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Τμήμα Γεωλογίας και
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Τομέας Ορυκτολογίας
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BSc Diploma Thesis – Προπτυχιακή Διπλωματική Εργασία

Recent Advances in Deep Diamond Genesis

Πρόσφατες Εξελίξεις στη Γένεση Διαμαντιών Πολύ Μεγάλου Βάθους

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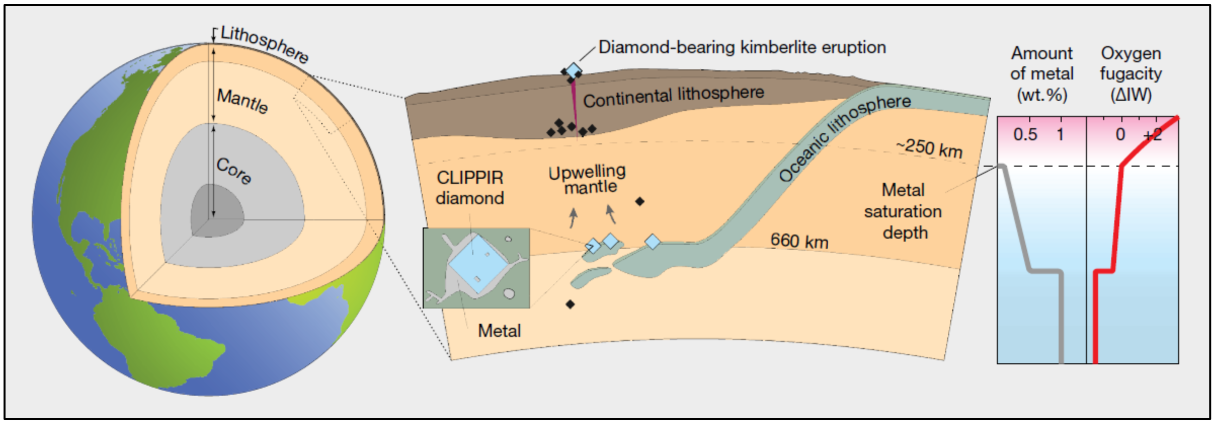

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ABSTRACT

Diamond is perhaps the most unique mineral on our planet. Apart from its aesthetic and commercial value, it is the information it preserves for parts of our planet that are completely inaccessible that makes it scientifically priceless. Through its mineral inclusions, we travel to depths inside the earth that could not even be conceived a couple of decades ago.

Less than 1% of the global diamond production is believed to come from depths greater than 250km. However, it is the mineral inclusions of these diamonds that provide extremely valuable information about the mineralogical constitution of the deep mantle, the pressure and temperature conditions prevailing at such depths as well as the deep carbon cycle.

The first part of this diploma thesis is concerned with the geotectonic setting of diamond genesis, the main carrier rocks, and the elemental substitutions in the diamond crystal lattice that are related with its depth of formation.

The second part deals with the diversity of mineral inclusions in the diamond and their connection to specific depths of formation, depths that can reach the top of the lower mantle (more than 660km).

Super-deep, CLIPPIR, ferropericlase, magnesium perovskite, walstromite

ΠΕΡΙΛΗΨΗ

Το διαμάντι είναι ίσως το πιο μοναδικό ορυκτό του πλανήτη μας. Εκτός από την αισθητική και εμπορική του αξία, έχει και ανεκτίμητη επιστημονική αξία καθώς μας μεταφέρει πολύτιμες πληροφορίες από περιοχές του εσωτερικού του πλανήτη μας που δεν είναι προσβάσιμες. Μέσα από τα ορυκτολογικά του εγκλείσματα, «ταξιδεύουμε» σε βάθη μέσα στη Γη, αδιανόητα λίγες δεκαετίες πριν.

Λιγότερο από το 1% της παγκόσμιας παραγωγής διαμαντιών πιστεύεται ότι δημιουργήθηκε σε βάθη μεγαλύτερα των 250km. Παρόλα αυτά, τα εγκλείσματα αυτών των διαμαντιών είναι από τα πλέον πολύτιμα όχι μόνο διότι παρέχουν πληροφορίες για τη σύσταση του βαθύτερου άνω μανδύα, αλλά επίσης διότι εμπεριέχουν πληροφορίες για τις συνθήκες P–T που επικρατούν εκεί καθώς και για την ανακύκλωση του άνθρακα στο εσωτερικό της Γης.

Στο πρώτο μέρος αυτής της διπλωματικής εργασίας γίνεται αναφορά στο γεωτεκτονικό περιβάλλον γένεσης των διαμαντιών, στα πετρώματα-ξενιστές των διαμαντιών καθώς και στην υποκατάσταση στοιχείων που λαμβάνει χώρα στο κρυσταλλικό πλέγμα των διαμαντιών, και η οποία είναι άρρηκτα συνδεδεμένη με το βάθος σχηματισμού τους.

Στο δεύτερο μέρος της διπλωματικής δίνεται έμφαση στην ποικιλία των ορυκτών εγκλεισμάτων των διαμαντιών καθώς και στη σύνδεσή τους με συγκεκριμένα βάθη σχηματισμού/κρυστάλλωσης, βάθη τα οποία μπορούν να φτάσουν μέχρι τα ανώτερα τμήματα του κατώτερου μανδύα, δηλαδή μεγαλύτερα από 660km.

Super-deep, CLIPPIR, Fe-περίκλαστο, Mg-περοβσκίτης, walstromite

INTRODUCTION

THE HISTORY OF DIAMOND

Diamond has always been admired and sought after. A testimony of this was what Roman naturalist Pliny stated in the first century AD: "Diamond is the most valuable, not only of precious stones but of all things in this world."

Some historians estimate that the diamond trade dates to the fourth century BC when Indians were gathering them from alluvial deposits in the country's rivers and streams for India's wealthy classes.

From the 1400s until about the end of the 19th century diamonds became fashionable accessories for Europe's elite and due to the increasing demand different mining sources were rising, since the alluvial deposits of India declined by the 1700s.

After India, Brazil emerged as an important source that dominated the diamond market for over 150 years followed by South African deposits which dominated during the 20th century.

This "diamond rush" affected the "scientific diamond rush", which led to intensive research on diamond and its properties as a mineral, its mode of formation, its applications, and so on. The research will continue since diamond truly is one of the unique minerals of our planet.

Among diamond's unique properties are its hardness (it is the hardest known naturally occurring mineral scoring 10 on Mohs's Scale), its inertia towards chemical reactions, its high thermal conductivity, and its high RI index (2.4) which gives it its adamantine luster as well as its outstanding brilliance and fire when properly cut and polished. Not to mention the variety of natural colors it occurs, which can only be compared with the variety of colors seen within the visible spectrum. Apart from being a breathtaking gem, diamond is a window to the Earth's mantle, its physical properties, its mineralogy, its processes, its redox state, and the deep C cycle.

GEOTECTONIC SETTING OF DIAMONDS

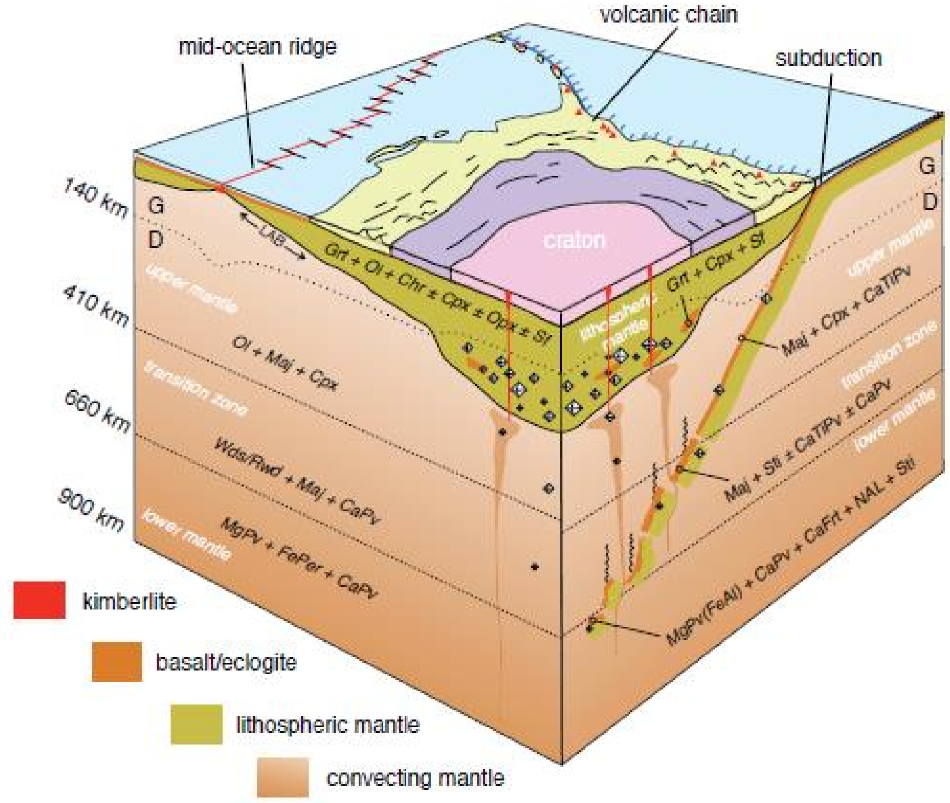


Fig. 1. Block diagram showing the relationships between a continental craton, its lithospheric mantle keel and diamond stable regions in it, and the convecting mantle. Under the appropriate *f*O_2 conditions, diamonds can form in the convecting mantle, the subducting slab, and the mantle keel.
G=graphite, D=diamond, LAB=lithosphere/asthenosphere boundary. Mineral assemblage information and abbreviations are defined in Tables 1 and 2. These assemblages give the expected inclusions to be found in peridotitic/ultramafic (left) and eclogitic/basaltic (right) rock compositions.
(From *Shirey et al.*, "Diamonds and the Geology of Mantle Carbon", 2013, their figure 2)

Experimental evidence suggests that the graphite-diamond transition takes place at depths exceeding 100km in the Earth's upper mantle at geologically reasonable temperatures (Fig. 2).

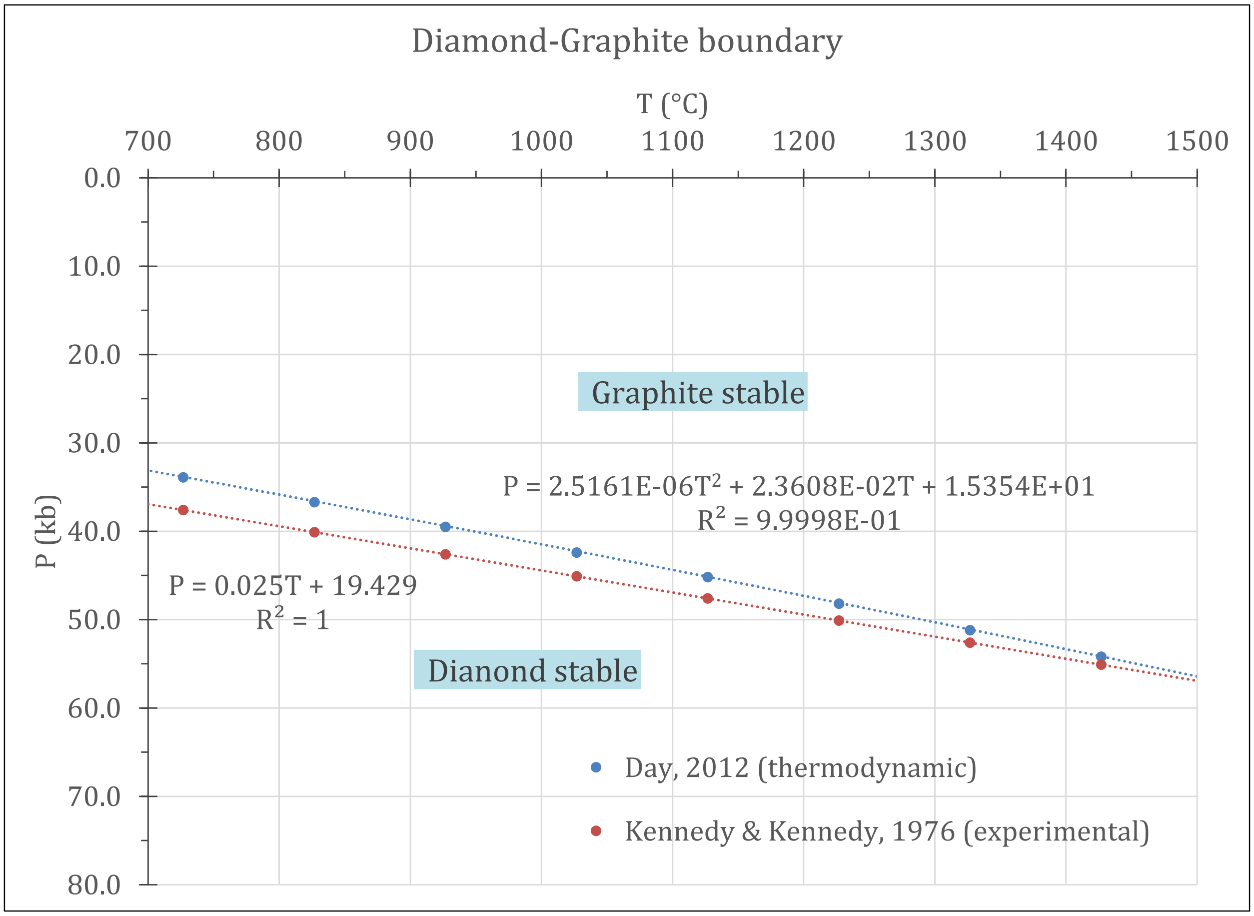


Fig. 2. Graphite-diamond boundary determined experimentally and calculated thermodynamically.

In general, most diamonds (including gem-quality ones) form at depths greater than ~150km (Fig. 1).

Within the mantle, we can distinguish two loci where diamonds are formed: i) the rigid part of the upper mantle, i.e. the subcratonic lithospheric mantle – these diamonds are referred to as *lithospheric diamonds* and ii) the asthenospheric mantle underneath, up to the 660km discontinuity (mantle transition zone) – these are referred to as *sub-lithospheric* or *"super-deep" diamonds*.

Additionally, we can have crustal diamonds that formed during ultra-high-pressure metamorphic events in subducted crustal rocks, and these are referred to as UHPM diamonds. UHPM diamond pressures can be comparable to lithospheric diamond pressures but are smaller than super-deep diamond pressures.

Significantly, UHPM diamonds are microdiamonds (<0.5 mm) and not macrodiamonds (>0.5 mm), like the ones derived from the mantle.

Finally, we can have meteoritic and impact diamonds. Meteoritic diamonds are the ones that make up a rare ingredient of meteorites' mineralogy. We can find these diamonds in iron, ureilite, and chondritic meteorites but they have a different origin in each meteorite category. The diamonds found in iron and ureilite meteorites are possibly the result of extra-terrestrial collisions whereas the chondritic meteorite diamonds have a very distinct carbon isotopic composition which suggests that they were formed outside our solar system and they "could be pre-solar dust grains of interstellar origin incorporated into the chondritic meteorites as exotic mineral components".

Impact diamonds formed during the impact of a meteorite on the Earth's surface. The pressure at the impact site can temporarily be so great as to lead to the crystallization of diamonds (usually only fractions of a millimeter in size).

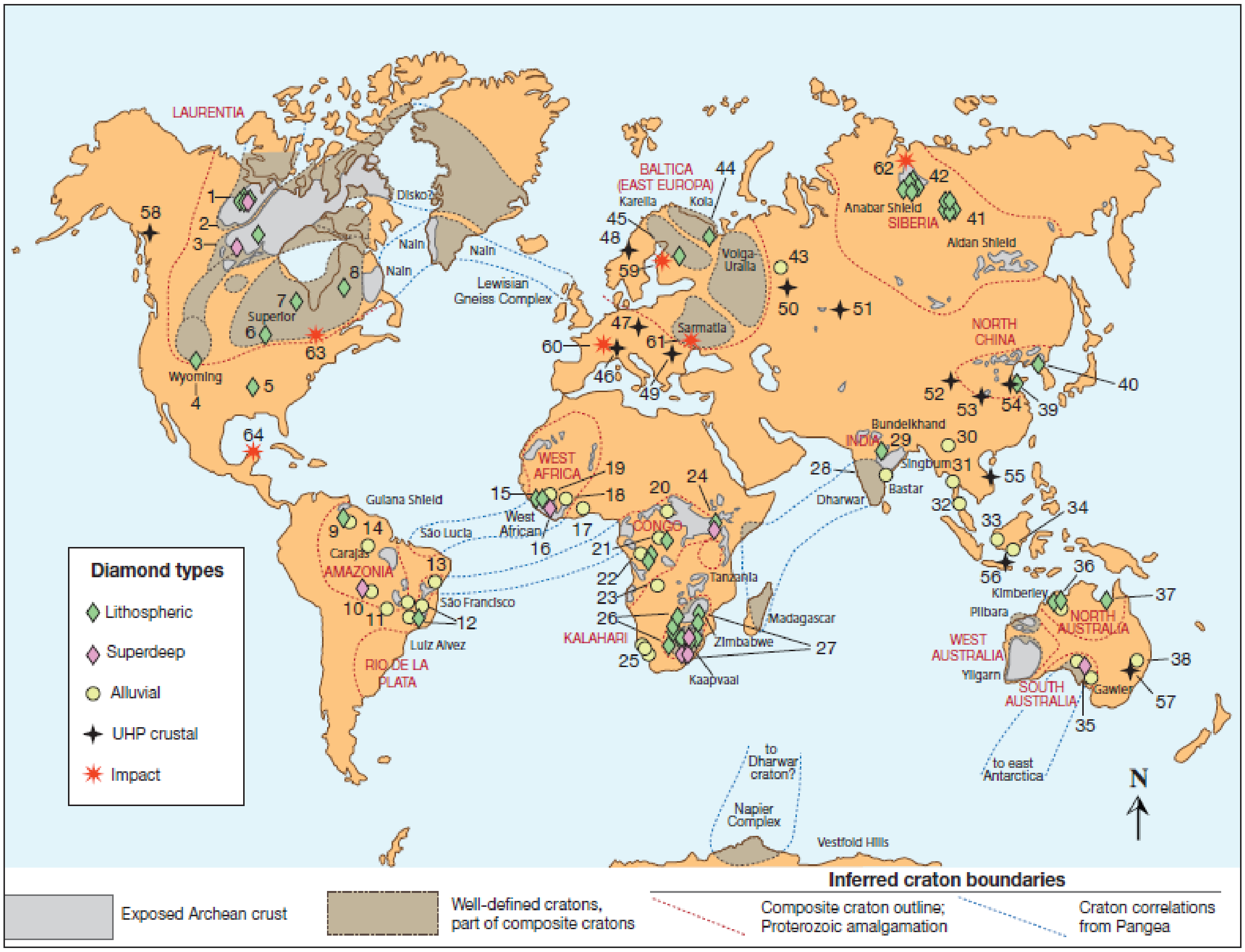


Fig. 3. World diamond localities are shown here in relation to Archean cratons and classified as either kimberlite-hosted and from mantle keels (lithospheric), kimberlite-hosted and from the convecting mantle (superdeep), of surface origin (alluvial), from ultra-high-pressure crustal terranes (UHP crustal) or formed by the shock of a meteorite impact (impact). Only a subset of these localities is rich enough to be mined for diamonds. The crustal age/craton base map is from Pearson and Wittig (2008). Locality information is from Tappert et al. (2009), Harte (2010), Harte and Richardson (2011), Tappert and Tappert (2011), Dobrzhinetskaya (2012), and Shirey et al. (2013).

