Ideal and real structures of different forms of carbon, with some remarks on their geological significance

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Abstract: Carbon is found in nature in a huge variety of allotropic forms and recent research in materials science has encouraged the development of technological materials based on nanocarbon. Carbon atoms with sp2 or sp3 hybridization can be thought of as building blocks. Following a bottom-up approach, we show how graphene and diamond molecules are built up from functional materials (Haber carbon) and how their properties vary with size, reaching an upper limit with bulk graphite and diamond. Carbon atoms with sp2 hybridization give rise to an impressive number of different materials, such as carbon nanotubes, graphene nanoribbons, porous carbon and fullerene. As in any crystalline phase, the crystal structures of natural carbon allotropes (i.e. graphite and diamond) contain various types of imperfections. These so-called lattice defects are classified by their dimensions into 0D (point), 1D (line), 2D (planar) and 3D (volume) defects. Lattice defects control the physical properties of crystals and are often a fingerprint of the geological environment in which they formed and were modified. Direct observations of lattice defects are commonly accomplished by transmission electron microscopy. We present and discuss the ideal and real structures of carbon allotropes, the energetics of lattice defects and their significance in understanding geological processes and conditions.

Introduction

Notwithstanding its abundance on Earth, which classifies it as a rare element (concentration c. 0.01 wt%, Palme & O’Neill, 2014), carbon is found in a huge variety of forms, spanning beyond all experimentally accessible stability fields. This variety of forms is a result of its electronic structure, which allows the formation of stable chemical bonds in various configurations. The four valence electrons (two s and two p electrons) of carbon occupy the L shell, while the inner K shell is occupied by two s electrons (Fig. 1). Figure 1 shows that the binding energies of the p electrons in carbon are very close to one another, a fundamental assumption in the interpretation of chemical bonds in the framework of hybrid atomic orbitals. The linear combination of valence carbon orbitals results in the formation of hybrid atomic orbitals with a symmetry that can give rise to 1D, 2D and 3D polymeric structures. The possibility of forming 1D chains (referred to as polymers) has been exploited in nature to build the tissues of living beings and by humans to develop plastics. 2D carbon structures (e.g. polycyclic aromatic hydrocarbons) dominate the world of aromatic compounds, which have a fundamental role in both the geosphere and in the development of functional materials (Haber et al. 2008; Bussetti et al. 2014). 3D carbon structures (e.g. diamondoids) are distinguished by their inertness and stability, making such carbon forms ubiquitous throughout the universe.

The topic of carbon allotropes is so overwhelmingly broad that it is beyond the scope of this paper to provide a comprehensive review on all aspects of carbon materials. The following sections provide some insight into the principles of the bonding, polymerization and structural arrangements of carbon allotropes. Following a bottom-up approach, we show how the progressive assembly of carbon atoms and low-dimensional building blocks brings about the formation of allotropic forms with different dimensionalities. We discuss their relative stability, including a description of the defects found in the crystalline phases of carbon and their significance in identifying their geological origin.

1D allotropes: carbon chains

The sp2 hybridization of atomic orbitals provides the basis for the formation of unidirectional bonds among carbon atoms (Fig. 1). In a system composed solely of carbon, for each contiguous pair of carbon atoms, one bond is due to the overlap of sp orbitals (σ bond) and one to the overlap of a p orbital (π bond). Electrons in π orbitals are those with the highest potential energy and govern the chemical reactivity of the allotrope. The overlap of two p orbitals, each containing one electron, brings about the formation of a bonding orbital (σ) occupied by two electrons and an unoccupied antibonding state (π*) separated by an energy gap of c. 10 eV (1 eV = 1.6 × 10−19 J = 23 kcal mol−1) (Fig. 2).

