Comprehensive analysis of nanodiamond evidence reported to support the Younger Dryas Impact Hypothesis

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ABSTRACT: During the end of the last glacial period in the Northern Hemisphere near 12.9k cal a BP, deglacial warming of the Bølling-Ållerod interstadial ceased abruptly and the climate returned to glacial conditions for a $\approx 1,300$ year interval known as the Younger Dryas stadial. The Younger Dryas Impact Hypothesis proposes that the onset of the Younger Dryas climate reversal, Pleistocene megafaunal extinctions, and disappearance of the Clovis paleoindian lithic technology were coeval and caused by continent-wide catastrophic effects of impact/bolide events in North America. While there are no known impact structures dated to the Younger Dryas onset, physical evidence of the impact/bolide events is argued to be present in sediments spanning several continents at stratigraphic levels inferred to date to the Bølling-Ållerod / Younger Dryas boundary (YDB). Reports of nanometer to submicron-sized diamonds in YDB sediments, in particular the rare 2H hexagonal polytype of diamond, lonsdaleite, have been presented as strong evidence for shock processing of crustal materials. We review the available data on diamonds in sediments and provide new data. We find no evidence for lonsdaleite in YDB sediments and find no evidence of a spike in nanodiamond concentration at the YDB layer to support the impact hypothesis.

KEYWORDS: Nanodiamonds; cubic diamond; hexagonal diamond; lonsdaleite; Younger Dryas Impact Hypothesis
Introduction

The Younger Dryas (YD) Impact Hypothesis attempts to explain the rapid and dramatic changes that occurred at the end of the Pleistocene as arising from catastrophic extraterrestrial mechanisms. The earliest versions of the YD Impact Hypothesis speculated that North America was impacted by intense cosmic rays from a supernova (Brakenridge, 1981, 2011; Firestone and Topping, 2001, 2002; Firestone et al., 2006), mineral debris that condensed in the supernova outflow (Firestone and Topping, 2001, 2002; Firestone et al., 2006), and a comet (Melton and Schriever, 1933; Sass, 1944) whose orbit was perturbed into the inner solar system by the supernova shockwave (Firestone et al., 2006). Multiple comet fragments have also been hypothesized to have struck the oceans across the globe (Kristan-Tollmann and Tollmann, 1992, 1994; Tollmann, 2001). A planet-sized fragment of a supernova has even been speculated to have entered the solar system, modified planetary orbits, and caused terrestrial impacts (Allan and Belair, 1994, 1997). A body ejected from a supernova has also been suggested to have struck North America (Firestone, 2009). Other early versions speculated that, during the Late Pleistocene, the Earth was irradiated by a burst of cosmic rays from the galactic core (LaViolette, 1987, 2005) and/or impacted by large solar flares in addition to coronal mass ejections from the sun (LaViolette, 2005, 2011), where the solar eruptions were induced by a supernova shockwave (Firestone et al., 2006). The YD Impact Hypothesis has since evolved into several highly-controversial versions, most proposing that the abrupt YD climate reversal, Pleistocene megafaunal extinctions, and disappearance of the Clovis paleoindian lithic technology were coeval and caused by continent-wide catastrophic effects of one or more impact/bolide events in North America 12.9k cal a BP (e.g., Firestone et al., 2007).

The coeval timing of the above events, a requirement for a singular causal mechanism, has not been firmly established (see van Hoesel et al., 2014) and is a point of controversy. The onset of the YD stadial either spanned, or is dated to within, a couple hundred years of 12.9k cal a BP, depending on the applied chronometer (see, Meltzer and Holliday, 2010; Fiedel, 2011; van Hoesel et al., 2014; Meltzer et al., 2014). However, the chronologies of the Pleistocene megafaunal extinctions (timing and rate of population decline) are not well constrained and are debated. During the Pleistocene, at least 33 (or > 70%) of North American
megafaunal genera disappeared (Barnosky et al., 2004) and, of these, the extinction of 16 genera (e.g., mammoths, mastodons, giant short-faced bears, saber-tooth tigers) are constrained between 12,000 and 10,000 $^{14}$C a BP (~13,800 - 11,400 cal a BP) (Grayson, 2007; Faith and Surovell, 2009; Woodman and Athfield, 2009). Additionally, a recent study that compared ancient DNA and radiocarbon data over the last 56k a concluded that the megafauna extinction events are correlated with the multiple Dansgaard-Oeschger interstadial warming events (Copper et al., 2015), suggesting the YD stadial is not unique. Furthermore, Pleistocene megafaunal extinctions were not limited to North America and also occurred at different times in South America, the Caribbean, Africa, Eurasia, and Australia. For discussions on the climatic changes that define the YD stadial see e.g., Berger (1990) and Carlson (2013), and on the dynamics of the paleoindian populations during this period see Collard et al. (2010).

There are no recognized impact structures in North America that date to the onset of the YD stadial. Several geomorphic features have been suggested as possible YD craters: oriented shallow depressions in Alaskan, Canadian, and Siberian permafrost (Allan and Belair, 1994, 1997), the Carolina Bays (Melton and Schriever, 1933; Allan and Belair, 1994, 1997; Firestone and Topping, 2001; Firestone et al., 2007, 2010a; Firestone, 2009; Kinzie et al., 2014, Kenneth et al., 2015a), small playa basins of the High Plains (Firestone et al., 2006), and deep depressions in four of the Great Lakes (Firestone et al., 2007, 2010a; Firestone, 2009); however, there is no evidence to support their impact origin (see Holliday et al., 2014). The 4 km-diameter, circular Corossol structure in the Gulf of St. Lawrence has also been suggested as a possible YD-age crater based on the discovery of a single 4 cm long breccia clast suggesting impact metamorphism (Higgins et al., 2011). However, the breccia clast could have been deposited by glacial activity from one of many distal impact structures in Quebec (Reimold et al., 2014). More importantly, the age of the Corossol structure is poorly constrained between the Mid-Ordovician to just prior to the Quaternary glaciations (Lajeunesse et al., 2013).

To account for a non-crater-forming YD impact event, the inferred YD impactor has been variously interpreted as a porous, loosely-bound, low-density impactor (Firestone et al., 2006); as highly fragmented multiple impactors (Kristan-Tollmann and Tollmann, 1992, 1994; Firestone et al., 2007; Firestone, 2009; Kennett et al., 2009a,b; Bunch et al., 2012; Wittke et al., 2013; Napier et al., 2013; Petaev et al.,
2013a,b); as oblique-trajectory impactors into the Laurentide ice sheet (Firestone et al., 2007); or as a bolide airburst similar to the Tunguska event, but orders of magnitude larger (Firestone, 2009; Israde-Alcántara et al., 2012a). However, bolide/impact scenarios that produce catastrophic environmental effects on an intercontinental scale and disperse shock-transformation products globally – while not forming a crater – have been argued to be improbable and inconsistent with geologic evidence and physical models (Deutsch et al., 1994; Melosh, 2009; French and Koeberl, 2010; Boslough 2012; Boslough et al., 2012, 2013; Boslough, 2013a; Holliday et al., 2014). It has further been suggested that the YD impact crater remains undiscovered (Kristan-Tollmann and Tollmann, 1994; Firestone et al., 2010a; Kinzie et al., 2014), despite suggestions that such a large and geologically young crater should be easily recognized.

While there are no known impact structures in North America that date to the YD onset, YD impact proponents nonetheless argue that physical evidence of the impact/bolide event is present in sediments, at multiple sites in North America, South America, Europe, and the Middle East that are claimed to be chronologically synchronous with the Bølling-Ållerod / YD boundary (YDB) layer (see, Kennett et al., 2015a,b). Elevated concentrations of a range of minerals interpreted as products of impact/bolide processes and geochemical indicators of the impactor/bolide are reported in these inferred YDB layers. Multifarious criticisms have been raised regarding the identification, analysis, and interpretation of these materials as impact markers (Deutsch et al., 1994; Southon and Taylor, 2002; Pinter and Ishman, 2008; Marlon et al., 2009; Surovell et al., 2009; Gill et al., 2009; Paquay et al., 2009, 2010; Haynes et al., 2010a,b; Scott et al., 2010; Daulton et al., 2010; Daulton, 2012; Pinter et al., 2011; Pigati et al., 2012; Hardiman et al., 2012; Boslough, 2013a,b; van Hosesel, 2014; van Hoesel et al., 2014; 2015; Holliday et al., 2014; Thy et al., 2015; Scott et al., 2015) as well as regarding the dating of their host sediment horizons (e.g., see Blaauw et al., 2012; van Hoesel et al., 2013, 2014; van Hosesel, 2014; Ives and Froese, 2013; Meltzer et al., 2014; Holliday et al., 2014, Boslough et al., 2015; Holliday et al., 2015). Accurate dating of stratigraphy at high resolution (required for proper evaluation of the YD Impact Hypothesis) is difficult because sites frequently have complex depositional/erosional histories and, except for lakebeds or ice sheets, rarely preserve a continuous record of sedimentation. Consequently, measurements that can provide sufficient chronological control are often poorly constrained or
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nonexistent. Meltzer et al. (2014) performed a critical analysis of the chronologies at 29 sites (including the Greenland ice sheet) in which the YDB layer has been studied in detail. The nature of the site, luminescence and radiocarbon ages, and age-depth models were examined. Meltzer et al. (2014) concluded that sediments at only three sites (Daisy Cave, San Miguel Island, California; Sheriden Cave, Ohio; and Big Eddy, Missouri) could be dated with any confidence to the YD onset.

