Structural characterization of natural diamond shocked to 60 GPa; implications for Earth and planetary systems

Published version:

DOI:10.1016/j.lithos.2016.09.023

IRIS AperTO

UNIVERSITÀ
DEGLI STUDI
DI TORINO

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in LITHOS, 265, 2016, 10.1016/j.lithos.2016.09.023.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

(1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.

(2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.

(3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en), 10.1016/j.lithos.2016.09.023

The publisher's version is available at:
http://linkinghub.elsevier.com/retrieve/pii/S0024493716303127

When citing, please refer to the published version.

Link to this full text:
http://hdl.handle.net/2318/1633328

This full text was downloaded from iris - AperTO: https://iris.unito.it/

iris - AperTO

University of Turin's Institutional Research Information System and Open Access Institutional Repository

LITHOS APJ Lonsdaleite v 8.3 5/5/2016

Structural Characterization of Natural Diamond Shocked To 60 GPa; Implications for Earth and Planetary Systems.

Adrian P Jones[a], Paul F McMillan[b], Christoph G. Salzmann[b], Matteo Alvaro[c], Fabrizio Nestola[c], Mauro Prencipe[d], David Dobson[a], Rachael Hazael[b] and Moreton Moore[e]

[a]Department of Earth Sciences, University College London, UK WC1E 6BT
adrian.jones@ucl.ac.uk (corresponding author), d.dobson@ucl.ac.uk
[b]Department of Chemistry, University College London, UK WC1E 6BT
p.f.mcmillan@ucl.ac.uk, c.salzmann@ucl.ac.uk, rachael.hazael@ucl.ac.uk
[c]Department of Geosciences, University of Padua, Italy
matteo.alvaro@gmail.com, fabrizio.nestola@inipd.it
[d]Earth Sciences Department, University of Torino, Italy
mauro.prencipe@unito.it,
[e]Royal Holloway, University of London, UK TW20 0EX,
M.Moore@rhul.ac.uk

Abstract

The possible presence of the high-density carbon polymorph with hexagonal symmetry known as lonsdaleite provides an important marker for shock impact events. It is typically considered to form as a metastable phase produced from graphite or other carbonaceous precursors. However, its existence has recently been called into question. Here we collected high-resolution synchrotron X-ray diffraction data for laboratory-shocked and natural impact diamonds that both show evidence for deviations from cubic symmetry, that would be consistent with the appearance of hexagonal stacking sequences. These results show that hexagonality can be achieved by shocking diamond as well as from graphite precursors. The diffraction results are analyzed in terms of a general model that describes intermediate stacking sequences between pure diamond (fully cubic) and lonsdaleite (fully hexagonal) phases, with provision made for ordered *vs* disordered stacking arrangements. This approach provides a "hexagonality index" that can be used to characterize and distinguish among samples that have experienced different degrees of shock or static high pressure-high temperature treatments. We have also examined the relative energetics of diamond and lonsdaleite structures using density functional theoretical (DFT) methods. The results set limits on the conditions under which a transformation between diamond and lonsdaleite structures can be achieved. Calculated Raman spectra provide an indicator for the presence of extended hexagonal stacking sequences within natural and laboratory-prepared samples. Our results show that comparable crystallographic structures may be developed by impact-generated shockwaves starting from ambient conditions using either of the two different allotropes of carbon (diamond, graphite). This broadens the scope for its occurrence in terrestrial and planetary systems.

Keywords: Diamond, graphite, Raman spectroscopy, shock, X-ray diffraction, lonsdaleite, stacking disorder, hexagonality.

Highlights

- Hexagonal features can form in diamond shocked to 60 GPa so that observations of "lonsdaleite" do not require precursor graphite.
- Coexisting hexagonal and cubic diamond features in laboratory-shocked and impact diamond is explained by stacking disorder.
- A metastable pathway for formation of mixed cubic-hexagonal carbon phases is proposed, that can explain fast energetic shock formation of both lonsdaleite and impact diamond.
- Raman spectra for hexagonal diamond calculated from first principles provide a marker for the presence of extended hexagonal sequences in diamond.
- We briefly review the status of nomenclature for diamond the mineral, the element and cubic-hexagonal polytypes.

1. Introduction

Since the discovery of hexagonal symmetry in diamond from the iron meteorite Canyon Diablo in Meteor Crater, Arizona, the identification of lonsdaleite has been interpreted as occurring *via* shock-transformation of graphite (Bundy, 1967; Frondel and Marvin, 1967; Garvie, 2009; Lonsdale, 1971; Roy et al., 1981; Sharp and DeCarli, 2006). Lonsdaleite was identified on the basis of X-ray crystallographic reflections additional to those of cubic diamond, that could be indexed on a hexagonal cell. Single crystals of lonsdaleite were first reported in natural samples of regionally metamorphosed rocks from Russia (Shumilova et al., 2011). Hexagonal diamond with preferred orientation has been synthesized in large volume high pressure (HP) experiments at a wide range of temperatures, identified *in situ* by synchrotron X-ray diffraction (Utsumi and Yagi, 1991; Utsumi et al., 1994). Lonsdaleite has also been observed in other synthesis studies, including during the thermal decomposition and HT annealing of diamond to graphite (Blank et al., 2011), by CVD growth on a Si substrate (Chiem et al., 2003) and as polytypes and twins formed by high pressure-high temperature (HPHT) treatment of graphite (Kulnitskiy et al., 2013). The HPHT synthesis of the apparently fully hexagonal polymorph of carbon was first reported (Bundy and Casper, 1967) in the same year that it was recorded to occur in natural samples from the Canyon Diablo iron meteorite and Goalpara ureilite (Hanneman et al., 1967). The name lonsdaleite was proposed and accepted to designate this as a new mineral phase (Frondel and Marvin, 1967).