As the number of carbon atoms in the chain increases, the bonding states are populated accordingly and, simultaneously, the energy of the highest occupied molecular orbital (HOMO) increases, whereas that of the lowest unoccupied molecular orbital (LUMO) decreases. Finite chains of carbon atoms bonded through contiguous double bonds are called cumulenes (Banhart 2015). In the limiting case of an infinite chain (carbyne), the number of bonding and antibonding states is so large that they form a continuum of energy levels, which is referred to as an energy band. The valence band originates from the bonding states, whereas the conduction band originates from the antibonding states. A single level, the Fermi energy level (E_F), separates the occupied and unoccupied states. The electronic structure of a solid system of
bonded atoms can always be described in terms of valence and conduction bands. An important point is that the electrons that occupy a band state cannot be assigned to a parent atom—that is, they are delocalized. For this reason, the reactivity of a solid in terms of its redox potential is described by parameters such as the ionization potential and electron affinity, which allows the identification of the energy position of the HOMO and LUMO levels or the valence band maximum and conduction band minimum levels (Kahn 2016).

In such a configuration, the system behaves like a metal because the thermal energy is sufficient to promote electrons from the Fermi level to the conduction band, where they are free to move throughout the chain, transporting their charge. However, 1D metals are inherently unstable towards distortion (dimerization), which lowers the energy of the valence band and opens up an energy gap (Peierls 2001). Such distortion brings the system towards a configuration more similar to a polyyne, where triple bonds (one $\sigma$ and two $\pi$ bonds) are alternated with single bonds within the chain. A theoretical quantification of such a distortion shows a variation in bond lengths of <2% (Cahangirov et al. 2010). The appearance of an energy gap gives rise to a transition from a metal to a semiconductor. In a semiconductor, the charge carriers need to be energetically activated to occupy states in the conduction band.

1D carbon chains are often the product of the degradation of more complex frameworks of carbon atoms, such as graphene layers. For example, Chuvilin et al. (2009) demonstrated the in situ formation of carbon chains through real-time imaging of graphene constrictions interacting with the electron beam of a transmission electron microscope.

### 2D allotropes: from benzene to graphene

The stabilizing effects of delocalization are also evident in 2D systems of carbon atoms, particularly when the atoms are arranged...
in planar cyclic arrays with $4n + 2$ (where $n$ is an integer number) $\pi$ electrons. Such systems are called polycyclic aromatics. They are produced geologically when organic sediments are chemically transformed into fossil fuels (e.g. oil and coal) and account for 10–30% of cosmic carbon. The smallest aromatic molecule is benzene ($C_6H_6$, Fig. 3), where six $sp^2$ carbon atoms are arranged at the vertices of a regular hexagon and the six $\pi$ electrons are paired in three bonding orbitals with a HOMO – LUMO gap of $c. 5$ eV. The energy gain of benzene due to aromaticity is $1.6$ eV ($36$ kcal mol$^{-1}$) and can be estimated from a comparison of the hydrogenation heat of cyclohexene and benzene. Planar aromatic systems are the result of fusing benzene rings with the formation of polyacenes (e.g. the coronenene structure in Fig. 3). Similar to the assembly of polynyle, polyacenes tend to a metallic state when approaching an infinite 2D configuration, which we refer to as grapheme. Much of the technological development of optoelectronic devices based on graphene layers relies on the possibility of exploiting the semiconducting properties of the active material. This is accomplished by reducing the dimensionality of the otherwise metallic 2D layer from a nanosheet to a nanoribbon (Han et al. 2007).

3D allotropes: nanotubes and fullerene

1D carbon chains have been demonstrated to be suitable building blocks for the production of 2D and 3D structures. Six-membered polynyle assemble spontaneously in solution to form either nanotubes (at temperatures between 0 and 40°C) or graphene layers (at temperatures $\geq$40°C) (Hlavaty et al. 2000). In this framework, the structural relationship between carbon chains, layers and tubes appears to be obvious, with the only stability constraint being the diameter of the tubular structure, which cannot be much less than 1 nm (Zhao et al. 2004). Single-walled carbon nanotubes can, in turn, interact with graphene layers to form multi-walled structures (Han et al. 2016).

A spontaneous assembly mechanism has been proposed to relate 1D carbon chains and fullerene. If the terminal carbons of long chains partially react with one another to produce the first hexagonal and pentagonal cycles, then the full $C_{60}$ and $C_{70}$ fullerene structures can be viewed as the result of a spiralling and zip-up mechanism of the rest of the carbon atoms of the chain around the first aromatic nuclei (Hunter et al. 1994). The interaction of carbon allotropes might then proceed further towards the formation of complex structures, such as the so-called peapods, which represent the arrangement of fullerene molecules within hollow carbon nanotubes (Smith et al. 1998; Hornbaker 2002).

