein). Even though fibrous diamonds often are homogeneous (typically 3‰; Cartigny et al. 2003) they can also document, sometimes within single growth zones, a consistent increase of 3‰ in δ^{13}C-range starting from a value near −8 up to −5‰ (e.g., Boyd et al. 1992; Klein-BenDavid et al. 2010; and references therein). These observations are again consistent with precipitation from oxidized carbon. It is worth noting, however, that in most cases, and especially for sub-lithospheric diamonds, this direct inference cannot be made. In this case, additional tracers are needed to better characterize the proportion of diamond precipitating from reduced/oxidized carbon.

Diamond crystallization alone from its source melt/fluid seems unlikely to account for the largest range in δ^{13}C values of diamonds, because otherwise eclogitic and peridotitic diamonds

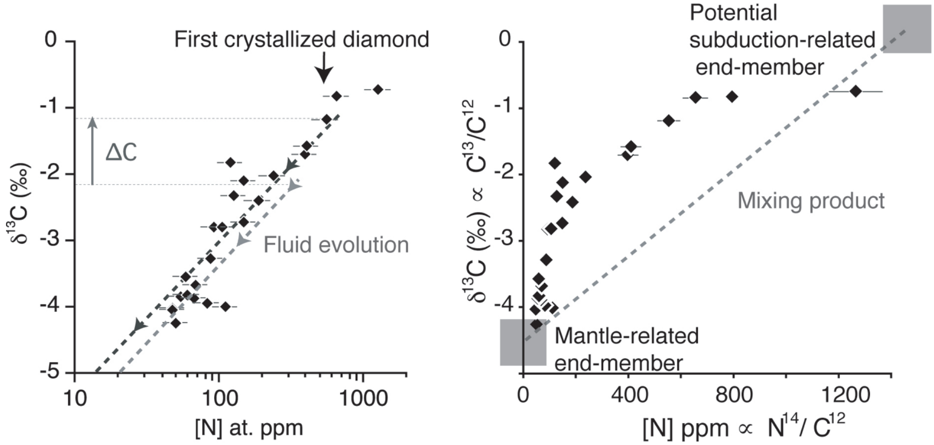


Figure 8. An illustration of the δ^{13}C-N variability that can be produced during the crystallization of diamonds in a natural lithospheric peridotite. The trends are modeled to record diamond growth from methane of multiple diamonds that all found in the same xenolith. Each data point represents a single diamond. [Adapted with permission of Elsevier from Thomassot et al. (2007), *Earth Planet Sci Lett*, Vol. 257, Figs. 2,3, p. 366.]

would display similar distributions. This fundamental observation is the basis for suggesting that diamond growth can be a recorder of mantle $\delta^{13}C$-variability (Javoy et al. 1986; Galimov 1991) by being inherited from various mantle sources. There are two schools of thought. Following the early suggestion of Deines et al. (1993) that diamond would record primordial isotopic heterogeneity, the occurrence of primordial carbon has been suggested for a few diamonds from Kankan, that have a $\delta^{13}C$ value close to −3.5‰ (i.e., being neither isotopically heterogeneous nor depleted in the ^{13}C-isotope; Palot et al. 2012). While the existence of primordial mantle carbon reservoirs can explain the general range of diamond $\delta^{13}C$ (e.g., Haggerty 1999), it still fails to account for the distinct $\delta^{13}C$-distributions among the general population of eclogitic and peridotitic diamonds. The alternative, non-exclusive interpretation is that mantle $\delta^{13}C$-variability recorded in diamonds (i.e., primarily eclogitic) reflects the persistence of isotope variability resulting from the subduction of sedimentary carbon (e.g., Sobolev and Sobolev 1980). The basaltic crust of the oceanic lithosphere contains considerable organic carbon, which is isotopically light (low) in its $\delta^{13}C$ composition. The oceanic lithosphere also is hydrothermally altered and takes on anomalous compositions in $\delta^{18}O$. Subduction of this material and its conversion to eclogite, a common and ongoing geological process, can account for both the anomalous $\delta^{13}C$ of diamonds and $\delta^{18}O$ of eclogite xenoliths in kimberlite. The possibility that diamond might form from subducted carbon is usually also addressed from the study of diamond structural impurities and mineral inclusions.

A contribution to the differences in eclogitic and peridotitic $\delta^{13}C$ isotope distributions also could result from distinctly different evolution of oxidized-C-bearing fluids in eclogite versus peridotite (Cartigny et al. 1998, 2001). Differences in evolution are due to differences in fluid H_2O/CO_2-ratio and the extent of decarbonation reactions in olivine-free eclogitic compositions. Because carbonate decarbonation is associated with $^{13}C/^{12}C$ fractionation (CO_2 being ^{13}C-enriched) this additional process can increase C-isotope variability found in eclogitic diamonds. Although this model is based on the previous experimental work (Luth 1993; Knoche et al. 1999) and finds increasing support (e.g., Stachel and Harris 2009), it is worth noting that it relies on a limited series of experiments. In particular, experiments involving methane are still lacking. Future work is likely to highlight new reactions that might be relevant to better understand eclogitic diamond formation.

Nitrogen in diamonds: contents, speciation, and isotopic composition. Interest in studying N-isotopes in diamonds originates from the original identification that mantle nitrogen is deprived in the ^{15}N isotope compared to surface reservoirs such as the atmosphere (0‰) and the crust and its sediments, which are enriched in ^{15}N (Javoy et al. 1984). This view has since been supported by a wealth of data (Fig. 9). Analysis of fibrous diamonds, mid-ocean ridge basalts, and older mantle derived-samples such as peridotitic diamonds that show predominantly negative $\delta^{15}N$ values. In contrast, metasediments show enrichment the ^{15}N-isotope (positive $\delta^{15}N$) both in the present and the Archean; the amount of negative $\delta^{15}N$ values in sediments is very rare (as reviewed by Thomazo et al. 2009). Furthermore, during sediment subduction, if any devolatilization occurs it would preferentially release ^{14}N, leaving a further ^{15}N-enriched subducted material (Bebout and Fogel 1992; Busigny et al. 2003) as shown by data on metamorphic diamonds (Cartigny et al. 2004 and references therein). Although a limited dataset is available, altered ocean crust and oceanic lithosphere also display positive $\delta^{15}N$ (Philippot et al. 2007; Busigny et al. 2011). Nitrogen in sedimentary/crustal rocks occurs as ammonium ions substituting for potassium and therefore the behavior of nitrogen in subduction zones is expected to follow the fate of potassic minerals, some of which have been experimentally demonstrated to be stable to mantle depths (Watenphul et al. 2009, 2010). If eclogitic diamonds form from subducted carbon and nitrogen, they would be predicted to display positive $\delta^{15}N$-values, as seen in subducted metamorphic rocks (i.e., values distinctly higher than a homogeneous mantle with $\delta^{15}N$ isotopic composition near −5‰). This is certainly

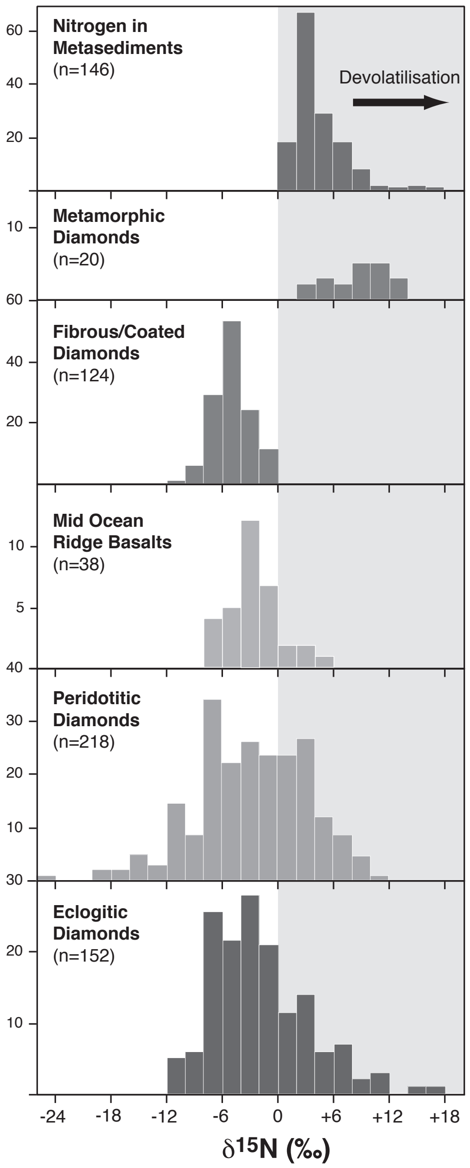


Figure 9. The rationale in using the $^{15}N/^{14}N$-values in diamonds lies in the distinct distributions displayed by surface and mantle reservoirs. Nitrogen in metasedimentary and metamorphic diamonds, metagabbros and metaophioloites (not shown) being enriched in ^{15}N compared to the mantle shown here by fibrous/coated diamond, mid-ocean ridge basalts (not shown) and peridotitic diamonds. The similarities of the $^{15}N/^{14}N$-distributions of eclogitic and peridotitic diamonds must be explained if the source of carbon and nitrogen in eclogitic diamond is to be largely related to subduction (see text for discussion). From Cartigny (2005).

the case for most of the deep diamonds from the mantle transition zone such as at Jagersfontein, South Africa and the Sao Luis-Juina fields, Brazil (Tappert et al. 2005a; Palot et al. 2012) and possibly at Dachine, French Guyana (Cartigny 2010; Smith et al. 2012). But many eclogitic diamonds worldwide show a $\delta^{15}N$-distribution similar to most peridotitic diamonds, pointing to a mantle origin of their nitrogen and therefore of their carbon (Fig. 9). About half of eclogitic diamonds with low-$\delta^{13}C$ values also show negative $\delta^{15}N$-values. These $\delta^{13}C$-$\delta^{15}N$-N co-variations have been argued to be inconsistent with simple mixing of subduction components (see Cartigny 2005 for review) and the data thus have been interpreted to reflect decarbonation reactions occurring in eclogites. However, the remarkably low-$\delta^{15}N$ compositions of the peridotitic diamonds from Pipe 50, China (Cartigny et al. 1997) suggests that variability in the N isotopic composition of mantle exists, and might mask the straightforward assignment of a positive $\delta^{15}N$ to recycled components involved in diamond formation. With a heterogeneous mantle, the $\delta^{13}C$-$\delta^{15}N$ mixing relationships become more complex. Evidence for subduction is clear from many studies: sulfur isotope of sulfide inclusions, oxygen isotopes of eclogitic silicate inclusions and eclogite nodules, and geological considerations. But subduction seems to require some decoupling of carbon from other elements, like N. This view can be reconciled by metasomatic processes during diamond formation. But it remains unclear, if carbon is a massively cycled element, why the presence of low $\delta^{13}C$ for recycled carbon in eclogitic diamonds remains rarer than the normal mantle-like $\delta^{13}C$. Perhaps the amount of C recycled form the mantle portion of the slab which should have $\delta^{13}C$ near –5‰ has been underestimated.

INCLUSIONS HOSTED IN DIAMONDS

Thermobarometry

Chemical thermobarometry. Chemical thermobarometers are expressions that allow one to retrieve the temperature (or pressure) of formation of a mineral species or mineral assemblage knowing the chemical compositions of the minerals and how these compositions are expected to vary with P (or T) of formation. In principle, thermobarometers are based on chemical equilibria between at least two mineral species, but approximate formulations can sometimes be devised that consider the composition of a single mineral, which is assumed to be in equilibrium with another phase capable of buffering its composition under certain P and T. Single-mineral thermobarometers are particularly useful for diamond studies, inasmuch as (1) most inclusions in diamonds are made of isolated mineral grains, (2) non-touching mineral grains included in the same diamond may have been incorporated at different times and P-T conditions and thus may not have been in equilibrium, and (3) polymineralic inclusions made of touching mineral grains presumably had enough time to re-equilibrate at depth after diamond formation during long-standing storage in the mantle. Single-mineral thermobarometry of monomineralic inclusions will provide an indication of the P-T of formation of the diamond, provided the inclusions are syngenetic, or had time to re-equilibrate completely during diamond-forming processes, and did not undergo any transformation afterwards. In contrast, two-mineral thermobarometry of touching inclusions may not necessarily provide the temperature of diamond formation, although the pressure estimate will still provide an indication of the depth of provenance of the diamond.

The reader is referred to Stachel and Harris (2008) for a review of P-T estimates for lithospheric diamonds based on single- and two-mineral thermobarometry of their inclusions. Estimates for over one thousand stones indicate that lithospheric diamonds can form at any depth within the appropriate P-T conditions for diamond stability, with a temperature mode around 1150-1200 °C. Rather than reflecting a favored condition for diamond formation, this mode may simply represent the most "probable" temperature range within the limits imposed by diamond stability, depth of the lithosphere and mantle adiabat under typical cratonic thermal regimes.