Localities are 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) Chapada Diamantina; (14) Boa Vista; (15) Koidu; (16) Kan; (17) Akwatia; (18) Tortiya; (19) Aredor; (20) Bangui; (21) Mbuji-Mayi; (22) Camafuca, Cuango, Catoca; (23) Masvingo; (24) Mwadui; (25) Luderitz, Oranjemund, Namaqualand; (26) Orapa/Damtshaa, Letlhakane, Jwaneng, Finsch; (27) Murowa, Venetia, The Oaks, Marsfontein, Premier, Dokolwayo, Roberts Victor, Letseng-la-Terae, Jagersfontein, Koffiefontein, Monastery, Kimberley (Bultfontein, Kimberley, De Beers, Dutoitspan, Kamfersdam, Wesselton); (28) Kollur; (29) Majhgawan/Panna; (30) Momeik; (31) Theindaw; (32) Phuket; (33) West Kalimantan; (34) South Kalimantan; (35) Springfield Basin, Eurelia/Orroroo, 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) Lappajärvi; (60); Ries; (61) Zapadnaya; (62) Popigai; (63) Sudbury; and (64) Chixculub. Adapted from Shirey et al. (2013), with permission of the Mineralogical Society of America.
(From *Shirey et al.* "Recent Advances in Understanding the Geology of Diamonds", 2013, their figure 4)

Lithospheric Diamonds (~150km – ~300km)

The lithosphere consists of the lithospheric mantle and the overlying crust which, together, constitute the plates that drift on the convecting asthenosphere.

The parts of the lithospheric mantle that favor diamond formation are the regions where we have high enough pressures combined at relatively low temperatures. These areas can be found at cratons – composed of granites and gneisses – they are regions of very low geothermal gradient that are generally confined to the geologically old parts of continents and are underlain by exceptionally deep-reaching mantle keels that mostly formed during the Proterozoic, ~1.5 billion years ago.

The mantle keels or roots have mainly peridotitic composition, depleted in Al, Ca and Fe and the diamonds inside them are believed to crystallize mainly from carbon-rich fluids that percolate through them (Fig. 4).

The maximum depth of lithospheric diamond formation based on thermobarometry on cratonic peridotite xenoliths worldwide is up to 250km with an estimated maximum temperature of ca. 1350 to 1400°C (*Stachel and Harris 2008*) stretching perhaps to 300km (*Shirey et al. 2013*).

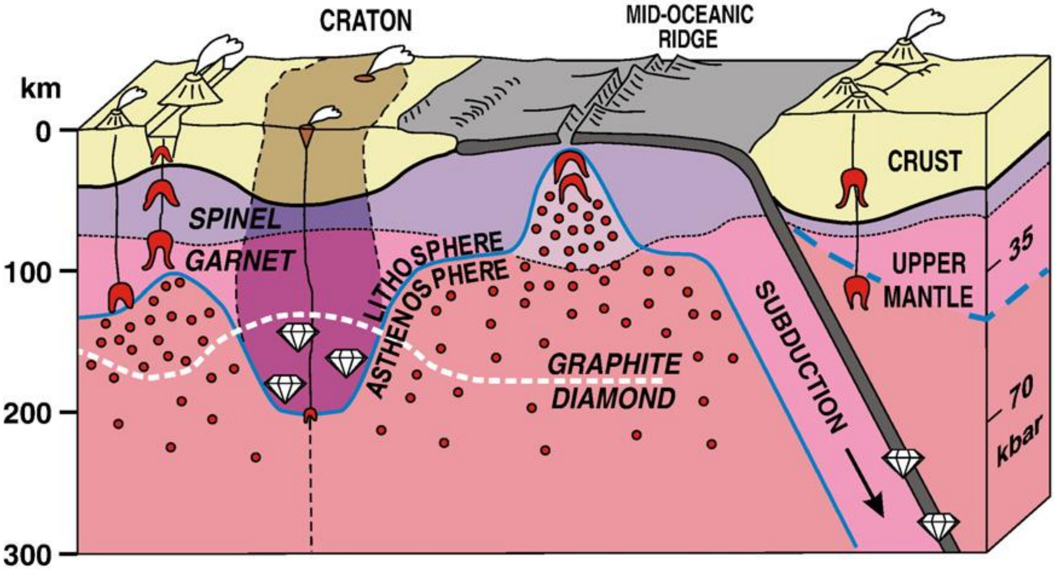


Fig. 4. Schematic vertical section through the Earth's crust and part of the upper mantle. The upper mantle is separated into two mineralogical layers, spinel facies (lilac) and garnet facies (purple to pink). The red dots are small volume melt fractions in the asthenosphere (causing low seismic velocities). Beneath Archean cratons, the lithosphere may extend to over 200km in depth. Compared to the asthenosphere at a similar depth, the subcratonic lithospheric mantle is cooler causing the graphite/diamond transition to occur at lower pressure. The resulting region where lithosphere and diamond stability overlap ("diamond window") is the principal source region of diamonds worldwide. Only beneath cratons may very deep-seated magmas (kimberlite, olivine lamproite) sample diamondiferous lithosphere during rapid ascent. Except for subducting oceanic slabs, the sub-lithospheric upper mantle appears to be void of macro-diamonds.
(From *Stachel et al.*, "The origin of cratonic diamonds — Constraints from mineral inclusions", 2008, their figure 1)

Sub-lithospheric or "Super-Deep" Diamonds (~300km – ~800km)

"Super-deep" diamonds are considered those having a sub-lithospheric origin, which means a depth of formation below 250-300km.

The depth of formation of these diamonds can be assessed by examining the different mineral inclusions in monocrystalline diamonds (originating from such depths) and comparing them to similar minerals synthesized experimentally in a laboratory.

One of the mineral inclusions that is used to characterize the geotectonic setting of super-deep diamonds is $CaSiO_3$-walstromite, as it is the most abundant Ca-bearing mineral inclusion found in them and is believed to derive from $CaSiO_3$-perovskite, which is stable only below ~600km depth (although its real depth of origin is controversial) (*Anzolini et al.*, 2018). Experimental data from *Anzolini et al.* (2018) showed for $CaSiO_3$-walstromite to have entrapment pressures ranging from 8.10 to 9.27GPa [P_{inc} = 4.26 (±0.07) GPa] which corresponds to 240-280km depth, with these numbers being the minimum estimate.

Figure 5 depicts phase changes in the $CaSiO_3$ system with increasing depth in the mantle as well as the graphite-diamond boundary.

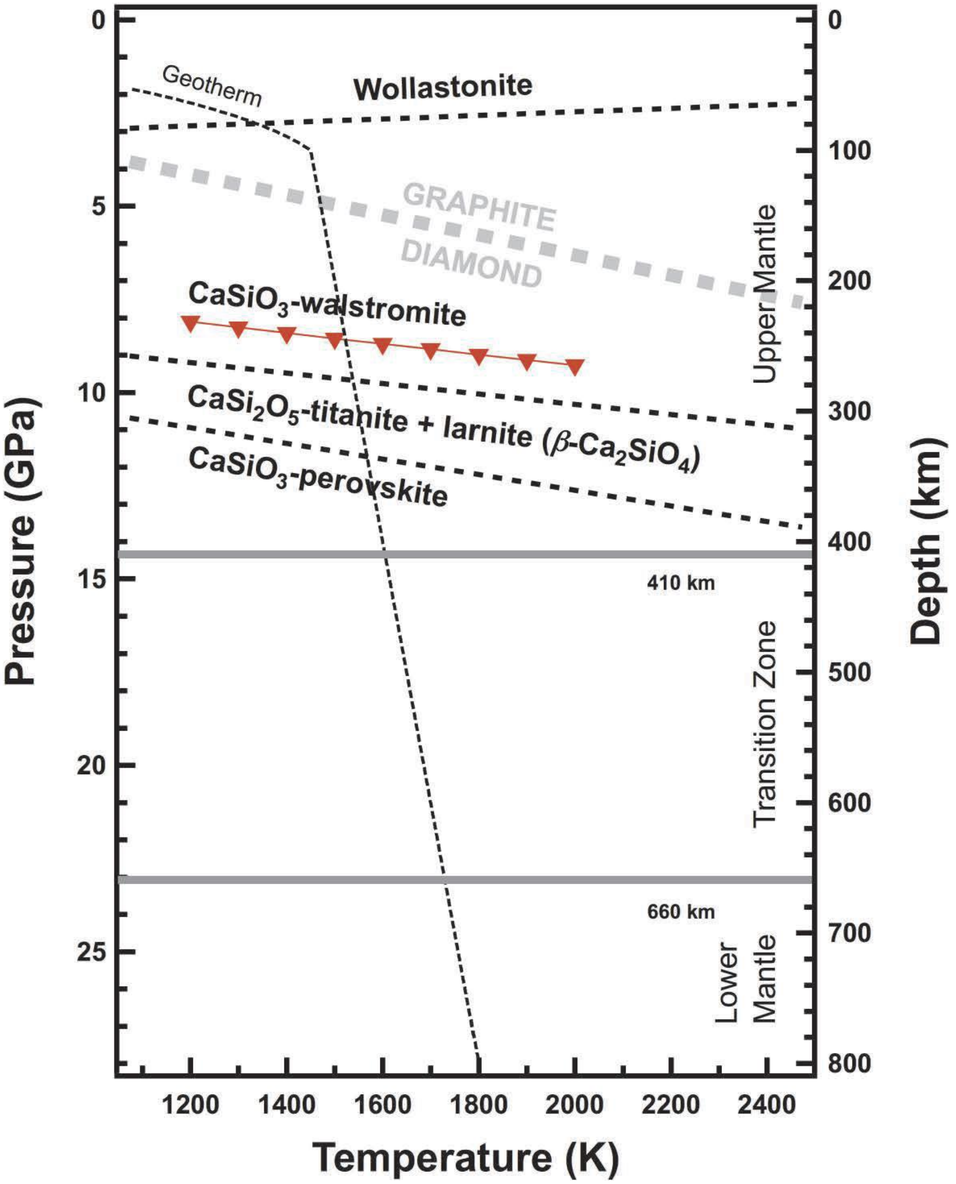


Fig. 5. Phase diagram of the $CaSiO_3$ system, in which the phase boundaries are given as dotted lines. The graphite-diamond phase boundary is shown as a gray dashed line. The geotherm is shown as a black dashed line. The 410 and 660km discontinuities enclosing the transition zone are indicated by bold lines. Entrapment pressures from which $CaSiO_3$-wasltromite may have originated are represented with red symbols.
(From *Anzolini et al.*, "Elastic Barometry of Super-Deep Diamonds", 2018, their figure 6)

It is worth noting here that only a small portion of diamonds ~6% are interpreted to crystallize between 300 and 800km depth because some of the inclusions entrapped are thought to result from retrograde transformation from lower-mantle or transition-zone precursors (*Anzolini et al.*, 2018).

Thus, the different mineral phases we come across in super-deep diamonds correspond to different depths of formation inside the lower upper mantle, transition zone, lower mantle, and even the lower mantle-core boundary.

The mineral inclusions in diamonds that have super-deep origin will be analyzed in a separate chapter.

HOST ROCKS

Characteristic	Kimberlite	Lamproite	Lamprophyre
Color of rock in outcrop	Green, dark bluish green	Dark gray, black	Dark gray, black
Volatiles	$CO_2 > H_2O$, halogens (Cl, F)	$H_2O > CO_2$, halogens	$H_2O > CO_2$, halogens
Composition	Not peralkaline, hybrid, $K_2O > Na_2O$	Peralkaline, hybrid to magmatic	Peralkaline, magmatic
Setting	Cratonic	Mobile belt, craton margin	Subduction zone
Depth of origin	200–300 km mantle, can be sourced >400–700 km	>140 km, but probably not much deeper	>140 km, but probably not much deeper
Eruptive style	Explosive volcanic pipes, pyroclastic	Small volcanic pipes and cones	Dikes
Diagnostic phenocryst minerals	Olivine	Ti-phlogopite	Biotite, amphibole
Typical matrix mineralogy	Olivine, carbonate	Phlogopite	Feldspar
Diamond potential	Common, can range to high diamond grade	Rare, but can range to high diamond grade	Rare, few diamondiferous known

Notes: A hybrid composition is one that is substantially modified by incorporation of early-crystallizing minerals, xenoliths, and pieces of country rock so that determining a real magmatic composition is difficult; magmatic composition can be directly related to its igneous source.

Table 1. Characteristics of known diamond-carrying magmas.
(From *Shirey et al.*, "RECENT ADVANCES IN UNDERSTANDING THE GEOLOGY OF DIAMONDS", 2013, their table 2)

Diamonds are formed at mantle depths. Their host rocks include peridotite and eclogite. Peridotite primarily consists of olivine and variable amounts of orthopyroxene, clinopyroxene, garnet, and/or spinel (chromite) whereas eclogite is mainly composed of magnesium-rich garnet and chromium-poor sodic clinopyroxene.

Diamond-bearing peridotites and eclogites are brought to the surface by three rare types of magma: kimberlite, lamproite, and lamprophyre (table 1) (*Shirey et al.* 2013). Once these magmas reach the Earth's surface, they erupt violently but on a small scale creating small craters (rarely larger than a few hundred meters in diameter) and volcanic structures underlying these craters that are commonly referred to as pipes or diatremes. After the eruption, the magmas cool and form volcanic rocks.

The common characteristics of these magma types are that: they come from small degrees of deep mantle partial melting, they are relatively rich in volatiles (H_2O, CO_2, F, or Cl) and MgO, they erupt rapidly, and are not oxidizing (*Shirey et al.* 2013).

Typically, all these rock types that carry diamonds are younger than the diamonds themselves and the ancient cratons or peri-cratonic regions they intrude.

Usually, diamondiferous eclogites survive transport (by kimberlite) whereas diamondiferous peridotite is exceptionally rare, and nearly all peridotite xenoliths are diamond-free (*Shirey et al.*, 2013). Possibly the reason for that is the ready reaction of CO_2-

rich diamond-forming fluids with abundant magnesian silicates to form friable magnesite ($MgCO_3$) along silicate grain boundaries that promote disaggregation of the xenoliths and release of the diamonds, thus destroying the textural relationship with their parental rock (*Shirey et al.* 2013).

Fig. 6. On the **left**, a piece of peridotite xenolith from the Bultfontein mine, Kimberley, South Africa (diameter ~30 cm), which consists mainly of olivine (dark green), garnet (purplish red), Cr-diopside (bright green), and orthopyroxene (light brown). On the **right**, a piece of eclogite xenolith from the Roberts Victor mine, South Africa (diameter ~30 cm), which consists mainly of garnet (reddish-brown) and clinopyroxene (grayish-green). Eclogites are a minor constituent of the lithospheric mantle, but they can be important diamond source rocks.
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 1-04 and 1-05)

Kimberlites

Kimberlites are the most important of the diamond host rocks since we have several thousands of them known and of which ~30% are diamondiferous (*Shirey et al.* 2013) – only 3% though are significantly diamondiferous i.e., containing macrodiamonds at a grade > 1 carat per hundred tons (*Giuliani et al.*, 2019). They were named after the town of Kimberley in South Africa where they were first discovered.

Kimberlites are volatile-rich, potassic, ultramafic igneous rocks that vary enormously in chemical and isotopic composition, mineralogy, and texture, and show evidence that they are derived from depleted, enriched, and/or fertile mantle source (*Torsvik et al.*, 2010).

The reason for this heterogeneity in kimberlitic composition is due to the relative proportions of disaggregated mantle xenoliths, phenocryst phases (e.g., olivine), assimilated country rock, the ratio of H_2O to CO_2 in the volatile phase, as well as the extent of interaction with metasomatic minerals in the subcontinental lithospheric mantle.

For diamond petrogenesis, it is very important to classify the kimberlites as diamond carriers. Thus, we can distinguish Group I (GI) kimberlites that contain non-metasomatic mantle minerals and initial isotopic compositions for Sr, Nd, Hf, and Pb that are indicative of equilibration chiefly with the convecting mantle and Group II (GII) kimberlites that 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 (*Shirey et al.*, 2013).

Experimental petrology suggests that the minimum depth of generation of such magmas is about 150km, but the maximum depth, as suggested by Torsvik et al.(2010) could have been as deep as the core-mantle boundary (CMB), which agrees with the general view that these magmas have the deepest origin of all terrestrial magmas. Torsvik et al. (2010) using plate reconstruction, supported that most kimberlites generated during the past 540 million years (Myr) are probably related to plumes that had risen from the two plume generation zones (PGZs) (where hot spots are created) at the core-mantle boundary (CMB) but there is not enough supporting evidence yet to state this as a scientific fact.

The way these magmas reached the surface of the Earth from such great depths is because they reputedly had higher ascent rates than other xenolith-bearing magmas. The mechanism behind this rapid ascent is thought to be the exsolution of dissolved volatiles (CO_2 and H_2O) which is essential to provide sufficient buoyancy for the ascent of these dense, crystal-rich magmas. Of course, kimberlitic magmas also exploit pre-existing, upper lithospheric zones of mechanical weakness.

Kimberlites are exclusively related to the most ancient parts of the continental crust, the cratons (stable nuclei), which are those that formed in the Archean eon, 3.8 to 2.5 billion years ago. A small portion of them (diamond-bearing kimberlites) are also present in younger parts of cratons that formed in the Proterozoic eon, 2.5 to 1.5 billion years ago, and are referred to as mobile belts.

The association between diamondiferous kimberlites and cratons (or peri-cratonic regions) was first formalized by Clifford in the 1960s which later became known as “Clifford’s rule”, implying that kimberlites erupted through younger rocks are non-diamondiferous. The reasoning behind that rule is that lithospheric roots beneath non-cratonic continental crust (crust younger than 1.5 billion years) generally have high geothermal gradients and reach depths of less than 100km which is not deep enough to have diamond formation.

The kimberlitic magmatism is generally much younger than the cratons since most of it occurred in the last 1.2 billion years with the peak of its activity being from 250 to 20 million years. After that period ended, that kind of magmatism seems to have ceased worldwide with the explanation of the mechanism behind it remaining unknown.

If we would like to broadly classify the variable styles of kimberlite emplacement, we would divide them between intrusive (i.e., sub-volcanic hypabyssal kimberlites) and extrusive (i.e., volcaniclastic kimberlites) (*Giuliani et al.*, 2019).

The hypabyssal kimberlites mainly occur as dikes and, less commonly, as sills, often in swarms, commonly associated with the root zones of many kimberlite pipes. Pipes, which is the most common volcanic feature produced by kimberlites, consist of downward-tapering structures that range in diameter from ~1 km to <100 m and have variable vertical extents of 100s meters to 2–3 km. Pipes are infilled with units of volcaniclastic and hypabyssal kimberlite, which represent discrete phases of magmatic activity (*Giuliani et al.*, 2019).

The reason we do not usually come across volcanic edifices on the surface of the Earth is that they are rarely preserved, as kimberlites are all older than 20-30 Ma and so they have eroded to or below ground level. Instead, the surface expression of the kimberlitic pipes can be lakes as in many areas of northern Canada, or rarely modest positive topography, such as at Kimberley (South Africa) or Somerset Island (Canada).

Fig. 7. Aerial view of an open pit (A-154 kimberlite pipe) at the Diavik mine, Northwest Territories, Canada, in the early stages of development. The kimberlite is exposed in the central part of the pit.
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 1-14)

Lamproites

Lamproites are next in importance to kimberlites as they host the world's largest diamond producer by carat weight, the Argyle mine in Australia, and known diamond occurrences in India and the United States. Among lamproites, ~30% are diamondiferous.

Lamproites are peralkaline, ultrapotassic rocks that are characterized by the presence of titanium phlogopite, titanium potassium richterite, titanium tetraferriphlogopite, sodium- and aluminum-deficient leucite, iron-rich sanidine, aluminum-poor diopside, potassium barium titanates (priderite, jeppeite), and potassium zirconium or titanium silicates (wadeite, davenite, shcherbakovite) (*Mitchell et al.*, 1991).

They possess some of the most extreme isotopic and trace-element compositions of any terrestrial mantle-derived magma (*Nowell et al.*, 2008).