3D allotropes: diamondoids

In the framework of real structures, i.e. finite sized systems, the transition from a molecule (hydrocarbon) to a true allotrope is ill-defined. For hexagonal systems, it is universally accepted that benzene is a molecule and not a carbon allotrope. This also holds for coronenene and higher oligoacenes and, in principle, as long as the fraction of heteroatoms (mainly hydrogen) does not reach zero. However, what we consider to be graphene and even graphite or other allotropes of carbon, still contain finite fractions of heteroatoms (e.g. nitrogen impurities in diamond).

The same scenario holds for systems with tetrahedrally coordinated carbon. When the size of a diamond crystal is so small that the fraction of hydrogen atoms saturating the dangling bonds of the surface carbon atoms cannot be neglected, we are prone to consider it as a molecule: a diamondoid. The smallest diamondoid is adamantane, formed by a carbon cage of ten carbon atoms ($C_{10}H_{16}$). Higher diamondoids have multiples of four additional carbon atoms arranged in a cage. In this manner, we have diamantane ($C_{14}H_{24}$) (Fig. 3) and triamantane ($C_{18}H_{32}$) systems, which retain the superior properties of diamond in terms of hardness, stiffness, thermal stability, chemical resistance and biocompatibility at the nanoscale (Dahl et al. 2003).

With the aim of defining a general way to assess the relative stability of the various allotropic forms of carbon, in relation to their molecular size, we follow the approach of Badziag et al. (1990), who calculated the heat of formation (the inverse of binding energy) of hexagonal and tetrahedral hydrocarbons assuming a surface terminated with H atoms (Fig. 3). At the limit of H/C = 0, we find the binding energies of ideal bulk diamond and graphite (5.06 and 4.11 kcal mol$^{-1}$, respectively). The lower binding energy of graphite shows its higher stability with respect to diamond. However, the dependence of the binding energy of tetrahedral hydrocarbons on size is very strong, whereas that of hexagonal hydrocarbons is weak. This results in the presence of an H/C ratio at which the stability of diamond-like and graphite-like molecules is the same, regardless of the pressure. This corresponds roughly to an octahedral diamond crystallite of 3–5 nm and a graphene layer containing c. 100 carbon atoms (Fig. 3).

This result accounts for a large number of experimental observations, where diamond nanoparticles are energetically favoured over polycyclic aromatics, without requiring the high pressures or extreme conditions usually invoked when the presence of diamond is detected. To explain this behaviour, we must consider that diamond is only slightly unstable with respect to graphite (at room temperature and 1 atm, the difference in free energy between diamond and graphite is only $c. 0.03$ eV per atom, which is virtually the available thermal energy of 0.025 eV) and also that heteroatoms, such as hydrogen, play a fundamental part in the growth process. Following Volmer’s rule, the first phase nucleating from a saturated carbon vapour is expected to be graphite due to its lower density (2.26 v. 3.51 g cm$^{-3}$). Once formed, graphite will not spontaneously transform into diamond because it is the stable phase and due to the high activation energy barrier between the two forms (c. 0.4 eV per atom). Atomic hydrogen is the key reactant and changes the relative energy of small graphitic and diamond clusters, providing a means of circumventing the large activation barrier. Diamond nucleation at metastable conditions is then possible within the framework of a mechanism in which graphitic intermediates are subsequently hydrogenated by atomic hydrogen to saturated
structures, which then can act as sites for diamond growth (Angus et al. 1993). Another way of escaping the energy barrier for the formation of diamond is heterogeneous nucleation in the epitaxial orientation relationship: diamond (111) $\parallel$ graphite (0001), diamond [110] $\parallel$ graphite [1120].