The formation mechanism, structural description and even the existence of lonsdaleite is currently the focus of renewed research(Nemeth et al., 2014). Transmission electron microscopy (TEM) observations of mixed hexagonal and cubic phases in shocked graphite have provided a new nanoscale understanding of the phase behavior. (Nemeth et al., 2014) presented results of a study that demonstrated that the hexagonal symmetry attributed to lonsdaleite could instead be produced by twinning and stacking faults. A new approach pioneered by Salzmann et al (2015) assessed the degree of disorder arising from interlaced cubic-hexagonal stacking which can be achieved in materials including those related to diamond and lonsdaleite. Analysis of published X-ray diffraction data suggests that the highest fractions of hexagonal stacking in claimed lonsdaleite materials are below 60% (Salzmann et al., 2015). Samples of the pure lonsdaleite phase were only reported recently for the first time. The fully hexagonal sp^3-bonded carbon polymorph was achieved in shock synthesis experiments at peak pressures in the170-230 GPa range at calculated T = 6000-7000K, close to the solid-liquid phase boundary (Kraus et al., 2016). These studies used pyrolytic non-porous graphite as a precursor material.

Impact diamond is considered to be a diagnostic mineral for shock metamorphic events in terrestrial impact craters (Bunch et al., 2008; Hough et al., 1995; Schmitt et al., 2005; Shelkov et al., 2010). Impact diamond usually occurs in plate-like form consistent with replacement of graphite. It exhibits X-ray and Raman characteristics of cubic and hexagonal symmetry. The impact diamond fractions can be physically separated by acid dissolution methods (Hough et al., 1995).

The presence of lonsdaleite or hexagonal diamond is widely cited as providing evidence for shockwave HP conditions extending into the >100 GPa range, in a wide variety of host rocks. Thus, in addition to the impact crater-related occurrences (eg (Bunch et al., 2008), lonsdaleite in ultra-high pressure (UHP) rocks may record shock-damaged crust (Smith et al., 2011). Hexagonal-diamonds in airfall carbon-rich layers of Younger Dryas age, are interpreted as evidence for a large cosmic impact at the end of the last ice-age (Israde-Alcántara et al., 2012; Kennet et al., (2009)). Lonsdaleite associated with nanodiamond has been reported in interplanetary dust particles (IDPs) and widely in meteorites with a variety of growth mechanisms, which include primitive nebular vapor condensates, large body HPHT growth, collision shock-modification of low-P carbon phases, and chemical vapor deposition (CVD), including crystalline graphite (Tielens et al., 1987) to which we now add diamond precursors.

Here we observe that mixed cubic and hexagonal signatures can also be produced in shocked diamond samples. This discovery not only extends the range of partially hexagonal diamond occurrence in natural systems but it also places constraints on the ongoing debate on pre-solar carbon provenance by excluding graphite as a necessary precursor (e.g. (Lewis et al., 1989; Tielens et al., 1987).

2. Samples

2.1 Popigai impact diamond (POP)

This impact diamond represents a shock-metamorphosed mineral found in the impact melt-breccias and the impact melt sheet within the large ~100 km diameter Popigai crater in Siberia, Russia, which formed in the Late Eocene at ~35.7 Ma. The impact smashed into the regional geological Precambrian-Phanerozoic boundary through a 1-2 km thick cover of sedimentary rocks and >5 km deep into basement rocks containing graphite-bearing gneisses, producing peak pressures ~ 600 GPa vaporizing the ~5 km impactor and leaving ~2000 km^3 of impact melt in less than one second. It is estimated that shocked graphite was transformed throughout a large central region, within ~13.6 km of ground zero, into lonsdaleite-bearing “impact diamond” (Masaitis V, 1998). The impact diamond appears as microcrystalline (~ 1 micron) aggregates paramorphous after graphite retains mm-scale physical features like cleavage and twinning attributed to graphite, and has diagnostic optical birefringence (<0.020) in ~0.2 mm grains. The Popigai impact diamond contains up to ~50% diamond and 50% diamond-related materials with significant hexagonal characteristics, interpreted as lonsdaleite. Similar impact diamond is known from other continental impact craters (Hough et al., 1995; Koeberl, 2002; Masaitis V, 1998; Schmitt et al., 2005).