In Australia they occur in mobile belts, they contain diamonds that are about 1.5 billion years old and some metamorphic crustal rocks that are slightly older, 1.8 billion years old. The *thermal pulse* revealed by the study of crustal rocks at the surface is thought to result from a tectonic process that heated and recrystallized older lithospheric mantle while permitting the formation of diamonds at the same time (*Shirey et al.*, 2013).

Fig. 8. Aerial view of the Argyle diamond mine, Western Australia, showing processing plant, tailings piles, and tilted sedimentary rocks of Proterozoic age, which form the wall rocks of the mine.
(From *Tappert & Tappert*, “Diamonds in Nature – A guide to rough diamonds”, 2011, their figure 1-15)

Lamprophyres

Lamprophyres until some years ago were considered igneous rocks in the form of “rotten” dikes (*N. M. S. Rock*, 2013) that were almost impossible to classify due to the great alteration they have gone through. Only recently we started to realize their importance among igneous rocks since they offer a window into the deep mantle and mantle processes, they are possible indicators for precious mineral deposits like diamond and gold, they are parental magmas to a very wide range of other igneous rock-types, and they are a source of innumerable exotic mineral varieties and geochemical compositions (*N. M. S. Rock*, 2013).

Diamondiferous ultramafic lamprophyres are mainly of petrological interest as they host the oldest known diamonds, with its main representative the Wawa belt in Ontario, Canada where the macrodiamonds are 2.7 billion years old. Another locality but with microdiamonds is in the Japan islandic arc.

In both cases, diamonds appear to have been created by late-stage magmas that produced the lamprophyre and then they were intruded as dikes and transported diamonds to the surface, but these diamonds may have been created elsewhere in the mantle.

ELEMENTAL SUBSTITUTION – DIAMOND "TYPE" CLASSIFICATION

The elemental substitution in the diamond crystal lattice has long been studied since it affects the gem qualities and thus the value of natural gem diamonds as well as, and more importantly, their physicochemical properties.

The elements trapped in the diamond lattice defects can be used to get estimates of the temperature that prevailed during the residence of a diamond in the mantle and can help get estimates of the return path of carbon to the surface (*Shirey et al.*, 2019). Pressure and temperature co-vary with depth in Earth, and the structure of these defects in the diamonds can record the temperature history that, in turn, can provide us an estimated location inside the mantle.

These measurements are complementary to those used on inclusions to determine the pressure and temperature conditions during their trapping as the diamond growth happens inside the mantle.

We can find more than 60% of the elements of the periodic table inside a diamond but the most important of them is nitrogen, boron, hydrogen, silicon, and nickel that substitute carbon in routinely measurable quantities (*Shirey et al.*, 2013).

Nitrogen is the main impurity, and, for historical reasons, it forms the basis of diamond classification into Type I (nitrogen-bearing) diamonds and Type II (nitrogen so low as to be thought of as essentially nitrogen-free) diamonds. With modern instrumentation, it became possible to detect traces of N in diamonds that previously would have been classified as Type II. Pearson et al. (2003) suggest defining Type II as <20 ppm N, but this value may decrease in the future (*Shirey et al.*, 2013).

The importance of nitrogen as a diamond impurity can be better understood by the usage of nitrogen defect aggregation as a thermochronometer since its general concepts and calibration are well established (*Shirey et al.*, 2019).

The technique is based on the kinetics of aggregation of pairs of nitrogen atoms (called A centers) into groups of four nitrogen atoms around a vacancy (called B centers) and measurement of these defect concentrations using Fourier-transform infrared (FTIR) spectroscopy (*Shirey et al.*, 2019). The aggregation of nitrogen impurities in diamonds is dependent on nitrogen content, temperature, and residence time in the mantle (*Smart et al.*, 2017).

What follows is the diamond "Type" classification scheme according to the presence or relative lack of nitrogen impurities.

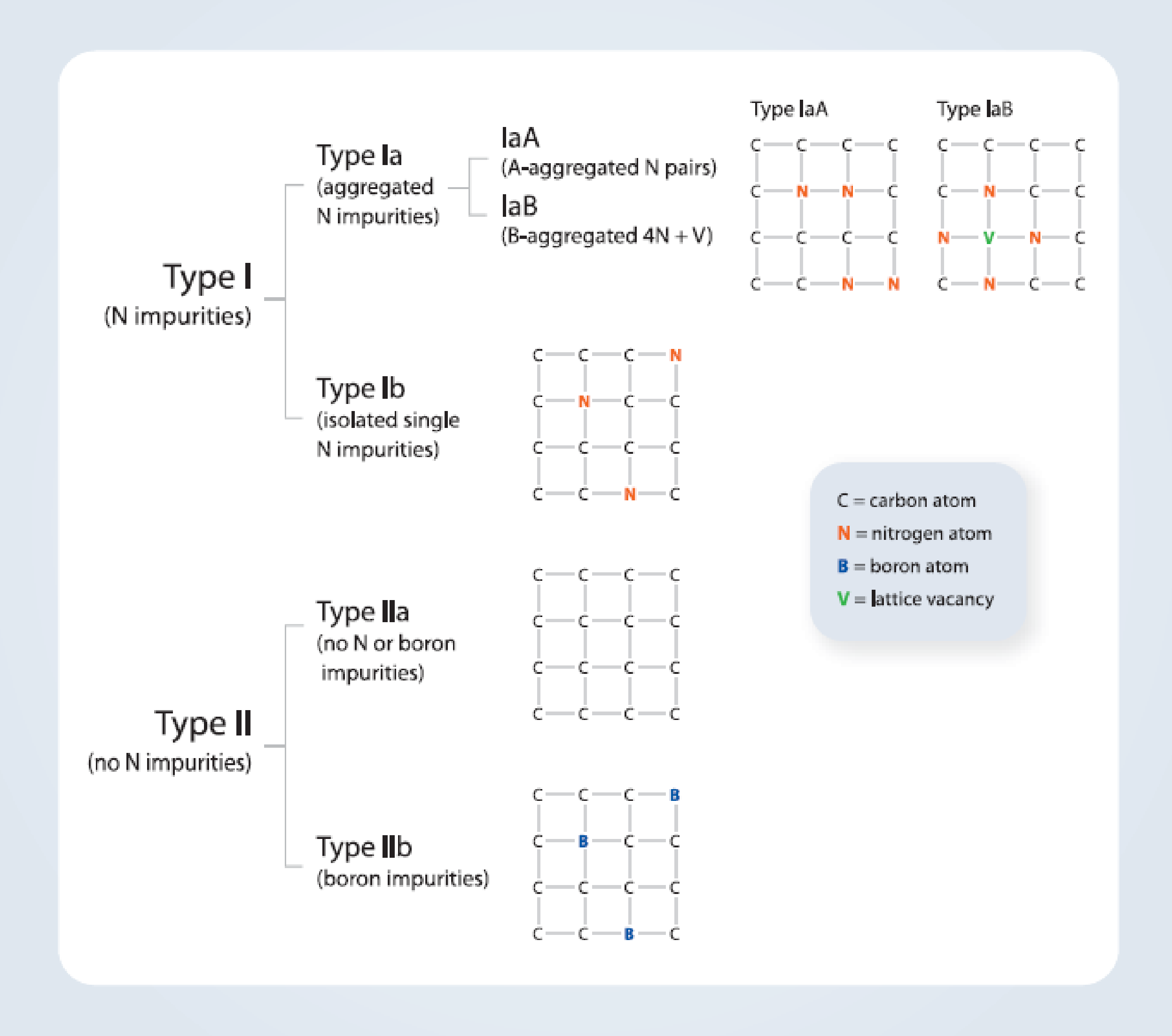


Fig. 9. Diamond "Type" Classification Table.
(From *Breeding et al.*, "The "type" classification system of diamonds and its importance in gemology", 2009, their figure 2)

Type I

Diamonds in this group contain sufficient N to be measurable by IR absorption spectroscopy and are then subdivided into type Ia and type Ib. Both subgroups contain N atoms, but they are arranged differently in each.

a. Type Ia

Diamonds of Ia type contain N atoms that are "close to one another in one of two spectroscopically detectable configurations".

A. *Type IaA*

The first configuration is the most common one and contains “two N atoms adjacent to each other in the lattice”. Although these two atoms occupy neighboring sites, each pair is isolated from other N atoms in the lattice). “These N impurities are referred to as A aggregates (or A centers)”.

B. *Type IaB*

The second configuration is four N atoms that symmetrically surround a vacancy (of C atom) in the crystal lattice of the diamond. This configuration is formed when two A aggregates combine and are named B aggregates (or B centers).

b. Type Ib

Diamonds of the Ib type contain “single N atoms that have replaced C atoms in the lattice and are isolated from one another”, which means that usually, they do not occur in “adjacent lattice positions”. These N impurities can be called isolated N, single substitutional N, or C centers.

Type II

These diamonds do not contain enough N to be detected by the IR spectrometers and are further subdivided into types IIa and IIb. It is this category that super-deep (or sub-lithospheric) diamonds typically belong to, showing quite variable C isotopic compositions (*Shirey et al*, 2019).

a. Type IIa

They contain neither N nor B that can be easily measured. Type IIa diamonds, where CLIPPIR diamonds also belong, will be analyzed later, in a separate chapter, along with their inclusions.

b. Type IIb

These diamonds do not contain N that can be IR-measured but they do contain B impurities that are thought to be configured as “isolated single atoms that replace C” in the diamond crystal.

The presence of B gives some unique properties to the diamonds of this category such as their electrical conductivity and their blue to greyish blue and grey color.

But the most important question these diamonds arise and thus challenge us to answer is where this boron came from. A possible answer to this question will be given in a following chapter.

However, most diamonds we encounter in nature belong to more than one diamond type and this must do partly with the conditions of the geotectonic environment in which they form.

Apart from the gemological “Type” classification, there is the geological classification based on inclusions of silicate minerals (garnet and pyroxene) that allow classifying gem diamonds into two groups according to their parental host rocks in the mantle, peridotite, and eclogite.

Peridotitic diamonds are known as "P-type" which can be further subdivided into harzburgitic and lherzolitic in descending order of abundance that parallels the occurrence of these types of peridotites in the population of mantle xenoliths in diamondiferous kimberlites (*Shirey et al.*, 2013); eclogitic diamonds are known as "E-type."

We can also use sulfide mineral inclusions such as pyrrhotite and pentlandite to classify diamonds into P-type or E-type (based on Ni content) but the opacity of sulfides and their obscuration by internal fracturing makes the classification possible only after breakage of the host diamond and removing the inclusion for study.

For sub-lithospheric diamonds, the geological classification process becomes more challenging because of the rarity of specimens, the small grain size of inclusions, and difficulties in recognizing original high-pressure minerals from their low-pressure forms (*Shirey et al.*, 2013).

To distinguish peridotitic diamonds, we use Mg-rich, ultramafic mineral assemblages, such as Mg-perovskite, ringwoodite, wadsleyite, and olivine with ferropericlase, majorite, and Ca perovskite to relate them, whereas for the eclogitic diamonds we use basaltic mineral assemblages such as majorite, clinopyroxene, CaTi-perovskite, Ca-perovskite, Ca-ferrite, stishovite, and the Na- and Al- bearing phase to relate them.

MINERAL INCLUSIONS IN DIAMONDS AS A DEPTH INDICATOR

Diamond occurs in three main forms: polycrystalline, monocrystalline, and coated, as well as many subtypes.

After a short reference to each category as well as to the relative age of inclusions compared to their diamond host, there will be a categorization of the ones we come across in monocrystalline sub-lithospheric diamonds according to their crystallization depth and mineralogy.

The emphasis of the research is placed on the results coming from single-mineral chemical thermobarometry on monomineralic inclusions (provided they are syngenetic) because they reflect more accurately the P-T conditions of diamond formation.

Chemical thermobarometry is a scientific method that allows us 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.

The challenges we come across with two-mineral thermobarometry of touching inclusions, the reliability of some of the thermometers – for example, those based on Fe-Mg exchange reactions between garnet and orthopyroxene, clinopyroxene or olivine – and the thermobarometry of eclogitic inclusions result in our inability to obtain the diamond formation temperature or in large uncertainties.

DIAMOND FORMS

Polycrystalline Diamonds

Polycrystalline diamonds can be divided into mantle-derived diamonds, impact diamonds, and diamonds of unknown origin.

In the mantle-derived polycrystalline diamonds we can have 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 (*Shirey et al.*, 2013). Some other subtypes that belong to the mantle-derived diamonds are framesite and ballas. In the impact category, we have the yakutite subtype and in the category of unknown origin, we have carbonado.

Monocrystalline Diamonds

They are the diamonds that are coming from a single crystal either in the micro-scale (<0.5 mm) or the macro-scale (>0.5 mm). These diamonds can display a complicated internal growth history with episodes of resorption and regrowth as well as simple composite forms like macles and intergrowths (twin forms) (*Shirey et al.*, 2013).

These diamonds are the most important of all because from these we have the gem-quality ones (thus cut and polished) and most importantly these are an important source of inclusions for study and therefore we will focus on inclusions coming from these diamonds.

Via geochronology on the inclusions of these diamonds, their age has been calculated as Proterozoic to Archean.

Larger diamonds statistically contain more inclusions, and these inclusions are more likely to be larger. The abundance of diamonds containing visually recognizable mineral inclusions (other than graphite) is generally quite small, but the percentage depends on the deposit (*Tappert et al.*, 2011).

Coated Diamonds

They are a mixture of polycrystalline and monocrystalline diamonds. Monocrystals have been overgrown by a thick, cloudy, polycrystalline coat laden with micro inclusions of fluid (*Shirey et al.*, 2013).

A special category is the fibrous diamond where the coat is composed of rods or blades of diamond and it exhibits a fibrous structure.

The coating is believed to occur during the transportation in the kimberlite and thus represent young, new diamond growth surrounding the often-ancient diamond.

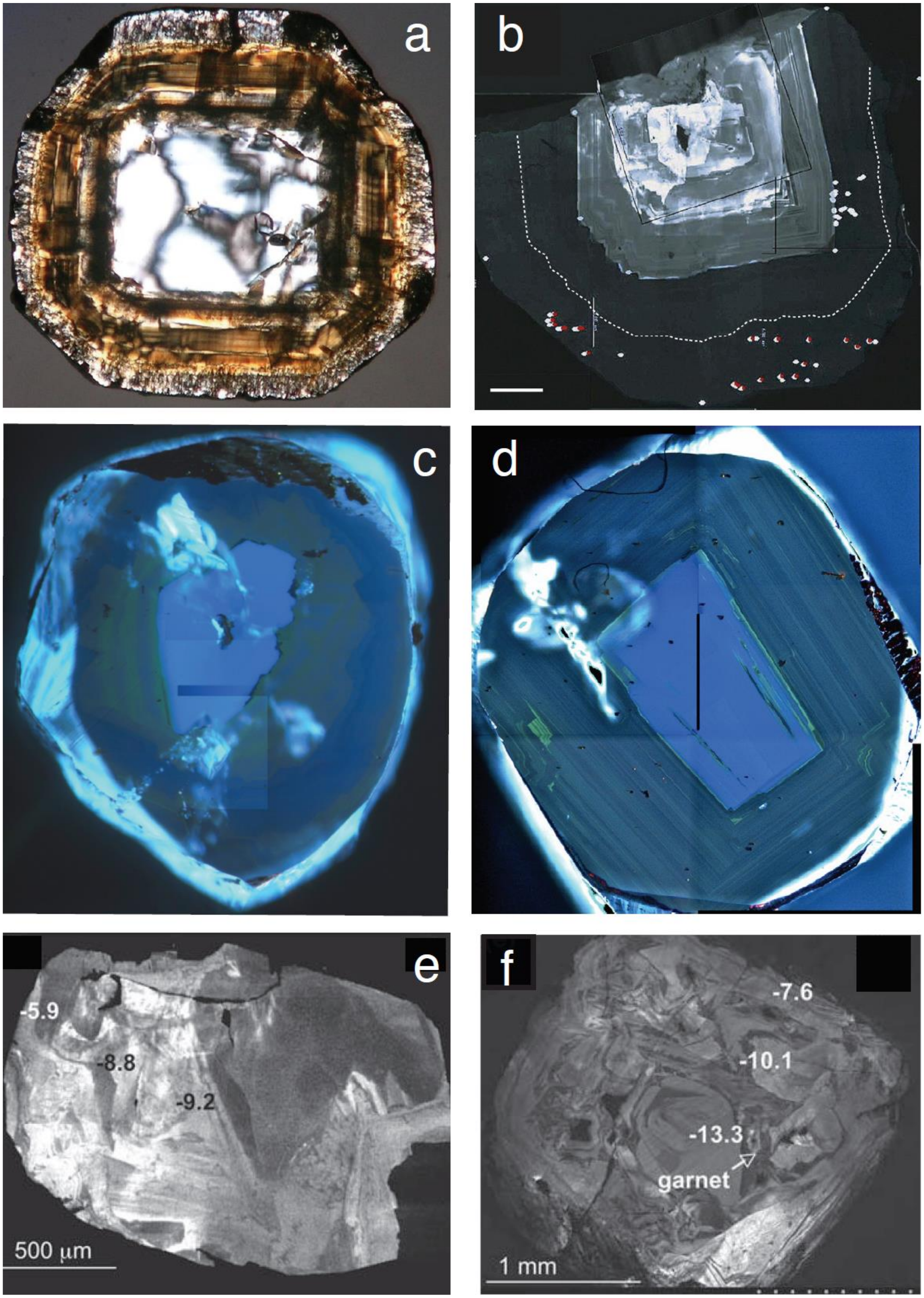

a
b
c
d
e
-5.9
-8.8
-9.2
500 µm
f
-7.6
-10.1
-13.3
garnet
1 mm

Fig. 10. 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. The diameter of the diamond is 1 cm. Coated diamond (b) from the Congo (alluvial) is a cathodoluminescence (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; the 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 the 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.
(From *Shirey et al.*, "Diamonds and the Geology of Mantle Carbon", 2013, their figure 1)

RELATIVE INCLUSION AGE

Inclusions in diamonds can be classified as protogenetic, syngenetic, or epigenetic according to their time of crystallization with respect to that of their diamond host (*Shirey et al.*, 2013).

Protogenetic

Protogenetic inclusions are generally the ones that were formed earlier than their host. They represent conditions that existed before their encapsulation, but this translates to a very broad geologic timescale. If the inclusion was formed much earlier in (the geologic) time than its host then it can be unrelated to diamond formation but although we would not be able to obtain an accurate (diamond formation) age from such an inclusion, we would get a maximum age and potentially a general age pattern of diamond growth in a region of the lithospheric mantle. "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" (*Shirey et al.*, 2013).

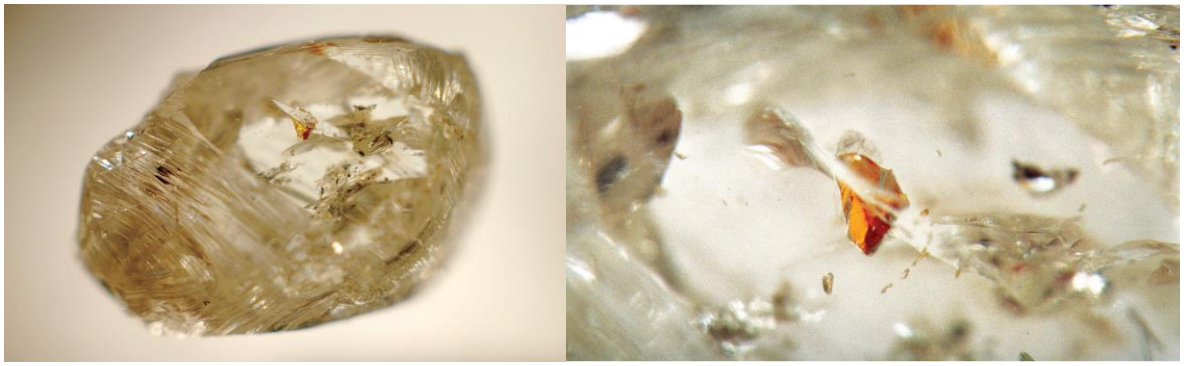


Fig. 11. Left: Eclogitic garnet inclusion with its characteristic orange color in a strongly resorbed and slightly distorted diamond (Ø: ~6 mm). The diamond surface is polished for better visibility.
Right: Close-up of the eclogitic garnet inclusion. The lack of a distinctive crystal shape indicates that the garnet may be protogenetic.
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-04)

Syngenetic

Syngenetic are the ones forming contemporaneous with the diamond. The discrimination between the protogenetic and the syngenetic inclusions is less straightforward and its importance lies in the fact that 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 (*Shirey et al.*, 2013).