3D allotropes: graphite, diamond and polytypes

Once the polymerization of carbon atoms has passed the nanoscale, we can definitely consider the phases as crystalline carbon allotropes. Graphite and diamond are generally regarded as the main stable forms of native carbon and have well-defined crystal structures (Hazen et al. 2013). There is some discussion about whether lonsdaleite, the hexagonal high-pressure phase of carbon, is also a stable polymorph of carbon (Langenhorst 2002; Langenhorst & Deutsch 2012; Németh et al. 2014; Jones et al. 2016; Shiell et al. 2016). Here we restrict our discussion to a brief description of the crystal structures of these three polymorphs and their possible polytypes.

The ideal graphite structure is composed of a series of stacked planar layers (Fig. 4). Each layer represents a hexagonal dense plane of carbon atoms and each carbon atom within these layers shows a trigonal planar coordination with strong covalent ($\sigma$) bonds to three other carbon atoms. The bond length between these $sp^2$ hybridized carbon atoms is short (0.142 nm). The unhybridized fourth $p_z$ valence electron is paired with another delocalized electron of the adjacent plane by a much weaker van der Waals bond, resulting in a relatively large spacing between the layers of 0.341 nm. The common stacking sequence of the layers is hexagonal with an ABAB order. There is also a rhombohedral form of graphite with a cubic sequence (ABCABC), which is regarded as a metastable variant.

Diamond shows a honeycomb structure with open channels when viewed along the [110] direction (Fig. 4). In this projection, its structure can also be visualized as a stacking of puckered layers along the [111] direction. Each carbon atom in the layers has a tetrahedral coordination with four covalent bonds forming 109.5° angles to neighbouring $sp^3$ hybridized carbon atoms at a distance of 0.154 nm. The stacking sequence of the {111} planes is cubic with an ABCABC order, such that every third layer is identical. As a result of the cubic symmetry of diamond, there are four orientations of the {111} planes with this stacking order.

Lonsdaleite is composed of the same puckered layers with the same covalent bonding as diamond, but shows a hexagonal ABAB stacking sequence such that every second layer is identical (Fig. 4). As a result of the hexagonal symmetry, the layers are indexed as (0001) planes. The coordination of carbon atoms is also tetrahedral and the densities of lonsdaleite and diamond are identical.

Analogous with the silicon carbide system (Ownby et al. 1992), we can also imagine mixed cubic and hexagonal stacking sequences of the puckered layers, such as ABCACB. These phases have a predominantly hexagonal symmetry with an increased periodicity along the $c$-axis. As the structural changes affect only one lattice direction, these variants are called polytypes. In addition to the classical description in terms of stacking sequences, there are further notations to describe the structures of polytypes. In the common Ramsdell notation, diamond is a 3C (C for cubic and with three layers in the stacking sequence), lonsdaleite is a 2H (H for hexagonal and with two layers in the stacking sequence) and the ABCACB phase is a 6H polytype (Ramsdell 1947).

Lattice defects in 3D carbon allotropes

The following sections give an introduction to the lattice defects typical of carbon allotropes. Like all crystals, carbon polymorphs are never perfect and show deviations from an ideal 3D structure. These imperfections locally disturb the regular arrangement of the atoms and usually increase the internal energy of the crystal. The different types of defects are subdivided according to their dimensions into point (0D), line (1D), planar (2D) and surface or volume (3D) defects. They are often intimately related and their presence can significantly modify the chemical and physical properties of carbon phases, playing an important part in their industrial applications.

In geological systems, the entity of defects (i.e., the defect microstructure of minerals) is commonly a fingerprint for the...
genesis and evolution of carbon polymorphs and provides a geological record of the host rocks. The defects in carbon phases are thus a geological archive complementary to the information from geochemical (trace elements and isotopes) markers. Here, we will briefly discuss the principles and different types of lattice defects (excluding the volume defects), based on typical examples of carbon minerals. This will allow us to understand the geological significance of defect microstructures, which is then finally demonstrated for the mineral diamond.

**Point defects in graphite and diamond**

Point defects or 0D defects can be either intrinsic or extrinsic (Fig. 5). Intrinsic point defects are either vacancies (i.e. vacant sites in the regular lattice) or self-interstitial carbon atoms (i.e. a carbon atom at an irregular interstitial site). The formation of vacancies is energetically more favourable because the distortion of the lattice environment is less severe than for self-interstitial carbon atoms. The concentration of vacancies is exponentially related to temperature and they are the only lattice defect that, as a result of a gain in entropy, can lower the internal energy of a crystal up to a certain threshold concentration. A typical concentration of intrinsic defects in diamond at ambient temperatures is 0.1–10 ppm.