The reliability of some of the thermometers used by Stachel and Harris (2008) and by many previous workers, particularly those based on Fe-Mg exchange reactions between garnet and orthopyroxene, clinopyroxene or olivine, and the popular two-pyroxene thermometer of Brey and Köhler (1990), is questionable (Nimis and Grütter 2010). The accuracy of the widely used Opx-Grt barometers at $P > 5$ GPa and for orthopyroxenes with excess Na over Cr + Ti (i.e., about 13% of reported Opx inclusions) also remains to be explored in detail (Carswell et al. 1991; Nimis and Grütter 2012). In particularly unfavorable cases, errors can exceed 150-200 °C and 1.5 GPa (i.e., 45 km in estimated depth). Especially at a local scale and for specific inclusion populations, these errors may obscure possible heterogeneities in the vertical distribution of diamonds. Thermobarometry of eclogitic inclusions remains particularly problematic, because Fe-Mg exchange thermometry of Grt-Cpx pairs is affected by large uncertainties (at least ±100 °C), mostly owing to Fe^{3+} problems (Krogh Ravna and Paquin 2003), and fully satisfactory, well-tested barometers are not yet available (Fig. 10).

It is also worth noting that in some diamond suites non-touching inclusions apparently yield hotter conditions than touching inclusions and xenoliths from the same kimberlite (e.g., Meyer and Tsai 1976; Stachel et al. 1998b; Viljoen et al. 1999; Phillips et al. 2004) and that no relationship occurs between the non-touching inclusion temperatures and those deduced from the N-aggregation state of the diamond. This result suggests diamond formation during transient thermal perturbations, secular cooling of the lithosphere after diamond formation or, simply, disequilibrium. In many other cases, however, no discrepancy exists (Hervig et al.

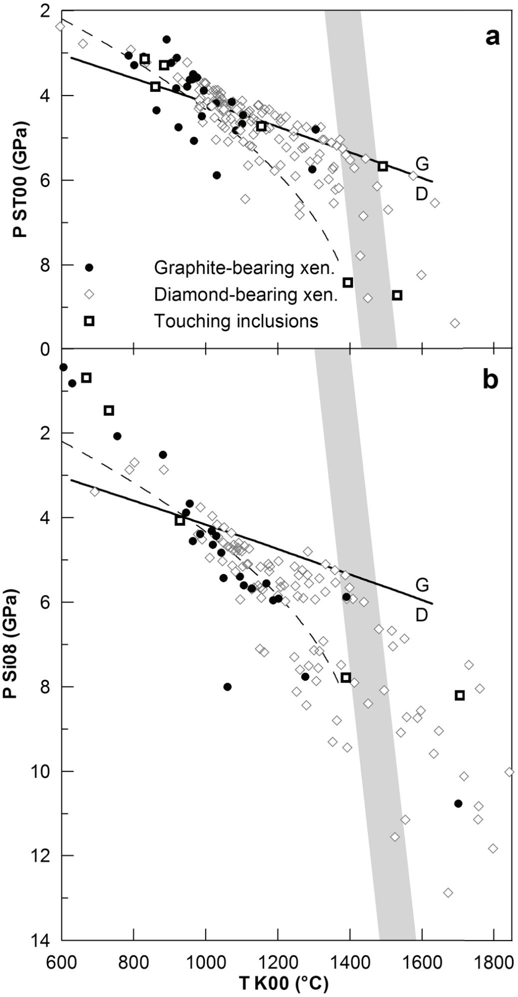


Figure 10. *P-T* estimates for eclogitic xenoliths and touching Grt-Cpx pairs included in eclogitic diamonds using a combination of the Fe-Mg exchange thermometer (K00; Krogh Ravna 2000) with two different versions of the Grt-Cpx barometer (ST00: Simakov and Taylor 2000; Si08: Simakov 2008). Both combinations produce a substantial overlap of diamond-bearing and graphite-bearing eclogites, a significant proportion of diamond-bearing samples in the graphite stability field, and variable proportions of excessive *T* and *P* values (much greater than expected for majorite-poor garnets), suggesting poor reliability of eclogite thermobarometry. Dashed line: conductive geotherms for a surface heat flow of 40 mW/m^2 after Pollack and Chapman (1977); black solid line: graphite-diamond boundary after Day (2012); grey band: *T* range for mantle adiabat based on mantle potential temperatures of 1300 to 1400 °C.

1980; Sobolev et al. 1997; Nimis 2002), suggesting that diamond-forming fluids were thermally equilibrated with the ambient mantle. This result implies that the lithospheric mantle had already cooled to a conductive thermal regime billions of years ago when the diamonds formed and that this thermal regime was comparable to that recorded in mantle xenoliths erupted during emplacement of the much younger host kimberlite (e.g., Cretaceous in the case of the Kaapvaal and Slave cratons). The possibility that these inclusions are all protogenetic and did not re-equilibrate completely during diamond crystallization should also be considered.

In view of the above complications, in the present review particular emphasis is placed on the results of single-mineral thermobarometry on monomineralic inclusions, because they have the best potential to reflect the true *P-T* conditions of diamond formation. Considering the wide range of pressures and temperatures under which diamonds may form, the potentially large influence of input *P* on *T* estimates (and vice versa), and the possible formation of diamond under perturbed or ancient thermal conditions, the most useful mineral species will be those that demonstrably allow sufficiently accurate retrieval of both *P* and *T* of formation. At present, the choice is restricted to diopsides belonging to the ultramafic paragenesis that can be assumed to be in equilibrium with garnet and orthopyroxene and allow application of the Cr-in-Cpx barometer and enstatite-in-Cpx thermometer of Nimis and Taylor (2000; Fig. 11a). Thermal re-equilibration of Cpx with Grt alone (± olivine) causes negligible effects on *P-T* estimates; therefore Cpx + Grt ± olivine polymineralic inclusions should provide the same information as monomineralic Cpx inclusions (Nimis 2002). The enstatite-in-Cpx thermometer has proved to be a very robust method (Nimis and Grütter 2010). The Cr-in-Cpx barometer has two limitations: first, tests against experiments indicated progressive underestimation at $P > 4.5$ GPa (up to ca. −0.8 GPa at $P = 7$ GPa; Nimis 2002); second, typical analytical uncertainties may propagate large errors for Cpx with low values of $a\mathrm{Cr} = \mathrm{Cr} - 0.81 \cdot \mathrm{Na} \cdot \mathrm{Cr}/(\mathrm{Cr} + \mathrm{Al})$ (atoms per formula unit), which is the main building block in the barometer formulation. Standard analytical conditions may result in errors exceeding 1-2 GPa for compositions with $a\mathrm{Cr} < 0.005$ (i.e., for about 10% of reported diopside inclusions). This error accounts well for the larger overall scatter in *P-T* points for inclusions using single-Cpx thermobarometry compared with Opx-Grt thermobarometry (Fig. 11a). Filtered *P-T* estimates confirm the mode around 1150-1200 °C, the distribution of most *P-T* values along typical cratonic geotherms, and the existence of a few "hot" inclusions approaching the mantle adiabat (Fig. 11a). Systematic shift of most

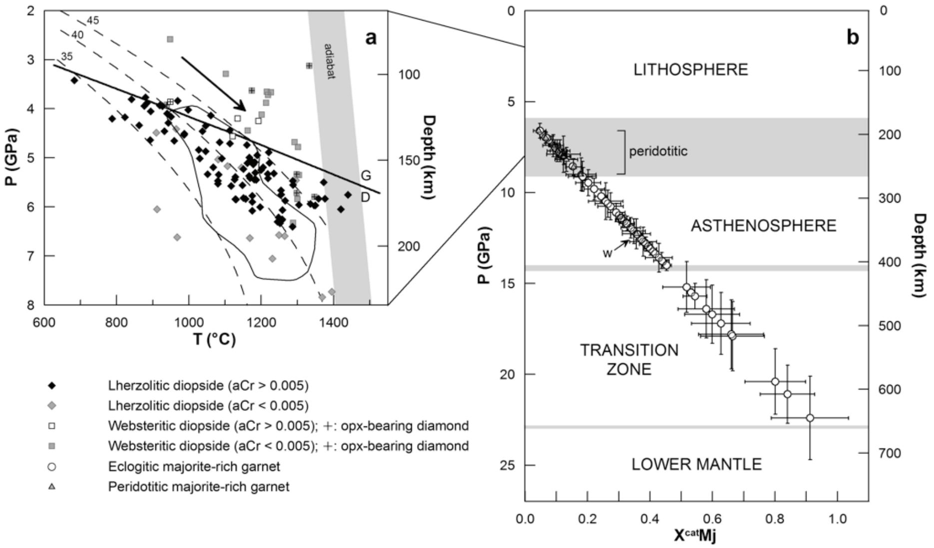


Figure 11. (a) *P-T* estimates for lherzolitic and websteritic Cpx inclusions (monomineralic and Opx-free polymineralic inclusions) in worldwide diamonds based on single-Cpx thermobarometry (Nimis and Taylor 2000). The estimates should correspond to the conditions of formation of the diamonds, with some *P* underestimation at $P > 4.5$ GPa. The scatter is considerably reduced if one excludes diopsides with aCr < 0.005, for which *P* estimates can be severely in error (see text for further explanation). Inclusions in websteritic diamonds containing also non-touching Opx inclusions are indicated with crossed-symbols. For all other websteritic inclusions equilibrium with Opx is not proved and *T* (and hence *P*) estimates may be strongly underestimated; the arrow shows the effect of an increase of *T* on calculated *P*. Outlined field encompasses *P-T* estimates for touching and non-touching inclusions from worldwide sources based on Opx-Grt thermobarometry (Harley 1984; Brey and Koehler 1990) after Stachel and Harris (2008). Conductive geotherms for different surface heat flows (mW/m^2) after Pollack and Chapman (1977); graphite-diamond boundary after Day (2012). *T* range for mantle adiabat is based on mantle potential temperatures of 1300 to 1400 °C. (b) Relationships between molar fraction of majoritic components and *P* for isolated inclusions of majorite-rich Grt in worldwide diamonds based on majorite barometry (Collerson et al. 2010). Bracket indicates *P* range for non-wehrlitic peridotitic inclusions.

websteritic diopsides to lower *P* may be due to *T* underestimation owing to absence of Opx in the original assemblage or to poor reliability of the Cr-in-Cpx barometer for very low-Cr# compositions—the barometer calibration only included diopsides with Cr# = 0.09-0.44 (Nimis and Taylor 2000).

Majorite-rich garnet inclusions allow retrieval of *P* from the fraction of majoritic component (Collerson et al. 2010). Although *T* remains undetermined, the majorite barometer appears to be thermally and compositionally robust, thus allowing the minimum pressure of formation to be estimated. Even allowing for generous uncertainties, the results for isolated monomineralic inclusions indicate beyond any doubt that diamonds containing majoritic garnet could form at very great depth (Fig. 11b). Ranges of possible temperatures of formation may vary over several hundred °C, depending on the interpreted formational setting: <1200 °C for eclogitic diamonds formed in a subducting slab (Stachel et al. 2005), about 1250-1400 °C for peridotitic diamonds formed in a deep lithosphere (Pokhilenko et al. 2004), >1400 °C for diamonds formed in ascending mantle plumes (Davies et al. 2004; Bulanova et al. 2010). Although the abundance of diamonds with majorite-rich garnet inclusions decreases with increasing *P*, existing estimates indicate a more or less continuous spreading from the deep lithosphere to the deep transition zone (Fig. 11b). Such distribution supports a potential genetic link between many majoritic garnet-bearing diamonds and the rare super-deep diamonds with inclusions of interpreted lower-mantle origin (Stachel et al. 2005; Tappert et al. 2009; Walter et al. 2011). Harte (2010) cautioned that many of the relatively low-*P* majoritic inclusions may originally have formed at much greater depth. If they formed in a clinopyroxene-poor medium, the pyroxene can be consumed by dilution into the garnet with no further change in composition recorded with increasing depth. Furthermore, slow rise of the diamond during mantle upwelling may lead to subsolidus re-equilibration of the inclusion (e.g., clinopyroxene exsolution) to lower *P* (Harte and Cayzer 2007). Although special care is given when investigating the chemical composition of diamond inclusions, the possibility that cryptic exsolution has been overlooked in some of these inclusions should be considered.

Elastic methods for geobarometry of diamonds. Elastic methods provide a potential, generally non-destructive alternative to chemical thermobarometry for the evaluation of the pressure of formation of a diamond containing a monomineralic inclusion. These methods are based on the measurement of the "internal pressure" (hereafter P_i and also called "residual" or "remnant" pressure), that is the pressure exerted by the diamond on the inclusion when the diamond-inclusion pair is at room *P-T*. Such pressure can be retreived by using three different techniques: (1) microRaman spectroscopy (e.g., Izraeli et al. 1999; Sobolev et al. 2000; Nasdala et al. 2003; Barron et al. 2008); (2) strain birefringence analysis (Howell et al. 2010), and (3) single-crystal X-ray diffraction (Harris et al. 1970; Nestola et al. 2012). Combining the P_i with data on the thermoelastic parameters (i.e., volume bulk modulus and its pressure and temperature derivatives, volume thermal expansion, shear modulus) of the diamond and of the inclusion allows one to calculate an "isomeke", i.e., a curve in *P-T* space along which the volume of the inclusion is equal to the volume of the cavity within the diamond for a fixed value of P_i. Such line constrains the possible conditions under which the diamond and the inclusion formed. If *T* is known independently, e.g., from FTIR data, or the isomeke is not strongly dependent on *T*, then the *P* at the time of encapsulation of the inclusion can be determined.