The proof for concluding syngenesis is when we find the morphology of the diamond imposed on the inclusion as well as when there is compositional consistency among them.

In the first case (morphology) we usually observe cubo-octahedral morphology, often distorted to some extent, even to minerals like olivine or pyroxene that under normal growth conditions they would not develop any cubic crystal faces.

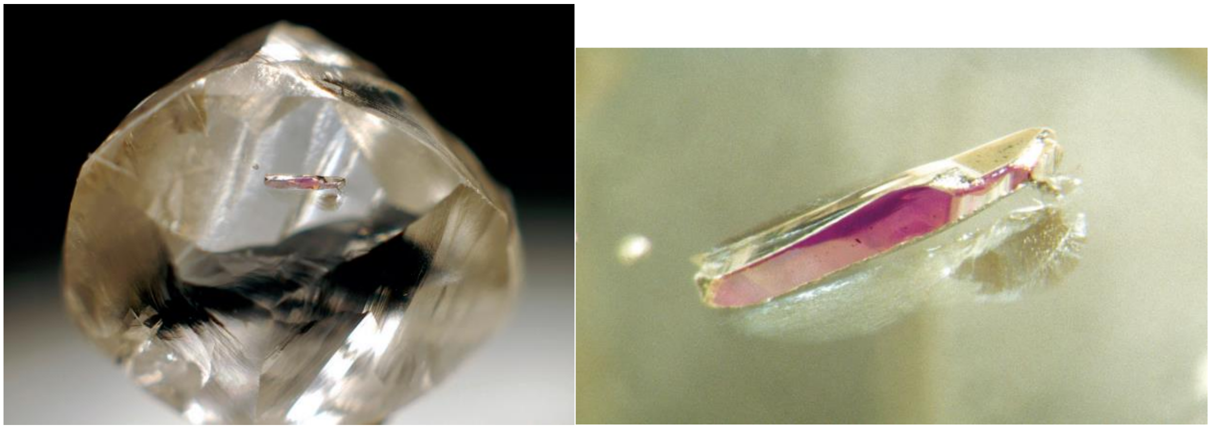


Fig. 12. Left: Strongly elongated peridotitic garnet inclusion (~1 mm in length). The crystal faces of the garnet are oriented parallel to the octahedral growth directions of the diamond, which are marked by terraces. This indicates that the inclusion and diamond crystallized, or re-crystallized, at the same time. One of the dodecahedral crystal faces of the diamond has been polished for better visibility.

Right: Close-up of the peridotitic garnet inclusion. The garnet has crystal faces that resemble a strongly distorted cubo-octahedron.

(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-01)

Epigenetic

They are the ones that formed later in relevance to their diamond host. In that category, we can have inclusions that formed along with fractures, deep etch pits, ruts, or ones made of alteration minerals after former syn- or protogenetic inclusions. It is not always possible to determine if an inclusion mineral has been affected by alteration or if it is a secondary precipitate, thus when located close to visible fractures or the surface of the diamond they should be examined with caution as they are especially prone to alteration.

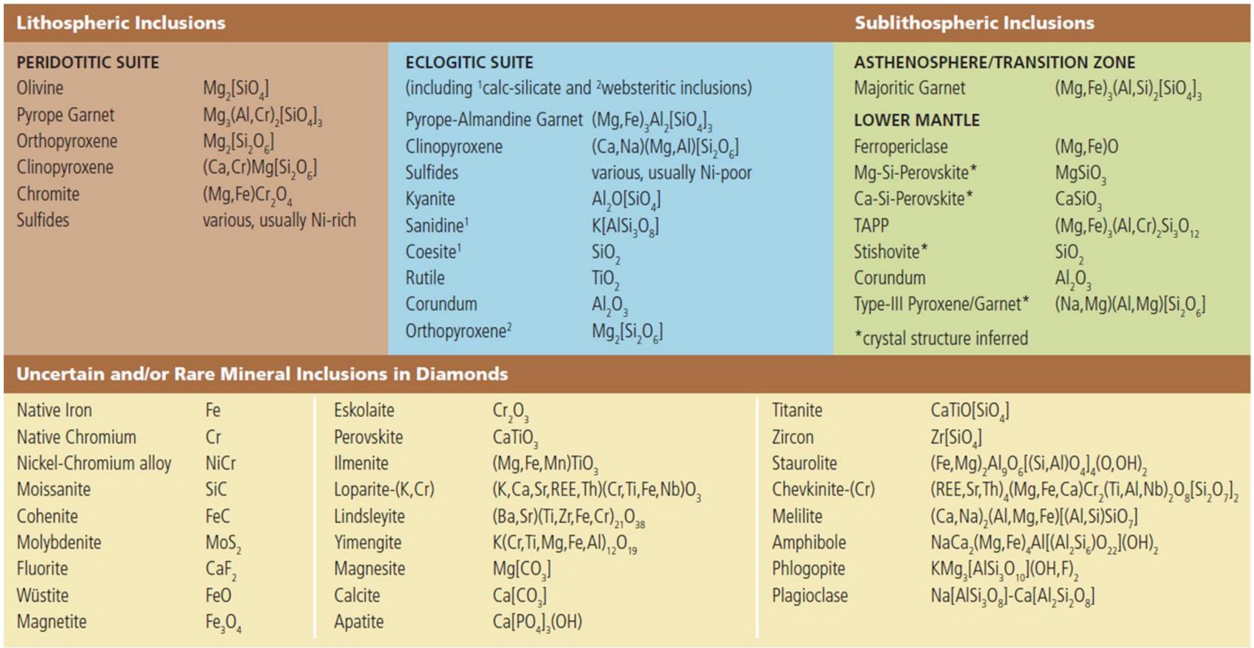
They are usually linked to processes that took place during the transportation of the diamond by kimberlitic magmas or during the residence on the Earth's surface.

A common epigenetic mineral is graphite, especially inside fractures, and they commonly appear cloudy.

Fig. 13. Left: Rounded dodecahedral diamond containing an altered (epigenetic) mineral inclusion (Ø: ~7 mm). The diamond surface is polished for better visibility.

Right: Close-up of the inclusion, which contains dark cloudy patches that are characteristic of altered inclusions.

(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-05)



Lithospheric Inclusions

PERIDOTITIC SUITE	
Olivine	$Mg_2[SiO_4]$
Pyrope Garnet	$Mg_3(Al,Cr)_2[SiO_4]_3$
Orthopyroxene	$Mg_2[Si_2O_6]$
Clinopyroxene	$(Ca,Cr)Mg[Si_2O_6]$
Chromite	$(Mg,Fe)Cr_2O_4$
Sulfides	various, usually Ni-rich

ECLOGITIC SUITE (including [1]calc-silicate and [2]websteritic inclusions)	
Pyrope-Almandine Garnet	$(Mg,Fe)_3Al_2[SiO_4]_3$
Clinopyroxene	$(Ca,Na)(Mg,Al)[Si_2O_6]$
Sulfides	various, usually Ni-poor
Kyanite	$Al_2O[SiO_4]$
Sanidine[1]	$K[AlSi_3O_8]$
Coesite[1]	SiO_2
Rutile	TiO_2
Corundum	Al_2O_3
Orthopyroxene[2]	$Mg_2[Si_2O_6]$

Sublithospheric Inclusions

ASTHENOSPHERE/TRANSITION ZONE	
Majoritic Garnet	$(Mg,Fe)_3(Al,Si)_2[SiO_4]_3$
LOWER MANTLE	
Ferropericlase	$(Mg,Fe)O$
Mg-Si-Perovskite*	$MgSiO_3$
Ca-Si-Perovskite*	$CaSiO_3$
TAPP	$(Mg,Fe)_3(Al,Cr)_2Si_3O_{12}$
Stishovite*	SiO_2
Corundum	Al_2O_3
Type-III Pyroxene/Garnet*	$(Na,Mg)(Al,Mg)[Si_2O_6]$

*crystal structure inferred

Uncertain and/or Rare Mineral Inclusions in Diamonds

Native Iron	Fe	Eskolaite	Cr_2O_3	Titanite	$CaTiO[SiO_4]$
Native Chromium	Cr	Perovskite	$CaTiO_3$	Zircon	$Zr[SiO_4]$
Nickel-Chromium alloy	$NiCr$	Ilmenite	$(Mg,Fe,Mn)TiO_3$	Staurolite	$(Fe,Mg)_2Al_9O_6[(Si,Al)O_4]_4(O,OH)_2$
Moissanite	SiC	Loparite-(K,Cr)	$(K,Ca,Sr,REE,Th)(Cr,Ti,Fe,Nb)O_3$	Chevkinite-(Cr)	$(REE,Sr,Th)_4(Mg,Fe,Ca)Cr_2(Ti,Al,Nb)_2O_8[Si_2O_7]_2$
Cohenite	FeC	Lindsleyite	$(Ba,Sr)(Ti,Zr,Fe,Cr)_{21}O_{38}$	Melilite	$(Ca,Na)_2(Al,Mg,Fe)[(Al,Si)SiO_7]$
Molybdenite	MoS_2	Yimengite	$K(Cr,Ti,Mg,Fe,Al)_{12}O_{19}$	Amphibole	$NaCa_2(Mg,Fe)_4Al[(Al_2Si_6)O_{22}](OH)_2$
Fluorite	CaF_2	Magnesite	$Mg[CO_3]$	Phlogopite	$KMg_3[AlSi_3O_{10}](OH,F)_2$
Wüstite	FeO	Calcite	$Ca[CO_3]$	Plagioclase	$Na[AlSi_3O_8]-Ca[Al_2Si_2O_8]$
Magnetite	Fe_3O_4	Apatite	$Ca[PO_4]_3(OH)$		

Table 2. Mineral inclusions in monocrystalline diamonds (other than graphite and diamond).
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their table 5-01)

Less than 1% of the global diamond production is believed to have genesis in depths greater than 250-300km, which means sub-lithospheric origin. The scientific evidence of that is the mineral inclusions that were found to be contained in some diamonds, which (inclusions) originate from much greater depths beneath the base of the lithosphere. As mentioned above, monocrystalline diamonds are a great source of such mineral inclusions, including silicates, oxides, sulfides (among the most common inclusions in diamonds - *Palot et al.*, 2013), and rarely carbonates. The diamond host has protected them from alteration, and they are pristine samples from parts of the Earth's mantle that are otherwise inaccessible (*Tappert et al.*, 2011).

Many minerals have been identified as inclusions in diamonds, which can be seen in Table 2, but most of these are rare and even some have only been identified once. From these, only about a dozen occur frequently and the silicates are the easiest to relate to specific conditions of formation due to the extensive high-pressure experimental work done on silicate compositions (*Harte*, 2010).

In addition, attention will be put on discerning retrograde and primary minerals as well as identifying the associations of these primary minerals with single diamonds; this provides potential equilibrium inclusion assemblages whose depths of formation may be estimated with reference to experimental studies (*Harte et al.*, 2013).

Classification of Diamond Inclusions

Inclusions in diamonds are usually classified based on their composition. Most of these mineral inclusions belong to one of two distinct suits: peridotitic (ultramafic) or eclogitic (basaltic), related to the two main rock types. Respectively, the diamonds containing each "kind" of these inclusions can be classified as peridotitic or eclogitic diamonds. A single diamond can contain more than one mineral inclusions, but it is extremely unusual for it to contain inclusions belonging to both suits.

Rarely diamonds contain inclusions that belong to less common and compositionally distinct suites, like the websterictic (mineral compositions that fall between the typical peridotitic and eclogitic ones) and calc-silicate ones. The presence of such inclusions indicates that the diamond host formed in unconventional mantle rocks, of regional scale.

Finally, we have some rare minerals that are found as inclusions in diamonds, but they cannot be linked to any suite because their composition is not diagnostic for a particular type of mantle rock.

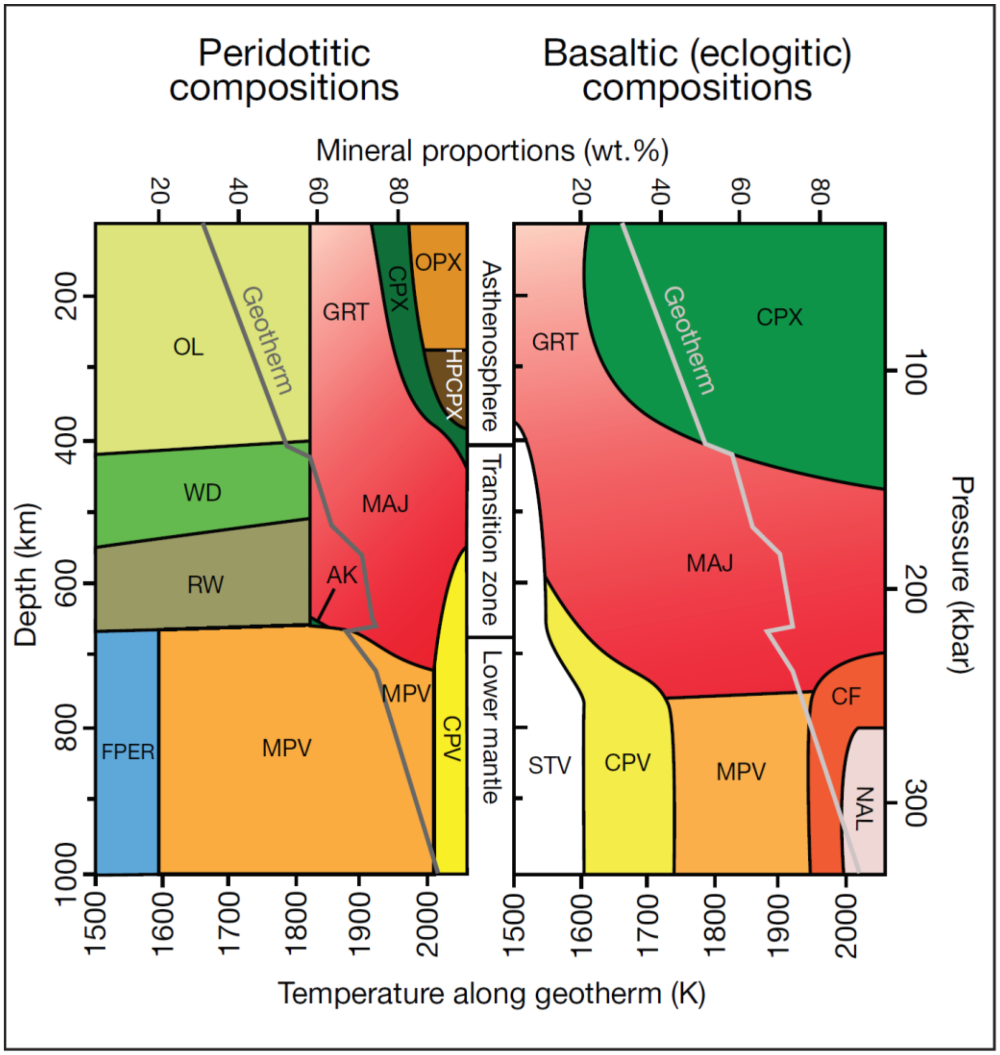


Fig. 14. This diagram shows the mineralogy with depth for two different rock compositions that would be expected at great depth in the mantle. The peridotitic (ultramafic) compositions on the left, make up most of the mantle by volume. The compositions on the right are typical of basalt that would be subducted to high pressure and recycled into mantle peridotite. The basaltic composition is more SiO_2-rich and therefore has much more clinopyroxene (CPX) and garnet (GRT) than the peridotitic composition. At 200 km depths, for example, the basaltic composition contains only clinopyroxene, and garnet, whereas the peridotitic composition has olivine (OL), garnet, clinopyroxene, and orthopyroxene (OPX). MAJ=majorite, WD=wadsleyite, RW=ringwoodite, FPER=ferropericlase, MPV=magnesium perovskite, CPV=calcium perovskite, STV=stishovite, CF=calcium ferrite, NAL = Na- and Al-bearing phase.
(From *Shirey & Shigley*, "Recent Advances in Understanding the Geology of Diamonds", 2013, their figure 20)

Sub-lithospheric Diamond Inclusions

The sub-lithospheric diamond inclusions are not as extensively studied as the inclusions coming from lithospheric diamonds partly because of the rarity of specimens, small grain size, and difficulties in recognizing original high-pressure minerals from their low-pressure, retrograde assemblages (Table 3).

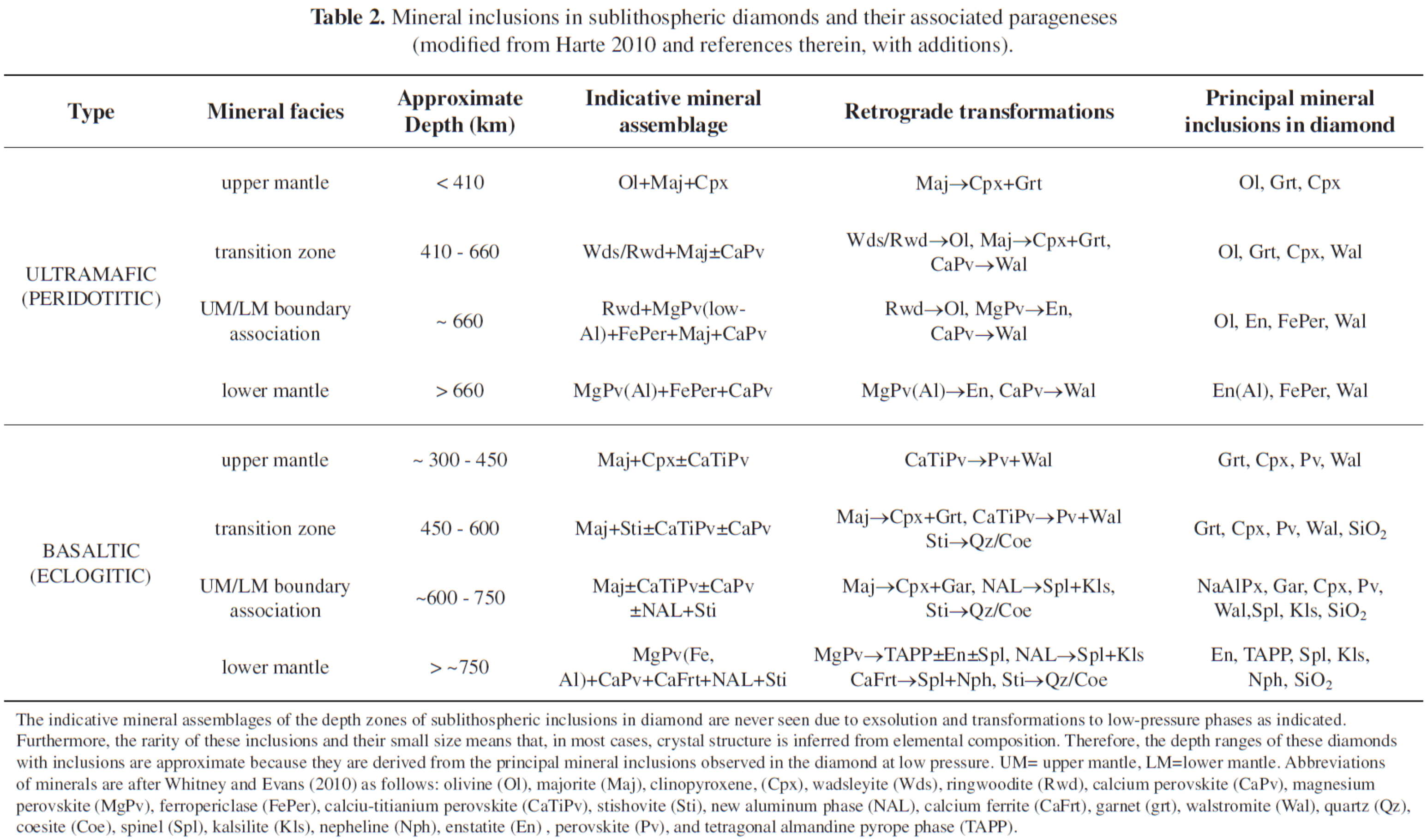


Table 2. Mineral inclusions in sublithospheric diamonds and their associated parageneses (modified from Harte 2010 and references therein, with additions).