2.2 Experimentally shocked diamond (DeCarli)

Shock experiments were carried out in 1960 at Stanford Research Institute by P. DeCarli[*] using a large diameter (65mm) single-stage gas gun. The natural diamond sample was a ~1 carat gem quality octahedral type II (low nitrogen) inclusion-free flawless gem (as viewed with x10 hand lens). This was mounted in pure copper and surrounding momentum traps, designed to avoid reverberation from reflected shock waves. The diamond sample was mounted at ambient temperature in vacuum and shocked to propagate a single plane-wave shock calculated to produce a peak impact pressure of 60 GPa. The disrupted copper and diamond samples were collected from a large capture chamber and the copper carefully removed from diamond fragments by chemical dissolution in nitric acid. The laboratory-

---

[*] P. DeCarli unfortunately passed away in 2013 while this study was being initiated, and so some of the experimental details are no longer available.

shocked products were first analyzed by Dr. J. Milledge at UCL in ~1960 using laboratory X-ray techniques. Those studies revealed the presence of only cubic diamond. In 2004 AP Jones examined diamond fragments from the same experiment under a microscope, edge-mounted on glass slides with double-sided Scotch tape for optical and micro–Raman examination. The brownish coloration and second order birefringence indicated deviations from optically isotropic material and the possible presence of lonsdaleite was suspected. The optical and spectroscopic properties of the DeCarli laboratory shocked sample were similar to those found among natural impact diamonds from Popigai. Some brownish fragments show "thousands" of penetrative linear to curved lines with ~micron-scale spacing (Figure 1), reminiscent of planar deformation features (PDFs) observed in shocked quartz (De Carli et al., 2002; Hough et al., 2003). Shock deformation can thus produce diamonds containing high concentrations of planar defects, as also observed by other researchers (Nemeth et al., 2014).

3. Synchrotron X-ray data

Samples of natural Popigai impact diamond (POP) and DeCarli laboratory shocked diamond (DC) were mounted on a goniometer head and observed during a single continuous 12-hour session using monochromatic radiation at station I15 of the Diamond Light Source (DLS), Harwell UK. X-ray diffraction data were collected with incident wavelength λ=0.4134Å using a six-circle Newport diffractometer and an Atlas (Agilent Technologies) CCD detector. A preliminary series of vertical scans were carried out using a 20 μm Pt pinhole and a step size of 25μ.□A□□□□□□□□□□□data were collected during 180^o rotation around the sample mounting ϕ-axis. Initial diffraction peak positions were assigned from library X-ray data for diamond and lonsdaleite (Fayes, 1999). Signatures for cubic (diamond) and hexagonal (lonsdaleite) stacking were determined to be present to varying degrees in both the Popigai (POP) and DeCarli (DC) samples (Fig. 2). The highest concentration of features assigned to "lonsdaleite" was recorded in a 50μm area of the ~200 μm DeCarli subsample DC8, where a maximum content of ~50% hexagonal diamond was initially calculated from the relative intensity of shoulders on the main diffraction peak.

In Figure 2a we show the integrated X-ray diffraction pattern for sample POP20 of the Popigai impact diamond, where the main (111) diffraction peak for cubic diamond shows distinctive shoulders on both its low and high angle sides. The laboratory-shocked DeCarli diamond sample DC4 exhibits sharper diffraction features (Fig. 2b). The 2D diffraction images for this sample (Fig. 2c) show the emergence of a pattern of ten diffuse reflections concentrated around the main (111) diffraction ring indicating that the original diamond crystal has broken up into nanoscale domains with slightly different orientation according to a multiple twin law. Such twinning is commonly observed in face-centered cubic (fcc) structures including CVD diamond (Hoffmeister, 1999). We can see the emergence of the separate features at slightly smaller diffraction angles that give rise to the main shoulder at larger *d*-spacing observed in the integrated diffraction patterns (Fig. 2d), that we associate with the appearance of domains with hexagonal stacking sequences.

4. Layer stacking analysis

The relationship of purely cubic (diamond) to hexagonal (lonsdaleite) stacking sequences can be conveniently expressed and analyzed from X-ray diffraction data using the new approach described in (Salzmann et al., 2015). The crystal structures of the two end members are shown in Figure 3(a,b). Both consist of puckered layers made up of six-membered rings of sp^3 bonded carbon atoms in the “armchair” conformation. In cubic diamond, identical layers are placed on top of one another but shifted halfway across the diagonal of a six-membered ring of the previous layer. In hexagonal diamond, each layer is the mirror image of the previous layer. Due to these different stacking recipes the six-membered rings *linking* between the layers are also "armchair" in cubic diamond, but take the alternative "boat" conformation in hexagonal diamond. These two different stacking possibilities give rise to a wide variety of structural polytypes ranging from purely cubic, $(c)_n$, representing diamond, to fully hexagonal, $(h)_n$, of lonsdaleite, with in principle any conceivable stacking sequence in between (e.g. …chhcchchhchchcchc…), with the possibility for ordered *vs* disordered arrangements within the sequence.