Materials that have been reported in YDB layer sediments and interpreted as markers of supernova/impact/bolide processes include: tektites including one embedded in a YD-dated tree trunk (Kristan-Tollmann and Tollmann, 1994); paleoindian chert artifacts with high-velocity particle tracks, with embedded chondritic micrometeorites, and with isotopic anomalies in K, U, and Pu (Firestone and Topping, 2001; Firestone et al., 2006, 2010a; Firestone, 2009); millimeter-scale magnetic particles embedded in mammoth tusks and other Pleistocene megafaunal remains (Firestone et al., 2006); iron micrometeorites and mammoth tusks with rusty pits (Baker et al., 2008); radioactive sediment; radioactive mammoth bones and teeth (Firestone et al., 2006, 2007, 2010a,b); magnetic grains and elevated Ir concentrations inside an extinct horse skull (West et al., 2007; Firestone et al., 2010a); magnetic grains (Darrah et al., 2007) and fullerences with isotopically anomalous helium (Darrah et al., 2007; Firestone et al., 2007); high abundance of unoxidized Fe-Ni, Cu-Ni, Fe-Sn-Ni, and Pt minerals (Darrah et al., 2007), anomalously high concentrations of elements including U, Th, Ir, Pt, Ni, Cr, and Cu (see Firestone et al., 2007; Bunch et al., 2010; Petaev et al., 2013a,b; Andronikov et al., 2014); chondritic iron oxide framboids (Fayek et al., 2012); pyrite framboids (Israde-Alcántara et al., 2012a); shocked quartz with planar deformation features (Mahaney et al., 2010); siliceous “scoria-like objects”; and lechatelierite (amorphous SiO2) (Bunch et al., 2012; Wittke et al., 2013a,b,c). While all the proposed impact markers discussed up to this point are reported in one or several YDB sediments, the following markers are reported in many to most YDB sediments studied: magnetic minerals (“grains”, “microspherules”); carbonaceous combustion products (charcoal/soot, “glass-like carbon,” “carbon elongates,” and “carbon spherules”) (e.g., see Firestone et al., 2007; Kennett et al., 2008); nanometer to submicron-sized diamonds (loosely termed “nanodiamonds”); as well as controversial phases “n-diamond” and “i-carbon” (e.g., see Kennett et al., 2009a,b; Kinzie et al., 2014). Further, excess 14C (defined by the difference between radiocarbon dates and actual dates) is reported in terrestrial YDB
sediments, including tree remains, carbon spherules, glass-like carbon, and charcoal contained within those sediments, as well in Icelandic YDB marine sediments (see Kristan-Tollmann and Tollmann, 1994; Firestone and Topper 2001; Firestone et al., 2006; Firestone, 2009; LaViolette, 2011). A number of these reported markers are no longer considered credible, some are currently considered credible by only a few YD impact proponents, and others continue to be widely debated (for reviews see Pinter et al., 2011; Boslough et al., 2012; van Hosesel, 2014; van Hoesel et al., 2014; Holliday et al., 2014; Taylor and Bar-Yosef, 2014).

Reports of nanodiamonds, in particular the rare 2H hexagonal polytype of diamond, lonsdaleite, in YDB sediments; carbonaceous forms in these sediments (carbon elongates, carbon spherules, and glass-like carbon); and Greenland ice, all reportedly dating to the YDB, continue to be presented as strong evidence for multiple impact/bolide events. We review the available data on diamonds as well as associated carbonaceous minerals in sediments and provide additional data for evaluating the YD Impact Hypothesis.

**Experimental Methods**

Millimeter-scale carbonaceous spherules and/or their fragments were isolated from Arlington Canyon, Santa Rosa Island California sediments AC-003 (Kennett et al., 2008; 2009b) and SRI 09-28A from Locality III (Scott et al., 2010; 2016) that were dated to the YDB (12,800-13,100 cal a BP and 12,718-13,079 cal a BP, respectively). Full details describing the collection/acquisition of those sediments are provided in the accompanying paper, Scott et al. (2016). Three different specimen sets were separately crushed between sapphire discs: 1) five spherules/fragments from SRI 09-28A; 2) eight spherules/fragments from AC-003; and 3) 13 acid-washed spherules/fragments from AC-003. Each specimen set should contain at least one spherule containing nanodiamonds given that Kinzie et al. (2014) state, “For carbon spherules, 111 of 153 samples investigated (73%) contained no detectable NDs [nanodiamonds]” and “ND concentrations in carbon spherules is >35% at three sites.”

The finely crushed material from each set was deposited directly on amorphous carbon-coated Cu transmission electron microscopy (TEM) grids (dry mount). Additional TEM grids were prepared by depositing several µL aliquots of ethanol- or nanopure water-suspended particles on the support film of the TEM grids (wet mount).
In addition, a sequence of sediment from Lommel Belgium that bracketed and included the presumed YDB-aged black mat that is reported to contain nanodiamonds (Tian et al., 2011) was provided by Ph. Claeys. Black mat sediment (7.064g) was processed by acid dissolution. The sediment was first treated with 10M HF - 1M HCl followed by 6M HCl, and this alternating treatment was repeated eight additional times to remove silicates. This was followed by an alternating treatment of 6M HCl - 2M HF followed by 6M HCl - 0.6M H$_3$BO$_3$ and this was repeated four additional times to dissolve remaining silicates. The residue was divided into colloidal and non-colloidal fractions by colloidal separation using NaOH (pH = 10) following the procedure commonly used to concentrate nanodiamonds from primitive meteorites (see Lewis et al., 1987). Due to the surface charge on the diamonds, they are expected to stay in suspension in basic solution (Lewis et al., 1989). The colloidal fraction was then oxidized with Cr$_2$O$_7^{2-}$ for 20.5 hours at ~80°C, and the remaining residue was treated with HClO$_4$ for 2.0 hours at 204°C to further remove carbonaceous matter other than the diamond. Colloidal separation of the residue was again carried out in an attempt to further concentrate diamonds. Several µL aliquots of the final colloidal suspension were deposited on TEM grids.

Specimen nanostructure was characterized using a JEOL JEM-2100F field emission scanning transmission electron microscope. This instrument was equipped with a high-resolution pole piece and a Schottky field emission gun: 0.5 nA at 1 nm full width at half maximum probe diameter. This instrument was operated at 200kV and, at that energy, has a rated point resolution of 0.23 nm and a lattice resolution of 0.1 nm. The instrument was equipped with a Bruker Quantax 200-STEM energy dispersive X-ray spectroscopy (EDXS) system that consisted of an XFlash 60 mm$^2$ active-area silicon drifted detector (SDD) as well as drift correction and HyperMap software packages for spectral mapping. The instrument was also equipped with a Gatan Model 863 Tridiem electron energy-imaging filter (GIF) with spectrum imaging package (model 777 STEMPack) capable of electron energy loss spectroscopy (EELS), EELS spectral imaging, and electron energy-filtered imaging. The GIF utilized an Ultrascan 1000 FT 2048 x 2048 pixel, 16-bit, fiber optically coupled, peltier-cooled, charge-coupled device (CCD) camera as the main detector. For scanning (S)-TEM imaging, the instrument is equipped with Gatan Model 805 dark-field (DF) and bright-field (BF) STEM detectors as well as a Gatan Model 806 high angle annular (HAA)-DF STEM detector capable of Z-contrast imaging. For
conventional TEM imaging, the instrument has a retractable Gatan Orius SC1000B
2672 x 4008 pixels, 14 bit, fiber optically coupled, peltier-cooled CCD camera
mounted on-axis directly above the GIF.