Extrinsic point defects are foreign elements at substitutional and interstitial sites (Fig. 5). The most common element that replaces carbon in the diamond structure is nitrogen, occurring at typical concentrations of c. 5000 ppm. Mantle diamonds are classified into different types depending on the kind and concentration of impurities such as nitrogen (Harlow 1998). Diamonds with a high nitrogen content are classified as type Ia diamonds. Most of the nitrogen atoms in these diamonds are arranged in pairs, but a particular type of nitrogen-rich defect referred to as platelets may also be present. Nitrogen generally causes the yellowish colour of diamonds. By contrast, boron causes a blue colour in diamonds.

**Line defects in graphite and diamond**

Line (1D) defects are dislocations – that is, displacements of atoms along a line in a crystal structure. If the displacement vector (i.e. the Burgers vector \( b \)) is perpendicular to the line direction, then the dislocation has an edge character. If the displacement vector is parallel to the line direction, then the dislocation is a screw dislocation. The movement of dislocations allows the crystal to deform by slip on specific lattice planes \{hkl\} along specific displacement vectors \(<uvw>\). Both the slip plane and Burgers vector \( b \) define the slip system \(<uvw>\{hkl\}\) of a material and depend on its crystal structure. In general, the energy of a dislocation is proportional to the square modulus of the Burgers vector: \( E \sim |b|^2 \).

To minimize the dislocation energy, the preferred Burgers vectors are thus the shortest lattice vectors and the slip planes are most densely packed planes in a crystal structure (Fig. 6).

The densest plane in graphite is (0001) and the shortest possible displacement vectors in this plane are \( \frac{1}{3} <1120> \) (i.e. the \( a \)-axes; Fig. 6a). This yields the slip system \( <1120>\{0001\} \), which has also been confirmed by transmission electron microscopy (Amelinckx & Delavignette 1960). The stacking fault energy in graphite is fairly low as a result of the weak van der Waals interlayer bonding, which often leads to the dissociation of perfect dislocations into two partial dislocations.

For diamond, the densest lattice planes are \{111\} and the shortest possible displacement vectors in these planes are \( \frac{1}{2} <11\overline{1}0> \), defining the slip system as \( \frac{1}{2} <11\overline{1}0>\{111\} \) (Fig. 6b). This slip system was observed early on in natural diamond by Hornstra (1958). Because the \{111\} planes are puckered, there are two distinct atomic positions at which an extra half-plane can end in the crystal lattice. These two types of dislocations are called the shuffle and glide sets (Fig. 6c).

Although the slip system of lonsdaleite has never been determined, it should be the same as for graphite.

**Planar defects: stacking faults and microtwins in graphite and diamond**

As both graphite and diamond can be interpreted as derivatives of closest packed structures, there are many possibilities for planar
faults in the stacking sequences. Hexagonal graphite with the stacking sequence ABAB is believed to be the thermodynamically stable low-pressure phase of carbon. However, graphite with a rhombohedral symmetry has also been reported to exist naturally as a rare unstable polymorph (Laves & Baskin 1956). Rhombohedral graphite has a cubic stacking sequence of ABCABC and can be interpreted as an extended stacking fault of hexagonal diamond. Many natural graphites contain both types of structure and numerous stacking faults (Amelinckx et al. 1965).

The nature of stacking faults and their relationship with microtwins is illustrated schematically in Figure 7 for the diamond structure projected along the [110] axis. In this projection, the diamond structure can be considered as a cubic closest packing of A, B and C layers (ABCABC ...), stacked along the [111] direction. Disordering in the cubic stacking sequence results in stacking faults and microtwins (Angus et al. 1992). Pairs of stacking faults are classified by the number (n) of layers of correct stacking between the faults. An intrinsic stacking fault does not have a layer (n = 0) of correct stacking between the faults. This corresponds to a missing C layer in the stacking sequence, resulting in a local hexagonal stacking sequence of ABAB. By contrast, an extrinsic stacking fault results from an additional C layer between the A and B layers. In this case, the number of layers with correct stacking is 1. A close look at both stacking faults shows a local twin configuration. The intrinsic stacking fault produces a twin extending over one layer, whereas the extrinsic stacking fault extends over two layers. If the fault in the stacking sequence extends over more than two layers, i.e. if the number of layers with correct stacking is >1, the defect is, by definition, referred to as a microtwin. There is therefore a close structural relationship between stacking faults and twins and both are oriented parallel to (111).