Available estimates of the pressure of formation for coesite inclusions based on P_i data are generally much too low for diamond stability (Fig. 12). On the whole, *P* estimates for olivine are more acceptable, but they still straddle the graphite-diamond boundary, indicating again some *P* underestimation at least for some samples (Fig. 12). The limited success of elastic methods thus far indicates that either the diamonds did not behave in a solely elastic fashion or that thermoelastic data for the minerals are inaccurate (see the recent review by Howell et al. 2012). The potential applicability of elastic methods to inclusions of important minerals for which

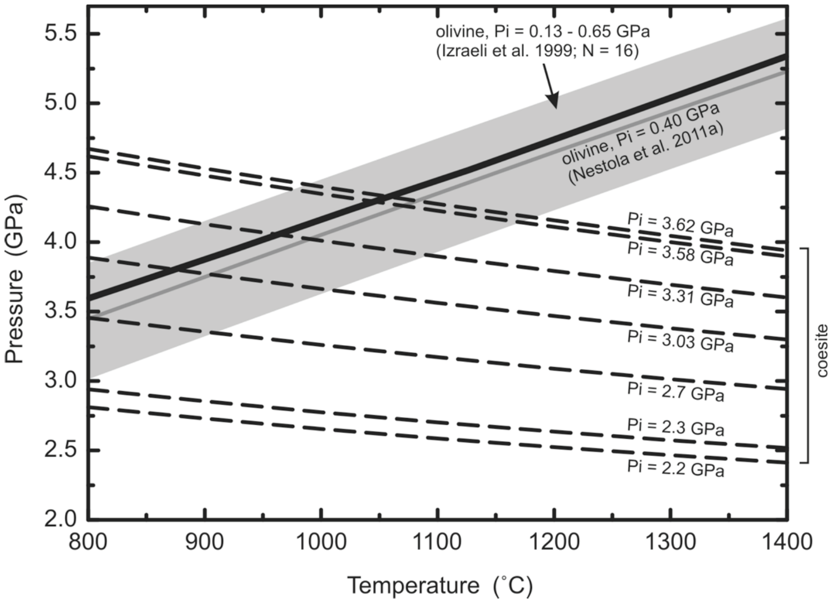


Figure 12. Isomekes for inclusions in diamonds based on P_i estimates (see text for details) obtained using different techniques and thermoelastic parameters as in Howell et al. (2010). Sources of P_i data: olivine - Izraeli et al. (1999; Raman, grey band), Nestola et al. (2011; X-ray diffraction, grey line); coesite - Sobolev et al. (2000; Raman), Nasdala et al. (2003; Raman), Barron et al. (2008; Raman), Howell et al. (2010; birefringence analysis). Black solid line: graphite-diamond boundary after Day (2012).

single-mineral chemical barometers do not exist (e.g., olivine, chromite, coesite) makes these methods worthy of further testing. However, re-assessment of thermoelastic parameters for the minerals included in diamond using state-of-the-art techniques and equipment is necessary before these methods can be considered trustworthy.

Geochemistry and age

Syngenesis or protogenesis? Mineral inclusions can be classified as protogenetic, syngenetic, or epigenetic according to the timing of their crystallization (earlier, contemporaneous, or later) with respect to that of their diamond host (Meyer 1987). Inclusions forming along fractures or made of alteration minerals after former syn- or protogenetic inclusions can be identified as epigenetic. Discrimination of syngenetic and protogenetic inclusions is less straightforward. Such distinction is important, because in the case of syngenesis any geological information extracted from the inclusion (e.g., *P*-*T* of formation, geochemical environment, age) would also unequivocally apply to its host diamond. A protogenetic inclusion would record conditions that existed before its encapsulation but this might range from geologically short to very long timescales. In the latter case a protogenetic inclusion could be unrelated to diamond formation. Demonstrably protogenetic inclusions would support models of diamond formation involving fluxes of C-bearing fluids through pre-existing mantle rocks and could help explain occurrences of isotopically different inclusions in the same generation of diamond (e.g., Thomassot et al. 2009). In cases of protogenicity, although absolutely accurate ages of diamond formation would not be obtained from the inclusions, a maximum age would be obtained and a general age pattern of diamond growth in a region of lithospheric mantle might still be evident (see section on "*Age systematics and isotopic compositions*").

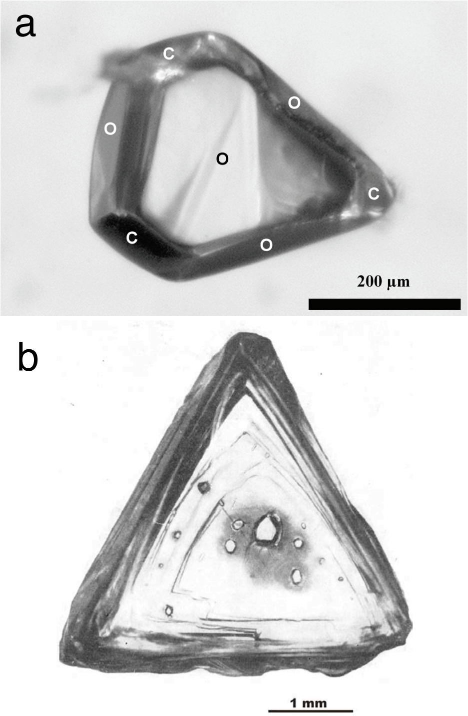


Figure 13. (a) Inclusion of olivine in diamond showing diamond-imposed, flattened cubo-octahedral habit (modified from Nestola et al. 2011). Faces of the dominant octahedral (o) and cubic (c) forms are indicated. (b) Diamond macle (twinned and flattened) with a number of olivine inclusions having major faces parallel to the octahedral diamond face (modified from Sobolev et al. 1972).

The most commonly used proof of syngenesis is the imposition of the morphology of the diamond on the inclusion (Fig. 13; e.g., Harris 1968; Sobolev et al. 1969, 1972; Sobolev 1977; Harris and Gurney 1979; Meyer 1985, 1987; Pearson and Shirey 1999; Sobolev et al. 2009). Compositional consistency with associated mineral inclusions is another important criterion as, for example, in the syngenetic low-Si mica inclusions that are documented in peridotite (U/P-type) and eclogitic (E-type) diamonds as phlogopite and biotite, respectively (Sobolev et al. 2009). The recognition of several inclusions of harzburgitic garnet with diamond-imposed morphology having trace element compositions indicative of multistage geochemical evolution has challenged the morphology criterion (Taylor et al. 2003). The observation that in many cases diamond growth zones, as revealed by cathodoluminescence studies, do not wrap around the inclusions is consistent with, although it does not prove, syngenesis (Bulanova 1995). An epitaxial relationship between an inclusion and its host would represent a more robust proof of syngenicity (e.g., Futergendler and Frank-Kamenetsky 1961; Harris 1968; Harris and Gurney 1979; Wiggers de Vries et al. 2011). Although some apparently recurrent crystallographic orientations with potential epitaxial significance have been found for some inclusions, such orientations are rarely determined and a systematic survey for the different mineral species is lacking or has been restricted to limited sets of samples (see review in Harris and Gurney 1979).

A more recent approach to investigating diamond-inclusion relationships relies on the combination of high-resolution techniques to better understand diamond growth, especially in relation to inclusions. For example Wiggers de Vries et al. (2011) applied the CL technique along with electron backscatter diffraction (EBSD), using FIB-SEM, to study the three-dimensional growth zonation around inclusions in diamond. EBSD orientation mapping revealed that three chromite inclusions in a single diamond studied by these authors have a potential epitaxial relation with the host, within ±0.4°. One of the chromite inclusions is surrounded by a non-luminescent CL halo that has apparent crystallographic morphology with symmetrically oriented pointed features. The CL halo has ~200 ppm Cr and ~75 ppm Fe and is interpreted to have a secondary origin as it overprints a major primary diamond growth structure. The diamond zonation adjacent to the chromite and the morphology of the inclusion records changes in the relative growth rates and habits at the diamond-chromite interface, thus supporting a syngenetic relationship.

A resolutive approach would be one that combines accurate measurement of the crystallographic orientations of the inclusion and its host with calculations of their interfacial energies in a number of possible reciprocal orientations. Crystallographic orientations can be determined with high accuracy and precision by *in situ*, non-destructive, single-crystal X-ray diffraction on the inclusions still trapped in their diamond hosts by adapting the methods developed for high-pressure studies of single crystals in diamond-anvil cells (e.g., Nestola et al. 2011). These methods overcome technical issues related to the accurate visual centering of the inclusions, a common difficulty in routine X-ray diffractometry, thus allowing investigation of diamonds with unfavorable morphology or with multiple inclusions. *Ab initio* quantum-mechanical calculations may then show whether any particular orientation is energetically favored and should hence be expected in the case of syngenesis. This combined methodology cannot be used routinely because it requires dedicated laboratories and equipment. In particular, interfacial energy calculations have never been performed on inclusions in diamond. Until a statistically significant number of crystallographic and interfacial energy data are produced, the classification of any inclusion as syngenetic based purely on morphological or crystallographic criteria should be considered with caution.

Inclusion type and paragenesis. Silicate inclusions in lithospheric diamonds are commonly classified into 2 dominant parageneses—peridotitic (P-type, with harzburgitic and lherzolitic members) and eclogitic (E-type). A minor websteritic paragenesis is present at some localities and a wherlitic paragenesis also can be tentatively identified (Stachel and Harris 2008 and references therein; Fig. 14, Table 1). For garnets, this classification is clearly resolved on the basis of Cr contents, with P-type garnets having > 1 wt% Cr_2O_3 (e.g., Schulze 1983; Fig. 14) and on the basis of Cr# (100Cr/[Cr + Al]) for clinopyroxenes where P-type clinopyroxenes (Cr-diopsides) have a Cr# of 7 to 10 (Stachel and Harris 2008). The websteritic inclusion suite is not as clearly defined and has been used to classify silicates with transitional mineral chemistry between P- and E-type paragenesis. For instance, Gurney et al. (1984) use this classification for garnets with Cr_2O_3 contents > 1 wt% that have abnormally low Mg#. Aulbach et al. (2002) have applied the websteritic classification to garnets and clinopyroxenes that have E-type chemical affinities (Cr_2O_3 in garnet generally <2.5%; low Cr# in clinopyroxene) and chemical traits implying coexistence with orthopyroxene. Grütter et al. (2004) distinguish websteritic garnets as having

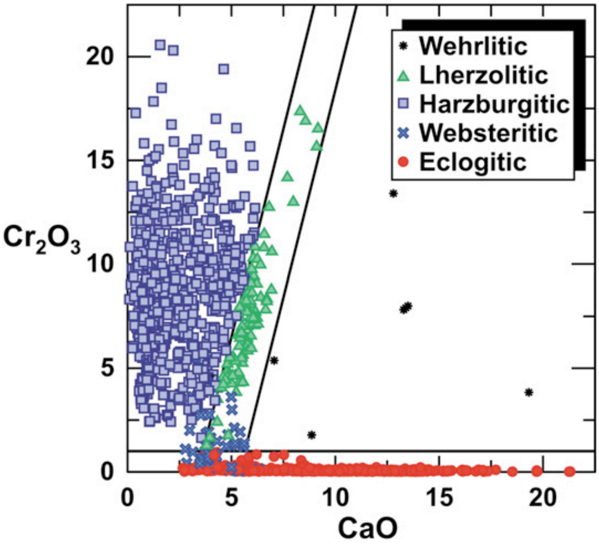


Figure 14. Garnet from a worldwide database on the classification in a plot Cr_2O_3 versus CaO (wt%) with compositional fields of Grütter et al. (2004). See text for discussion. (Figure and caption used by permission of Elsevier Limited, from Stachel and Harris (2008) *Ore Geology Reviews*, Vol. 34, Fig. 4, p. 8).

Table 1. Mineral inclusions in lithospheric diamonds and their associated parageneses (modified from Sobolev 1983).