Elemental maps were acquired by STEM-EELS and STEM-EDXS spectral
imaging in which EELS and EDXS spectra, respectively, were collected at each pixel
position within a STEM region of interest. For STEM-EELS, a spectrometer 5 mm
diameter entrance aperture, a collection angle of $2\beta = 22.66 \pm 0.06$ mrad, and an
energy dispersion of 0.2 eV/channel were used to measure an energy loss region of
640 to 1050 eV. The EELS spectra were corrected for dark current and channel-to-
channel gain variation of the CCD detector array and collected in the diffraction mode
of the microscope (i.e., image coupling to the EELS spectrometer). Ratios of
integrated EELS core-loss signal between elements were converted to their
corresponding atomic ratios using partial cross-sections that were calculated from
theoretical Hartree-Slater models. Unlike maps of EELS core-loss signal, maps of
relative elemental compositions are, in principle, not influenced by variations in
specimen thickness and electron diffraction. Ratios of integrated EDXS signal
between elements were converted to their corresponding atomic ratios using
standardless k-factors.

Experimental Results

Grain fragments of crushed carbonaceous spherules deposited on the TEM grids
were systematically examined using a variety of techniques, including: selected area
electron diffraction (SAED); bright-field, dark-field, and high-resolution imaging; and
EDXS spot analysis. In total for all specimens, approximately 2000 grains were
individually examined. The carbonaceous spherules primarily consisted of
amorphous material (~95%) dominated by C and O, but also exhibiting a range of
common elements that varied and included: Al, Ca, Fe, K, Mg, Na, P, S, Si, and/or Ti.
A small fraction of these amorphous grains (~several percent thereof) contained
nanocrystals embedded within their matrix. In no case were any of these nanocrystals
found to be carbonaceous, and no nanocrystals of diamond were observed. The
remainder of the material (~5%) on the TEM grids from the crushed spherules
consisted of submicron- (hundreds of nanometer-) sized monocry stalline non-
carbonaceous minerals (e.g., aluminosilicates, pyrite), disordered graphite, and
polycrystalline aggregates of graphene/graphane/graphite (with some trace elements present). In comparison, spherules examined in Daulton et al. (2010) contained higher abundances of graphene/graphane/graphite aggregates than those examined here. No diamonds were observed.

The acid-dissolution residues of YDB Lommel sediments contained submicron crystals that were rich in O, Al, Si, Zr, and/or Ti. No diamonds were observed. The Lommel residue was subsequently subjected to harsher acid dissolution treatment to remove more of the non-diamond minerals. These further-processed residues still contained abundant non-carbonaceous submicron crystals that survived acid dissolution. Again no diamonds were observed, although an exhaustive search was not performed. It was our intention to perform mass balance measurements of the nanodiamond abundance in Lommel sediment horizons across the YDB. In the mass balance approach, abundance is estimated from the initial mass of the sediment and the mass of the resultant acid dissolution residue (assuming pure diamond isolates). For non-pure isolates, mass modal abundances of minerals present in the residues are required to estimate the initial diamond abundance. Due to the large amounts of surviving non-diamond minerals in the Lommel black mat acid residue, and as will be discussed latter, quantitative mass balance measurements are incapable of yielding any reliable abundance estimations for diamond. Therefore, it was not possible to determine if there was a peak in the diamond concentration at the Lommel YDB.

van Hoesel (2014) were similary unable to find nanodiamonds in their acid dissolution residues of “black mat” YDB sediment from Lommel or from Murray Springs, Arizona. As is the case for any mineral phase that was not observed, lack of observation of diamond does not demonstrate the total absence of said mineral in the samples examined; it can, at best, only constrain its possible abundance. For the specimens we examined, it was not possible to accurately constrain the possible abundance of nanodiamonds.

**The Nanodiamond Evidence**

One of the main lines of evidence presented to support the YD Impact Hypothesis has been the reports of cubic and hexagonal nanodiamonds within bulk terrestrial and lacustrine sediments; carbonaceous forms in these sediments (carbon elongates, carbon spherules, and glass-like carbon); and Greenland ice, all reportedly dating to
the YDB (Firestone et al., 2007, 2010a; Kennett et al., 2009a,b; Kurbatov et al., 2010; Israde-Alcántara et al., 2012a,b; Kinzie et al., 2014). In a culmination of several connected studies, Kinzie et al. (2014) report a nanodiamond-containing YDB sediment horizon (with nanodiamonds completely absent above and below this horizon) that span several continents at 9 out of 22 YDB sites studied. If correct, this would suggest that a unique event occurred at the time this layer was deposited. In regard to the nature of this event, much emphasis has been placed on the reported discovery of lonsdaleite in YDB sediments (Kennett et al., 2009b; Redmond and Tankersley, 2011; Israde-Alcántara et al., 2012a; Kinzie et al., 2014).

**Lonsdaleite**

Lonsdaleite is the 2H hexagonal polytype of diamond (space group 194, \(P6_3/mmc\): \(a = 2.508\) Å, \(c = 4.183\) Å: Yoshiasa et al., 2003) that differs structurally from the 3C cubic polytype of diamond (space group 227, \(Fd3m\): \(a = 3.567\) Å) in the stacking sequence of tetrahedral close packed planes. In cubic diamond, the stacking sequence is \((A^b)(B^c)(C^a)\)\(_\ldots\), whereas in lonsdaleite it is \((A^b)(B^a)\)\(_\ldots\) (Fig. 1). Lonsdaleite was first discovered in laboratory experiments to synthesize diamond. Bundy and Kasper (1967) after discovering lonsdaleite in transformation products of their high-static-pressure compression experiments, became aware of a Netherlands patent (1965) reporting the formation of hexagonal diamond by shock compression. They subsequently identified lonsdaleite in the Canyon Diablo iron meteorite and attributed it to shock formation (Bundy and Kasper, 1967). Additional reports of lonsdaleite soon followed in meteorites (Hanneman et al., 1967; Frondel and Marvin, 1967; Clarke Jr. et al., 1981; Daulton et al., 1996); interplanetary dust (Rietmeijer and Mackinnon, 1987); material from Ries, Popigai, Sudbury, and Obolon impact structures (Hough et al., 1995; Koeberl et al., 1997; Goryainov et al., 2014; Shumilova et al., 2014; Masaitis et al., 1999; Gurov et al., 2009); and peat from the Tunguska bolide epicenter (Kvasnitsa et al., 1979; Kvasnytsya et al., 2013). This has led to the perception that natural lonsdaleite was exclusively associated with shock metamorphism. Although in the case of interplanetary dust, Rietmeijer and Mackinnon (1987) argued against shock formation of the lonsdaleite they observed.

By contrast, the broader literature contains reports of natural lonsdaleite with no directly connected association with shock processes. The Russian literature reports
lonsdaleite within titanium placers of the Ukrainian Shield (Sokhor et al., 1973); eclogites in Sal’niye Tundra, Kola Peninsula and the Urals (Golovnya et al., 1977); metamorphosed and metasomatically modified rocks of the Kumdykol diamond deposit in North Kazakhstan (Shumilova et al., 2011); and metamorphic rocks of the Kokchetav Massif in North Kazakhstan (Dubinchuk et al., 2010). Additionally, lonsdaleite is reported in polycrystalline diamonds from the Udachnaya kimberlite pipe, Yakutiya (Gorshkov et al., 1999; Titkov et al., 2001) and in similar polycrystalline diamond from placers in Yakutiya (Kaminsky et al., 1985; Petrovsky et al., 2013). The situation is complicated further in that some published data identifying natural lonsdaleite, whether at impact structures or not, is not rigorously convincing, with identifications sometimes based on several diffuse X-ray lines or a few transmission electron microscopy (TEM) electron diffraction patterns. In some studies (Koeberl et al., 1997; Masaitis et al., 1999; Titkov et al., 2001), no data are presented to support the lonsdaleite identification.

Microanalysis of lonsdaleite is difficult because it is always reported intergrown with cubic diamond and sometimes graphite on the nanometer to submicron scale. These phases often have high defect densities (e.g. dislocations, stacking faults, twin planes, and disordered grain boundaries). Consequently, the interpretation of structural measurements performed at a spatial scale greater than the grain size of these polycrystalline diamonds (such as with X-ray diffraction and TEM SAED) is not straightforward (see Daulton et al., 2003). Németh et al. (2014) go so far as to speculate that lonsdaleite does not exist and is an illusion created by lattice faults in polycrystalline cubic diamond having nanometer grain size. Earlier, Cayron et al. (2008) had shown that many reports of hexagonal-diamond Si had misinterpreted micro/nanotwins in cubic-diamond Si; note that these Si phases are isostructural to carbon’s lonsdaleite and cubic diamond, respectively. A stacking fault of tetrahedral close-packed planes in cubic diamond, \((A^b)(B^a)(A^b)(B^c))\)\((C^a)\)\)\(…\) where a \((C^b)\) plane is missing and the preceding \((B^c)\) plane is altered to \((B^d)\), necessarily forms a unit cell and a half wide lamellae of lonsdaleite. While such lamellae should not be considered a 2H hexagonal phase, there is sufficient evidence that well ordered \((A^b)(B^a)\)\)\(…\) stacking of tetrahedral planes (Fig. 1, 2) occurs at scales up to, at least, tens of nanometers for C (e.g., see Chen et al., 1996; Daulton et al., 1996; Lifshitz et al., 2001; Kulnitskiy et al., 2013), Si (Dahmen et al., 1989; Cerva, 1991; Algra et al.,
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2011; Hauge et al., 2015), Ge (Xiao and Pirouz, 1992; Vincent et al., 2014), and SiC (Daulton et al., 2003). Therefore, lonsdaleite, as well as other 2H hexagonal-diamond isostructural phases, do exist on at least this spatial scale. Nevertheless, some previous diffraction studies of heavily disordered cubic diamond minerals may have overestimated or misidentified the presence of lonsdaleite.