The formation of these planar defects can be attributed to growth, deformation or transformation. A stacking fault bound by partial dislocations is usually of a mechanical or transformational nature, whereas the absence of partial dislocations is indicative of an origin during growth. A stacking fault in deformed diamond is terminated by two partials with \( b = \frac{1}{2}[110] \). A mechanical stacking fault in graphite can be created by the splitting of a perfect dislocation according to the reaction \( 1/3[2110] \rightarrow 1/3[1010] + 1/3[1100] \).

![Figure 6](image-url)

(a) (0001) projection of a layer of the graphite structure showing the unit cell (pale blue), lattice directions and one Burgers vector \( b \) with a length of \( \frac{1}{3}[2110] \). (b) Unit cell of the diamond structure showing a densely packed (111) plane (pale blue) with three possible Burgers vectors (shortest lattice translations) in this plane. (c) (110) projection of the diamond structure with a 60° glide dislocation (modified after Blumenau et al. 2004). Note that the Burgers vector is 30° inclined to the projection, resulting in a 60° angle to the dislocation line.
Other defect microstructures characteristic of graphite and diamond

Both graphite and diamond show peculiar defect microstructures unique to each mineral. During the natural carbonization of organic matter and graphitization (e.g. during high-temperature metamorphism), graphitic carbon develops an intermediate so-called turbostratic structure (Fig. 8; Buseck & Beyssac 2014). In this structure, the carbon layers are randomly oriented and arranged in a folded and crumbled manner. Turbostratic carbon materials are considered to contain a combination of highly concentrated defects, such as vacancies, dislocations and disclinations (i.e., line defects violating rotational symmetry). The individual graphitic crystallites within the turbostratic structure coarsen and line up with increasing degrees of metamorphism, potentially resulting, under the optimum conditions, in a large single crystal graphite.

Kimberlitic diamonds with high nitrogen contents (type Ia) show two unusual lattice defects that are absent in nitrogen-poor type II diamonds. The defects are called platelets and voidites and were originally believed to contain nitrogen. Platelets are planar defects oriented parallel to the {100} planes. Platelets show a similar fringe pattern to stacking faults in transmission electron microscopy images (Fig. 9a) because they disrupt the normal stacking sequence in the crystal. Voidites are tiny {111}-faceted cavities that lie in the {100} platelets, suggesting that they are a kind of precipitate on the platelets.

The precise nature of platelets and the apparently variable nitrogen content in them are long-standing subjects of diamond research (Harris 2018). The generally accepted model postulates that platelets consist of an interstitial layer of carbon atoms bonded pentagonally to the surrounding diamond matrix. Nitrogen tends to accumulate as paired nitrogen defects in this defect environment (Fallon et al. 1995). Advances in aberration-corrected electron microscopy enabled recently the imaging of platelets at sub-Angström resolution, revealing a zigzag ordering of these defect pairs (Olivier et al. 2018). By contrast, voidites are rich in nitrogen and may even represent solid nitrogen exsolved from diamond during uplift into crustal regimes. This occurs because the solubility of nitrogen in diamonds decreases with decreasing pressure and/or temperature. Thus both platelets and voidites could be indicators of the pressure–temperature paths of kimberlitic diamonds.

Defect microstructures of natural diamonds as a genetic fingerprint

Diamonds form in a wide range of environments, from the deep interiors of planets to molecular clouds in space, via a diverse range of processes (metastable and stable) and conditions. Four types of diamond can be distinguished based on their genesis and geological setting: (1) kimberlitic, (2) ultra-high pressure (UHP) metamorphic, (3) impact and (4) pre-solar diamonds.