Type	Mineral parageneses	Principal mineral inclusions in diamond	Specific compositional features	Polycrystalline	Xenoliths
ULTRAMAFIC (PERIDOTITIC)	harzburgite-dunite	**Cr-Prp** (Mg# >85; Ca# <15; Cr# >15), **Ol** (Fo_{92-94}), **Chr** (Cr# >85), **Sf** (Ni > 17 wt%), [Esk, Phl]	Ca-poor Cr-Prp	+	+
	lherzolite	**Prp** (Mg# >80; Ca# >15), **Ol** (Fo_{90-92}), **En**, **Cr-Di**, **Sf** (Ni >17 wt%), [Chr, Phl, Mgs, Ilm, Rt]	Prp with moderate CaO (4-7 wt%)	+	+
	wehrlite	**Cr-Prp** (Mg# >80; Ca# >20 +Ol (Fo_{92}), **Cr-Di**, **Sf** (Ni > 17 wt%), [Chr]	Ca-rich Cr-Prp (Ca# > 20)	+	–
WEBSTERITIC	websterite-pyroxenite	**Prp** (Mg# >70), **Cpx**, **Sf** (Ni 10-17 wt%), [En]	Absence of Ol	+	+
ECLOGITIC	eclogite	**Grt** (Ca# < 50), **Omp**, **Sf** (Ni < 10 wt%), [Rt, Phl (Bt), Dol]	Na in Grt K in Omp	+	+
	coesite eclogite	**Grt** (Ca# < 50), **Omp**, **Coe**, **Sf** (Ni < 10 wt%), [Rt]	Coe	–	+
	ilmenite eclogite	**Grt**(Ca# < 50), **Omp**, **Ilm**, **Sf** (Ni< 10 wt%), [Rt]	Ilm	+	–
	kyanite eclogite	**Grt** (Ca# < 50), **Omp, Ky**, **Sf** (Ni < 10 wt%), [Sa, Rt, Coe]	Ky	–	+
	corundum eclogite	**Grt** (Ca# < 50), **Omp**, **Crn**, **Sf** (Ni < 10 t%), [Ky, Rt]	Crn	–	+
	grospydite	**Grt** (Ca# >50), **Omp**, **Ky**, **Sf** (Ni < 10 wt%), [Crn, Rt]	Grt (Ca# > 50)	–	+

The more common mineral inclusions in diamond are shown in boldface; the rarer inclusion minerals are in normal typeface within brackets. Sulfides are common minerals in all diamond parageneses. Sometimes rare minerals like ferropericlase, moissanite and others may be present as inclusions in diamonds. (+) indicates the presence diamond type or rock associated with the paragenesis; whereas (–) indicates their absence. Abbreviations of minerals are after Whitney and Evans (2010) as follows: chrome-pyrope (Cr-Prp), olivine (Ol), chromite (Chr), sulfide (Sf), eskolaite (Esk), phlogopite (Phl), pyrope (Prp), enstatite (En), chrome-diopside (Cr-Di), magnesite (Mgs), ilmenite (Ilm), rutile (Rt), clinopyroxene (Cpx), garnet (Grt), omphacite (Omp), kyanite (Ky), sanidine (Sa), coesite (Coe), and corundum (Crn). Polycrystalline diamond includes boart, framesite and diamondite (see text for details). Mg# = 100Mg/(Mg+Fe); Ca# = 100Ca/(Ca+Mg+Fe+Mn); Cr# = 100Cr/(Cr+Al).

relatively low Cr_2O_3 (<2.5%) and CaO contents of <6 wt%. Sodium content can be useful as Sobolev and Lavrent'ev (1977) noted that E-type garnets contained elevated Na_2O (>0.1%)

The Cr_2O_3 versus CaO plot for garnets (Fig. 14) has developed into a central means of classifying garnets and is a key diamond exploration tool (Gurney and Switzer 1973; Sobolev et al. 1973; Schulze 1983; Gurney et al. 1984; Grütter et al. 2004). In this compositional space, Sobolev et al. (1973) first identified garnets that had not equilibrated with clinopyroxene as having low-Ca, high-Cr characteristics and designated these garnets as having come from highly-depleted harzburgitic to dunitic lithologies. In contrast, lherzolitic garnets occupy a distinct linear trend originating from circa 2.5 wt% Cr_2O_3 and 3 wt% CaO with a slope of ~ 0.3 CaO to 1 Cr_2O_3 (Fig. 14). Gurney (1984) defined a similar lherzolitic trend based on a line that separated 85% of diamond inclusion garnets with Cr_2O_3 >4 wt%, extending upwards in Cr-Ca space with a similar slope to the Sobolev trend. Grütter et al. (2004) proposed more precise boundaries to the lherzolitic field, which are largely the same as the early classifications as well as more clearly defining the eclogitic and websteritic compositional fields on this plot. Sobolev (1977) likewise distinguished high-Mg and Cr chromites (Fe/(Fe + Mg) <50%; Cr_2O_3 >62 wt%) as characterizing diamond inclusion spinels and reflecting a harzburgite association.

Mirroring the approach to silicates, a basic subdivision of sulfides into P- and E-type chemistries, based predominately on Ni-content (Table 1) was proposed by Yefimova et al. (1983), although Deines and Harris (1995) showed a clear compositional overlap. Subsequent studies of sulfides for Re-Os dating, while adding to this continuum, have demonstrated that Os content (i.e. 3-200 ppb for E-types and ~2,000-30,000 ppb for P-types) is a more sensitive discriminant (e.g, Pearson and Shirey 1999).

The study of mineral inclusions in sublithospheric diamonds is in a youthful stage compared to the study of inclusions in lithospheric diamonds in part due to the rarity of specimens, small grain size, and difficulties in recognizing original high-pressure minerals from their low-pressure, retrograde assemblages (e.g., Table 2). Regardless, sublithospheric inclusions can be divided into ultramafic (peridotitic) and basaltic (eclogitic) types in a parallel manner to inclusions in lithospheric diamonds. Ultramafic types are characterized by high-pressure magnesium-rich phases such as Mg-perovskite, ringwoodite, wadsleyite, and olivine with ferro-periclase, majorite, and Ca-perovskite and their low pressure breakdown products (Table 2). Basaltic types are characterized by assemblages richer in basaltic components such as Ca, Al, Si, and Ti including majorite, clinopyroxene, CaTi-perovskite, Ca-perovskite, Ca-ferrite, stishovite, and the "new aluminum phase" (NAL; Table 2).

Trace elements. Pioneering work (Sobolev and Lavrent'ev 1971; Sobolev et al. 1972; Hervig et al. 1980), using elevated beam currents and extended counting times, allowed the measurement of a limited number of trace elements in silicates included in diamonds. The advent of the ion microprobe allowed the first analyses of a broad spectrum of trace elements, including the petrogenetically useful rare earth elements (REE), which indicate the extreme enrichment of incompatible elements in fluids that formed them (Shimizu and Richardson 1987). While laser-ablation ICPMS has the potential to make the same analyses (Davies et al. 2004), the significantly more destructive nature of this technique has meant that trace element studies focused almost exclusively on the ion-microprobe technique (Ireland et al. 1994; Shimizu and Sobolev 1995; Shimizu et al. 1997; Stachel and Harris 1997; Stachel et al. 1998b, 1999, 2000, 2004; Harte et al. 1999; Aulbach et al. 2002; Promprated et al. 2004; Tappert et al. 2005b).

Stachel et al. (2004) pointed out that, from a global perspective, peridotitic garnets included in diamonds from cratonic lithosphere show a full spectrum of REE patterns from those known as sinusoidal (i.e., they have positive slopes from La to Nd or even Eu, negative slopes in the middle REE and positive slopes again from Ho or Er to Lu; Fig. 15a), to those that are light REE depleted with flat middle REE- to heavy REE sections. The light REE enrichment

Table 2. Mineral inclusions in sublithospheric diamonds and their associated parageneses (modified from Harte 2010 and references therein, with additions).

Type	Mineral facies	Approximate Depth (km)	Indicative mineral assemblage	Retrograde transformations	Principal mineral inclusions in diamond
ULTRAMAFIC (PERIDOTITIC)	upper mantle	< 410	Ol+Maj+Cpx	Maj→Cpx+Grt	Ol, Grt, Cpx
	transition zone	410 - 660	Wds/Rwd+Maj±CaPv	Wds/Rwd→Ol, Maj→Cpx+Grt, CaPv→Wal	Ol, Grt, Cpx, Wal
	UM/LM boundary association	~ 660	Rwd+MgPv(low-Al)+FePer+Maj+CaPv	Rwd→Ol, MgPv→En, CaPv→Wal	Ol, En, FePer, Wal
	lower mantle	> 660	MgPv(Al)+FePer+CaPv	MgPv(Al)→En, CaPv→Wal	En(Al), FePer, Wal
BASALTIC (ECLOGITIC)	upper mantle	~ 300 - 450	Maj+Cpx±CaTiPv	CaTiPv→Pv+Wal	Grt, Cpx, Pv, Wal
	transition zone	450 - 600	Maj+Sti±CaTiPv±CaPv	Maj→Cpx+Grt, CaTiPv→Pv+Wal Sti→Qz/Coe	Grt, Cpx, Pv, Wal, SiO_2
	UM/LM boundary association	~600 - 750	Maj±CaTiPv±CaPv ±NAL+Sti	Maj→Cpx+Gar, NAL→Spl+Kls, Sti→Qz/Coe	NaAlPx, Gar, Cpx, Pv, Wal,Spl, Kls, SiO_2
	lower mantle	> ~750	MgPv(Fe, Al)+CaPv+CaFrt+NAL+Sti	MgPv→TAPP±En±Spl, NAL→Spl+Kls CaFrt→Spl+Nph, Sti→Qz/Coe	En, TAPP, Spl, Kls, Nph, SiO_2

The indicative mineral assemblages of the depth zones of sublithospheric inclusions in diamond are never seen due to exsolution and transformations to low-pressure phases as indicated. Furthermore, the rarity of these inclusions and their small size means that, in most cases, crystal structure is inferred from elemental composition. Therefore, the depth ranges of these diamonds with inclusions are approximate because they are derived from the principal mineral inclusions observed in the diamond at low pressure. UM= upper mantle, LM=lower mantle. Abbreviations of minerals are after Whitney and Evans (2010) as follows: olivine (Ol), majorite (Maj), clinopyroxene, (Cpx), wadsleyite (Wds), ringwoodite (Rwd), calcium perovskite (CaPv), magnesium perovskite (MgPv), ferropericlase (FePer), calciu-titianium perovskite (CaTiPv), stishovite (Sti), new aluminum phase (NAL), calcium ferrite (CaFrt), garnet (grt), walstromite (Wal), quartz (Qz), coesite (Coe), spinel (Spl), kalsilite (Kls), nepheline (Nph), enstatite (En) , perovskite (Pv), and tetragonal almandine pyrope phase (TAPP).

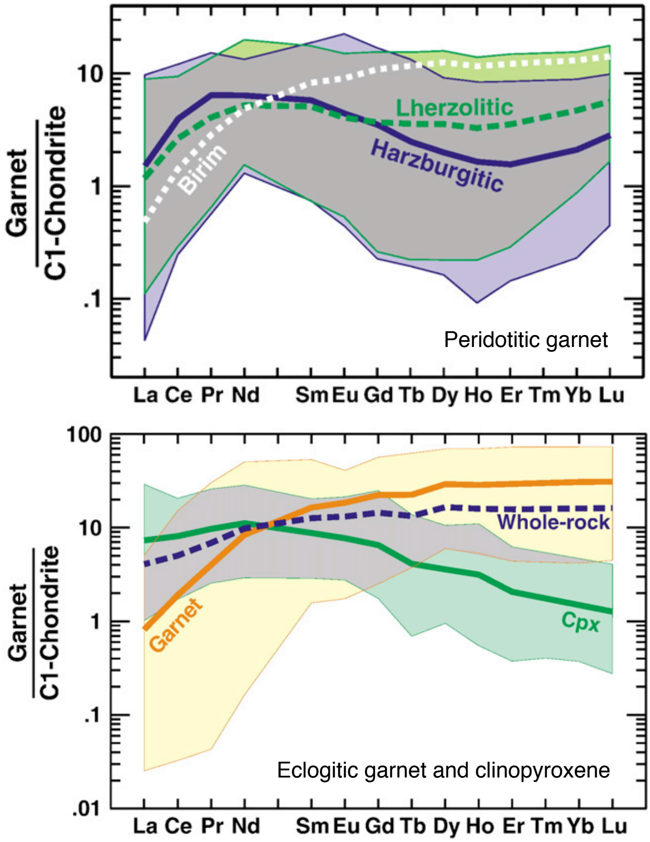


Figure 15. REE in peridotitic and eclogitic garnet inclusions from the database of Stachel et al. (2004) and normalized to C1-chondrite (McDonough and Sun 1995). The top diagram shows the compositional fields and average compositions of harzburgitic and lherzolitic garnets. The average composition of lherzolitic garnets from Birim diamonds (Akwatia, Ghana; Fig. 3) is shown to represent "normal" REE patterns generally (but not exclusively) restricted to the lherzolitic paragenesis. The strongly sinusoidal REE patterns typically observed for the harzburgitic paragenesis represent depleted garnets that have been re-enriched in light REE. This pattern requires a metasomatic agent with extremely high light REE to heavy REE, believed to indicate fluid metasomatism. Ranges and average REE contents of eclogitic garnet and clinopyroxene inclusions are shown in the bottom panel. Calculated REE pattern for eclogitic whole-rock (blue dashed line) assumes a modal garnet-clinopyroxene ratio of 1:1. (Figures and captions used by permission of Elsevier Limited, from Stachel and Harris (2008) *Ore Geology Reviews*, Vol. 34, Figs. 21 and 22, pp. 17 and 19).

and strongly sinusoidal patterns are generally restricted to very depleted (high-Cr, low-Ca), harzburgitic major element chemistries in diamond inclusions (Stachel et al. 2009) and garnets in diamond-bearing peridotites (Nixon 1987; Pearson et al. 1995; Shimizu et al. 1997; Stachel et al. 1998b; Klein-BenDavid and Pearson 2009) and this pattern has led to the suggestion that this signature is characteristic of the imprint left on wall-rocks by the passage of diamond-forming fluids. Garnets with strongly sinusoidal REE patterns often have Sr enrichments of 10 to >40 ppm (Pearson et al. 1995; Shimizu and Sobolev 1995) and these features, together with other characteristics, have led to the prevalent interpretation that these garnets equilibrated with C-O-H fluids (e.g., Stachel et al. 2004) or carbonatitic fluids/melts (Navon 1999) associated with diamond formation. The classic light REE depleted, typically more fertile lherzolitic garnets seem to have last equilibrated with a silicate melt. Stachel et al. (2004) see the continuum between these two end-member garnet types as resulting from a spread of melt-fluid compositions generated by fractional crystallization and reaction with lithospheric wall rocks. Burgess and Harte (2004) called such a process "percolative fractionation." Isotopic studies of diamond-forming fluids indicate that there are multiple fluid sources involved in diamond genesis (McNeill et al. 2009; Klein-BenDavid et al. 2010) and hence the "C-O-H fluid" designation is likely to encompass fluids of differing types. The co-variation of Zr with Y in garnets can also be used to characterize the different metasomatic interactions that mantle garnets may have experienced (Griffin et al. 1999). When garnets included in diamonds are examined in this way (Stachel and Harris 2008; their Fig. 22), the majority of harzburgitic garnets plot in the field for garnets that have experienced large amounts of melt depletion, with a clear trend of Zr enrichment that is usually associated with phlogopite metasomatism. This trend may be reflective of one of the sources of fluids being derived from mica-rich metasomes within the lithosphere (Klein-BenDavid et al. 2010). In contrast, lherzolitic garnets range from the melt-depleted field into the regions of coupled Zr and Y enrichment that signifies silicate melt metasomatism.