The extent of cubic/hexagonal stacking within such polytypic structures is conveniently expressed *via* two parameters within a "stackogram" derived from analysis of the X-ray diffraction patterns (Salzmann et al., 2015) (Fig. 4). These parameters are the stacking probabilities, Φ_{cc} and Φ_{hc}, that define the probabilities of cubic stacking following a cubic or a hexagonal stacking event, respectively. The diagonally opposite corners of the stackogram represent the fully cubic ($\Phi_{cc} = \Phi_{hc} = 1$) and fully hexagonal polytypes ($\Phi_{cc} = \Phi_{hc} = 0$). The line connecting these two corners indicates various randomly stacked polytypes with $\Phi_{cc} = \Phi_{hc}$, implying that the layer arrangement is independent of the stacking history. Moving up from the random line, structures with higher probabilities of staying within a given stacking sequence are found ($\Phi_{cc} > \Phi_{hc}$). The extreme case for this is the corner representing a physical mixture of pure cubic and hexagonal diamond. Structures lying below the random line ($\Phi_{cc} < \Phi_{hc}$) on the other hand are characterized by greater probabilities of switching between cubic and hexagonal stacking. The most extreme case for this is the strictly alternating $(ch)_x$ polytype. The dashed lines emanating from the physical mixture corner indicate lines of constant hexagonalities, Φ_h, the overall fraction of hexagonal stacking. As described in (Salzmann et al., 2015) it is straight forward to calculate the hexagonality from Φ_{cc} and Φ_{hc}. The corresponding fraction of cubic stacking of a given sample, Φ_c, is simply 1-Φ_h since there is only either cubic or hexagonal stacking.

Stacking disorder leads to broad and asymmetric features in the diffraction patterns that only affect those Bragg peaks (hkl) where (h – k)/3 is not an integer (Pusey et al., 1989). The powder pattern of any stacking disordered structure can be calculated using the DIFFaX software (Treacy et al., 1991). The input parameters are the lattice constants, atomic coordinates within the layers, symmetry relationships between the layers for the different types of stacking, peak profile parameters and the stacking probabilities. The MCDIFFaX extension introduces a least-squares refinement of the various parameters (Malkin et al., 2015; Salzmann et al., 2015). The program randomly suggests a change in one of the parameters. If this leads to an improvement of the fit to the diffraction data, the step is accepted and the program carries on performing another random change in one of the parameters. A Monte Carlo-type parameter ensures that a small number of unfavorable changes are accepted which enables the fitting procedure to avoid local minima. Figure 5 shows that the POP20 X-ray diffraction data could be fitted well using MCDIFFaX. More than 30,000 steps were required in this particular case to achieve convergence of the fitting routine. The refined Φ_{cc} and Φ_{hc} stacking probabilities were determined as 0.7233 and 0.7750, resulting in an overall hexagonality of about 24%. The location of the POP20 diamond within the stackogram plot shows that this material out of all stacking disordered diamonds analyzed to date lies closest to the random stacking line, providing insights into the possible conditions of its formation. For example, it can be argued that the POP20 diamond sample experienced the fastest cooling out of all the stacking disordered diamond samples shown in the stackogram, leading to a close to random stacking sequence.

In natural diamond, lonsdaleite has rarely been reported from mantle samples, for example using TEM to study diamond microcrystals from Liaoning in China (Gorshkov et al., 1997) that have a HPHT kimberlitic source (Chris Smith Pers comm 2016). The diffraction patterns of these minerals were interpreted as representing intergrowths of cubic and hexagonal diamond supported by the presence of additional reflections of different symmetry (Gorshkov et al., 1997), whereas a possible alternative interpretation in terms of multiple incoherent twins was discarded as being less probable. There appeared to be a high degree of alignment between the cubic and hexagonal layers, that are not randomly distributed within the samples.

5. Interpretation of Raman Spectra of lonsdaleite

The strong characteristic Raman peak of cubic diamond at 1332 cm^{-1} is often used to diagnose the presence of this phase, even when it is present as nanocrystals and in trace quantities within mineral samples. Subtle shifts in the peak position along with peak broadening can reveal the presence of non-isotropic strains, due to impurity content or structural defects within the samples. The occurrence of broadening as well as shifts in the peak position have also been interpreted as indicating the presence of lonsdaleite, or mixed cubic-hexagonal polytype structures, within natural and laboratory-prepared samples (Gogotsi et al., 1998; Le Guillou et al., 2010; Ross et al., 2011; Smith and Godard, 2009). Microdiamonds containing lonsdaleite are a characteristic feature of the group of carbon-rich diamond-bearing meteorites called ureilites. The Raman spectra for ureilite diamond have been well reviewed (Le Guillou et al., 2010; Ross et al., 2011).

The zone-center vibrational modes for lonsdaleite, diamond and cubic-hexagonal polytypes have been analyzed by Spear et al. (1990). Cubic diamond (Fd-$3m$ symmetry) contains Z=2 atoms per primitive unit cell resulting in a single Raman active peak with T_{2g} symmetry. Lonsdaleite ($P6_3/mmc$) has Z=4 atoms per cell, giving rise to expected zone center Raman modes with symmetries $A_{1g} + E_{1g} + E_{2g}$, with B_{1u}, B_{2g} and E_{2u} modes inactive (Ivanova and Mavrin, 2014; Spear et al., 1990; Wu, 2007). In Figure 6 we compare the Raman spectra for both phases calculated using *ab initio* methods implemented at the hybrid HF/DFT level (Prencipe et al., 2014a; Prencipe et al., 2012; Prencipe et al., 2014b). The calculations were carried out at T = 0 K using the Wu-Cohen GGA exchange functional (Wu and Cohen, 2006) corrected by 16% of Hartree-Fock exchange, and the Lee-Yang-Parr (LYP) correlation functional (Lee et al., 1988), that is expected to provide a good interpretation of the structural and vibrational properties of the two phases (Prencipe et al., 2014a).