While the literature on lonsdaleite can be murky, it is clear that shock metamorphism has not been established as the exclusive mechanism by which lonsdaleite is formed in terrestrial deposits. Recall that lonsdaleite has been reported to form under high-static pressure (Bundy and Kasper, 1967). With the exception of lonsdaleite, none of the studies of YDB sediments report identification of any of the generally accepted and recognized shock minerals found at known impact structures (c.f., French and Koeberl, 2010; van Hosesel, 2014; van Hoesel et al., 2014). Therefore, in the absence of other shocked minerals, the presence of lonsdaleite in sediments can only provide tenuous evidence for an association with shock processing. While it can be debated under what circumstances lonsdaleite can be used as an impact marker, it is premature to consider this question further in assessing the YD impact hypothesis as the reports of lonsdaleite in YDB sediments are not well supported.

Daulton et al. (2010) demonstrated that Kennett et al. (2009b) misidentified polycrystalline aggregates of graphene and graphane present in various carbonaceous forms within the sediments as lonsdaleite. Independent studies have confirmed this conclusion (Madden et al., 2012; van Hoesel et al., 2012; van Hosesel, 2014; Bement et al., 2014) and have failed to observe lonsdaleite in YDB sediments (Tian et al., 2011). Graphene is a two-dimensional, single-atom-thick planar molecule with sp² bonded carbon (1.42 ± 0.1 Å bond length) in a hexagonal arrangement of 2.46 ± 0.02 Å edge length (Geim and Novoselov, 2007; Elias et al., 2009). Graphene was first observed as randomly oriented and uncorrelated sheets (i.e., a polycrystalline aggregate) within the cores of many circumstellar graphite spherules isolated from chondritic meteorites (Bernatowicz et al., 1996). When graphene sheets are periodically stacked normal to their plane (e.g., AB, AA, or ABC stacking), they form various graphite polytype structures or turbostratic graphite if the stacking is disordered. Graphane is a hydrogenated form of graphene, with H bonded on the surface resulting in a out-of-plane puckering of C bonds and an effective contraction of the hexagonal edge length to between ≈ 2.34 - 2.46 Å (Elias et al., 2009).
Kuratov et al. (2010) and Israde-Alcántara et al. (2012a), in which Kennett is a coauthor, also misidentified lonsdaleite. For example, the high-resolution (HR)-TEM lattice image of a nanocrystal from residues of Greenland ice shown in Figure 6 of Kuratov et al. (2010) and identified as lonsdaleite is inconsistent with the crystal structure of lonsdaleite. No crystallographic zone axis of lonsdaleite exists that can display two differently oriented sets of 2.06 Å spaced \{002\} planes because there is only one such set of planes in the structure (Fig. 3). The HR-TEM lattice image of a nanocrystal from Lake Cuitzeo identified as twinned lonsdaleite and shown in Figure 11B of Israde-Alcántara et al. (2012a) is inconsistent with the crystal structure of lonsdaleite. Using as spatial calibration the annotated 1.93 Å \{101\} spacing and scale marker of their figure, we measure a spacing of 1.75 ± 0.05 Å for the nearly vertical atomic planes (whose plane normal is perpendicular to the direction of the arrows in the figure) with cross plane angle of 67.4 ± 0.4°. Lonsdaleite lacks 1.75 Å spaced planes (see Table 1). If the plane spacings were both 1.93 Å (i.e., closest lonsdaleite spacing to our measured 1.75 Å spacing, see Table 1), the cross plane angle is restricted to 52.41° for \(<011>\), 55.81° for \(<110>\), or 80.15° for \(<121>\), and all are inconsistent with the HR-TEM image. Furthermore, the most common twin configuration in diamond is twinning across the tetrahedral basal plane (e.g., \{111\}_{3C} and \{002\}_{2H}) with twin angle of 70.53° (\(\Sigma=3\)) (see, Daulton et al., 2003), and this twin configuration will not alter the 2H lonsdaleite structure (i.e., stacking sequence). Although stacking faults in lonsdaleite are frequently reported, twining in lonsdaleite is yet to be reported, with the exception of Israde-Alcántara et al. (2012a).

The recent study by Kinzie et al. (2014) reports no new or convincing evidence for lonsdaleite. Contrary to earlier publications (Kennett et al., 2009b; Kuratov et al., 2010; Israde-Alcántara et al., 2012a), the term “lonsdaleite-like” is now used to describe these grains in Kinzie et al. (2014); note that all of these publications share at least one coauthor. Curiously, Kinzie et al. (2014) also state that “lonsdaleite has never been observed in any deposits of any age in Europe or North America, where YDB lonsdaleite-like crystals are currently found.” The reason the term lonsdaleite-like is now used is simple; these grains are not consistent with lonsdaleite. Kinzie et al. (2014) argue that the grain shown in their Fig. 15, which is the same grain as shown in Figures 2a-c and S2 of Kennett et al. (2009b), is a lonsdaleite-like grain. The original identification of this grain by Kennett et al. (2009b) as lonsdaleite was
questioned by Daulton et al. (2010). Kinzie et al. (2014) wrote in response, “He [Daulton et al. (2010)] questioned figure 2A-2C of Kennett et al. (2009b). Although the analyses were insufficient to conclusively identify the nanocrystal shown as lonsdaleite, we find no evidence to eliminate it as a possibility.” Despite their inability to conclusively identify the grain, Kennett et al. (2009b) categorically identified it as lonsdaleite, and Kinzie et al. (2014) identified it as lonsdaleite-like.

The grain in question displayed an azimuthally asymmetric polycrystalline diffraction pattern with partial rings (forming doubled rings, see Fig. 4), and this is indicative of heterogeneity either in the form of texturing or a multiphase mixture. Texturing (defined as a distribution of crystallographic orientations of polycrystalline grains, in which all possible orientations do not occur with equal probability) can produce asymmetric ring intensity. However, texturing can be ruled out because this diffraction pattern completely lacks intensity from many lonsdaleite reflections (see Fig. 4) including (101) and (102) (see Table 1; Bundy and Kasper, 1967; Frondel and Marvin, 1967) even for a wide range of specimen orientations achieved by tilting the TEM goniometer. The diffraction pattern is thus inconsistent with the lonsdaleite structure; however it is consistent with a two-phase aggregate of polycrystalline graphene/graphane, a mineral assemblage (Fig. 5) observed ubiquitously in the sediments (Daulton et al., 2010; van Hoesel et al., 2012; Bement et al., 2014).

The identification by Kinzie et al. (2014) of other reported lonsdaleite-like grains is based on the same analysis used by Israde-Alcântara et al. (2012a) to identify lonsdaleite. Both use single, off-zone-axis HR-TEM lattice images and their fast Fourier transformations (FFTs) that can easily yield misleading results (e.g., see Kohno et al., 2003; Cayron et al., 2008; den Hertog et al., 2012) and cannot provide a conclusive mineral identification. In particular, Kohno et al. (2003) demonstrated that HR-TEM images of twinned nanocrystals of cubic-diamond Si can be confused with hexagonal-diamond Si. The structural information contained in an individual HR-TEM image and its associated diffraction pattern is incomplete because they are two-dimensional projections of three-dimensional structures with potentially complex twin and stacking-fault configurations (see, Daulton et al., 2003; den Hertog et al., 2012). The analysis of a single HR-TEM image cannot conclusively determine the structure of a nanocrystal; instead, methods such as comparison of simulated phase-contrast lattice images to a through-focus series of HR-TEM images must be applied for a range of nanocrystal orientations (see also Billinge and Levin, 2007).
Kinzie et al. (2014) comment on an EELS analysis of a lonsdaleite-like grain, “Figure 17B is an HR-TEM image of a rounded 10-nm lonsdaleite-like crystal. The ED[X]S results were presented in Kurbatov et al. (2010), confirming that the crystal is carbon, and an EELS spectrum indicated high sp\(^3\) bonding.” However, the only EDXS and EELS results presented in Kurbatov et al. (2010) are found in their Figure 8 for a grain they claim is “n-diamond,” not lonsdaleite. Further, the EELS C-K edge spectra and the associated low-loss plasmon peak at 22 eV reported by Kurbatov et al. (2010) are consistent with amorphous C (e.g., see Kincaid et al., 1978; Fallon and Brown, 1993) from the ~70 nm thick TEM support film upon which the nanocrystals were mounted. The EELS spectra shown by Kinzie et al. (2014) for “n-diamond” is also consistent with amorphous C; as in the case of Kurbatov et al. (2010) and others, the spectra is likely dominated by contributions from the amorphous C TEM support film. Nevertheless, no C-K edge EELS spectrum of the lonsdaleite-like grain was published that can be evaluated here. Adding to the confusion, Kinzie et al. (2014) state in their Figure 17b caption, “B, HR-TEM image of a 10-nm lonsdaleite-like monocrystal from Lake Cuitzeo (YDB: 493 ppb at 280 cmbs).” However, Kurbatov et al. (2010) did not examine Lake Cuitzeo specimens.