A subset of very depleted, high-Cr garnets with either very high equilibration temperatures (Buffalo Head Hills, Alberta; Banas et al. 2007) or majoritic (high-Na) compositions (Promprated et al. 2004) could indicate, in some locations, the possible presence of very deep (>300 km) lithospheric mantle in places, or derivation from detached slabs of basal lithosphere by kimberlites on route to the surface. Such occurrences, while rare, offer a valuable opportunity to better understand mantle geodynamics and further study is warranted.

Despite the plethora of analyses from many different cratons, the exact nature of the parental diamond melt-fluid to peridotitic diamonds remains unconstrained, because of the multiple stages of depletion and metasomatism that silicates included within diamonds have experienced. Difficulties in the geochemical interpretations include the assumption of equilibrium to calculate parental fluids/melts using trace element partitioning data and the likely lack of applicability of the partitioning data due to strong differences in distribution coefficients related to poorly constrained parental fluid compositions. Trace element partitioning data between lherzolitic and high-Cr harzburgitic garnets over a range of C-O-H and carbonatitic fluid/melt compositions, would greatly assist our understanding of P-type diamond formation, notwithstanding the technical difficulties of such experiments.

E-type silicates included in diamonds show much less trace element variability that P-type silicates. Eclogitic garnet inclusions have light REE depleted patterns that show broad similarities to garnets from crustal eclogites, with light REE ~ 1× chondritic abundances and heavy REE ~ 30× chondritic (Fig. 15b; e.g., Ireland et al. 1994; Taylor et al. 1996; Stachel et al. 1999, 2000, 2004). REE patterns for clinopyroxenes (omphacites) appear in broad equilibrium with the garnets, with light REE enrichment and heavy REE at ~ 1× chondritic. Ireland et al (1994) noted that the major and incompatible trace element compositions of eclogitic silicates included in diamonds were more depleted than host eclogite xenoliths and interpreted these compositions as reflecting the extraction of a TTG melt during subduction of an oceanic crustal precursor that experienced eclogite facies metamorphism. The observation of positive and negative Eu anomalies in both garnet and clinopyroxene inclusions supports an origin via oceanic crustal protoliths (e.g., Promprated et al. 2004; Stachel et al. 2004), in agreement with the widely accepted origin of most eclogite xenoliths erupted by kimberlites through cratons (e.g., MacGregor and Manton 1986; Jacob 2004).

While the parentage of the E-type silicates seems straightforward with the available data, the origin of the diamonds that surround E-type silicates is not. The simplest hypothesis for the origin of E-type diamonds would be via solid-state growth from a carbon-bearing crustal precursor. However, there is little evidence for the solid-state growth of most diamonds (see review in Stachel and Harris 2009) and increasing evidence for their metasomatic growth. The strongest evidence for a metasomatic origin for diamonds come from studies that document extreme chemical variations across multiple inclusions in the same diamond (Sobolev and Efimova 1998; Taylor et al. 1998; Keller et al. 1999; Bulanova et al. 2004), and relations between diamonds and host silicates in diamondiferous xenoliths revealed by microscopy (Spetsius et al. 2002; Spetsius and Taylor 2008) and X-ray micro-tomography (Keller et al. 1999; Taylor et al. 2003; Anand et al. 2004). The range in silicate inclusion equilibration temperatures indicated by diamond inclusion thermobarometry, from supra- to sub-solidus, has also been used to support a metasomatic origin for most diamonds under melt-dominated (eclogite and lherzolite) and C-O-H fluid-dominated (harzburgitic) conditions (Stachel and Harris 2008). A temporal variability has been suggested in this process, on the basis of lithospheric redox and C-isotope compositions, with Meso- to Paleoarchean diamonds possibly forming via reduction of methane-rich fluids permeating the lithosphere, whereas in post-Archean times, reduction of carbonate-rich melts better explains the C isotopic systematics (Stachel and Harris 2009). This view contrasts however with vanadium-scandium systematics (e.g., Canil 2002), which do not highlight any significant secular change in mantle oxygen fugacity.

Key aspects of these models require better understanding: 1) the temporal evolution of the lithospheric mantle redox state, 2) the mechanism of diamond formation via interaction of melt and C-O-H fluid with mantle wall rocks, and 3) the origin of the proposed metasomatic fluids—are there local sources of carbon that are remobilized over centimeters, or fluids streaming through the lithosphere on kilometer scale-lengths?

Age systematics and isotopic compositions. Currently, it is not possible to date monocrystalline diamonds by direct analysis of the diamond crystal. Fibrous diamonds, being related to the kimberlite magmatism, have an age very close to that of kimberlite. But with only poorly aggregated nitrogen, the exact residence time (million year time scales) and temperature(s) in the mantle remains unclear. As such, all viable ages produced so far have been obtained by the analysis of solid inclusions within diamonds that are assumed to be syngenetic (see above) with the diamonds; the reader is directed to the isotopic age dating review of Pearson and Shirey (1999) for more details. The first dating studies were performed on sulfide (Kramers 1979) and silicate (Richardson et al. 1984) inclusions and indicated the likely antiquity of the host diamonds. Both these groundbreaking studies were made by pooling together numerous (sometimes >100) inclusions because of analytical constraints. Subsequently, the Sm-Nd isotope system became the method of choice and yielded a number of isochron ages from suites of diamonds from southern Africa (Smith et al. 1991; Richardson et al. 1990, 1999, 2004), Siberia (Richardson and Harris 1997), and Western Australia (Richardson 1986).

Some studies have questioned the validity of ages obtained on composites of inclusions (see discussion in Navon 1999) and this uncertainty drove the need to make analyses on single inclusions. The Ar-Ar method was the first to be applied to single clinopyroxene inclusions in diamonds (Phillips et al. 1989; Burgess et al. 1992) because eclogitic omphacite contains sufficient potassium to allow age determinations. It soon became clear that unexposed, pristine inclusions are essential for this approach due to potential diffusion of radiogenic Ar to the silicate-diamond interface, yielding ages that range upwards from the kimberlite eruption age in cleaved diamonds (Burgess et al. 1992). Because of the potential for incorporation of the locally abundant ambient ^{40}Ar in the mantle (e.g., Pearson et al. 1998), the ages can be viewed as absolute maxima for encapsulation of the inclusion by the diamond. Orapa eclogitic pyroxenes analyzed by Burgess et al. (2004) gave ages of 906 to 1032 Ma, consistent with previously determined Sm-Nd ages, with a few samples yielding ages >2500 Ma, hinting at the presence of multiple diamond age populations in this kimberlite. These authors also found ages of 520 Ma for eclogitic omphacites from the Venetia kimberlite, indicating a population of diamonds that formed shortly before kimberlite eruption. In summary, Ar-Ar geochronology studies of eclogitic pyroxenes from southern Africa largely confirm the results of the Sm-Nd approach, indicating E-type diamond formation from the Neoarchean onwards.

Analysis of single inclusions in diamond has been most effectively realized using the Re-Os isotope system in sulfides. The relatively high Re and Os contents of sulfides from both E- and P-type parageneses, allow analyses of Os in the sub-picogram to nanogram range (Pearson et al. 1998, 1999b; Pearson and Shirey 1999). The focus on obtaining relatively large sulfides for analysis has lead to an apparent bias towards dating studies involving E-type diamonds (e.g., Pearson et al. 1998; Richardson et al. 2001, 2004; Shirey et al. 2004a, 2004b; Aulbach et al. 2009a) although P-type sulfide inclusions have been analyzed in some instances (Pearson et al. 1999a, 1999b; Westerlund et al. 2006; Smith et al. 2009; Smit et al. 2010).

The general picture of lithospheric diamond formation revealed by Re-Os dating is that there are multiple diamond ages within one kimberlite (e.g., Pearson et al. 1998; Richardson et al. 2004; Aulbach et al. 2009a) and that all E-type sulfide-bearing diamonds analyzed so far appear to have formed in the Neoarchean and later (Pearson et al. 1998; Pearson and Shirey 1999; Richardson et al. 2001, 2004; Shirey et al. 2004b, 2008; Aulbach et al. 2009a,b; Laiginhas et al. 2009; Shirey and Richardson 2011). In contrast, diamonds containing P-type sulfides are older, having started to form from the Mesoarchean onwards (Pearson et al. 1999a, 1999b; Westerlund et al. 2006; Aulbach et al. 2009b; Smit et al. 2010; Shirey and Richardson 2011), with the exception of a single Mesozoic diamond from Koffiefontein (Pearson et al. 1998) and one from Jagersfontein (Aulbach et al. 2009b).

In addition to these "mainstream" approaches, there has been a small number of studies using the U-Pb system on zircon (Kinny and Meyer 1994) and yimengite (Hamilton et al. 2003). Bulanova et al. (2004) also made Ar-Ar age determinations on yimengite inclusions in a diamonds from the Sese kimberlite, Zimbabwe, producing apparent ages from 538 to 892 Ma. These studies yielded relatively young formation ages. Such phases that may be related to the proto-kimberlite melts, and are part of a growing body of evidence, augmented by Re-Os isotopes (Pearson et al. 1998; Aulbach et al. 2009a), Sm-Nd and Ar-Ar studies in E-type clinopyroxenes (Richardson 1986; Burgess et al. 2004) and N-aggregation systematics, that indicate a proportion of gem diamond growth shortly before kimberlite eruption.

So far only 2 age determinations have been made on ultra-deep, sub-lithospheric diamonds. Bulanova et al. (2010) made a U-Pb ion probe determination of a Ca-silicate perovskite (re-equilibrated to walstromite) diamond inclusion from the Collier-4 kimberlite, Brazil that yielded an age of 107 ± 7 Ma, only 14 Ma older than the pipe emplacement age of 93 Ma. This study did not use matrix-matched standards and, as such, the date must be viewed as preliminary. However, the results are supported by nitrogen aggregation data for super deep diamonds from this pipe, which imply, for an assumed temperature of ~1500 °C, a maximum mantle residence time of <10 Ma (Bulanova et al. 2010). In contrast, a single sulfide inclusion in an ultra-deep diamond from Juina examined by Hutchinson et al. (2012) indicated a formation age likely to be significantly in excess of 500 Ma, considerably older than the circa 90-Ma pipe emplacement age. This sort of age (400 to 800 Ma) is seen for some radiogenic isotopic systems (e.g., Sm-Nd, Lu-Hf) in oceanic basalts and abyssal peridotites and thus is consistent with this diamond having grown deep in the convecting oceanic mantle. A similar conclusion can be drawn from the Sr and Nd isotopic compositions reported in majoritic garnet inclusions in diamonds from the mantle transition zone, also from the Brazilian craton (Sao Luis), which plot in the middle of the oceanic Sr and Nd isotopic array and distinctly different from the garnet inclusions from lithospheric diamonds (Harte and Richardson 2011). The scarcity of data from sulfides in ultra-deep diamonds has so far restricted age information on ultra-deep diamonds and this is certainly an area that will see more effort in the future.