Our calculated Raman spectra can provide improved constraints for recognition of hexagonal diamond layering sequences and domains within natural and synthetic samples. For example, in the extensive reviews provided by Le Guillou et al. (2010) and Ross et al. (2011) (Le Guillou et al., 2010; Ross et al., 2011), the shift of the main "diamond" peak to lower wavenumber (e.g., 1318 cm^{-1}) along with the appearance of an additional weak shoulder at ~1350 cm^{-1} for a very few of the samples studied, such as the Almahata Sitta grain 7 shown in Figure 2 of Ross et al. (2011), could be consistent with the presence of significant hexagonal "lonsdaleite" domains within such samples.

Gogotsi et al. (1998) published micro-Raman spectra of indentation zones created within diamond under extreme and highly localized stresses with a significant shear component, and noted the appearance of an apparent "satellite" peak at lower frequency than that assigned to diamond (see Fig. 5(b) in their paper). They attributed this to the presence of some hexagonal diamond component. In fact, the main peak occurs at higher wavenumber than the diamond T_{2g} feature, and so both peaks could correspond to the A_{1g} + E_{1g} modes predicted for pure lonsdaleite by our *ab initio* calculations (Fig. 6).

One previous shock study of diamond also reported evidence for the formation of hexagonal diamond, identified using Raman spectra (He et al., 2002) by a main peak occurring within the 1318-1325 cm^{-1} range among 5 samples shocked at 54-196 GPa. They suggested formation of lonsdaleite by a kinetically controlled mechanism coupled with the presence of both shear stresses and elevated temperature. Their Raman data (see figure 3 in (He et al., 2002) show some correspondences with our calculated lonsdaleite spectrum.

Our new results reveal that micro-Raman spectroscopy combined with an improved understanding of the polytypic cubic-hexagonal structures can provide an important new marker for materials formed with different layer stacking within the diamond-lonsdaleite system, and can be developed as a diagnostic for the appearance of such structures within natural and laboratory-prepared samples.

6. Stable and Metastable Phase Relations: Diamond, Lonsdaleite and Graphite Polymorphs

We used our *ab initio* approach to model the energy-volume ($E(V)$) relations at T=0K to examine the possible metastable transitions between graphite-diamond-lonsdaleite, as well as the formation of intermediate cubic-hexagonal structures (Wu 2007) (Fig. 7). Diamond is more stable than lonsdaleite by approximately ΔE = -0.0042 Hartree/mol (referenced to lonsdaleite), or ~2.6 kcal/mol. Interestingly, the reverse situation has been found for cubic *vs* hexagonal polymorphs of Si, where lonsdaleite-Si was found to be stabilized relative to the diamond structure (Wu, 1999). The $E(V)$ curves for the two dense phases of elemental carbon lie directly above one another, negating the possibility of a direct diamond-lonsdaleite transition at any finite pressure, at least if vibrational entropy effects can be ignored. This is also shown by the calculated enthalpy-pressure relations, which form two parallel lines with no obvious signs of crossing. We can see that in principle, if diamond is compressed sufficiently along its $E(V)$ curve, we can estimate how much pressure is needed to take it above the lonsdaleite stability range, which sets an upper limit for formation of any cubic-hexagonal "intergrowth" of phases. We show schematically in Figure 7 that a diamond phase with some degree of hexagonality could be formed *via* a metastable transformation during pressure release, along one of the possible common tangents to the $E(V)$ curves.

The energetic relations may become modified if the anharmonic phonon density of states for the two phases are sufficiently different to cause the vibrational entropy contributions as a function of pressure and temperature to diverge, and result in crossing of the respective Helmholtz ($F(T,V)$) or Gibbs' ($G(P,T)$) curves. This is already known to occur for cubic (sphalerite) and hexagonal (wurtzite) polymorphs of ZnS and other materials with similar structural and phase relationships.

We did not extend our calculations to include graphite because of the difficulties associated with accurate modelling the interlayer interactions, but we constructed a schematic diagram illustrating the energetic relations between the three phases (Figure 7). Graphite transforms to diamond *via* a first order phase transition at ~0.7 GPa, determined by extrapolating experimental data sets to low temperature. However, the transition is kinetically hindered and it usually requires a high temperature or the presence of a catalyst to be enabled efficiently. It can be bypassed readily either during rapid timescale shock processes, or by compressing graphitic starting materials at low temperature. In that case, lonsdaleite, or one of a family of intermediate phases with mixed cubic-hexagonal layer stacking, might be produced instead at slightly higher pressure than the equilibrium graphite-diamond transformation. That would agree with the recent report by (Kraus et al., 2016) of lonsdaleite formation from graphite on nanosecond shock timescales, as well as in natural impact environments. Lonsdaleite and other cubic-hexagonal polytypic materials can also form in a similar way.

The key difference between laboratory experiments and natural shock events during impact cratering relates to the enormous energy released during natural impacts, and long duration of a large natural shock pulse (~1 second) that may be many orders of magnitude longer than those (~ns-μs) that can be replicated in the laboratory (De Carli et al., 2002; DeCarli et al., 2002) (Sharp and DeCarli, 2006). Additional processes related to mineralogical complexity may include the transient appearance of very hot (3000-4000K) impact melts (Kenkmann et al., 2005).