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).

Table 3. Mineral inclusions in sub-lithospheric diamonds and their associated parageneses (From *Shirey et al.*, “Diamonds and the Geology of Mantle Carbon”, 2013, their Table 2)

For the classification of deep mantle diamond inclusions, researchers usually use their depth of formation to do so.

The reason for that is that the mineral assemblages change several times with depth and thus cease to represent peridotite and eclogite rock suits from mineralogical and petrographic viewpoint (*Harte*, 2010). As with increasing depth we recognize series of major metamorphic facies (*Harte*, 2010), all mineral phases can still be matched to ultrabasic (or ultramafic-peridotitic) and basic (or basaltic-eclogitic according to *Shirey et al.*, 2013) bulk rock compositions, and that is why they will be referred to from now on as metaperidotite and metabasite affinities according to Harte (2010).

Typically, it is considered that ultramafic inclusions are the prevailing minerals of the lower mantle (they are of in situ source) whereas the basaltic ones (from eclogite assemblages) originate from subducting lithosphere (*Litvin et al.*, 2014).

The **metaperidotite (or 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 3) (*Shirey et al.*, 2013). The **metabasite (or 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 3) (*Shirey et al.*, 2013).

In addition, when researchers compared these sub-lithospheric diamond inclusions with experimental data, they noticed that there is a selective distribution of them with respect to depth. This translates to basic inclusion compositions coming predominantly from the depths of the lower asthenosphere and upper transition zone, and ultrabasic ones coming from the base of the transition zone and the uppermost lower mantle.

According to the above, we have sub-lithospheric diamond formation in three areas of the mantle: the asthenosphere (250-410 km), the transition zone (410-670 km), and even in the lower mantle (>670 km). These areas are then categorized into two main depth zones (*Harte*, 2010):

1. The lower asthenosphere and upper transition zone (TZ)
2. The Upper Mantle/Lower Mantle (UM/LM) boundary region and the uppermost LM.

The inclusions from zone 1 are very largely majoritic garnets (with or without clinopyroxene) which indicate bulk compositions of eclogitic/metabasic (basaltic) affinity (Fig. 14). The minerals from zone 2 include Ca-Si and Mg-Si perovskites and ferropericlase and are predominantly of metaperidotitic (ultramafic) bulk composition but include some possible metabasite assemblages. In many of these natural assemblages, the tetragonal almandine pyrope phase (ex-TAPP, now jeffbenite) occurs rather than the garnet found in experiments. Armstrong and Walter (2012) have suggested that jeffbenite (ex-TAPP) must be a retrograde product, forming mainly from Al bridgmanite (MgSi perovskite), but possibly also from garnet because it is stable only at relatively low pressures (up to 13GPa at 1973°C). This observation makes enigmatic the association of jeffbenite with ferropericlase and bridgmanite in some superdeep diamonds. However, the stability field of jeffbenite has been extended to ~23GPa (~660 km), demonstrating that this mineral may represent one of the most reliable markers for diamonds of super-deep origin (*Zedgenizov et al.*, 2020).

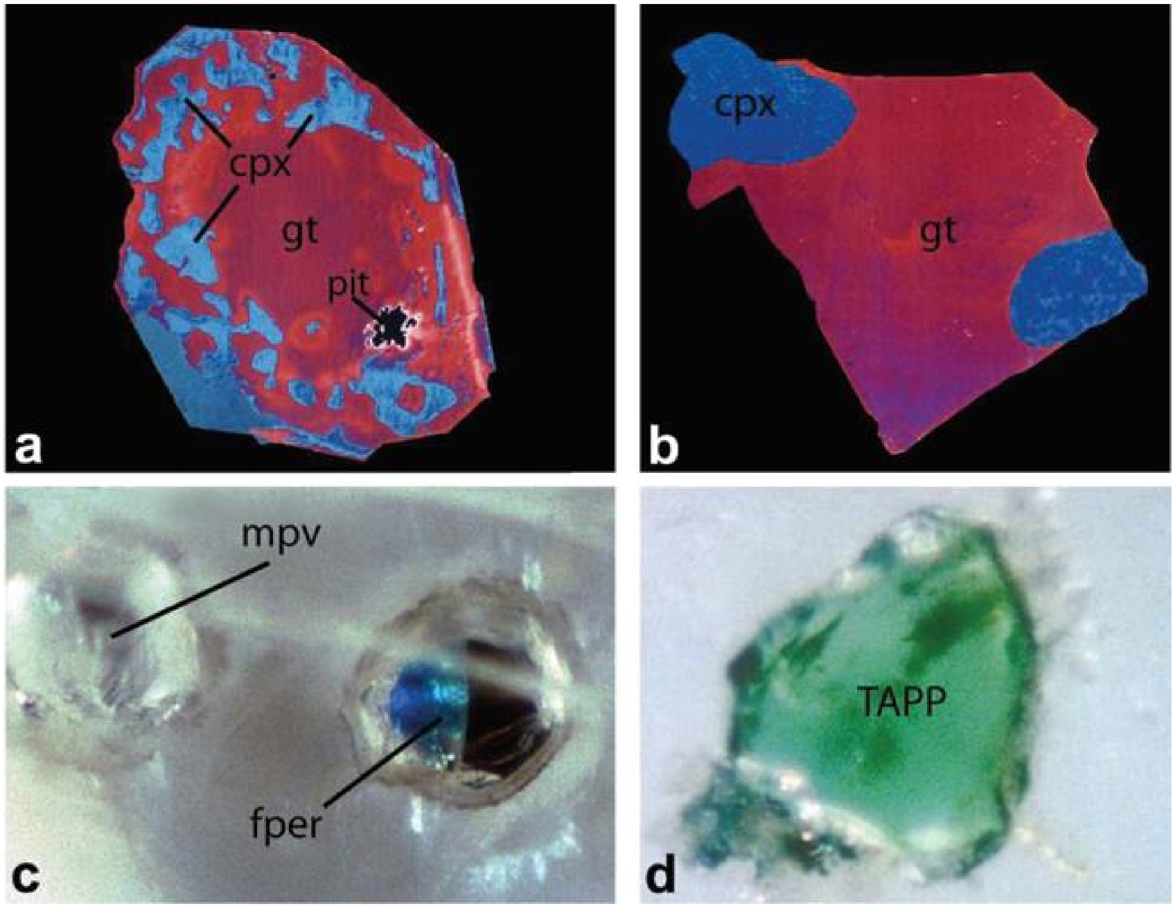


Fig. 15. Images of deep mantle inclusions in diamonds. a and b BSE images showing two majorite-eclogite inclusions (150-200 mm) after break-out from their host diamonds. The intensity of the backscattered signal has been converted to a blue-red scale so that clinopyroxene appears blue and garnet (both with and without a majoritic component) appears in magenta to red colors. **a.** Inclusion BZ43 with extensive areas of omphacitic clinopyroxene in the outer part of the inclusion; the garnet in the central area is darker colored (and has a high majorite component) compared to the usually redder (and more normal Si) garnet adjacent to clinopyroxene. Note that despite a generally irregular appearance, some of the edges of the clinopyroxenes have straight segments with common orientations and are believed to result from exsolution from original very Si-rich majorite. **b.** Inclusion BZ20 has homogenous normal-Si garnet and omphacitic clinopyroxene in smooth-edged grains (slight variations in color result from polishing). The sharp kink in the garnet-clinopyroxene boundary in the top left coincides with a grain boundary within the clinopyroxene. This 'eclogite' inclusion is believed to have formed by recrystallization from an original majoritic garnet (*Harte and Cayzer*, 2007). (c) and (d) Photographs of inclusions (40-50 mm) within diamonds. **c.** Shows a FPER with

an iridescent blue effect on a polished surface together with a colorless perovskite (probably MPV) lying below the surface. **d.** TAPP (now jeffbenite).
(From *Harte*, "Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones", 2010, his figure 3)

1. Inclusions in the lower asthenosphere and upper transition zone diamonds (250-670 km)

Diamond inclusions of **ultramafic** (metaperidotite) affinities in the lithosphere are characterized by the typical mineral assemblage of olivine, garnet, orthopyroxene, and clinopyroxene.

With increasing depth, and as we move towards the lower asthenosphere and the transition zone (TZ), the dominant (Mg, Fe)$_2$SiO$_4$ phase changes from olivine (OL) to wadsleyite (WD) (12-16GPa) and then ringwoodite (RW) (18-22GPa) (Fig. 14).

The transition zone is dominated by WD and RW phases which coincides with the well-recognized seismic discontinuities. The upper and lower boundaries of the TZ do not seem to be strongly affected by considerable variations in temperature, Mg-Fe, and the potential presence of H or H$_2$O in the WD and RW compositions (*Harte*, 2010).

The additional aforementioned phases of ultramafic affinities are garnet, orthopyroxene, and clinopyroxene. With increasing depth, the latter two pass effectively into a solid solution with garnet giving birth to a special variety containing majoritic end-member components. That consequently results in majoritic garnet being one of the dominant phases of the transition zone with WD and RW in metaperidotites.

In the upper part of the transition zone, majoritic garnets show a wide range of Mg-Fe-Ca compositions, which is not the case for the lower transition zone, where we observe CPV becoming stable as well as the main Ca-bearing phase as we transcend to the lower mantle.

Diamond inclusions of **basaltic** (metabasite) affinities present changes in the garnet + pyroxene component of the ultramafic compositions (Fig. 14). The dominant change we come across as we move from the asthenosphere towards the transition zone is that garnet undergoes expansion of its composition phase compared to lower depths where clinopyroxene is the dominant phase (followed by garnet). In the transition zone, majoritic garnet commonly forms >80% of the rock.

As mentioned earlier, there is selective distribution of inclusion assemblages according to depth, and at the depths of the lower asthenosphere and upper transition zone we mainly have basaltic (eclogitic) inclusion compositions thus the dominant mineral phase is the majoritic garnet of eclogitic affinities (only a few diamonds contain majoritic garnets of peridotitic and websteritic composition).

They result from the dissolution of pyroxene into the crystal structure of garnet, which occurs at pressures of more than 80 kilobars (depths > than 250km). Compositionally, majoritic garnets are characterized by higher Si contents compared to garnet inclusions from shallower parts of the lithosphere. They exhibit the distinctive orange color of eclogitic garnet inclusions from lithospheric diamonds and thus visually they cannot be distinguished from their non-majoritic counterparts.

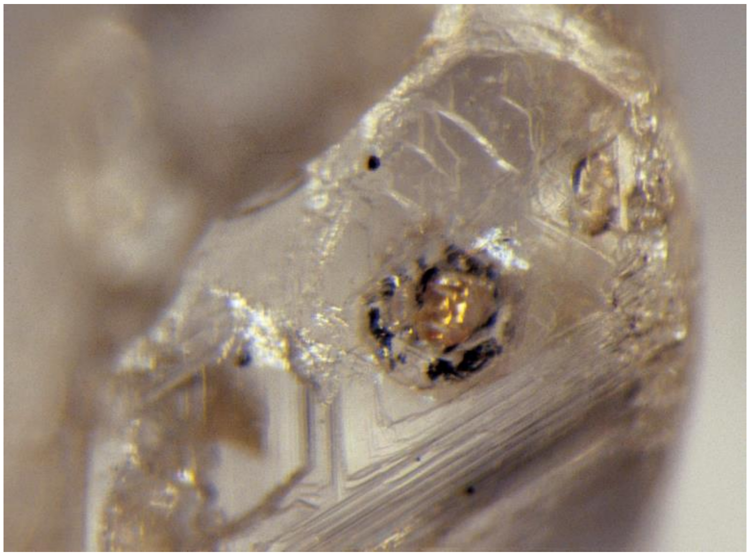


Fig. 16. Minerals from the asthenosphere – transition zone: a majoritic garnet inclusion in a diamond from the Jagersfontein mine, South Africa. The garnet inclusion has the typical orange color of eclogitic garnets. The inclusion is surrounded by graphite-coated fractures. The field of view is ~2 mm.
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-26)

2. Inclusions in the Upper Mantle/Lower Mantle (UM/LM) boundary region and the uppermost LM diamonds (>670 km)

The boundary between the transition zone and the lower mantle, at depth of about ~670km, is one of the most important geophysical features of the earth and it is caused by a change in the mineralogical composition of the mantle. The importance of this boundary is deriving from the conversion of the dominant mineral phases of the upper mantle to denser high-pressure minerals.

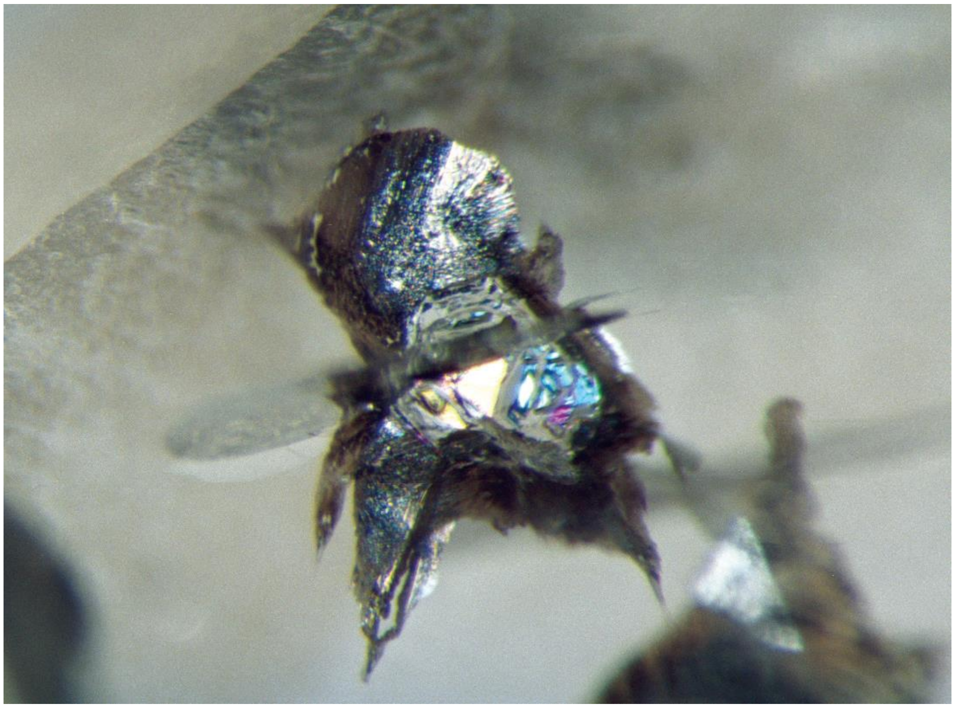


Fig. 17. Inclusion of ferropericlase in a diamond. A fine graphite film on the inclusion-diamond interface probably causes the iridescence. The inclusion is surrounded by graphite-coated fractures. The field of view is ~1 mm.
(From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-29)

The **ultramafic** (metaperidotite) compositions at the UM/LM boundary, are characterized by the replacement of RW (it ceases to be stable) by ferropericlase (FPER) and MPV (magnesium perovskite – bridgmanite) in the reaction:

$$\mathbf{(Mg,Fe)_2SiO_4 = (Mg,Fe)O + (Mg,Fe)SiO_3}$$

Ferropericlase is the most common inclusion in lower mantle diamonds. It has a characteristic brown color, caused by the presence of Fe (Fig. 18) and the interface between the diamond and the FPER often shows iridescence, most likely due to the presence of a thin layer of graphite (Fig. 17). Most FPER diamond inclusions are Mg-rich, and they are called magnesiowüstites, but also Fe-rich varieties exist which are classified as wüstites (*Tappert et al.*, 2011).

They are particularly common in diamonds coming from the Sao Luiz, Juina area in Brazil. Although ferropericlase inclusions are generally considered to be lower mantle minerals, especially if they occur along with MgSi-perovskite, it has been pointed out that when a diamond only contains FPER inclusions it can also point out to a formation outside the lower mantle, in compositionally unusual source rocks (*Tappert et al.*, 2011).

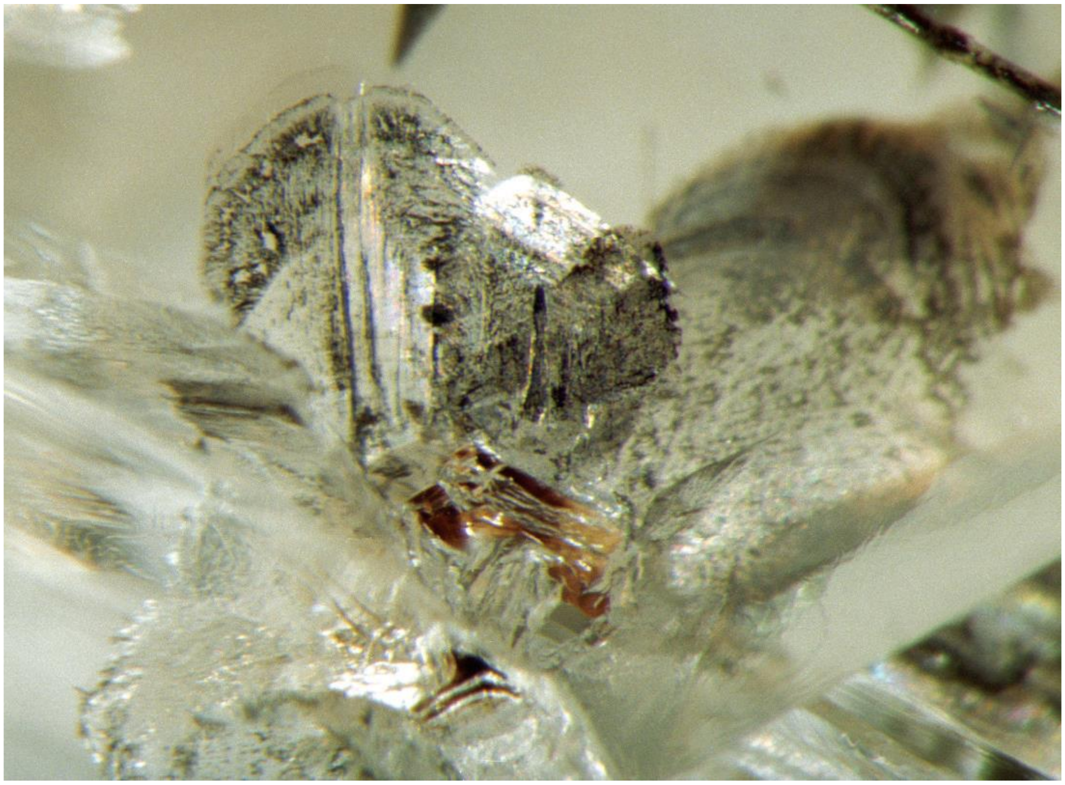


Fig. 18. Minerals from the lower mantle: a brown ferropericlase inclusion in a diamond. The inclusion, which is partially masked by reflections on the inclusion-diamond interface, is surrounded by an extensive fracture system. Many of the fractures are covered by graphite. The field of view is ~2 mm. (From *Tappert & Tappert*, "Diamonds in Nature – A guide to rough diamonds", 2011, their figure 5-27)

The MPV has a chemical composition like orthopyroxene (enstatite) but with the crystallographic structure of perovskite. That is why outside the lower mantle it converts to (its low-pressure polymorph) orthopyroxene and also that explains why when we find it (pyroxene) by itself it is not enough proof to conclude that a diamond has a "super-deep" genesis. Only with the presence of FPER in the same diamond, we can have indirect evidence that the orthopyroxene was once MPV in the lower mantle. Former MPV may also be identified by their nickel contents, which are expected to be considerably lower (<0.02 wt.% Ni) than true lithospheric orthopyroxene inclusions (0.1-0.2 wt.% Ni) (*Tappert et al.*, 2011).