Cubic Diamond

Nanometer-sized grains of the 3C cubic polytype of diamond in YDB sediments has also been interpreted as supporting the YD Impact Hypothesis. This interpretation is based on reports of cubic diamonds of nanometer to tens-of-micron size in Cretaceous/Tertiary boundary sediments (Carlisle and Braman, 1991; Hough et al., 1997); of submicron to millimeter size at Ries, Popigai, Sudbury, Gardnos, and Obolon impact structures (Hough et al., 1995; Koeberl et al., 1997; Masaitis et al., 1999; Gilmour et al., 2003; Gurov et al., 2009); and of submillimeter size in peat at the Tunguska bolide epicenter (Kvasnitsa et al., 1979; Kvasnytsya et al., 2013). Furthermore, ureilite and iron meteorites contain submicron- to millimeter-sized cubic diamond believed formed by shock (see Ksanda and Henderson, 1939; Nakamuta and Aoki, 2000) and primitive carbonaceous chondrites contain presolar cubic nanodiamonds (0.5-10 nm diameter, mean 2.6 nm) believed formed primarily by gas condensation (Lewis et al., 1987; Daulton et al., 1996). Submillimeter to centimeter polycrystalline aggregates of cubic diamond found in alluvial placers, known as
carbonados (from Mesoproterozoic deposits in Brazil and Central Africa) and yakutites/carbonados (from Yakutiya, Russia), have been attributed to formation by shock metamorphism (see Smith and Dawson, 1985; Kaminsky, 1994). However, Cartigny (2010) argued that a mantle origin for carbonados cannot be excluded. Formation mechanisms other than shock such as crystallization from a carbon-supersaturated fluid have been suggested (Ketcham and Koeberl, 2013), and the origins of carbonados remain poorly understood (Haggerty, 1999; 2014; Heaney, 2005; McCall, 2009; Cartigny, 2010). Yakutites have been described as differing from carbonados in several aspects (but see McCall, 2009), one being that they contain lonsdaleite (Kaminsky, 1994; Heaney et al., 2005), which is traditionally associated with shock processing. However, yakutites have been reported in kimberlite pipes (Gorshkov et al., 1999; Titkov et al., 2001), which are volcanic in origin.

On the other hand, cubic diamonds of non-impact and non-shock origin occur widely in the crust. Centimeter-size down to tens-of-micron, or smaller, cubic diamonds (including polycrystalline aggregates variously known as framesite, boart, ballas, stewartite, diamondite, and sometimes carbonado/yakutite) occur as xenocrysts in volcanic rocks (e.g., kimberlites, lamproites, and ultramafic lamprophyres) of pipe structures formed during mantle eruptions through the crust (see Haggerty, 1999; Gorshkov et al., 1999; Kurat and Dobosi, 2000; Titkov et al., 2001; Nowicki et al., 2007; Dobosi et al., 2008; Shirey et al., 2013). Micron- to tens-of-micron-sized cubic diamonds (microdiamonds) have been found worldwide as inclusions within or in association with metamorphosed crustal rocks of regional metamorphic terrains: Kokchetav Massif, Kazakhstan (Rozen et al., 1972; Sobolev and Shatsky, 1990); Maksyutov Complex, Russia (Bostick et al., 2003); Western Gneiss region, Norway (Dobrzhinetskaya et al., 1995); Bohemian Massif, Germany (Stöckhert et al., 2001); Lago di Cignana Western Alps, Italy (Frezzotti et al., 2014); Rhodope Massif, Greece (Schmidt et al., 2010); Dabie Shan, Su-Lu, and Qinling regions, China (Xu et al., 1992, 2005; Yang et al., 2003); and Aklulâk minette dike system, Canada (Cartigny et al., 2004). Polycrystalline cubic microdiamonds have also been found in the ultrahigh-pressure metamorphic terrain of Erzgebirge, Germany (Dobrzhinetskaya et al., 2013). The formation of metamorphic microdiamonds has been attributed to deep continental subduction of primary crustal rocks followed by rapid tectonic uplift of recrystallized material to the crust (see Ogawara, 2005; Dobrzhinetskaya et al.,
However, fluid-metasomatic formation of microdiamond in the crust has also been suggested (see Pechnikov and Kaminsky, 2008). Hawaiian mantle-derived, garnet pyroxenite xenoliths have been found to contain cubic nanodiamonds within melt inclusions (Wirth and Rocholl, 2003) and CO₂-H₂O-H₂S fluid inclusions (Frezzotti and Peccerillo, 2007). Cubic nanodiamonds also may be prevalent in metamorphic terrains; MicroRaman spectra of inclusions in garnets from the Maksyutov Massif (Bostick et al., 2003) and the Rhodope Massif (Perraki et al., 2006) suggest the presence of nanodiamonds or nanodiamond aggregates, although this has not been confirmed by other microanalytical techniques. All of these diamonds can be eroded from their source rocks, transported, and deposited into placer deposits, sediments (see de Wit, 2004), and sedimentary conglomerates (see Fleischer, 1998).

Cubic nanodiamonds have also been reported in sediments and in carbonaceous forms within sediments without clear association with impact structures and which do not date to the YDB. Nanometer to submicron-sized diamond were reported in carbon spherules, similar to those reported at the YDB, but from modern forest soils in Germany and Belgium (Yang et al., 2008). Similar sized nanodiamonds were also reported in glass-like carbon from the Usselo horizon in Geldrop-Aalsterhut, The Netherlands; however that horizon postdates the YD onset by two centuries (van Hoesel et al., 2012, 2013).

Diamond is chemically inert, highly resistant to weathering (e.g., decomposition and transformation), and will persist in the surface environment. Erosion of diamond-bearing source rocks and transport by wind or water could widely redistribute nanometer- to submicron-sized diamonds into distant alluvial deposits and sediments that bear little resemblance to the diamond source rocks. Similarly could be the case for micron-sized host grains containing nanodiamond inclusions, and those inclusions would be extracted from their host minerals during laboratory acid dissolution of the sediments. It is intriguing that nanodiamonds are present in the Pleistocene to Holocene sediments, and work is clearly needed to understand their origin. Similar to lonsdaleite, the literature on nanometer- to submicron-sized cubic diamonds in terrestrial deposits is complicated by the varying strength of the published data. Also, questions of laboratory contamination have been raised for some metamorphic rocks (see Chopin and Sobolev, 1995). Nevertheless, it is clear that the presence of these cubic diamonds in sediments cannot be used as an impact marker because shock
metamorphism does not appear to be the predominant formation mechanism of diamonds of that size found in the crust.

**Nanocrystals of “n-diamond” and “i-carbon”**

In addition to the two known polytypes of diamond, impact proponents also report nanometer-sized crystals of “n-diamond” and “i-carbon” in YDB sediments and Greenland ice (Kinzie et al., 2014). While neither are polytypes of diamond, impact proponents often describe them as nanodiamonds. They also interpret these nanocrystals as evidence for a YD impact event. “N-diamond” is a hypothesized carbonaceous phase that displays diffraction lines strikingly similar to that of 3C diamond, with the notable exception that the Bragg reflections kinematically forbidden in 3C diamond are present. This has lead to the speculation that “n-diamond” is a modified form of 3C diamond polytype (Hirai and Kondo, 1991). Aggregates of nanocrystals that display “n-diamond” reflections sometimes exhibit additional reflections that are attributed to another hypothesized nanocrystalline carbon phase termed “C₈” or “i-carbon” (see, Matyushenko et al., 1979; Hirai and Kondo, 1991). The atomic structure of “n-diamond” has yet to be determined and its identification as a modified form of 3C diamond remains controversial (e.g., see Wen et al., 2007). Similarly, “i-carbon” is controversial, and its atomic structure has not yet been determined.