7. Discussion

Our studies have important bearing on the nomenclature used to describe "lonsdaleite" as well as other diamond phases in the carbon system. We have presented here a new interpretation of the degree of stacking disorder that can be achieved between cubic and hexagonal forms of sp^3-bonded carbon (Salzmann et al., 2015). That can now be applied to classify the degree of stacking disorder in natural impact diamond, e.g. from Popigai, allowing the recognition of a structural end member for a pure hexagonally stacked "diamond" polytype.

Synthesis of such pure hexagonal diamond samples has proved elusive, until the recent report of its formation under dynamic shock compression at transient HPHT conditions (Kraus et al., 2016) which these authors refer to as lonsdaleite. So, should the pure hexagonal form of diamond be called lonsdaleite, or should that name be reserved for the natural mineral corresponding to an intermediate stacking cubic/hexagonal polytype with some degree of stacking disorder as recorded from Canyon Diablo/Meteor Crater (see Fig. 4).

An important question arises from the different length scales of observational methods used to characterize the different cubic-hexagonal diamond phases, many of which may be metastable with respect to ordered crystalline end-members. Both natural and laboratory-prepared samples can display structural heterogeneities over several length scales, and even samples previously recognized as single crystals may contain polytypic structural elements. Some guidance in nomenclature for these elemental carbon polytype structures can be carried over from emerging research descriptions of crystalline H_2O ice structures (Malkin et al. 2015). We must now begin to distinguish between the usage of the term "diamond" to describe (a) a natural mineral as well as laboratory-synthetized material with essentially pure carbon composition, and (b) as a structure type based on sp^3-bonded atoms located within the tetrahedral interstices of a fcc crystallographic lattice. In that sense we propose the designations of "cubic" *vs* "hexagonal" diamond to represent the fully cubic or hexagonal layer stackings within the idealized crystalline materials. We then propose the use of the hexagonality as well as the stacking probabilities Φ_{cc} and Φ_{hc} to describe the presence and degree of incorporation of hexagonal layering within the initially cubic structure, along with the ordering of hexagonal *vs* cubic domains.

Given the geochemical cosmic abundance of carbon, the significance of carbon polymorphs and dynamic phase behavior can constrain the physical, chemical and geological history of carbon in extraterrestrial samples. The first textural evidence that lonsdaleite in meteorites predates the shock metamorphism associated with arrival at Earth, was demonstrated in carbonado-type lonsdaleite-diamond “nodules” in ALHA77283 (Roy et al., 1981).

8. Conclusions

Our synchrotron X-ray diffraction results demonstrate that hexagonal features previously attributed to the presence of hexagonal diamond or “lonsdaleite” can form within diamond samples shocked in the laboratory to peak pressures of 60 GPa , and hence do not require the presence of graphitic carbon precursors. Coexisting hexagonal and cubic structures found within impact and laboratory-shocked and impact diamonds can be interpreted using a new model for stacking disorder/disorder, that can be used to assign a new measure of the hexagonality index. Using *ab initio* computational techniques we propose an understanding of the relative energetics of cubic *vs* hexagonal diamond structures and use these $E(V)$ diagrams to understand the possible formation of diamond, lonsdaleite and mixed cubic-hexagonal polytype structures under static and dynamic HPHT conditions as well as by metastable syntheses from precursors.

9. Acknowledgements

The ~1 carat gem diamond used or shock experiments was provided by DeBeers through collaboration with Judith Milledge at University College London. Laboratory hypervelocity shock experiments were designed and conducted at SRI by the late Paul DeCarli, who provided early guidance to this project. Victor Masaitis provided samples of Popigai impact diamond to Judith Milledge and used in this study. Sincere thanks to Wilhelm Heribert on station I.15 at the Diamond Light Source and to DLS for supporting experiments *via* proposal EE8752. Chris Smith at Bristol University is thanked for discussions concerning the geology of mantle diamond from China. CGS thanks the Royal Society for a University Research Fellowship. APJ acknowledges support from DeBeers and the Leverhulme Trust. PFM, RH and DD were supported by the UK EPSRC and NERC. MA was supported by the MIUR-SIR grant “MILE DEEp” (grant number RBSI140351) to M. Alvaro. FN has been supported by the ERC starting grant number 307322 to Fabrizio Nestola.

10. References

Blank, V.D., Kulnitskiy, B.A., Nuzhdin, A.A., 2011. Lonsdaleite formation in process of reverse phase transition diamond–graphite. Diamond and Related MAterials 20, 1315-1318.
Bunch, T.E., Wittke, J.H., Kennett, J.P., Kennett, D.J., Que Hee, S.S., Wolbach, W.S., Stich, A., Mercer, C., Weaver, J.C., 2008. Hexagonal Diamonds (Lonsdaleite) Discovered in the K/T Impact Layer in Spain and New Zealand, American Geophysical Union Fall Meeting. American Geophysical Union, San Francisco, pp. PP13C-1476.
Bundy, F.P., 1967. Hexagonal diamonds: a new form of carbon. . Journal of Chemical Physics 46, 3437-3446.
Bundy, F.P., Casper, J.S., 1967. Hexagonal dimaond -a new form of carbon. Journal of Chemical Physics 46.
Chiem, C.V., Seo, H.-K., Ansari, S.G., Kim, G.-S., Seo, J.M., Shin, H.-S., 2003. Lonsdaleite diamond growth on reconstructed Si (100) by hot filament chemical vapor deposition (HFCVD). Korean Journal of Engineering 20, 1154-1157
.