Both FPER and MPV were predicted to be the LM dominant minerals from high-pressure experiments.

The majoritic garnet of ultramafic affinities transcends to CPV (dominant Ca-bearing phase) but MPV widens its composition field to take Al into a solid solution which has a result that with increasing depth the metaperidotite (ultramafic) bulk compositions soon cease to carry a pyrope-rich garnet or majoritic garnet as the dominant Al-bearing phase (*Harte*, 2010). At lower pressures, Ca-Si-perovskite (CPV) is not stable and converts to wollastonite. Since wollastonite is not a typical lithospheric mineral, its presence indicates a lower mantle origin for the diamond (*Tappert et al.*, 2011).

The first time a perovskite-structured polymorph of $CaSiO_3$ was discovered in a natural diamond was from Nestola et al. (2018) in a South African Cullinan kimberlite. The mineral is intergrown with about 6% calcium titanate ($CaTiO_3$) (Fig. 19) which (Ti-rich) indicates a bulk composition consistent with derivation from basaltic oceanic crust subducted to pressures equivalent to those present at the depths of the uppermost lower mantle. The relatively "heavy" carbon isotopic composition of the surrounding diamond, together with the pristine high-pressure $CaSiO_3$ structure, provides evidence for the recycling of oceanic crust and surficial carbon to lower-mantle depths (*Nestola et al.*, 2018).

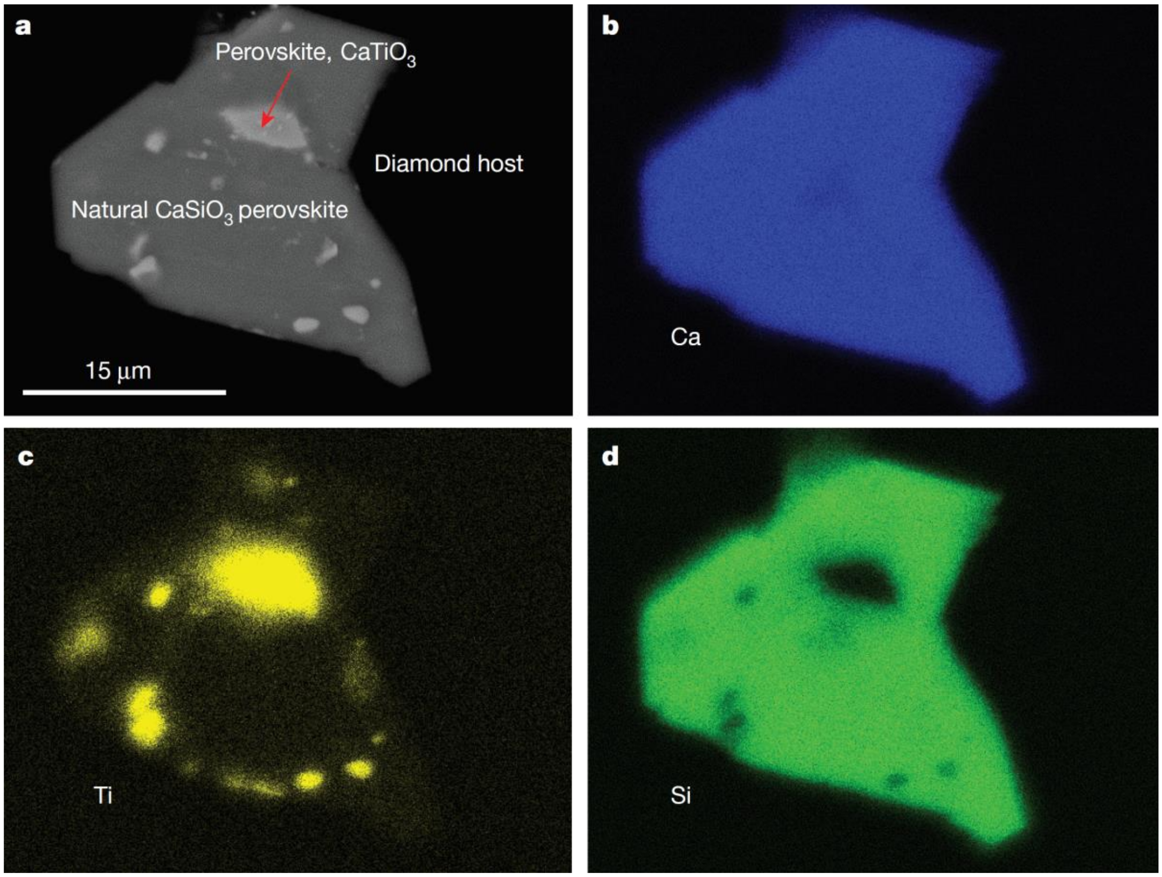


Fig 19. Backscattered-electron image of the Ca-Pv inclusion and energy-dispersive X-ray spectroscopy elemental maps. **a**: Backscattered electron image of the Ca-Pv inclusion (dark grey) surrounded by the diamond host (black), showing smaller inclusions of $CaTiO_3$ perovskite (light grey). **b–d**: Energy-dispersive X-ray spectroscopy elemental maps of Ca (b), Ti (c), and Si (d). The color intensity (black within the grain outline through to saturation in a specific color) is proportional to the element concentration.

(From *Nestola et. al*, “CaSiO3 perovskite in diamond indicates the recycling of oceanic crust into the lower mantle”, 2018, their figure 2)

Apart from the dominant ultramafic compositions that characterize the UM/LM boundary and the lower mantle sometimes we can come across mineral inclusions of **basaltic** (metabasite) affinities. As depth increases, first, the Ca components of majoritic garnet (dominant phase of the transition zone) give rise to CPV and then the Mg-Fe components form MPV. As we travel into greater depths in the LM, Al goes into MPV, but because of the larger Al contents of metabasite compositions, garnet (with decreasing majoritic component) persists to greater depths than in inclusions of metaperidotite (ultramafic) affinities (*Harte*, 2010).

Furthermore, in inclusions of basaltic composition we have larger Na and Al contents that result in the formation of additional phases like the Na- and Al-bearing phase (NAL) and a Na-Ca-Mg-Al-Si phase (CF) documented by Hirose and Fei (2002) and Perillat et al. (2006) (*Harte*, 2010).

Finally, it is important to refer to stishovite, a polymorph of silica (SiO_2), that becomes stable at the transition zone and continues into the lower mantle.

Fig 20. Small ferropericlase inclusions in a diamond from Kankan, Guinea (Ø: ~6 mm). The ferropericlase inclusions are surrounded by graphite-coated fractures. The brown color and the lack of well-defined crystal faces are characteristic features of Type II diamonds, which are prevalent among lower mantle diamonds.

(From *Tappert & Tappert*, “Diamonds in Nature – A guide to rough diamonds”, 2011, their figure 5-28)

3. Uncertain and/or rare mineral inclusions in diamonds

A variety of minerals has been found as inclusions in diamonds that cannot be linked to the typical lithospheric or sub-lithospheric inclusion suites or that are so rare that have only been recorded sporadically if not only once, and they usually occur as isolated inclusions.

Some of these inclusions indicate that the environment of source rocks, where the diamonds crystallized, was compositionally distinct from the conventional peridotitic or eclogitic. The presence of websteritic and calc-silicate minerals as inclusions in diamonds and as xenoliths proves that such unconventional source rocks exist.

A different type of unconventional source rock may be reflected in the phlogopite- and titanate-bearing mineral inclusions assemblages, such as those found in some diamonds from the Namibian coast. In this case, the diamonds probably formed in a possibly metasomatized part of the mantle. Although it is likely that more of these unconventional diamond source rocks exist within the mantle, it is unlikely that they are volumetrically significant (*Tappert et al.*, 2011).

Primary carbonate inclusions of aragonite $CaCO_3$, dolomite $CaMg(CO_3)_2$, nyerereite $Na_2Ca(CO_3)_2$, nahcolite $NaHCO_3$ in transition zone, and lower mantle diamonds are symptomatic for multicomponent carbonatite (carbonate-oxide-silicate) diamond-parental melts and feasibility of a mantle-carbonatite model to “super-deep” diamond genesis (*Litvin et al.*, 2014)

It is also worthy to make here a reference to the first finds of iron nitrides (Fig. 21) and carbonitride (Fig. 22) as inclusions in lower-mantle diamond from Rio Soriso, Brazil, as reported by Kaminsky and Wirth (2017). Among nitrides, both trigonal Fe_3N and orthorhombic Fe_2N were present and from the carbonitride the trigonal $Fe_9(N_{0.8}C_{0.2})_4$ one was present. These mineral phases are associated with iron carbide, Fe_7C_3, silicon carbide, SiC, Cr-Mn-Fe, and Mn-Fe oxides; the latter may be termed Mn-rich xieite (*Kaminsky et al.*, 2017).

The study concluded that the aforementioned iron nitrides and carbonitrides were formed in the lowermost mantle as the result of the infiltration of liquid metal, containing light elements from the outer core into the D″ layer, with the formation of the association: native Fe^0 + iron nitrides, carbides, and transitional compounds + silicon carbide. This, in turn, indicates that major reservoirs of nitrogen should be expected in the core and the lowermost mantle, providing some solution to the problem of nitrogen balance in the Earth (*Kaminsky et al.*, 2017).

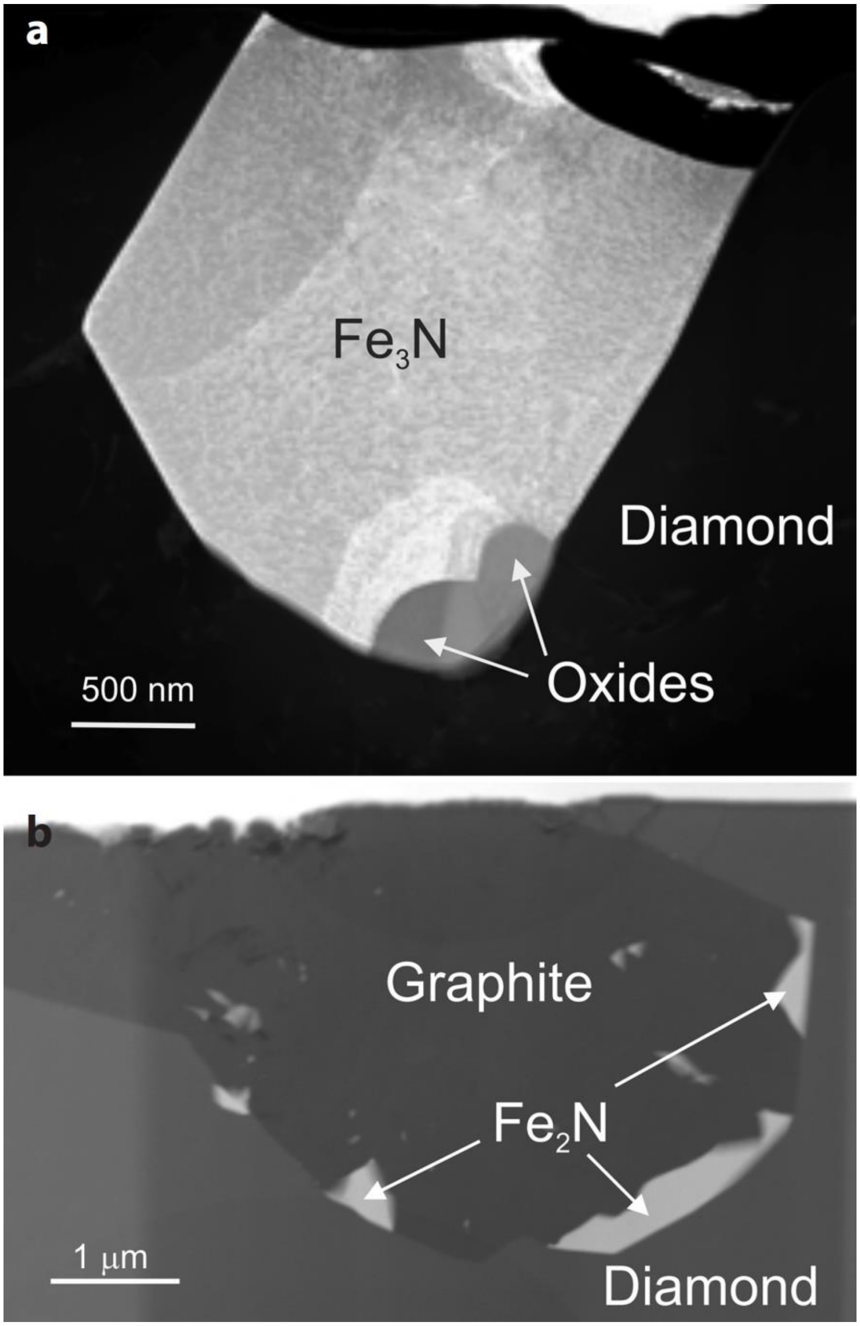


Fig. 21. TEM dark-field images of iron nitrides included in diamond no. 8/103. **a.** First type. A tabular grain of iron nitride, Fe_3N, intergrown with oxides. Foil no. 4592. **b.** Second type. Iron nitride, Fe_2N, resorbed with graphite, which occupies now the major part of the inclusion. Relics of Fe_2N have the same crystallographic orientations, confirming that they belong to a former, single large crystal. Foil no. 2934.

(From *Kaminsky And Wirth*, “Nitrides and carbonitrides from the lowermost mantle and their importance in the search for Earth’s “lost” nitrogen”, 2017, their figure 1)

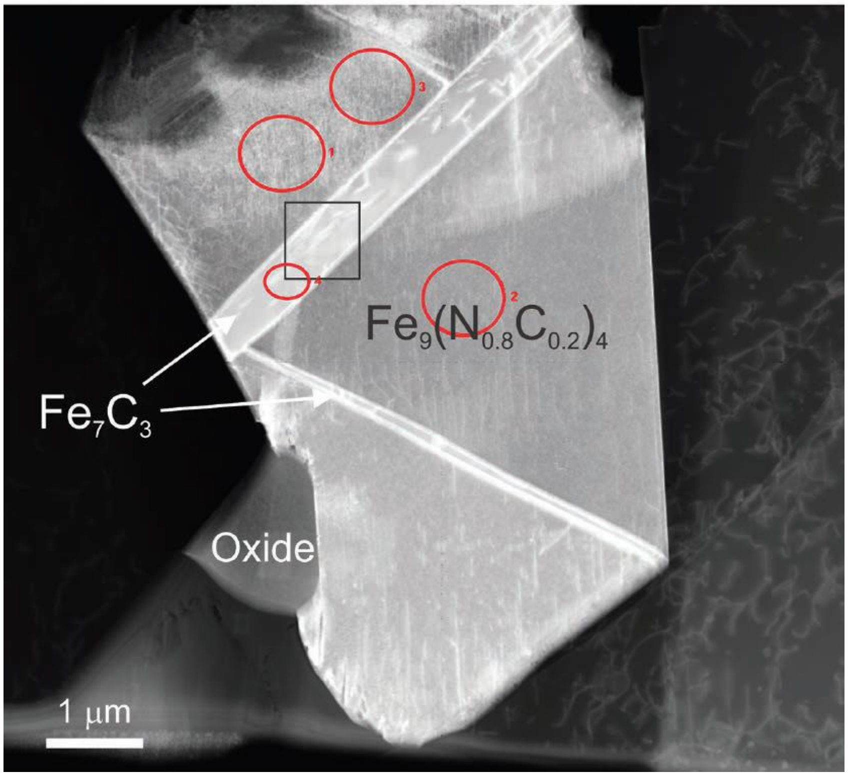


Fig. 22. HAADF image of iron carbonitride, $Fe_9(N_{0.8}C_{0.2})_4$, with lamellae of iron carbide, Fe_7C_3, hosted as inclusion in the diamond. In the lower-left part of the image, an idiomorphic crystal with spinel-type structure is observed intergrown with carbonitride. The volume below this grain is filled with redeposited Ga and sputtered material; originally it was likely filled with trapped fluid and/or vapor. The outlined square area corresponds to regions for Si and C elemental maps. Circles show areas for which EDX spectral analyses were determined. Foil no. 4588.
(From *Kaminsky And Wirth*, “Nitrides and carbonitrides from the lowermost mantle and their importance in the search for Earth’s “lost” nitrogen”, 2017, their figure 3)

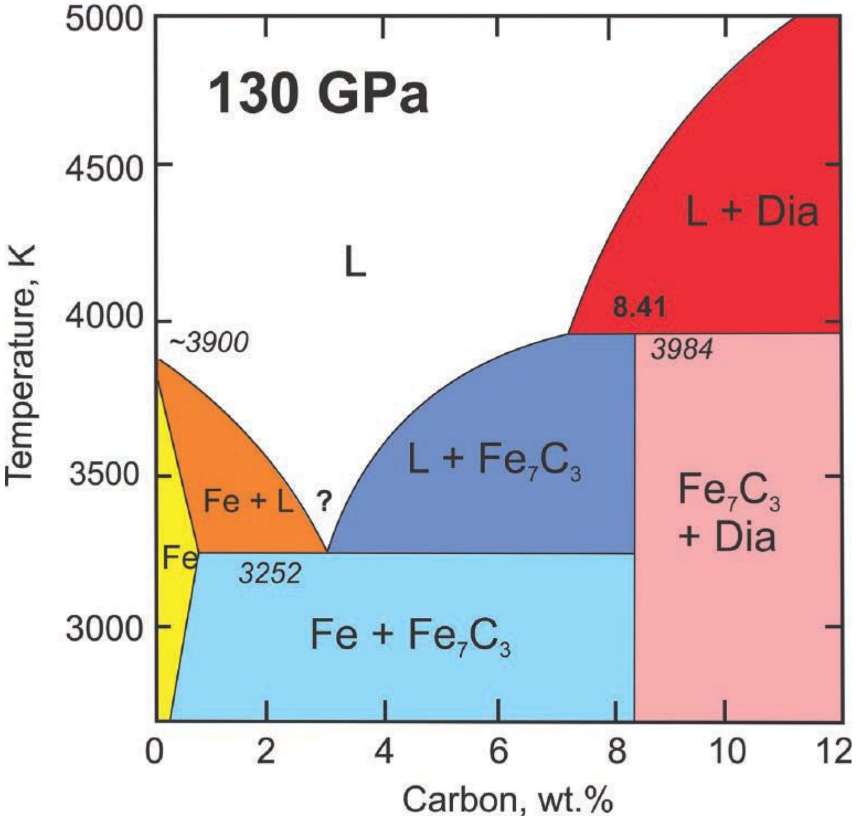


Fig. 23. The iron-rich portion of the Fe-C phase diagrams at 130GPa. L = liquid; Dia = diamond. Values in italics represent melting temperatures, and those in bold represent compositions. Modified from Lord et al. (2009).

(From *Kaminsky And Wirth*, "Nitrides and carbonitrides from the lowermost mantle and their importance in the search for Earth's "lost" nitrogen", 2017, their figure 7)

4. Retrograde minerals

One very important aspect of deep mantle diamond inclusions is that they were formed at great depths and thus at pressure and temperature conditions that differ tremendously from the ones that predominate on the surface of the earth. So, one query that might arise instantly is what happens to these inclusions during the ascent of the diamond to surface conditions, and how can we associate these products of retrograde transformation from lower-mantle or transition-zone precursors with specific diamond formation conditions.