In YDB sediments, “n-diamonds” are usually reported at much higher concentrations than cubic diamonds, and in many cases were “n-diamonds” are reported cubic diamonds are not observed. Table D2 of the supplementary materials of Kinzie et al. (2014) report “n-diamonds” present in 22 of 24 sites that date to the YDB, “i-carbon” in 20 of these sites, cubic diamonds were reported in only 8 of these sites, and hexagonal diamond in only 5. Israde-Alcántara et al. (2012a) report “n-diamonds” at Lake Cuitzeo, but write, “. . . we could not unequivocally identify the cubic allotrope. This may be due to masking by i-carbon and/or n-diamonds, which share some d-spacings with cubic NDs.” Kinzie et al. (2014) write in regard to Lake Cuitzeo, “Using HRTEM and FFT, we identified . . . n-diamonds, i-carbon, and cubics [cubic diamond] have a ratio of 3:1:1.”

The presence of “n-diamonds” in sediments cannot be used as an impact marker because they are also reported in sediments that do not date to the YDB and,
importantly, their formation by impact processes has not be demonstrated. Nanocrystals with diffraction patterns consistent with “n-diamond” were reported in surface forest soils in Germany and Belgium (Yang et al., 2008). At Bull Creek, Oklahoma, cubic nanodiamonds were not found, but nanocrystals of “n-diamond” were reported in multiple horizons (Madden et al., 2012) and in sediments dated <3000 14C a BP (Bement et al., 2014). Firestone et al. (2007) reported nanodiamonds in glass-like carbon from the rims of Carolina Bays using nuclear magnetic resonance (NMR); while that identification was questioned (Kerr et al., 2008), Kinzie et al. (2014) reported confirmation by TEM. Kinzie et al. (2014) wrote, “We used a focused ion beam to mill a piece of glass-like carbon extracted from the YDB layer at the M33 site, the rim of a Carolina Bay in Myrtle Beach, South Carolina (for site details, see Firestone et al., 2007). The TEM analyses showed that diamonds were present only from the surface down to a depth of ≈0.75 µm and were not observed in the interior (fig. 14A).” The caption for Figure 14 of Kinzie et al. (2014) identifies these nanocrystals as “n-diamond”. Firestone et al. (2010) earlier reported, “All of the Bay rims examined [15 in total] were found to have, throughout their entire 1.5-5-m sandy rims, a typical assemblage of YDB markers (magnetic grains, magnetic microspherules, iridium, charcoal, soot, glass-like carbon, nanodiamonds [emphasis added], carbon spherules, and fullerenes with helium-3).” However, Firestone et al. (2010a) did not disclose the methods and data by which the nanodiamonds were identified.

The Carolina Bays are thousands of shallow elliptical depressions with elevated rims scattered along the Atlantic Coastal Plain (see Brooks et al., 2010), which formed asynchronously over a significant period of time with multiple periods of rim accretion with intervening periods of erosion (Grant et al., 1998; Rodriguez et al., 2012). Meltzer et al. (2014) write, “Firestone et al. (2) subsequently admitted that the ages of the Carolina Bays vary but then suggested that because sediment from 15 Carolina Bays contained supposed impact markers and because such impact markers occur only in the supposed YDB layer and were ‘identical to those found elsewhere in the YDB layers that date to 12.9 ka,’ the supposed YDB layer in the Carolina Bays must be the same age (ref. 2, p. 16019).” Rodriguez et al. (2012) studied Lake Mattamuskeet, one of four Carolina Bays on the Albemarle-Pamlico Peninsula of North Carolina that Firestone et al. (2007, 2010a) reported contain impact markers (including nanodiamonds) and concluded that rim accretion significantly postdated
the YD stadial. In fact, Firestone (2009) measured radiocarbon ages between 685-8455 $^{14}$C a BP for glass-like carbon from several Carolina Bays including Myrtle that is reported to contain nanodiamonds (Firestone et al., 2007; Kinzie et al., 2014). Firestone (2009) suggests that the glass-like carbon from the Carolina Bays must be enriched in $^{14}$C relative to their assumed YD age and offered the implausible scenario that the YD impactor was ejected from a near-Earth supernova to account for the enrichment. A more probable explanation is that the assumed YD age of those Carolina Bays is incorrect.

**Nanodiamond Host Minerals**

Nanometer-sized diamond, “n-diamond”, and/or “i-carbon” have been reported within glass-like carbons (Firestone et al., 2007, 2010a; Firestone, 2009; Israde-Alcántara et al., 2012a supplemental materials; Kinzie et al., 2014), carbon elongates (Kennett et al., 2009b), and carbon spherules (Firestone, 2009, Firestone et al., 2010a; Kennett et al., 2009a; Israde-Alcántara et al., 2012a supplemental materials; Kinzie et al., 2014) from YDB sediments as well as acid dissolution residues of these sediments. Glass-like carbon was described by Firestone et al. (2007) as “Pieces up to several cm in diameter . . . associated with the YDB and [Carolina] Bays, and their glassy texture suggests melting during formation, with some fragments grading into charcoal.” Firestone et al. (2007) also describe “Carbon spherules (0.15–2.5 mm) are black, highly vesicular, subspherical-to-spherical objects (Fig. 3). SEM analyses show them to have cracked and patterned surfaces, a thin rind, and honeycombed (spongy) interiors. SEM/energy dispersive spectrometer and microprobe analyses show that the spherules are dominantly carbon (75%).” Kennett et al. (2009b) describes, “Carbon elongates differ from the carbon spherules in having an irregular array of walls and voids, whereas carbon spherule interiors display a well-organized honeycomb (reticulated) pattern. Both types are composed entirely of glass-like amorphous carbon indicative of high-temperature formation. The general shape of elongates ranges from angular (hexagonal in cross-section) to subrounded.” Kinzie et al. (2014), with Kennett as a coauthor, report carbon spherule abundances at Arlington Canyon that are equal to the sum of carbon spherule and carbon elongate concentrations reported by Kenneth et al. (2008, 2009b). No explanation was
provided by Kinzie et al. (2014) on why they reclassified the so-called carbon elongates as carbon spherules (see also Hardiman et al., 2012).

While carbon spherules may have multiple origins, most carbon spherules studied in YDB sediments have external and internal morphologies indistinguishable from sclerotia (Fig. 6) of saprobiic (e.g., Sclerotium Athelia rolfsii), phytopathogenic (e.g., Rhizoctonia solani, Botryotinia cinerea), and ectomycorrhizal (e.g., Cenococcum geophilum) fungi (Scott et al., 2010), to name a few. Sclerotia are resting bodies (i.e., persistent propagules) of fungi, composed of closely packed (pseudoparenchymatous) hyphae, which have a range of morphologies and form during periods of environmental stress (see Smith et al., 2015). Typically, they usually consist of an outer rind of tightly packed hyphal tips that develop an impervious thick-walled and pigmented (melanized) layer surrounding a medulla of hyphae with extended vacuoles that store reserves of glyocgen, proteins, lipids, and polyphosphates. Viable sclerotia can remain dormant for many years during adverse conditions and germinate in favorable conditions to produce mycelia. Sclerotia are ubiquitous in forest litter and soils, and even after death can persist for at least many thousands of years (see Trappe, 1969; Hormes et al., 2004; Benedict, 2011; McLaren et al., 2014). Further, fossil sclerotia (or similar structures) of Palaeosclerotium pusillum have been reported preserved in the matrix of coal dated to the Middle Pennsylvanian (≈ 310 Ma) (Rothwell, 1972; Dennis, 1976; Taylor et al., 2015). Consequently, sclerotia are common at archaeological sites (e.g., see McWeeney, 1989; Shay and Kapinga, 1997; Deal, 2005), and the common association of sclerotia with wood-charcoal in sediments has lead to the suggestion that charring of sclerotia by wildfires may contribute to their long-term preservation (Benedict, 2011). Carbon spherules were extracted from YDB sediments by flotation (Firestone et al., 2007; Kennett et al., 2008, 2009b; Israde-Alcántara et al., 2012a; Kinzie et al., 2014), and this method will readily collect dead sclerotia, which float in water (see Trappe, 1969; Shay and Kapinga, 1997, Benedict, 2011). Scott et al. (2010) suggested that carbon elongates in YDB and other sediments include non-spherical sclerotia and/or arthropod fecal material.