Stable isotopic signatures in diamond inclusions. The origin of diamond can also be addressed from the study of O- and S-isotopes in silicate and sulfide inclusions ($n < 20$ and $n < 50$, respectively). Although fairly limited data are available, both provide evidence for the involvement of subduction-related material. The $^{18}O/^{16}O$-isotope variability ($\delta^{18}O$ from +4 to +16‰) of eclogitic diamond inclusions, contrasts with the mantle homogeneity displayed by peridotite xenoliths and diamond inclusions and compares with the known range measured in altered ocean crust (see Lowry et al. 1999; Schulze et al. 2003; Anand et al. 2004). Although often equilibrated at lower pressure and temperature, eclogite xenoliths have O-isotope compositions consistent with those in eclogitic diamond inclusions (see Jacob 2004 for review). Eclogitic sulfide inclusions also display variable $^{34}S/^{32}S$ ratios ($\delta^{34}S$ from −11 to +14‰) that compare well with sediments and altered oceanic crust, but it must be emphasized that the most recent studies did not reproduce such a large range of values (Farquhar et al. 2002; Thomassot et al. 2009 and references therein). Unambiguous evidence for the involvement of subduction-related sulfur in eclogitic diamond inclusions is brought from the recognition of mass-independent fractionations of sulfur isotopes (i.e., $\delta^{33}S \neq 0.5 \times \delta^{34}S$) within sulfide diamond inclusions (Fig. 16; Farquhar et al. 2002; Thomassot et al. 2009). The only known geologically relevant process to be associated with sulfur isotopic compositions with mass-independent fractionations is the UV-photolysis of sulfur-bearing molecules in an O_2-deprived composition: on Earth, such conditions were met during the Archean Eon (Farquhar et al. 2000). Therefore the identification of mass-independent fractionations of sulfur isotopes within sulfides eclogitic diamond inclusions (Farquhar et al. 2002), and their absence within peridotitic diamonds (Cartigny et al. 2009), demonstrate the occurrence of recycled Archean sedimentary sulfur in the former.

GEOLOGY OF MANTLE CARBON FROM DIAMONDS

Geodynamics, carbon mobility and reservoirs

Diamond—the mechanisms by which it crystallizes, the relationship it bears to the explosive kimberlite host magmas that deliver it, and the distribution of different diamond types in a geologic context—provide the key to understanding the carbon cycle in the deep mantle.

Continent assembly, plate tectonics, and ancient carbon recycling. As a consequence of old cratons having preserved mantle keels, the diamond record remains one of the prime ways to examine continental tectonics from mantle depths and avoid the later overprinting effects of metasomatism. It is also a main way to get some idea of Earth's ancient igneous carbon cycle.

Shirey and Richardson (2011) extended the observations of isotopic ages to all diamond formation ages so far determined and combined them with the diamond type to show that only P-type diamonds were forming in the lithosphere during the Paleoarchean to Mesoarchean, whereas E-type diamonds began to form post-3 Ga and became the prevalent type of diamond formed (Fig. 17). These authors went on to propose, based on the diamond inclusion geochronology database that includes both the Sm-Nd data on silicate inclusions and the Re-Os data on sulfides, that continental dispersion and subduction tectonics as we know it in the modern Earth—the Wilson cycle—initiated in the Neoarchean. The transition to an Earth dominated by lateral tectonics and subduction is not well explained at the present time, but the 3-Ga shift to eclogitic inclusions does correlate with a major change in crustal geologic style (Van Kranendonk 2010, 2011) and crustal growth mechanisms (Dhuime et al. 2012), which do support the Wilson Cycle onset conclusion. It is not known, for example, whether the appearance of eclogite simply signals a more effective capture of slabs by a buoyant keel in which they can be retained or the actual appearance of large slabs in the geologic record. If it is the latter, this change may have important implications for the nature of carbon-bearing fluids and their delivery to diamond-forming depths in the mantle. Using skewness in the carbon isotopic composition histogram of P-Type diamonds,

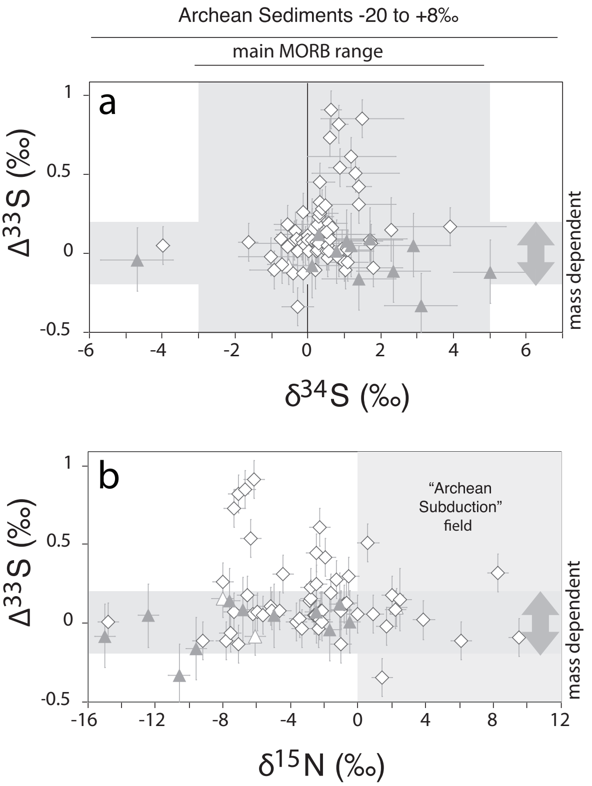


Figure 16. Illustration of δ^{34}S-Δ^{33}S (a) and δ^{15}N-Δ^{33}S (b) covariations in sulfide-bearing diamonds. Filled triangles and filled diamonds correspond to sulfides from peridotitic and eclogitic diamonds respectively from the Ekati mine, Canada (Panda kimberlite; Cartigny et al. 2009); open diamonds are eclogitic sulfides from the Jwaneng and Orapa kimberlites, Botswana (Farquhar et al. 2002; Thomassot et al. 2009). Note that almost no samples fall within the Archean subduction field. The inconsistency between the evidence for the occurrence for subucted sulfur in sulfide inclusion (from non zero Δ^{33}S) and absence (from negative δ^{15}N) could be reconciled considering metasomatic diamond formation enclosing a pre-existing sulfide although the N isotopic composition of the Archean mantle is poorly known (see text for details). Dashed line: conductive geotherms for a surface heat flow of 40 mW/m^2 after Pollack and Chapman (1977); black solid line: graphite-diamond boundary after Day (2012); grey band: *T* range for mantle adiabat based on mantle potential temperatures of 1300 to 1400 °C. (Used by permission of Elsevier Limited, from Cartigny et al. (2009) *Lithos*, Vol. 112S, Fig. 6, p. 861)

Stachel and Harris (2009) proposed that there may a change in the mechanism by which older diamonds form from methane oxidation in the Mesoarchean Era to the way that younger diamonds form by carbonate reduction in the Proterozoic Eon. If this observation is combined with the proposed onset of the Wilson Cycle, it could signify a change from the geodynamic processes that would favor primary mantle devolatilization and/or the outgassing of recycled reduced fluids, to the geodynamic processes that favor carbonate recycling via slab subduction.

Diamond inclusion populations and ages have also been linked to broad-scale regional lithosphere evolution. A number of authors have made the link between diamond formation events or pulses and large-scale thermo-tectonic events recorded in the craton crust (Shirey et al. 2002, 2004b; Richardson et al. 2004; Pearson and Wittig 2008; Richardson and Shirey 2008; Aulbach et al. 2009a,b). Shirey et al. (2002, 2004a,b) have noted that in southern Africa, mantle

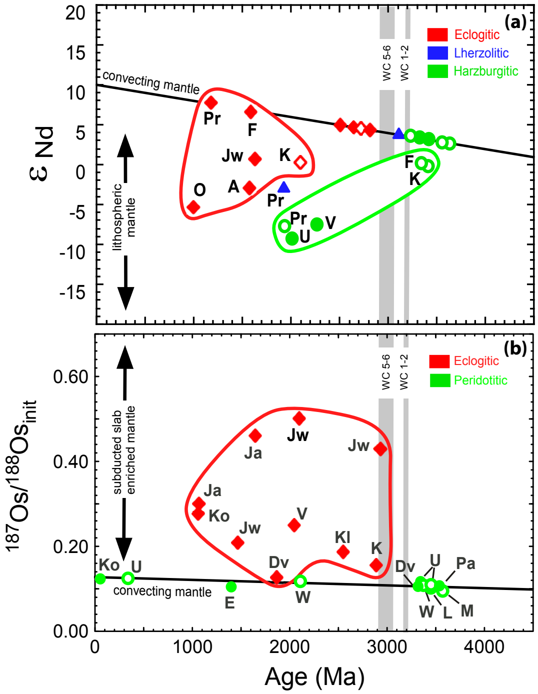


Figure 17. (a) Silicate inclusion initial Nd isotopic composition vs Sm-Nd age for diamonds of peridotitic (circles), lherzolitic (triangle), and eclogitic (diamonds) parageneses. Closed symbols are isochron studies for composites of garnet and clinopyroxene grains. Open symbols are model age studies for composites of garnet only. Unlabeled points on convecting mantle curve are mantle extraction ages extrapolated from labeled points. (b) Sulfide inclusion initial Os isotopic composition vs Re-Os age. Closed symbols are isochron studies; open symbols are model age studies for single grains. For isochron studies, mantle extraction ages extrapolated from labeled points are typically <100 million years (one scale division) older than the isochron age. WC 1-2 represents the Wilson Cycle rifting (stage 1-2) for the Pilbara craton (Van Kranendonk et al. 2010) whereas WC 5-6 represents the Wilson Cycle continental closure (stage 5-6) for the Kaapvaal craton. Locality abbreviations are as follows: (Pr) Premier, (O) Orapa, (A) Aryle, (Jw) Jwaneng, (F) Finsch, (Ko) Koffiefontein, (U) Udachnaya, (V) Venetia, (K) Kimberley pool, (E) Ellendale, (W) Wellington, (Dv) Diavik, (Kl) Klipspringer, (Pa) Panda, (M) Murowa, (L) Letseng. (Figure and caption used by permission of the American Association for Advancement of Science, from Shirey and Richardson (2011) *Science*, Vol. 333, Fig. 1, p. 434).

lithosphere with slower seismic P-wave velocity relative to the craton average correlates with a greater proportion of E-type versus P-type silicate inclusions in diamonds, a greater incidence of younger (Mesoproterozoic Era) Sm-Nd inclusion ages, a greater proportion of diamonds with light C-isotope compositions and a lower proportion of low-N diamonds (Fig. 18). This correlation was proposed to result from Proterozoic modification of Mesoarchean lithosphere by large-scale tectono-magmatic events in the Proterozoic Eon, which added new lherzolitic and eclogitic diamonds to an original harzburgitic inventory of diamonds. In this case, diamond-forming fluids equilibrated with pre-existing silicates and incorporated them as inclusions, retaining the mineralogical differences imparted by the sub-lithospheric magmatism of the Bushveld Complex, now retained as fossil seismic velocity differences (Fig. 18).

The craton-wide pattern for southern Africa displayed by sulfide-bearing diamonds is different than the pattern seen with silicate-bearing diamonds. This difference stems from the

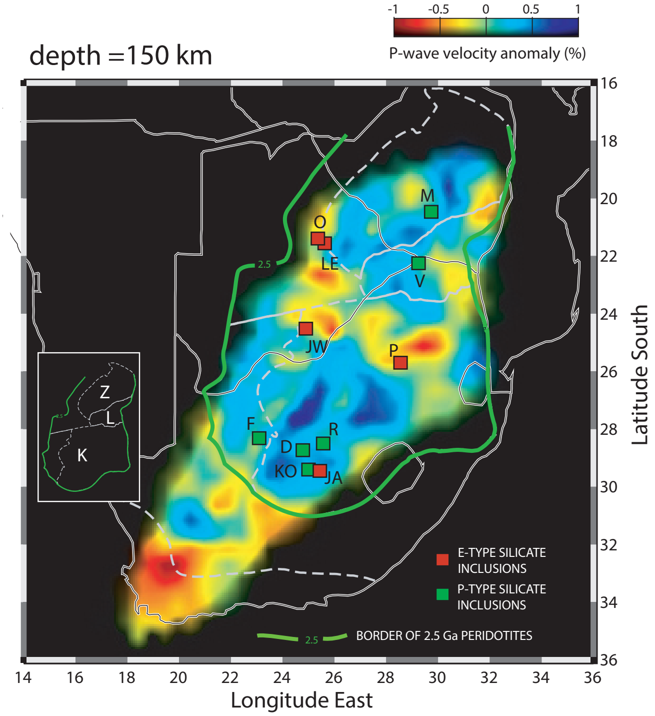
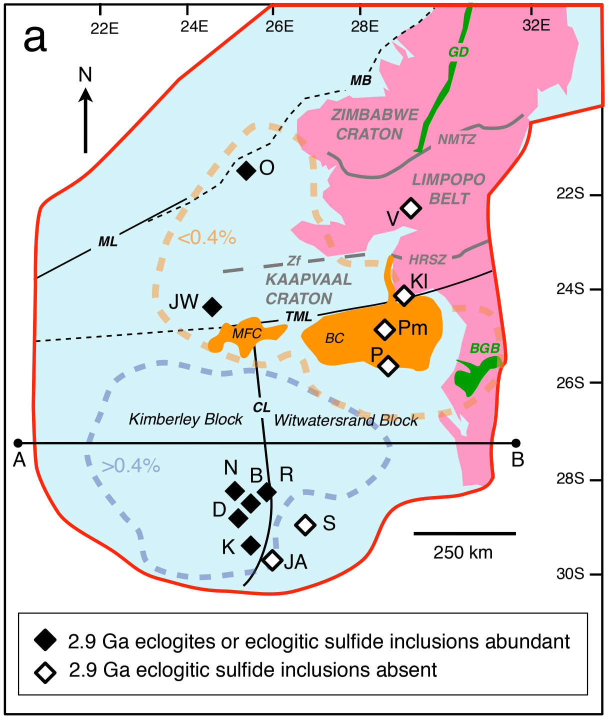