De Carli, P.S., Bowden, E., Jones, A.P., Price, G.D., 2002. Laboratory impact experiments versus natural impact events. Geological Society of America Special Paper 356, 595-605.
DeCarli, P.S., Bowden, E., Sharp, T.G., Jones, A.P., Price, G.D., 2002. Evidence for kinetic effects on shock wave propogation in tectosilicates, in: Furnish, M.D. (Ed.), Shock Compression of Condensed Matter 2001. American Institute of Physics, New York, pp. 1381-1384.
Fayes, J., 1999. Possible 3D carbon structures as progressive intermediates in graphite to diamond phase transition. Journal of Solid State Chemistry 148, 278-285.
Frondel, C., Marvin, U.B., 1967. Lonsdaleite, a hexagonal polymorph of diamond. Nature 214, 587-589.
Garvie, L.A.J., 2009. The structure of Canyon Diablo "diamonds", Lunar and Planetary Sciecnce Conference, p. 1346.pdf.
Gogotsi, Y.G., Kailer, A., Nickel, K.G., 1998. Pressure-induced phase transformations in diamond. Journal of Applied Physics 84, 1299-1304.
Gorshkov, A.I., Yanan, B., Bershov, L.V., Ryabchikov, I.D., Sivtsov, A.V., Lapina, M.I., 1997. Inclusions in diamond from the Liaoning Deposit (China) and their genetic meaning. Geochemistry International 35, 58-65.
Hanneman, R.E., Strong, H.M., Bundy, F.P., 1967. Hexagonal diamonds in meteorites: implications. Science 155, 995-997.
He, H., Sekine, T., T., K., 2002. Direct transformation of cubic diamond to hexagonal diamond. Applied Physics Letters 81, 610-612.
Hoffmeister, H., 1999. Fivefold Twinning in Nanosized Particles and Nanocrystalline Thin Films. Materials Science Forum 312-314, 325-332.
Hough, R.M., Gilmour, I., Pillinger, C.T., Arden, J.W., Gilkess, K.W.R., Yuan, J., Milledge, H.J., 1995. Diamond and silicon carbide in impact melt rock from the Ries impact crater. Nature 378, 41-44.
Hough, R.M., Lee, M.R., Bevan, W.R., 2003. Characterization and significance of shocked quartz from the Woodleigh impact structure, western Australia. Meteoritics and Planetary Sciences 38, 1341-1350.
Israde-Alcántara, I., Bischoff, J.L., Domínguez-Vázquez, G., Li, H.-C., DeCarli, P.S., Bunch, T.E., Wittke, J.H., Weaver, J.C., Firestone, R.B., West, A., Kennett, J.P., Mercer, C., Xie, S., Richman, E.K., Kinzie, C.R., Wolbach, W.S., 2012. Evidence from central Mexico supporting the Younger Dryas extraterrestrial impact hypothesis. Proceedings of the National Academy of Sciences 109, E738-E747.
Ivanova, T.A., Mavrin, B.N., 2014. Lattice dynamics and the incommensurability of the structures of hexagonal polytypes of diamond.
Kenkmann, T., Hornemann, U., Stoffler, D., 2005. Experimental shock synthesis of diamonds in graphite gneiss. Meteoritics and Planetary Science 40, 1299-1310.
Kennet, D.J., Kennet, J.P., West, A., Mercer, C., , Que Hee, S.S., Bement, L., Bunch, T.E., Sellers, M., Wolbach, W.S.N.i.t.Y.D.b.s.l., (2009). Nanodiamonds in the Younger Dryas boundary sediment layers. . Science 323, 94.
Koeberl, C., 2002. Mineralogical and geochemical aspects of impact craters. Mineralogical Magazine 66, 745-768.
Kraus, D., Ravasio, A., Gauthier, M., al, e., 2016. Nanosecond formation of diamond and lonsdaleite by shock compression of graphite. Nature Communications 10970.