(1) Kimberlitic diamonds originate from various depths in the Earth’s mantle and have attracted considerable interest in the earth sciences due to their inclusions of high-pressure phases (Stachel et al. 2005). The origin of mantle diamonds has been discussed for a long time, but there is now a common consensus that they form by redox crystallization from hydrous silicate–carbonate melts, with the oxygen fugacity as the controlling factor in their precipitation (Rohrbach & Schmidt 2011; Shirey et al. 2013; Stagno et al. 2013, 2015).

In this formation process, kimberlitic diamonds may take up impurities such as nitrogen, which aggregates into different types of point defects: A defects (pairs of nitrogen atoms in neighbouring interstitial sites), B defects (four substitutional nitrogen atoms surrounding a vacancy) and C defects (dispersed substitutional nitrogen atoms). Type Ia diamonds with B centres often contain platelets parallel to the {100} planes (Fig. 9a). A higher form of nitrogen aggregation is seen in voidites. Annealing experiments have confirmed that the sequence of aggregation from centres to platelets to voidites and dislocation loops is a function of temperature and the residence time in the Earth’s mantle (Kiflawi & Bruley 2000), thus these defects have the potential to be used as thermosteppers.

The other type of defect in kimberlitic diamonds is dislocations, usually occurring at moderate densities of 10^{12} m^{-2}. The slip system is the \( <110> \{111 \) system (Hornstra 1958), whereby the dislocation lines are mostly aligned along the <110> directions – that is, the...
Dislocations are of a screw or 60° character. Dislocation lines sometimes show helical configurations due to interactions with point defects (Fig. 9b). The dislocations may originate, in part, from inclusions that internally strain the diamond during upwelling as a result of the different compressibilities of the inclusion and the host diamond.

Ultra-high-pressure metamorphic diamonds were first discovered at the type locality Kokchetav in northern Kazakhstan (Sobolev & Shatsky 1990) and were subsequently found in various other localities worldwide, including the Ore Mountains (Erzgebirge) in southern Germany (Massonne 1999) and the Alps (Frezzotti et al. 2011). This type of diamond occurs exclusively in metamorphic crustal rocks formed by the deep subduction of continental lithosphere to mantle depths, followed by exhumation to the Earth’s surface. The diamondiferous metamorphic source rocks usually contain relict diamond in multiphase inclusions encapsulated in garnets. The diamond grains themselves show a facet-rich, sometimes skeletal, morphology and are commonly bound by octahedral faces. Transmission electron microscopy shows that metamorphic diamonds are often completely free of defects. The surrounding phases are mostly hydrous sheet silicates, indicating the presence of a COH fluid (Stöckhert et al. 2001) that reacted with the surrounding host garnet (Fig. 10a). Determination of the Fe³⁺/Fe⁺⁺ ratios by electron energy loss spectroscopy suggests that diamonds precipitated from this supercritical fluid via a redox reaction (Fig. 10b) involving the oxidation of iron from garnet and the reduction of CO₂ in the fluid (Langenhorst 2003; Stagno et al. 2015). This presumed redox reaction also implies that the source of carbon was carbonates from the subducted lithospheric slab. A Raman spectroscopic study of fluid inclusions in diamond-bearing garnets showed that carbonates do dissolve in subduction fluids, transferring carbon at the depth of diamond formation (Frezzotti et al. 2011). This agrees with thermodynamic calculations on the stability of COH fluids as a function of pressure, temperature and oxygen fugacity (Sverjensky et al. 2014).

Impact diamonds are produced by hypervelocity collisions on Earth or in space. The impact origin of such diamonds was first noticed for iron meteorites and ureilites (Lipschutz 1964) and their occurrence in terrestrial impact rocks was first recognized at the Popigai crater in northern Siberia (Masaitis et al. 1972). The source rocks of terrestrial impact diamonds are usually graphite-bearing gneisses or other crystalline rocks (Masaitis et al. 1972; Langenhorst et al. 1999; El Goresy et al. 2001). Graphite in these rocks was extremely rapidly transformed in the solid state by the passage of a shock wave (a dynamic high-pressure wave). The short transformation time resulted in a defect-rich microstructure and the inheritance of some features of the precursor graphite at various length scales.
Impact diamonds retain the tabular hexagonal morphology of graphite at the millimetre scale and sometimes preserve spectacular growth twins rotated about, or inclined to, the \(c\)-axis of graphite. Impact diamonds can therefore be regarded as pseudomorphs after graphite and are called apographitic diamonds (Masaitis et al. 1990; Koeberl et al. 1997).