Figure 18. Tomographic image of the lithospheric mantle derived from seismic P-wave data at a depth of 150 km (e.g., James et al. 2001; Fouch et al. 2004). The Kaapvaal and Zimbabwe cratonic blocks and the Limpopo mobile belt (K,L, and Z of inset) collectively comprise the Kaapvaal-Zimbabwe craton. Bold green line indicates the outermost boundary of the Kaapvaal-Zimbabwe craton as defined by the break between Archean and Proterozoic Re-Os ages for peridotite xenoliths (Carlson et al. 1996; Carlson et al. 1999; Janney et al. 2010). Colored squares are diamond mines: red = predominantly eclogitic silicate inclusions (Letlhakane, LE; other abbreviations in caption to Fig. 17) and green squares = predominantly peridotitic silicate inclusions (Roberts Victor, R; other abbreviations in caption to Fig. 17). (Figure and caption used by permission of the American Association for Advancement of Science, from Shirey et al. (2002) *Science*, Vol. 297, Fig. 1, p. 1634).

close association of the sulfide-bearing diamonds with sulfide-containing eclogite that is the source of the diamond fluids and the occurrence of sulfides in different diamonds than those that contain silicate inclusions. The Kaapvaal craton was assembled from two independent continental blocks after 2.97 Ga (Schmitz et al. 2004). Westward-facing subduction underneath the western or "Kimberley" block (Schmitz et al. 2004) effectively made the western block the hanging wall for the fluids and sulfur carried by the oceanic slab (e.g., Aulbach et al. 2009b) and the western cratonic keel the recipient of any eclogite that could be incorporated. The surface distribution of diamond ages and types is a result of this process. West of the suture, all diamond mines contain 2.9 Ga diamonds whereas east of the suture 2.9 Ga diamonds are absent (Fig. 19). If younger ages occur it is either where the lithosphere was subject to subduction at its margin or where persistent, pervasive sub-lithospheric magmatism took place (e.g., Bushveld complex; Fig. 19). The systematic relationship of diamond age and type to the geologic processes that have affected the deepest parts of the continental lithosphere, besides being an excellent exploration model, makes diamond formation a premier tracer of the passage of ancient carbon-rich fluids.



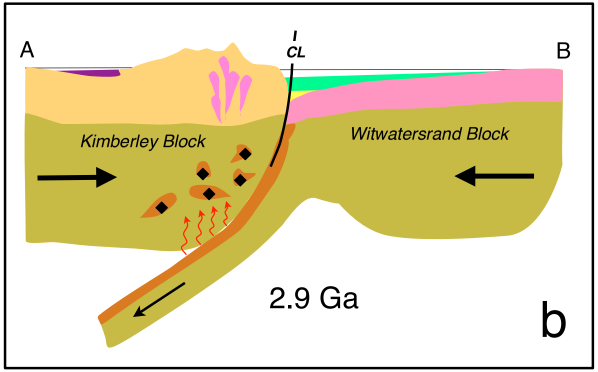


Figure 19. (a) Schematic map view of the Kaapvaal-Zimbabwe craton of southern Africa showing the localities where suites of eclogitic sulfide inclusions or whole rock eclogites have been studied and give 2.9 Ga ages (black diamonds) versus eclogitic sulfide suites where 2.9 Ga ages are absent (white diamonds) superposed on a geological basemap modified from McCourt et al. (2004) and Richardson et al. (2009). Note the assymmetry in age distribution. Data from the literature with locality abbreviations as in Figures 17, 18 with the addition of Star (S; Schmitz unpub data), Palmietgat (Pm; Simelane unpub data) and Klipspringer (Kl; Westerlund et al. 2004). Area of Archean outcrop in pink, Archean covered by supracrustal rocks in blue, outcrop of the Proterozoic Bushveld Complex (BC) and Molopo Farms Complex (MFC) in orange. The region of anomalously high P-wave velocity (>0.4%, blue dashed line) and low P-wave velocity (<0.4%, orange dashed line) is shown for the mantle lithosphere at 150 km depth (James et al. 2001; Fouch et al. 2004). The craton boundary (see sources in Fig. 18 caption) is shown by the red line, the suture between its two craton halves (Schmitz et al. 2004) by the black line labeled CL (Coleburg lineament). Other structural and igneous elements of the Kaapvaal-Zimbabwe craton (McCourt et al. 2004) as follows: Great Dyke (GD), Barberton greenstone belt (BGB), Thabazimbi-Murchison Line (TML), Hought River Shear Zone (HRSZ), Zoetfontein Fault (ZF), Northern Marginal Thrust Zone (NMTZ), southern margin of Magondi Belt (MB), Makgadikgadi Line (ML). (b) Cross section of craton along line A-B illustrating that the Kimberley Block was on the hangingwall for westward dipping subduction during continent collision at 2.9 Ga and received the bulk of diamond-forming fluids, sulfur, and eclogitic components at this time. Figure modified from Schmitz et al. (2004) and Aulbach et al. (2009b).

Lithospheric diamonds are old, typically 1.0 to 3.5 Ga, and crystallized during and after lithosphere construction. Both primordial mantle carbon and carbon sourced from subducted lithosphere could have participated in diamond-forming events in the lithosphere as a consequence of fluid and melt metasomatism. The thermodynamic and experimental observations described above are permissive of a large number of pathways for diamond crystallization, and from a wide compositional range of fluids, melts, and solids (Fig. 20a,b; see section on "*Diamond Formation*"). The considerable compositional range of mineral and fluid inclusions found in diamonds likely attests to many of these pathways being important in nature. What is clear from a mantle redox point of view is that diamond crystallization from fluids and melts in mantle lithosphere is an explicable and expected outcome of mantle metasomatism.

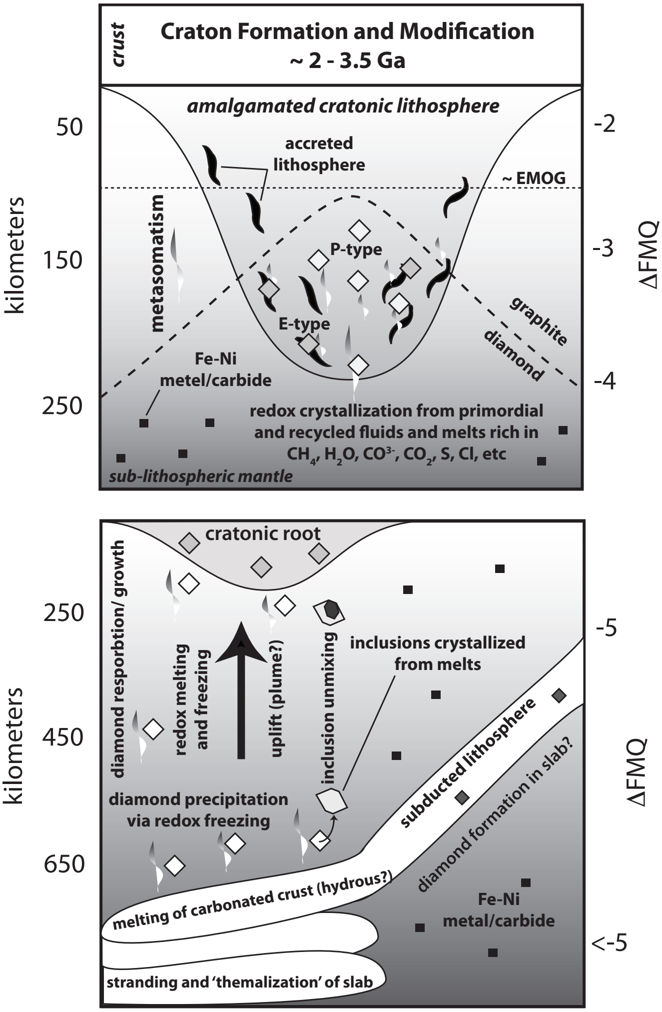


Figure 20. Schematic diagrams illustrating possible mantle conditions (e.g., depth, oxygen fugacity) and geodynamic settings in which lithopsheric and sub-lithospheric diamonds and their mineral inclusions are formed. The relative roles of mantle and subducted lithospheric protoliths, crystallization from partial melts, mantle redox, and mantle flow, can all be deduced and quantified through detailed, integrated studies of diamonds and their inclusions. See text for detailed discussion.

Deep carbon cycling with mantle convection: sub-lithospheric diamonds. Harte (2010) has suggested a link between the depth intervals over which sub-lithospheric inclusions most commonly occur (e.g., Table 2) based on geobarametry, and dehydration of hydrous or nominally anhydrous minerals in subducting lithospheric slabs. He postulated depth control by the position at which fluid or melt occurs. Harte suggested that dehydration of lawsonite in subducted mafic rocks provides a location for melt formation and the inclusion of the shallower (~300 km) majoritic inclusions. Deeper majoritic inclusions from the transition zone may occur as a consequence of dehydration melting at the wadsleyite-to-olivine transformation whereas the deepest diamonds possibly are related to dehydration of hydrous ringwoodite and dense hydrous Mg-silicates formed in subducted peridotites. A link between subducted protoliths and sub-lithospheric diamonds is strong in many cases. For example, Tappert et al. (2005a,b) showed that majorite garnets from Jagersfontein have Eu anomalies linking them to subducted oceanic crust, while the diamond hosts have extremely negative carbon isotope compositions possibly derived from a subducted carbon source. These authors postulate diamond formation by direct conversion from graphite in a subducted slab.

Many sub-lithospheric inclusions in natural diamonds provide ample evidence for the role of deep melts in their origin. Phase relations and abundances of incompatible trace elements show that effectively all reported inclusions in diamond interpreted as relic Ca-rich perovskite likely crystallized directly from melts derived from low extents of melting (Wang et al. 2000; Walter et al. 2008; Bulanova et al. 2010). The majority of majoritic garnet inclusions in sub-lithospheric diamonds could also have crystallized in equilibrium with low-degree, carbonate-rich melts (Keshav et al. 2005; Walter et al. 2008; Bulanova et al. 2010). Walter et al. (2008) and Bulanova et al. (2010) argue for a model involving diamond and inclusion co-precipitation from low-degree, carbonate-rich melts. These melts are envisioned to have originated within subducted oceanic lithosphere that became stranded in the deep transition zone or shallow lower mantle and thermalized with ambient mantle (Fig. 20b). Under such conditions, carbonated slab materials, including sediment, basalt, and peridotite, would potentially release low-degree, carbonate-rich melts, possibly hydrous, into the surrounding mantle. As illustrated in Figure 20b, the oxidized, carbonate-rich melts would be unstable in the ambient, reducing mantle, and when the highly mobile melts infiltrate the surrounding mantle, reaction with the mantle and reduction of carbonate results in diamond precipitation by "redox freezing" (Rohrbach and Schmidt 2011).

A feature of some inclusions in super-deep diamonds is unmixing of originally homogeneous phases into a composite of two or more phases (Table 2). Unmixing is common in majorite inclusions (Harte and Cayzer 2007) and occurs in Ti-rich Ca-perovskite (Walter et al. 2008; Bulanova et al. 2010). Walter et al. (2011) have argued that a suite of unmixed inclusions from Juina, Brazil, represents original Al-rich Mg-perovskite, CF-phase, and NAL-phase that formed in the lower mantle (Table 2). These observations indicate that the diamonds were transported upward by as much as hundreds of kilometers from their place of origin prior to incorporation into kimberlite magmas. The mechanism for upwelling beneath a craton is unclear, but could be related to a deep-seated mantle plume in the case of the sub-lithospheric mantle beneath Brazil (e.g., Harte and Cayzer 2007; Bulanova et al. 2010). Mantle that has undergone metasomatism and diamond formation via redox freezing would be locally more carbon-rich and more oxidizing than ambient mantle. Upon upwelling of such metasomatized mantle, carbonate will become stabilized at a depth that will depend on the carbon content and the ambient f_{O_2}. If this stabilization occurs, local oxidation of diamond to carbonate will drastically lower the solidus, resulting in "redox melting" (Fig. 20b; Taylor and Green 1988; Stagno and Frost 2010; Rohrbach and Schmidt 2011). Newly formed carbonated melts would then intrude more reducing mantle, and redox freezing could again occur. This process of repeated redox freezing, including melting, may in part explain the complex textures observed in many super-deep diamonds that include multiple growth centers, resorption and re-growth, and intense and complex zoning (Fig. 1, bottom).