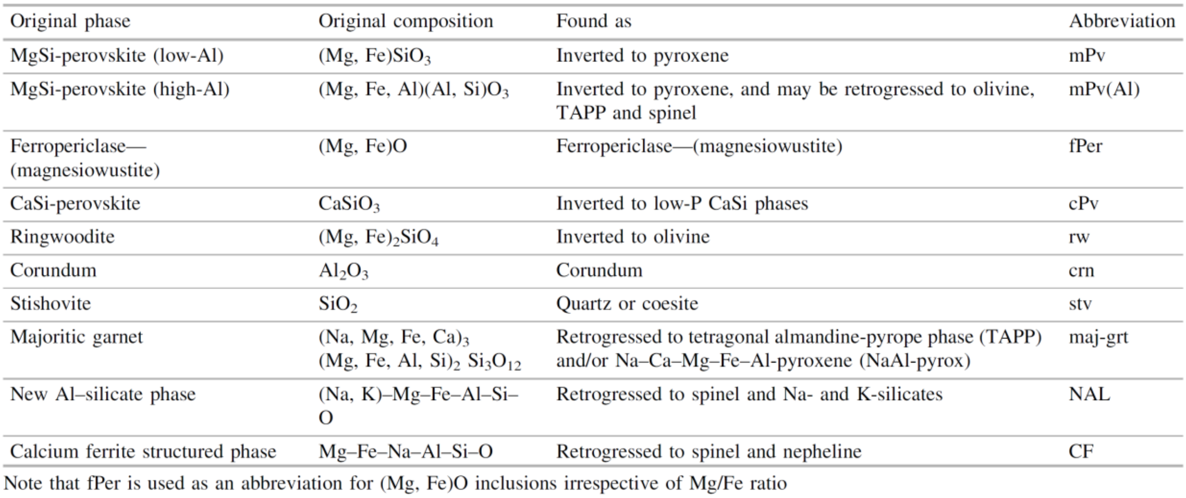
Although the answer is anything but simple, research on diamond inclusions from different localities has helped shed some light on a very complex question.

Ben Harte and Neil F. C. Hudson, in their paper "Mineral Associations in Diamonds from the Lowermost Upper Mantle and Uppermost Lower Mantle" (2013), have made a very thorough research on distinguishing retrograde and primary mineral inclusions, as seen in Table 4.

For Harte and Hudson (2013), associations in the same diamond of separate inclusions of $(Mg,Fe)SiO_3$, $(Mg,Fe)O$ and $(Mg,Fe)_2SiO_4$ – potentially representing the original phases MgSi-perovskite(mPv), ferropericlase (fPer) and ringwoodite (rw) – indicate formation at the Upper/Lower Mantle boundary.

Associations involving MgSi-perovskite and ferropericlase, without ringwoodite, are taken to indicate Lower Mantle assemblages of ultrabasic bulk composition, and these are further subdivided into two groups: those with low-Al MgSi-perovskite, mPv, from the shallowest Lower Mantle, and those with high-Al MgSi-perovskite, mPv(Al), from greater depths (*Harte and Hudson*, 2013).

In assemblages of basic bulk composition, the primary phases of mPv(Al), sodic majoritic garnet (maj-grt), new Al–silicate phase (NAL), and the calcium ferrite-structured phase (CF) are all represented by composite inclusions, which include a variety of retrograde products such as olivine, spinel, tetragonal almandine-pyrope phase (TAPP), NaAl-rich pyroxene phase (NaAl-pyrox) and nepheline. In both ultrabasic and basic bulk compositions, the principal Ca-bearing phase appears to be CaSi-perovskite (cPv) (*Harte and Hudson*, 2013).



Original phase	Original composition	Found as	Abbreviation
MgSi-perovskite (low-Al)	$(Mg, Fe)SiO_3$	Inverted to pyroxene	mPv
MgSi-perovskite (high-Al)	$(Mg, Fe, Al)(Al, Si)O_3$	Inverted to pyroxene, and may be retrogressed to olivine, TAPP and spinel	mPv(Al)
Ferropericlase—(magnesiowustite)	$(Mg, Fe)O$	Ferropericlase—(magnesiowustite)	fPer
CaSi-perovskite	$CaSiO_3$	Inverted to low-P CaSi phases	cPv
Ringwoodite	$(Mg, Fe)_2SiO_4$	Inverted to olivine	rw
Corundum	Al_2O_3	Corundum	crn
Stishovite	SiO_2	Quartz or coesite	stv
Majoritic garnet	$(Na, Mg, Fe, Ca)_3$ $(Mg, Fe, Al, Si)_2$ Si_3O_{12}	Retrogressed to tetragonal almandine-pyrope phase (TAPP) and/or Na–Ca–Mg–Fe–Al-pyroxene (NaAl-pyrox)	maj-grt
New Al–silicate phase	(Na, K)–Mg–Fe–Al–Si–O	Retrogressed to spinel and Na- and K-silicates	NAL
Calcium ferrite structured phase	Mg–Fe–Na–Al–Si–O	Retrogressed to spinel and nepheline	CF

Note that fPer is used as an abbreviation for (Mg, Fe)O inclusions irrespective of Mg/Fe ratio

Table 4. List of minerals occurring in the Perovskite and Periclase suite of deep diamonds inclusions. (From *B. Harte and N. F. C. Hudson*, "Mineral Associations in Diamonds from the Lowermost Upper Mantle and Uppermost Lower Mantle", 2013, their table 1)

Another important finding is that from Anzolini et al. (2018). According to them, $CaSiO_3$-walstromite is the most abundant Ca-bearing mineral inclusion found in super-deep diamonds and is believed to derive from $CaSiO_3$-perovskite (stable only below ~600km depth). They came to this conclusion by studying the remnant pressure (P_{inc}) retained by an inclusion, combined with the thermoelastic parameters of the mineral inclusion and the diamond host, that allowed them the calculation of the entrapment pressure of the diamond-inclusion pair.

CLIPPIR Diamonds

Fig. 24. Rough CLIPPIR diamonds have physical features akin to the historic Cullinan diamond, which forms the "C" of the CLIPPIR acronym. The size distribution for this variety of diamonds is skewed toward large sizes, with the examples shown here ranging from 14 to 91 carats. In rough form, CLIPPIR diamonds are irregularly shaped rather than well-formed crystals and sometimes appear to be broken fragments of once larger diamonds. Photo by Robert Weldon/GIA; courtesy of Gem Diamonds Ltd.
(From Smith et al., "THE VERY DEEP ORIGIN OF THE WORLD'S BIGGEST DIAMONDS", 2017, their figure 1)

This is a family of diamonds, like the famous Cullinan diamond (3,106ct, found in South Africa in 1905), that tend to be large, inclusion-poor, and relatively pure (usually type IIa), and in their rough state, they are irregularly shaped and significantly resorbed (Fig. 24). These characteristics are combined in the acronym "CLIPPIR" (**C**ullinan-like, **L**arge, **I**nclusion-**P**oor, **P**ure, **I**rregular, and **R**esorbed) (*Smith et al.*, 2017). Among larger diamonds, there is a striking increase in the prevalence of D color grades (the highest colour grade for diamonds in the D-Z colour range) and the proportion of type IIa diamonds, mainly due to their lack of nitrogen. As expected, these larger type IIa diamonds have very few inclusions and consequently high clarity grades. It is important to note here that not all type IIa diamonds are classified as CLIPPIR, and vice versa (*Smith et al.*, 2017).

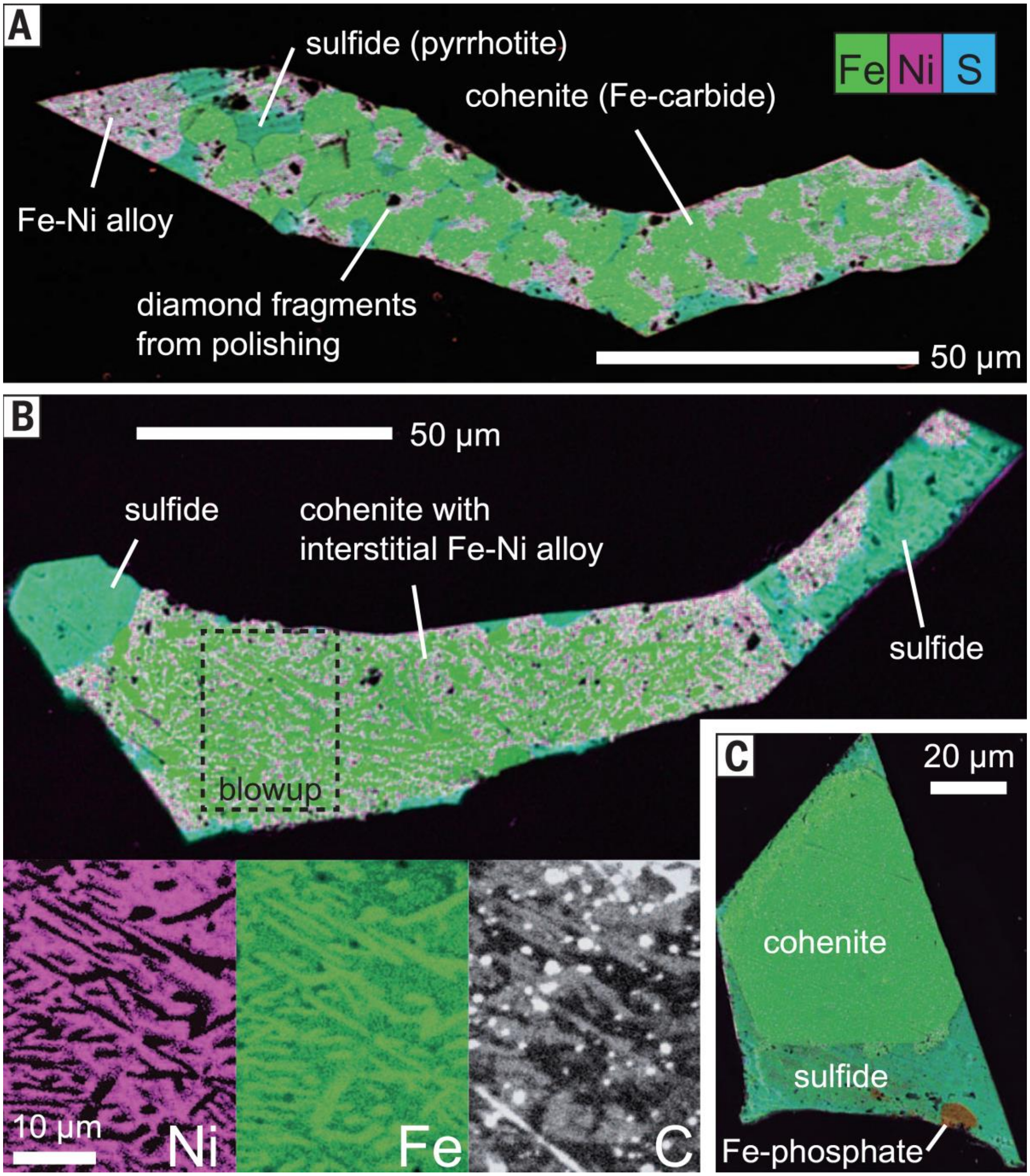


Fig. 25. Scanning electron microscopy x-ray maps of Fe-Ni-C-S melt inclusions. **A.** and **B.** Cohenite [$(Fe,Ni)_3C$] (green) is surrounded by interstitial Fe-Ni alloy (pink) and segregations of Fe-rich sulfide (teal), likely pyrrhotite. Detailed Ni, Fe, and C maps for the dashed area in **B.** show that the cohenite is relatively Ni-poor but Fe- and C-rich. **C.** Fe-phosphate bleb within sulfide and a large cohenite grain (no Fe-Ni alloy intersected). The samples shown are Letseng_889, inclusion E (A); Letseng_890, inclusion A (B); and OC2, inclusion D (C). (From Smith et al., "Large gem diamonds from metallic liquid in Earth's deep mantle", 2016, their figure 2)

The most intriguing part of this diamond family is nothing but its inclusions. Among the samples studied by *Smith et al.* (2016), the most common trapped material was a magnetic, metallic inclusion. In some other samples, they found a multiphase assemblage composed primarily of cohenite [$(Fe,Ni)_3C$], an interstitial Fe-Ni alloy, iron sulphide (pyrrhotite) segregations, and some more minor accessory phases like Fe-phosphate, Cr-Fe-oxide, and Fe-oxide (*Smith et al.*, 2016).

Also, small amounts of graphite occurred at the diamond inclusion interface and the fractures radiating from the inclusions. A thin fluid jacket of CH_4 was detected around most of the inclusions by Raman spectroscopy and in a few samples, it was also accompanied with H_2 (*Smith et al.*, 2016).

Smith et al. (2016) interpreted these inclusions to be coming from a former Fe-Ni-C-S melt with minor dissolved H, P, Cr, and O, indicating a reducing environment.

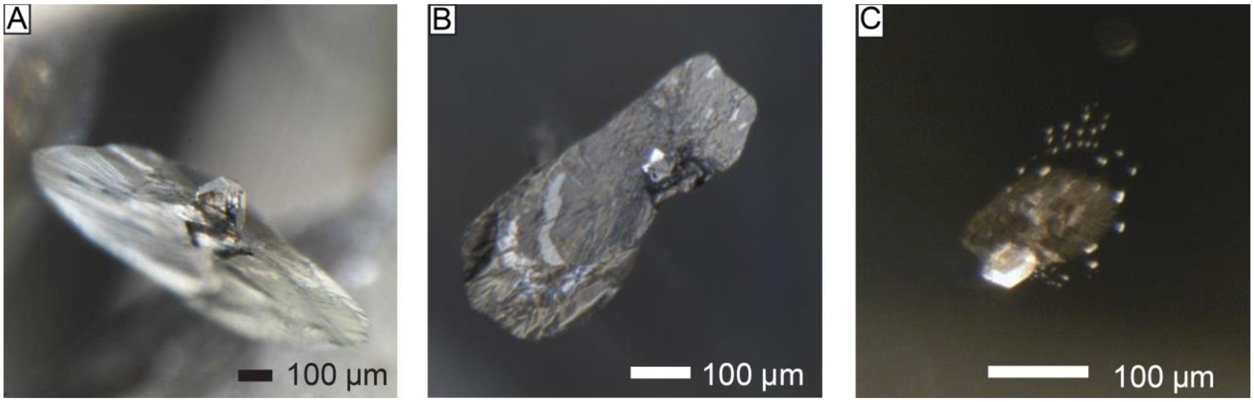


Fig. 26. Representative high-pressure silicate inclusions within CLIPPIR diamonds. **A.** Majoritic garnet with metal component and CH_4 in a colorless offcut from Letseng, Lesotho (sample Letseng_892). **B.** Wollastonite (inverted CaPv) with large, rounded graphitic fracture (sample 110207870803). **C.** $CaSiO_3$-walstromite (inverted CaPv) with metal-and-CH_4-bearing satellite inclusions defining a healed crack, and a later, graphitic fracture, not healed, that does not reach as far away from the central inclusion (sample 110206031373). The metallic component in A and C gives the inclusions detectable magnetism. It should be noted that CaSi-perovskite (CaPv) inclusions are inevitably inverted to assemblages of $CaSiO_3$-walstromite, Ca_2SiO_4-larnite, $CaSi_2O_5$-titanite, wollastonite, and $CaTiO_3$-perovskite.
(From Smith et al., "Large gem diamonds from metallic liquid in Earth's deep mantle", 2016, their figure S2)

Finally, for the remaining samples *Smith et al.* (2016) studied, they found mineral inclusions of silicate composition from a high-pressure origin, such as Cr-poor majoritic garnet and CaSi perovskite (CaPv) inverted to lower pressure phases. Some of these silicates also have coexisting metal and CH_4 ±H_2 fluid trapped in the same inclusion which leads to the conclusion that these silicate inclusion assemblages were trapped under similar reducing conditions as the metal-only population at minimum pressures of 12 GPa, 360 km depth.

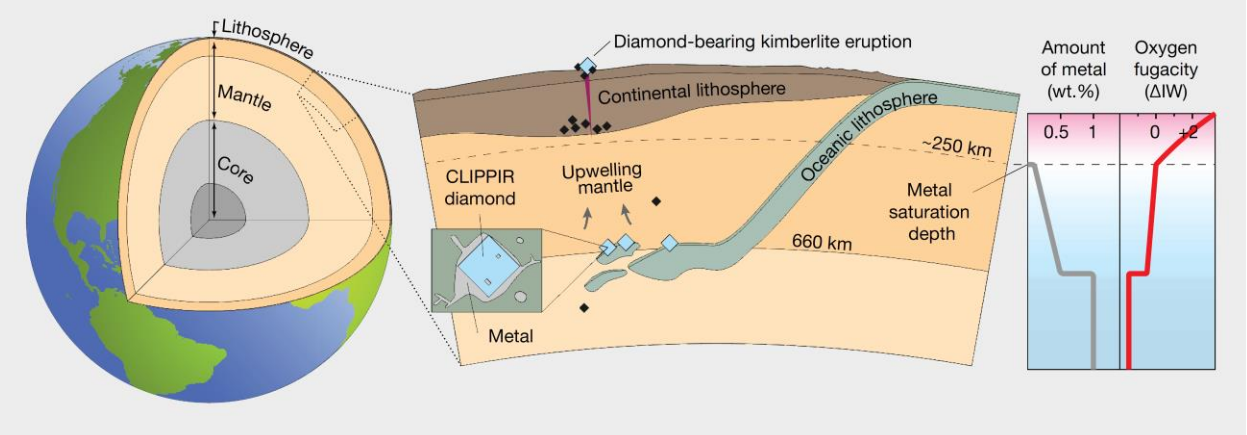


Fig. 27. Cross-section of the uppermost 1,000 km of the earth (center) illustrating the origin of CLIPPIR diamonds, shown as large blue diamond symbols. Smaller black diamond symbols indicate other varieties of diamond formed mainly in the continental lithosphere. The oceanic lithosphere subducted into the mantle provides the rocks necessary to explain the CaPv and majoritic garnet inclusions. CLIPPIR diamonds are thought to grow from liquid metal. Following growth, they may be carried upward with thermally or chemically buoyant upwelling mantle material and entrained in a kimberlite eruption to the surface. Profiles at the right show how the amount of metal in the mantle is expected to increase with depth starting from 250 km down, reaching up to approximately 1 wt.% below 660 km and buffering oxygen fugacity to reducing conditions (ΔIW, log units relative to the iron-wüstite buffer). Profiles after Rohrbach and Schmidt (2011). (From Smith et al., "THE VERY DEEP ORIGIN OF THE WORLD'S BIGGEST DIAMONDS", 2017, their figure 7)

From experimentation with synthetic diamonds grown in Fe-Ni alloy, researchers have observed that a metallic liquid is a favorable medium for growing large diamonds such as CLIPPIR, with few inclusions and little or no chemical zonation, because the carbon supply is well buffered and carbon diffuses rapidly.