Impact diamonds contain numerous kink or twin bands that appear to be parallel to \((hh2hl)\) planes of precursor graphite at the micrometre scale (Fig. 11a). Numerous \(\{111\}\) stacking faults and microtwins are observed at the atomic scale (Langenhorst et al. 1999; Langenhorst 2002; Fig. 11b). The micrometre bands were probably generated by the deformation of graphite at the time of shock wave transmission, i.e. directly before the phase transformation to diamond. As the numerous stacking faults in impact diamonds are bound by partial dislocations (Fig. 11b), they are indicative of rapid transformation in a very disordered manner.

Two atomic operations are, in principle, necessary to convert graphite into diamond. The hexagonal carbon layers have to be brought together by compression along the \(c\)-axis and the stacking sequence has to be changed from a hexagonal to a cubic array by shearing of the hexagonal carbon layers in their \(a-a\) plane. Neglecting the van der Waals bonds, it is not necessary to break any strong bonds within the layers. Such shear-induced transitions are called martensitic transformations (Porter et al. 2009); they are rapid and can operate at the speed of sound in the material.

The observation of a disordered microstructure with numerous stacking faults sheds some light on the question of the generally accepted existence of lonsdaleite in impact diamonds. The cubic stacking sequence changes into a hexagonal arrangement at the stacking faults. For example, an intrinsic stacking fault can be regarded as a monolayer of 2H lonsdaleite because the local stacking sequence changes to ABAB and this lonsdaleite would then show the reported epitaxial relationship to diamond with \((0001)_{\text{lons}}//(111)_{\text{Dia}}\). However, the stacking faults are not interpreted as a new phase due to their defect nature and because there is no 3D periodicity across the fault. This casts some doubt on the existence of lonsdaleite in impact diamonds, which can therefore be regarded as having a defect-rich diamond structure (Langenhorst 2002, 2003; Németh et al. 2014).

(4) Pre-solar diamonds are found as rare constituents of chondritic meteorites and are the oldest solid matter available for inspection, with an age older than that of the solar system (\(>4.56\) Ga). Their extrasolar origin was concluded from the
extraordinary carbon and nitrogen isotopes that are only compatible with nucleosynthesis in stars other than the Sun (Huss 2005). Pre-solar diamonds generally occur as nanocrystals with numerous multiple [111] stacking faults and microtwins, which are sometimes associated in a star-like fashion (Dautlton et al. 1996). These planar faults form an interconnected network throughout the crystal and always terminate at the grain surfaces. Thus they are not bound by partial dislocations and have to be regarded as a growth feature. These features are identical to the defect microstructures observed in diamonds synthesized by chemical vapour deposition, suggesting circumstellar condensation and the growth of pre-solar diamonds from the gas phase. The numerous stacking faults are thus interpreted as a consequence of imperfect and rapid growth from a vapour phase.

Conclusions

The peculiar electronic configuration of carbon atoms gives them the ability to form a virtually limitless number of allotropic forms. Each allotrope can be described by ideal structural models that help to identify their fundamental properties. However, the finite size of any system represents an intrinsic deviation from the ideal structure, with dramatic consequences for nanosized objects. It is the control of such effects that drives research on engineering nanomaterials based on nanocarbon, such as carbon nanotubes and graphene. From a naturalistic standpoint, the defects seen in carbon minerals, when investigated down to the atomic scale with the use of electron microscopy, can be considered as a fingerprint of their geological history. Their presence is not only linked to the specific chemical–physical environment that the crystal has experienced, but also to its transformation dynamics. The virtuous interplay between research focused on the determination of the natural origin of a carbon crystal phase and that focused on the controlled modification of the physical properties of a known carbon phase will drive the discovery of new carbon forms and technological applications.

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