Kulnitskiy, B., Perezhhogin, I., Dubitsky, G., Blank, V., 2013. Polytypes and twins in the diamond-lonsdaleite system formed by high-pressure and high-temoerature treatement of graphite. Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials B69, 474-479.
Le Guillou, C., Rouzaud, J.N., Remussat, L., Jambon, A., Bourot-Denise, M., 2010. Structures, origin and evolution of various carbon phases in the ureilite Northwest Africa 4742 compared with laboratory-shocked graphite. Geochimica Cosmochimica Acta 74, 4167-4185.
Lee, C., Yang, W., Parr, R.G., 1988. Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. Physical Review B, Condensed Matter 37, 785-789.
Lewis, R.S., Anders, E., Draine, B.T., 1989. Properties, detectability and origin of interstellar diamonds in meteorites. . Nature 339, 117-121.
Lonsdale, K., 1971. Formation of Lonsdaleite from single crystal graphite. The American Mineralogist 56, 333-336.
Malkin, T.L., Murray, B.J., Salzmann, C.G., Molinero, V., Pickering, S.J., Whale, T.F., 2015. Stacking disorder in ice. Physical Chemistry Chemical Physics 17, 60-76.
Masaitis V, 1998. Popigai crater: Origin and distribution of diamond-bearing impactites. Meteoritics and Planetary Science 33, 349-359.
Nemeth, P., Garvie, L.A.J., Aoki, T., Dubrovinskaia, N., Dubrovinsky, L., Buseck, P.R., 2014. Lonsdaleite is faulted and twinned cubic diamond and does not exist as a discrete material. Nature Communications, 5:5447 doi: 5410.1038/ncomms6447 (2014).
Prencipe, M., Bruno, M., Nestola, F., De La Pierre, M., Nimmis, P., 2014a. Toward an accurate ab initio estimation of compressibility and thermal expansion of diamond in the [0, 3000K] temperature, and [0. 30 GPa] pressure ranges, at the hybrid HF/DFT theoretical level. American Mineralogist 99, 1147-1154.
Prencipe, M., Mantovani, L.U., Tribuadino, M., Bersani, D., Lottici, P., 2012. The Raman spectrum of diopside: a comparison between ab iniitio calculated and experimetnally measured frequencies. . European Journal of Mineralogy 24, 457-464.
Prencipe, M., Maschio, L., Kirtman, B., Salustro, S., Erba, A., Dovesi, R., 2014b. Raman spectrum of NaAlSi2O6 Jadeite. A quantum mechanical solution. Journal of Raman Spectroscopy 45, 703-709.
Pusey, P.N., Van Megan, W., Bartlett, P., Ackerson, B.J., Rarity, J.G., Underwood, S.M., 1989. Structure of crystals of hard colloidal spheres. Physical Review Letters 63, 2753-2756.
Ross, A.J., Steele, A., Fries, M.D., Kater, L., Downes, H., Jones, A.P., Smith, C.L., Jenniskens, P.M., Zolensky, M.E., Shaddad, M.H., 2011. MicroRaman spectroscopy of diamond and graphite in Almahatta Sitta and comparison with other ureilites. Meteoritics and Planetary Science 46, 364-378.
Roy, S., Appleman, D.E., Ross, D.R., 1981. An Antarctic meteorite contains preterrestrial impact-produced diamond and lonsdaleite. Nature 291, 396-398.
Salzmann, C.G., Murray, B.G., Shephard, J.J., 2015. The extent of stacking disorder in diamond. Diamond and Related MAterials 59, 69-72.
Schmitt, R.T., Lapke, C., Lingemann, C.M., Siebenschock, M., Stoffler, D., 2005. Distribution and origin of impact diamonds in the Ries crater, Germany,. Geological Society of America Special Paper 384, 299-314.

Sharp, T.G., DeCarli, P.S., 2006. Shock effect in meteorites, in: Lauretta D. S., Jr, M.H.Y. (Eds.), Meteorites and the Early Solar System II University of Arizona Press Arizona, pp. 653–677.

Shelkov, D.A., Verchovsky, A.B., Milledge, H.J., Kaminsky, F.V., Pillinger, C.T., 2010. Carbon, nitrogen, argon and helium study of impact diamonds from Ebeliakh alluvial deposits and Popigai crater. Meteoritics and Planetary Science 33, 985-992.

Shumilova, T.G., Mayer, E., Isaenko, S.I., 2011. Natural monocrystalline lonsdaleite. Doklady earth Sciences 441, 1552-1554.

Smith, D.C., Dobrzhinetskaya, L.F., Godard, G., Green, H.W., 2011. DiamondLonsdaleiteGraphite Relations Examined by Raman Mapping of Carbon Microinclusions inside Zircon at Kumdy Kol, Kokchetav, Kazakhstan: Evidence of the Metamictization of Diamond, Ultrahigh-Pressure Metamorphism 25 Years After the Discovery of Coesite and Diamond. Elsevier, pp. 43-75.

Smith, D.C., Godard, G., 2009. UV and VIS Raman spectra of natural lonsdaleites: towards a recognized standard. . Spectrochimica Acta 73A, 428-435.

Spear, K.E., Phelps, A.W., White, W.B., 1990. Diamond polytypes and their vibrational spectra. Journal of Materials Research 5, 2277-2285.

Tielens, A., Seab, C., Hollenbach, D., McKee, C., 1987. Shock processing of interstellar dust-Diamonds in the sky. The Astrophysical Journal 319, L109-L113.

Treacy, M.M.J., Newsam, J.M., Deem, M.W., 1991. A general recursion method for calcuating diffracted intensities from crystals containing planar faults. Proceedings of the Royal Society of London A433, 499-520.

Utsumi, W., Yagi, T., 1991. Formation of hexagonal diamond by room temperature compression of graphite. Proceedings of the Japan Academy 67, 159-164.

Utsumi, W., Yamnaka, M., Yagi, T., Shimomura, O., 1994. In situ X-ray diffraction study of the phase transition from graphite to hexagonal diamond under high pressures and high temperatures. AIP Conference Proceedings 309, 535-538.

Wu, B.R., 1999. First-principles study on the high-pressure behaviour of the zone-center modes of lonsdaleite silicon. Physical Review B 61, 5-8.

Wu, B.R., 2007. Structural and vibrational properties of the 6H diamond: First-principles study. Diamond and Related MAterials 16, 21-28

.

Wu, Z., Cohen, R., 2006. More accurate generalized gradient approximation for solids. Physical Review B 73, 2-7.