Diamonds from the transition zone cover a large range in $^{13}C/^{12}C$ ratio (Fig. 7), yet display restricted and distinct ranges from one locality to another. For example, Kankan transition zone diamonds have higher $^{13}C/^{12}C$ ($\delta^{13}C$ ~1‰), whereas those from Jagerfontain are much lower $^{13}C/^{12}C$ ($\delta^{13}C \sim -20$‰; Fig. 7). As these diamonds are eclogitic in nature, it remains unknown whether these values are characteristic of larger transition zone domains or only apply to local eclogitic regions. The link between diamond formation in the transition zone and the subduction factory has been emphasized by the unique C-isotope characteristics of the diamonds and the trace element patterns their included eclogitic garnets (e.g., Tappert et al. 2005b), and is essential for the "redox-freezing" model for super-deep diamond growth (see above). N-isotope geochemistry of most studied transition zone diamonds also support the subduction-factory link (Palot et al. 2012), although this link has been challenging to confirm with $^{15}N/^{14}N$ studies because of the preponderance sub-lithospheric diamonds that are Type-II (nitrogen-free). Low $^{13}C/^{12}C$ compositions are rarer in the studied lower mantle diamond population (Fig. 7; Pearson et al. 2003), which might suggest eclogitic material rarely reaches the lower mantle. Recently, though, a suite of low $^{13}C/^{12}C$ ($\delta^{13}C \sim -24$‰) lower mantle diamonds containing a high-pressure basaltic mineral assemblage was studied, confirming that recycling can reach the lower mantle (Walter et al. 2011). In general, the complex growth pattern of super-deep diamonds identified by cathodoluminescence (Fig. 1; Araujo et al. 2013) is substantiated by C-isotope heterogeneity, illustrating multiple diamond growth events in a changing P-T environment (e.g., Bulanova et al. 2010; Palot et al. 2012).

Carbon mobility with melt: the diamond-kimberlite-carbonatite connection. With the exception of rare lamproite and lamprophyre, lithospheric and sub-lithospheric diamonds have been transported to the surface exclusively in rocks of kimberlitic composition (e.g., Gurney et al. 2010). Experimental studies and igneous petrology establish a petrogenetic link between kimberlite, carbonatite, and carbonated peridotite (Gudfinnsson and Presnall 2005; Keshav et al. 2005; Walter et al. 2008; Keshav et al. 2011; Russell et al. 2012; Jones et al. 2013). Where kimberlites originate and how they form are matters beyond simple diamond transport, for, although nearly all monocrystalline diamonds are much older (e.g., many tens of millions to billions of years older) than their host kimberlite, there is much that the study of kimberlites can contribute to understanding deep mantle fluids and melts in the region of diamond growth.

Kimberlites are rare but have been found on every continent and are associated with the cratonic portion that has a mantle lithospheric keel (e.g., Figs. 2, 3). Kimberlites are well known to have erupted more commonly in the Phanerozoic Eon than in the Pre-Cambrian (Gurney et al. 2010). The number of known kimberlite occurrences older than 1 Ga is fairly small, and although at the moment Archean kimberlites are not known, the presence of alluvial macro-diamonds in late Archean sediments indicates that such ancient kimberlites may indeed have existed (e.g., Gurney et al. 2010; Kopylova et al. 2011). Apparently the number of kimberlites that erupted globally increased dramatically around the Phanerozoic Eon (e.g., Smith et al. 1994; Heaman et al. 2004), although Tertiary kimberlites are much less abundant and only one Quaternary example has been reported (Dawson 1994).

Most kimberlites are not diamond bearing, but those that are must have originated at least as deep as the onset of diamond stability, which is at ~140 km, a depth that is consistent with results from thermobarometry on mantle xenoliths in kimberlites. The presence of sub-lithospheric diamonds in some kimberlites places kimberlite magma generation within the asthenosphere or deeper in the mantle, at least for these kimberlite pipes. The isotopic composition and mineralogy of Group I kimberlites also supports a sub-lithospheric origin, whereas the lithospheric affinity of Group II raises question of a shallower source that may be in the lithosphere for these kimberlites. Kimberlite magmas collect and transport a tremendous amount and variety of foreign material, including xenoliths and xenocrysts derived from both mantle and crustal sources. For this reason, establishing the bulk composition of primary kimberlite magma has long been problematic (e.g., Mitchell 2008). However, from rare hypabyssal aphanitic examples and from chemical re-constructions, a general consensus has emerged that kimberlites are silica-undersaturated (~15 to 35 wt% SiO_2) and MgO-rich (~20 to 35 wt%), and contain a high volatile component, possibly rich in both carbon (~5 to 20 wt%) and water (~5 to 10 wt%; see Mitchell 2008; Sparks et al. 2009). The lack of knowledge of the composition of primary kimberlite magma renders petrogenetic models for their origin non-unique. For example, their elemental enrichments and volatile-rich nature might indicate either very low-degree partial melting of cryptically metasomatized mantle (Dalton and Presnall 1998; Becker and Le Roex 2006) or higher-degree melting of pervasively veined mantle (Mitchell 1995, 2004).

Kimberlites also bear resemblance to carbonatitic rocks in terms of their high degree of silica undersaturation and enrichments in incompatible elements and volatiles, and for this reason there is a possible petrogenetic link between these magma types. On the basis of experimental melting phase relations of model carbonated peridotite, there is a continuum of compositions ranging from carbonatitic magmas (e.g., $SiO_2 < 5$ wt%) at the solidus to compositions akin to kimberlites at higher degrees of melting (Dalton and Presnall 1998; Gudfinnsson and Presnall 2005) at pressures at least up to up to 8 GPa. With this link to carbonatites, kimberlites themselves then would provide information about the deep carbon cycle by being generated from carbonatitic sources.

Another possible link is that carbonatitic melts may have been responsible for the metasomatic conditioning of the mantle source regions from which kimberlites form. Carbonatitic melts are probably highly mobile in the mantle (Minarik and Watson 1995; Hammouda and Laporte 2000; Jones et al. 2013) and are considered to be very effective metasomatic agents (Green and Wallace 1988; Hauri et al. 1993), influencing the mantle either chemically or modally. Melting of carbonate-metasomatized mantle, especially in the presence of water, may produce primary kimberlite magmas. Recently a model was developed whereby kimberlites form as the product of reaction of proto-carbonatitic melts with orthopyroxene-bearing mantle peridotite (Fig. 21). Dissolution of orthopyroxene into carbonatite increases the silica content, which at the same time decreases the solubility of volatiles (i.e., CO_2 and H_2O). Exsolution of the volatile phase provides buoyancy for the magma and a mechanism for rapid upward migration and incorporation of xenolithic material. Continued dissolution of orthopyroxene as the magma rises eventually changes the carbonatitic primary magma into a kimberlitic magma, and the progressively decreasing volatile solubility eventually leads to the rapid and explosive transport and emplacement of diamonds from the deep mantle to the shallow crust or surface (Fig. 21).

Carbon reservoirs: primordial versus recycled carbon. Carbon is a massively cycled element and it is likely that it is close to steady state in Earth's mantle (e.g., Javoy et al. 1982; Jambon 1994). In other words, the central question is not whether carbon is subducted but rather whether we can record the isotope heterogeneity introduced in Earth's mantle by subduction and distinguish it from the heterogeneity induced by intra-mantle processes (e.g., metasomatism), or even by mixing with a homogeneous (or heterogeneous) C-isotopic reservoir.

Furthermore, with mantle carbon having a long residence time, ca. 4.5 b.y. and other isotopic evidence for long-lived ancient mantle reservoirs (e.g., Jackson et al. 2010; Touboul et al. 2012), it is possible that a primordial C-reservoir might still exist and be sampled. The occurrence of low $\delta^{13}C$ in diamonds has been often ascribed to reflect a primordial heterogeneity of carbon in the mantle (Deines et al. 1991, 1993; Haggerty 1999) although this model, among others, fails to account for their occurrence among eclogitic rather than in peridotitic diamonds. The argument according to which mantle carbon might be isotopically heterogeneous was originally based on the similarities between the $\delta^{13}C$ distribution of carbon in iron meteorites and diamonds

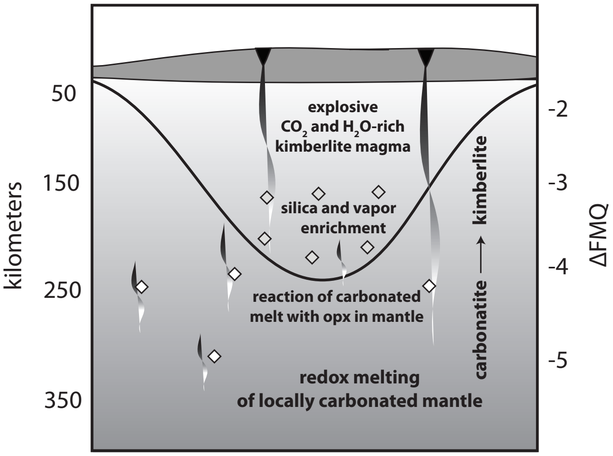


Figure 21. A schematic diagram illustrating the growth environment of lithospheric diamonds and their mineral inclusions. Studies show the importance of C-O-H-S metasomatic fluids in diamond growth, and the chemistry of mineral inclusions clearly reveals both peridotitic (P-type) and eclogitic (E-type) protoliths. The chemistry, age, and tectonic setting of the diamonds and their inclusions provide powerful constraints for models of the growth and evolution of cratonic mantle lithosphere. Carbonatite to kimberlite evolution after Russell et al. (2012).

but how such heterogeneities could survive mantle convection and homogenization during a period of a magma ocean remained unaddressed. In a model in which carbon is at steady state, it is anticipated that Earth's convective mantle (i.e., the reservoir from which the oceanic and continental crust are extracted and subducted ocean crust is recycled) and the primordial reservoir would have similar $\delta^{13}C$ close to –5‰. This similarity would also be the case for carbon exchanged between the surface and the mantle; degassed carbon and recycled carbon would display time-integrated $\delta^{13}C$ close to –5‰. In this context, the fact that ocean island basalts, mid-ocean ridge basalts, carbonatites, kimberlite, and diamonds have a $\delta^{13}C$ mode close to –5‰ is not inconsistent whatever the source of their carbon. The evidence for primordial carbon is therefore typically inferred from other systematics such as rare gases in ocean island basalts, but the respective contributions of carbon from the primordial and convective reservoirs remain to be established as their concentration in the primordial reservoir remains unknown. Additional evidence for primordial heterogeneity in diamonds has been suggested from three samples displaying low $\delta^{15}N$-values (< –25‰). In this case the $\delta^{13}C$-value close to –3.5 ‰ was suggested (Palot et al. 2012) but the size of the primordial reservoir and its carbon concentration cannot be addressed.

Several diamond populations (from the Dachine metakomatiite or metalamprophyre in French Guyana and from Jericho kimberlite in Northern Slave with $\delta^{13}C$-modes ~–28 ‰ and –38‰ respectively) are unique and difficult to interpret in the light of heterogeneity being either primordial, subducted, or mantle-related. This difficulty arises because there is almost no sediment with $\delta^{13}C$ as low as –40‰. Their preservation of such low $\delta^{13}C$ further requires the virtual absence of any (i.e., ^{13}C-enriched) carbonates in their sources, which is not consistent with observations in metamorphic rocks and sediments in general. Those odd C-isotope distributions might alternatively reflect an as yet unknown process(es), but we lack appropriate experimental work to investigate such a possibility.

Overall, the data suggest that the existence of a primordial carbon reservoir can be recognized and sampled from the study of diamonds, but its existence can only be established in the light of additional tracers (trace elements, radiogenic and other stable isotope systematics). Although usually at sub-ppm or ppb levels, diamonds contain many impurities that can be used in future studies to perhaps resolve the many open issues that have been highlighted in this review chapter.

OUTSTANDING QUESTIONS AND FUTURE WORK

The comprehensive, cross-disciplinary nature of this review identifies some of the areas where important unknowns in diamond research can be addressed with future work: (1) the quantitative partitioning of elements and fractionation of isotopes during diamond growth, (2) the co-genetic (or not) relationship of diamond to its host inclusions and the age of diamonds, (3) the recognition and significance of primordial carbon, primary mantle carbon, or subducted carbon in the composition of diamond, (4) the speciation of C in diamond-forming fluids and the processes that control the oxygen fugacity of the mantle, (5) the deepest diamonds, their ultra-high pressure inclusions and the geodynamic processes occurring in convecting the mantle, (6) the experimental simulation of diamond formation from a variety of mantle fluids and melts, and (7) the nanostructural characteristics of diamond as they relate to all aspects of diamond formation.

The expected answers to questions in these areas will lead to a new understanding of the conditions of diamond formation in the deep mantle, how diamond-forming and diamond-carrying melts interact with mantle peridotite, whether a significant reservoir of mantle carbon is primordial or recycled, and how carbon is transported and stored in the mantle now and in the past (as long as 3.5 billion years ago). Such integrated research on natural diamond has the potential to transform our knowledge about the sources of the surface volcanic flux of carbon, the connections between carbon in the biosphere to carbon in the deep mantle, the behavior of carbon in Earth's interior under extreme conditions, and the geodynamics of Earth's mantle.

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