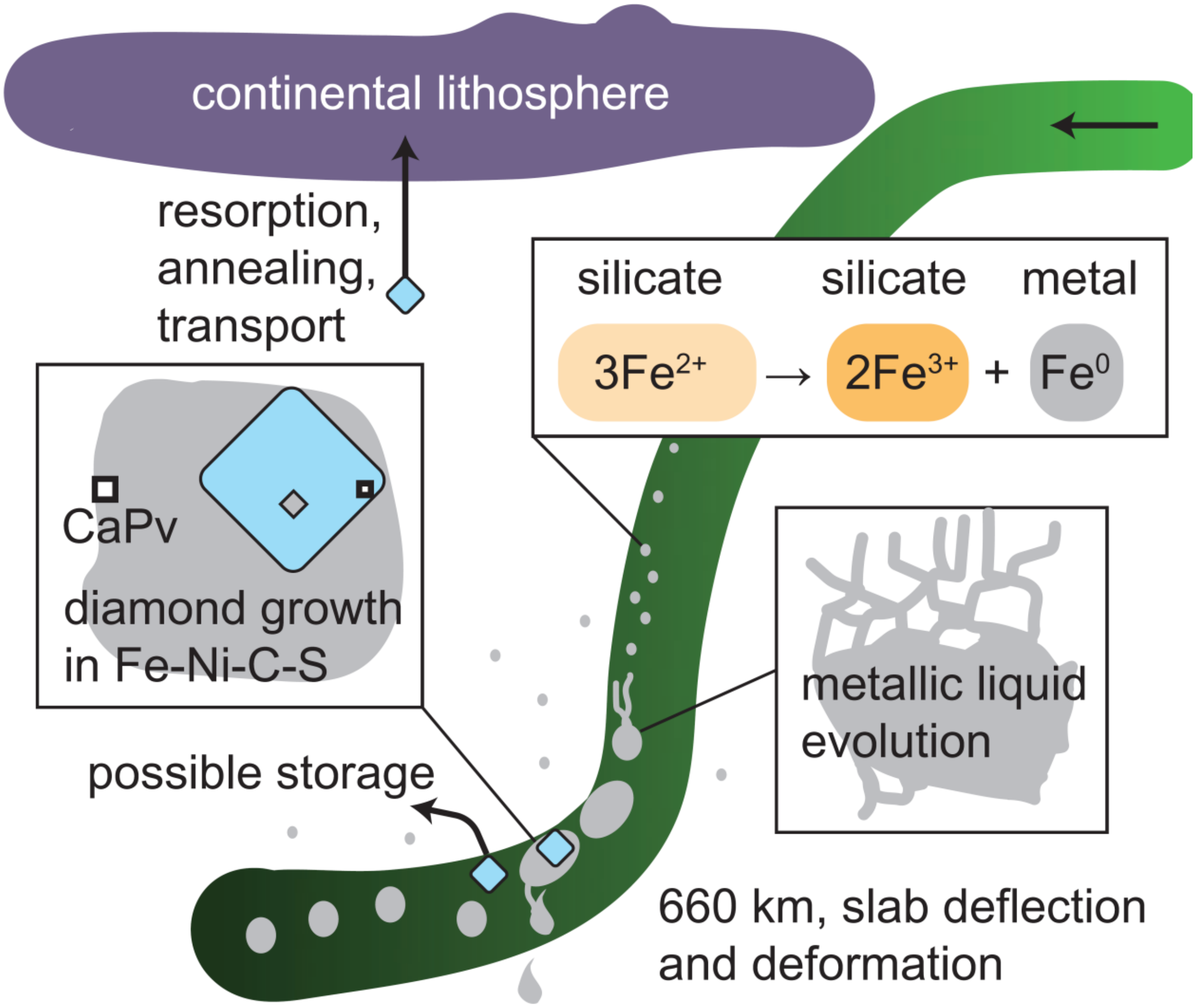


Fig. 28. Model of CLIPPIR diamond formation. Formation of metallic iron proceeds in subducting eclogite by disproportionation. Metal segregation may be aided by the deformation of the subducting slab in the transition zone. The liquid metal composition evolves to Fe-Ni-C-S, also dissolving P and H. Diamond crystallization occurs within metallic liquid pockets, likely in the pressure range of 12 to 25 GPa. Pocket walls become a site of CaSi-perovskite (CaPv) crystallization, where they can be included in a diamond. Carbon saturation is achieved by increasing pressure, assimilating further C, or another mechanism such as increasing S content. After growth, diamonds are physically separated from the growth environment and may be transported and entrained by a kimberlite eruption.
(From Smith et al., "Large gem diamonds from metallic liquid in Earth's deep mantle", 2016, their figure 3)

Blue Boron-Bearing Diamonds

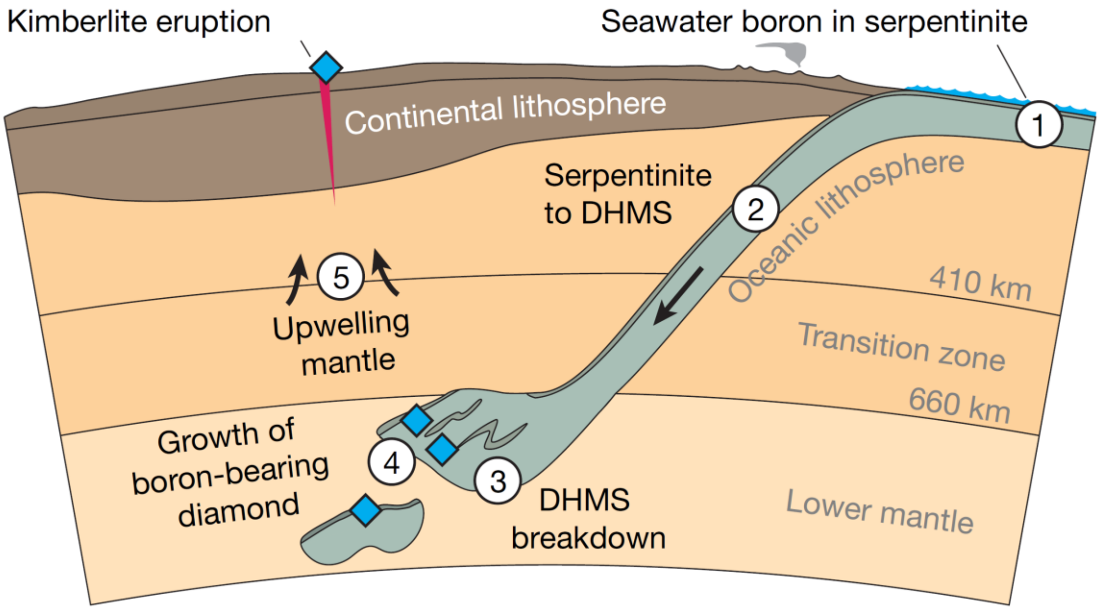


Fig. 29. Formation of type IIb diamond. (1) Seafloor hydrothermal circulation causes serpentinization, introducing boron into the oceanic lithosphere. (2) Subduction and metamorphism of serpentine to DHMS. (3) Breakdown of DHMS yields hydrous, boron-enriched fluid that migrates and evolves. It may gather carbon from the altered oceanic lithosphere. (4) Crystallization of boron-bearing diamond, triggered by redox reactions or in response to changing pressure, temperature, or composition of the fluid. (5) Vertical transport may involve localized buoyancy associated with diamond-related metasomatism or an external mechanism such as a plume, with ultimate exhumation to the surface due to kimberlite volcanism.
(From Smith et al., "Blue boron-bearing diamonds from Earth's lower mantle", 2018, their figure 3)

The blue-boron-bearing diamonds, which make up ≤0.02% of mined diamonds, belong also to Type II diamonds, and specifically to the Type IIb group.

Type IIb diamonds are mantle-derived minerals that contain boron at the 0.01-10p.p.m. level and show a lack of nitrogen absorption in infrared spectroscopy (*Smith et al.*, 2018). Boron imparts their blue color and p-type semi-conductivity. Their color and saturation of the blue hue depend on the boron concentrations (low or high) as well as on whether additional lattice defects are present. Because boron is a quintessential crustal element with a low concentration in Earth's mantle, blue diamonds, and their formation have long been a geochemical enigma (*Smith et al.*, 2018).

Boron as a chemical element is abundant in the continental and oceanic crust, and as proven by blue diamonds – like the renowned Hope diamond, it is also present in certain diamond-forming fluids at mantle depths.

Until recently, both the provenance of the boron and the geological setting of diamond crystallization were unknown but Smith et al. (2018) showed that boron-bearing diamonds carry previously unrecognized mineral assemblages (inclusions) whose high-pressure precursors were stable in metamorphosed oceanic lithospheric slabs at depths reaching the lower mantle. What *Smith et al.* (2018) suggest is that some of the boron in the seawater-serpentinized oceanic lithosphere is subducted into the deep mantle, where it is released with hydrous fluids that enable diamond growth. Type IIb diamonds are thus among the deepest diamonds ever found and indicate a viable pathway for the deep-mantle recycling of crustal elements (*Smith et al.*, 2018).

The inclusions that Smith et al. (2018) record are unmixed multiphase assemblages, as, during the ascent in the mantle, the originally sub-lithospheric inclusions destabilized, and broke down to lower-pressure minerals. It is highly doubtful that we could come across the same multiphase assemblages in samples from shallower, lithospheric depths.

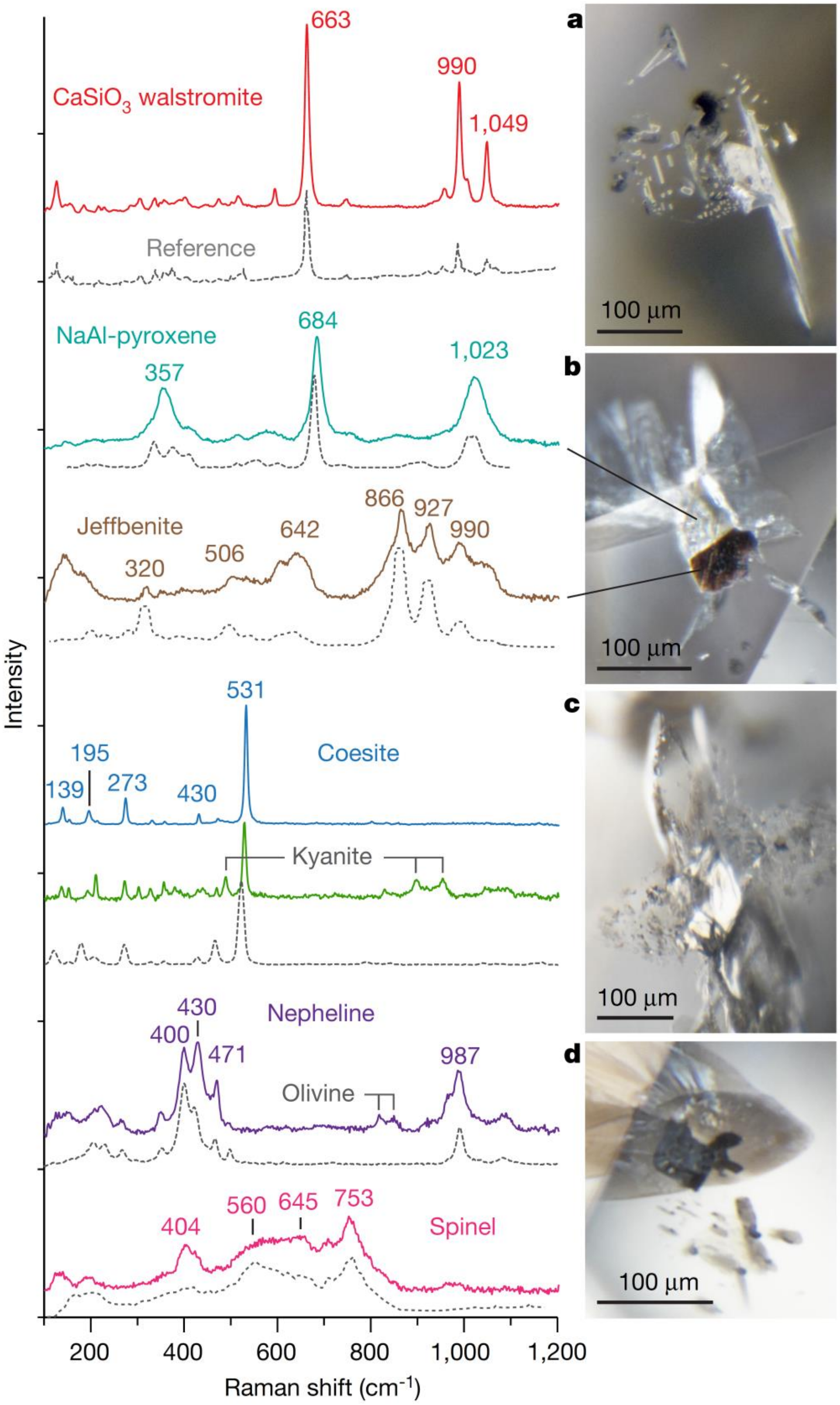

663
990
1,049
CaSiO$_3$ walstromite
Reference
NaAl-pyroxene
684
357
1,023
Jeffbenite
866
927
990
320
506
642
531
195
139
273
430
Coesite
Kyanite
430
400
471
Nepheline
987
Olivine
404
560
645
753
Spinel
Intensity
200
400
600
800
1,000
1,200
Raman shift (cm^{-1})
a
100 μm
b
100 μm
c
100 μm
d
100 μm

Fig. 30. Selected Raman spectra of inclusions in type IIb diamonds. **a.** Former Ca-Pv, now $CaSiO_3$ walstromite, in sample 110205945970. **b.** Former majoritic garnet, now a composite of NaAl-pyroxene and jeffbenite in sample 880000037816. **c.** Former stishovite, now coesite, in sample 101024478345. Also shown on the left is composite coesite plus kyanite spectrum (green) from sample 890000180201. **d.** Former CF, now composite of nepheline and spinel (with CH_4 fluid, not shown), in sample 110208245246. Dashed lines are reference spectra of $CaSiO_3$ walstromite, jeffbenite, nepheline, and spinel, plus omphacite R061129 and coesite X050094 from the RRUFF database. Spectra are stacked vertically for clarity. Source Data.
(From Smith et al., "Blue boron-bearing diamonds from Earth's lower mantle", 2018, their figure 1)

The most abundant inclusion identified, in the samples studied, was Ca-silicate dominated by $CaSiO_3$ walstromite, sometimes with larnite (β-Ca_2SiO_4) and other phases of $CaSiO_3$ composition. These inclusions are commonly interpreted as retrogressed $CaSiO_3$ perovskite (Ca-Pv). Retrogression of pure Ca-Pv alone should maintain a bulk Ca:Si ratio of 1, thus the presence of (Ca-rich) larnite in some inclusions may indicate that diamond growth occurred in a chemically evolving system with variable Ca enrichment (as seen in other super-deep diamonds) (*Smith et al.*, 2018).

Other recorded inclusions of retrogressed high-pressure mineral assemblages were orthopyroxene, with sharp Raman spectra matching enstatite, and minor amounts of coexisting olivine that are interpreted as retrogressed bridgmanite (lower-mantle Mg-silicate perovskite phase). Multiphase inclusions containing ortho- or clinopyroxene, coexisting with jeffbenite ($Mg_3Al_2Si_3O_{12}$) or spinel [$(Mg,Fe)Al_2O_4$], are interpreted as aluminous bridgmanite, although some bearing clinopyroxene may represent retrogressed majoritic garnet.

Another inclusion provides a convincing example of retrogressed majorite. It contained the two-phase assemblage of NaAl-clinopyroxene and jeffbenite (Fig. 30b) and was confirmed by *Smith et al.* (2018) with microanalysis by energy-dispersive X-ray spectroscopy and was interpreted as a former low-Ca, high-Na majoritic garnet. A separate inclusion of orthopyroxene in this diamond, interpreted as former bridgmanite, would then make a putative majorite–bridgmanite pair that would restrict its origin to within ~660–750km. Other observed inclusion phases are coesite (with accessory kyanite, interpreted as former stishovite) as well as ferropericlase (*Smith et al.*, 2018).

Finally, a multiphase inclusion was also analyzed from one diamond sample, that was dominated by nepheline and spinel, interpreted as former calcium-ferrite-type (CF) phase or possibly new aluminous (NAL) phase, which is compelling evidence of derivation from host rocks of basaltic composition at lower-mantle depths (Fig. 30). The same diamond also contained a multiphase inclusion of Fe carbide, Fe sulfide, and wüstite, that does not correspond to a known mineral but may represent a former metallic melt similar to those discovered in (boron-lacking) CLIPPIR diamonds. A few other type IIb samples were containing metallic-looking, magnetic inclusions like those of CLIPPIR diamonds, but these samples represent a minority population, whereas CLIPPIR diamonds are dominated by metallic Fe–Ni–C–S inclusions.

The observed inclusion mineralogy is consistent with the lithologies in subducted oceanic lithosphere reaching lower-mantle depths. Although some samples, particularly those containing Ca-Pv alone, may have grown in the mantle transition zone, the inclusion assemblages with former bridgmanite, ferropericlase, and CF phase require an origin in the lower mantle (*Smith et al.*, 2018).

CONCLUSION

Delving into the world of deep-mantle diamond formation, we experience an amazing journey into the deep earth, into the mineralogy of the sub-lithospheric mantle, the deep C cycle, as well as to the processes that brought these diamonds to the surface of the earth so we can mine today.

We come across two main lithotypes in these depths as diamond carriers, namely ultramafic (metaperidotite) and basaltic (metabasite), with a spatial distribution. At the depths of the lower asthenosphere and upper transition zone we mainly have basaltic (metabasite–eclogitic) compositions whereas at the depths of lower upper mantle and upper lower mantle we mainly come across ultramafic (metaperidotite–peridotitic) compositions.

Thus, starting from the lower asthenosphere and the upper transition zone, at about 250–670km, the peridotitic inclusions have the dominant $(Mg,Fe)_2SiO_4$ phase changing from olivine (OL) to wadsleyite (WD) (12–16GPa) and then ringwoodite (RW) (18–22GPa), accompanied by garnet, orthopyroxene and clinopyroxene. The latter two pass effectively into a solid solution with garnet giving birth to the majoritic end-member variety. That, consequently, results in majoritic garnet being one of the dominant phases of the transition zone along with WD and RW.

In the eclogitic inclusions, we observe the same changes in the garnet + pyroxene component as in the peridotitic-ultramafic inclusions and the dominant change taking place, as we move from the asthenosphere towards the transition zone, is that garnet undergoes expansion of its modal abundance (>80% in the transition zone) compared to clinopyroxene, which is the dominant phase in shallower depths. In the lower transition zone, we observe CPV becoming stable as well as the main Ca-bearing phase as we transcend into the lower mantle.

In the upper mantle/lower mantle (UM/LM) boundary region and the uppermost LM, at ~670km, we come across one of the most important geophysical boundaries of the earth since we have the conversion of the dominant mineral phases of the upper mantle to much denser high-pressure minerals. The ultramafic-peridotitic compositions at this boundary, are characterized by the replacement of RW by ferropericlase (FPER) (most common inclusion in lower mantle diamonds) and magnesium perovskite (MPV) – bridgmanite. But only when a diamond contains both FPER and MPV we can be sure of its “super-deep” origin.

Another important aspect we always need to take into account when examining the sub-lithospheric origin of the inclusions is, whether they are retrograde products such as olivine, spinel, tetragonal almandine-pyrope phase (TAPP, now jeffbenite), NaAl-rich pyroxene phase (NaAl-pyrox) and nepheline. In both ultrabasic and basic bulk compositions, the principal Ca-bearing phase appears to be CaSi-perovskite (CPV) which converts to wollastonite.

Finally, with regard to the CLIPPIR and blue boron-bearing diamonds, it is important to stress that they are both usually type II diamonds. Specifically, the former are type IIa whilst the latter are type IIb diamonds.

CLIPPIR diamonds have characteristic metallic inclusions like cohenite [$(Fe,Ni)_3C$], Fe-Ni alloy, pyrrhotite segregations, and some other minor accessory phases like Fe-phosphate, Cr-Fe-oxide, and Fe-oxide, which give away their deep mantle origin.

Blue boron-bearing diamonds have mainly $CaSiO_3$ walstromite inclusions, sometimes with larnite (β-Ca_2SiO_4) and other phases of $CaSiO_3$ composition, retrogressed majorite, containing the two-phase assemblage of NaAl-clinopyroxene and jeffbenite and others which are consistent with the lithologies in subducted oceanic lithosphere reaching lower-mantle depths.

A future project on deep mantle diamond genesis, that could benefit the scientific community as a whole, in subjects like plate tectonics, deep C cycle, deep mantle mineralogy, deep N cycle etc., could be the analysis of super-deep diamond inclusions from different localities, so as to create a database of inclusion mineralogies that could be used by scientists worldwide working on different aspects of deep mantle diamond genesis.

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