Israde-Alcántara et al. (2012a) responded to Scott et al. (2010), asserting that “... charred and uncharred sclerotia have textured, filamentous, low-reflectivity interiors, whereas at Cuitzeo [their study site], SEM imaging demonstrates that CSp have smooth, glassy, highly reflective interiors with no evidence of filamentous structure observed in fungal sclerotia (or cellular structure found in charcoal) (SI Appendix,
Fig. 5” (see also Israde-Alcántara et al., 2012b). However, fungal sclerotia can be hollow (see, Ferdinandsen and Winge, 1925; Trappe, 1931) and have smooth interior surfaces (Fig. 7) (private communication M. Watanabe). In the image of a carbon spherule from Arlington Canyon shown in the supplemental materials of Kennett et al. (2009b) septal pores which allow movement of cytoplasm and organelles in fungi hyphae (see, Reichle and Alexander, 1965; van Peer et al., 2009) are clearly evident (Fig. 8) and conclusively identify it as a fungal sclerotia at some undetermined stage of diagenesis (private communication M. Watanabe). Septa pores are also clearly evident in the image of a carbon spherule from a Carolina Bay that is attributed to Allen West (see, Largent, 2008). We also observed septal pores in carbon spherules from the YDB layer at Arlington Canyon provided to us by J. West and J. J. Johnson (e.g., see Fig. SSD of the supplemental materials of Scott et al., 2010). Further, our measured elemental composition of an Arlington Canyon carbon spherule is similar to that of fossil sclerotia. The amorphous matrix of the spherules had an elemental composition, as determined by EDXS, of 82.49 at.% C, 13.40 at.% O, and 0.35 at.% Si, consistent with that reported for YDB carbon spherules (Firestone et al., 2010a; Israde-Alcántara et al., 2012a). In comparison, fossilized sclerotia from sediments of Lake Biwa, Japan contained 83 at.% C, 15 at.% O, and 2 at.% Si (Itoh et al., 2013). Sclerotia undergo diagenetic changes in composition and structure while in sediments. Itoh et al. (2012) demonstrated that the high O/C ≈ 0.5 in initially viable C. geophilum sclerotia within soils decreased to 0.3 to 0.1 with increased diagenesis.

Israde-Alcántara et al. (2012a) also responded that “CSp also contain numerous noncarbon particles, including aluminosilicates, indicating that these cannot be primary biological entities, such as sclerotia.” Their reasoning is inconsistent with their own observation that “CSp are dominantly carbon (>87%) with minor particulates, such as Si, Al, and Fe, concentrated in the rind,” suggesting that the aluminosilicates are embedded in or present on the surface of the carbon spherules. Furthermore, Israde-Alcántara et al. (2012a) neglect studies such as Watanabe et al. (2001, 2004a) that found the exteriors and interiors of sclerotia contained inorganic components such as Al₂O₃, SiO₂, and Fe₂O₃. Inorganic nanocrystals (e.g., boehmite) were also reported in C. geophilum sclerotia and were thought to have formed by Al dissolution-precipitation reactions (Watanabe et al., 2004b).

Kinzie et al. (2014) claimed that, “There is no credible mechanism by which fungi can create NDs in sclerotia,” and “There is no plausible process by which sclerotia
could extract NDs from surrounding sediment.” Within crushed spherule fragments that we studied (from Arlington Canyon, AC-003), TEM revealed the presence of amorphous-carbonaceous grains with numerous rounded nanocrystals embedded with their matrix (Fig. 9) that were strikingly similar to nanodiamond containing fragments reported by Kennett et al. (2009b), Bement et al. (2014), and Kinzie et al. (2014). Electron diffraction from the embedded nanocrystals is nearly identical to that reported for “n-diamond” in YD boundary sediments (Fig. 10). Kinzie et al. (2014) report that “n-diamond” is far less resistant to oxidation by perchloric acid during acid dissolution than cubic diamond, and state, “This was an advantage when analyzing cubic NDs but a major disadvantage for the other allotropes, which were no longer present [in the acid residues].”

To further characterize the nanocrystals embedded in the Arlington Canyon carbon spherule fragments, EDXS and EELS spectral image maps were collected, and representative elemental maps are shown in Fig. 11. These maps revealed that the nanocrystals were Cu (see also Daulton et al., 2010). Native Cu (space group 225, \( Fm\-3m: a = 3.6149 \ \text{Å} \)) has the same diffraction lines as “n-diamond” that differ by \( \approx 1\% \) in plane spacing (Table 2). The Cu nanoparticles may be stabilized from oxidation by the amorphous carbon that surrounds them, by adsorbed surface groups, or by a protective oxide surface layer. The primary oxidation product of copper, \( \text{Cu}_2\text{O} \), is also present in the spherules (Daulton et al., 2010). Cuprite, \( \text{Cu}_2\text{O} \) (Space Group 224, \( Pn\-3m: a = 4.2696 \ \text{Å} \)), has essentially the same diffraction lines as the controversial “i-carbon”, with planar spacings differing by \( \approx 1\% \) (Table 2). The crushed spherules also contained nanocrystals that were not embedded in any matrix (Fig. 12). Elemental mapping demonstrated these nanocrystals were copper sulfides (e.g., covellite, chalcocite, digenite, geerite, anilite, djurleite and/or roxbyite). All the amorphous carbon fragments with embedded nanocrystals that we examined contained Cu nanocrystals. We found no nanocrystals (embedded within amorphous C or not) that were consistent with diamond, “n-diamond”, or “i-carbon”. While our observations cannot prove that diamond, “n-diamond,” and “i-carbon” are not present in the carbon spherules (and sediments), they clearly demonstrate that native Cu nanocrystals occur at far higher concentrations than “n-diamond” – should that modified form of 3C diamond exist and be present in the YDB. Since Cu nanocrystals were not reported in previous studies of YDB nanodiamonds, they were undoubtedly misidentified as “n-diamond” in the previous studies. Similarly, \( \text{Cu}_2\text{O} \)}
nanocrystals were not reported and were likely misidentified as “i-carbon” in those studies.

Interestingly, common wetlands plants (undoubtedly present in “black mat” forming environments) have been shown to form nanocrystals of Cu near roots with the possible assistance by endomycorrhizal fungi (Manceau et al., 2008), and such fungi include species known to form sclerotia (Münzenberger et al., 2009). The filamentous fungi Hypocrea lixii (Salvadori et al., 2013) and Trichoderma koningiopsis (Salvadori et al., 2014) have been shown to synthesize spherical nanocrystals of Cu from mine waste waters. Hypocrea lixii is the telomorph (i.e., sexual reproductive stage) of Trichoderma harzianum, a widely distributed fast growing soil fungal species (Chaverri and Samuels, 2002). Mycoparasitic species of Hypocrea/Trichoderma can grow on sclerotia surfaces and penetrate the rind (Elad et al., 1984; Benhamou and Chet, 1996). Sclerotia in forest soils have been shown to contain H. lixii (Asmaya et al., 2015). Further, the sclerotia colonizing fungus Fusarium oxysporum (Xu et al., 2008) has been shown to form nanoparticles of copper sulfide (chalcolite) (Hosseini et al., 2012). Biomineralization mechanisms (see Pantidos and Horsfall, 2014) could account for the nanocrystalline Cu and Cu compounds observed in the carbon spherules.

Furthermore, nanocrystals (e.g., aluminosilicates and other minerals including diamond, if present) associated with the carbon spherules could be located on surfaces or within the often-reported fissures and cracks that exist now (e.g., Fig. 10), or existed previously but were closed by organic carbon accumulation and/or by low-intensity burning/annealing in sporadic wildfires. Furthermore, nanometer-sized minerals including diamond can readily enter biological systems, and this has opened the possibility of their use for drug delivery and raised concerns over their toxicity in the environment (e.g., Zhang et al., 2012; Perevedentseva et al., 2013). For example, nanodiamonds labeled with tritium were shown to absorb on the surface of roots and penetrate into wheat shoots (Myasnikov et al., 2014).

**Nanodiamond Abundances**

Whether or not a unique event – but not necessarily an impact – occurred at the onset of the YD stadial depends on if nanodiamonds occur in YDB sediments at concentrations significantly elevated with respect to underlying and overlaying
Kinzie et al. (2014) reported nanodiamond concentrations of several hundred parts per billion (ppb) at the YDB layer and 0 ppb for multiple horizons at depths of tens to hundreds of centimeters above and below the YDB layer for 9 sites worldwide. However, it is technologically impossible with present instrumentation and techniques to accurately estimate concentrations of nanometer-sized minerals in sediments at and below ~tens to hundreds of parts per million (ppm) concentrations.

The problems associated with representative sampling and dating of fluvial sediment samples are discussed in Scott et al. (2016); therefore we focus on the methodology used by Kinzie et al. (2014) to measure nanodiamond concentrations. Similar methodologies were employed by several coauthors of Kinzie et al. (2014) (e.g., Kennett et al., 2009a,b; Kurbatov et al., 2010; Israde-Alcántara et al., 2012a), as well as by (Bement et al., 2014). Remarkably, Kinzie et al. (2014) tested their nanodiamond isolation and measurement methodology using a control sediment specimen loaded with a relatively large (0.01%) concentration of synthetic nanodiamonds, in contrast to the three to four orders-of-magnitude lower abundances (11-494 ppb) they reported for the YDB bulk sediments they processed by acid dissolution. Acid dissolution is the technique by which nanodiamonds were first isolated from carbonaceous chondrites (Lewis et al., 1987), and the isolates were initially thought to be relatively pure. However, it was later recognized they contain significant amounts of amorphous to poorly crystalline carbons that were difficult to quantify by TEM and X-ray diffraction. Acid-dissolution residues always contain non-diamond impurities, representing: minerals that survive acid dissolution, transformation products/residues/condensates of acid dissolution, and laboratory contaminants (e.g., Gilmour et al., 1992, 2003; Daulton et al., 1996; Stroud et al., 2011; Israde-Alcántara et al., 2012a; Heck et al., 2014; Kinzie et al., 2014). The amount of impurities is usually large, ~50% to near 100%, and can be dominated by amorphous to poorly crystalline carbons. Israde-Alcántara et al. (2012a) and Kinzie et al. (2014) subjectively estimated the purity of their acid residues at “about ±50%” and “< 50%”, respectively.

Due to the significant levels of non-diamond phases in the acid dissolution isolates, the abundance estimations of nanodiamonds in sediments based on mass balance are subject to large error. For nanodiamond concentrations below ~several ppm, where the recovered nanodiamond masses are very small (< micrograms per gram of processed material) and subject to greater relative contamination, the mass
The balance approach has extremely large error. In fact, contamination levels are greater and nanodiamonds are more readily lost when large amounts of matrix (> several tens of grams) are processed, and this is particularly problematic with small nanodiamond concentrations (i.e., less than a ppm). Kinzie et al. (2014) processed between 20 to 150 g of dry-sieved material per sediment horizon and state, “The acid extraction process commonly yielded very little residue that was nearly invisible to the naked eye inside the centrifuge tubes and often was detectable only by light microscope.” They further state in their supplemental materials that, “We placed all the residue on a single [TEM] grid, whenever possible. If not, we measured the total amounts used or not used to get a percentage per grid.”

The combined errors in measurement of the minuscule mass of the recovered residue, and the fraction thereof placed on the TEM grid, is compounded with the error in measuring relative modal (mass) abundance of the different minerals present in the non-pure residue. Accurate measurements of modal abundances are required for determination of the mass of the recovered nanodiamonds from the mass of acid residues or from the mass of crushed carbon spherules. Kinzie et al. (2014), Bement et al. (2014), and Kurbatov et al. (2010) estimated modal abundances by measuring projected areal densities (i.e., projected TEM support film coverage) of nanometer to submicron-sized grains deposited on TEM grids. Projected areal densities are not measurements of the relative mass of nanodiamonds with respect to the mass of non-diamond minerals, and their use will yield large errors in the determination of the nanodiamond abundance in sediments, carbon spherules, and ice cores. For example, to estimate the relative mass of the ubiquitous amorphous to poorly graphitized carbon within which the nanocrystals were observed requires measurement of the thickness and mass density of those carbon forms, in addition to a projected areal density. The thickness – and therefore mass – of the amorphous to poorly graphitized carbon can vary greatly on the TEM grids.

Furthermore, the greatest limitation of the approach of Kinzie et al. (2014) and others is that detailed measurements must be performed on each individual grain in order to correctly identify it as diamond (see, Daulton et al., 2010). Kinzie et al. (2014) state, “NDs represent <50% of the residue, and the remaining non-ND residue can mask the NDs, thus making them difficult to identify. In addition, there are inherent difficulties and uncertainties in correctly identifying tiny crystals ≤2 nm in diameter.” Kinzie et al. (2014) further state, “By themselves, SA[E]D patterns are
insufficient to identify NDs, and so further investigations, such as those using HRTEM, FFT, ED[X]S, and EELS, were performed on these nanoparticles to confirm that they are NDs and not some other mineral.” In their conclusions, Kinzie et al. (2014) wrote, “The identification of the isolated NDs involves two main methods, electron microscopy imaging and electron spectroscopy, using up to nine imaging, analytical, or quantification procedures: scanning electron microscopy, STEM, TEM, HRTEM, ED[X]S, SA[E]D, FFT, EELS, and EFTEM. The entire procedure is labor-intensive and technically demanding.” However, Kinzie et al. (2014) perplexingly describe in their supplemental materials, “... for the purpose of estimating abundances, we assumed that all rounded particles were NDs [emphasis added]. We also observed abundant amorphous carbon nanoparticles, but almost none were rounded, and therefore, we discounted them. This estimation procedure focused solely on the presence or absence of rounded particles [emphasis added].” Given the importance of this point, it is troubling that it was stated not in the main paper but only in the supplemental materials. We reiterate that Kinzie et al. (2014) measured projected areal densities of “rounded particles,” not necessarily nanodiamonds, and they certainly did not measure modal mass abundances. This is a critical flaw, given that the acid-dissolution residues and crushed spherules are not pure diamond.

Israde-Alcántara et al. (2012a) report that, “[Lake] Cuitzeo [Mexico] CSp [carbon spherules] contain numerous noncarbon particles including aluminosilicates.” We observed a range of non-carbonaceous crystalline minerals in carbon spherules from Arlington Canyon; their mass abundance was of the order of several percent of the spherule mass. We also found the carbon spherules contained amorphous-carbon with rounded nanocrystals embedded with their matrix (Fig. 6) that were strikingly similar to nanodiamond containing spherule fragments reported by Kennett et al. (2009b), Bement et al. (2014), and Kinzie et al. (2014). However, we found the embedded nanocrystals were native Cu in all spherule fragments examined. In no case did we observe diamond, “n-diamond,” and “i-carbon,” and while our observations cannot prove their absence in the carbon spherules, they clearly demonstrate that native Cu nanocrystals occur at far higher concentrations than “n-diamond.” As in the case for the carbon spherules, glass-like carbon from YDB sediments have been shown to contain nanocrystals of Ca-rich, Ti-rich, Ti-rich, and Fe-rich phases which can have rounded morphologies (van Hoesel, 2014). Nanocrystals of native Cu, Cu compounds, and other minerals that are present in
crushed carbon spherules are undoubtedly included in the counting statistics of Kinzie et al. (2014) and others that counted “rounded particles.”

The method of estimating TEM grid surface coverage of rounded particles by Kinzie et al. (2014) is further puzzling given that angular, octahedral, and euhedral nanodiamonds have been reported in YDB-aged sediments. Kennett et al. (2009b) claim, “. . . clusters of stable cubic diamonds (≈1,000 in total) were found with carbon elongates . . . These diamonds appear more angular than the associated n-diamonds,” and “TEM study revealed conspicuous subrounded, spherical, and octahedral crystalline particles . . . Analysis of the particles by electron diffraction show reflections consistent with . . . metastable ‘new-diamond’ polymorph or n-diamond.” Similar descriptions of the YDB nanodiamonds appear in Kennett et al. (2009a). Furthermore, an example of a cubic diamond from black mat sediments of presumed YDB-age at Lommel Belgium, and shown in Fig. 2 of Tian et al. (2011), is flake-like with an irregular non-rounded shape. van Hoesel et al. (2012) reported submicron cubic diamonds with irregular non-rounded shape (their Fig. 6) in the Usselo horizon at Geldrop-Aalsterhut, The Netherlands. Israde-Alcántara et al. (2012a) described the nanodiamonds they reportedly identified as, “. . . nanocrystalline carbon particles ranging in shape from spherical to elongate to euhedral . . . embedded in amorphous carbon, as Tian et al. (14) described. We identified three of four previously reported ND variants, of which, n-diamond was the most abundant.”

Kinzie et al. (2014) prepared TEM specimens by placing dried acid residues or crushed spherules into suspension using NH₄OH, depositing aliquots of suspended grains on the TEM grids, and allowing the aliquots to evaporate. Another limitation of the TEM approach for determining modal abundances is that depositing liquid-suspended grains on a TEM grid results in highly heterogeneous grain dispersions. This is problematic because variation in surface chemistry of different minerals or mineral grains of different sizes can result in different tendencies to cluster and/or adhere to the TEM support film. Consequently, measured modal distributions based only on analysis of the TEM-accessible regions, with nearly monolayer dispersions of spatially well-separated grains, can be greatly skewed from the true modal distribution. Often electron-transparent multilayer deposits form, consisting of overlapping grains that make it difficult to identify individual grains or determine modal abundances. Furthermore, thick grain aggregates are electron-beam opaque and cannot be analyzed by TEM. These regions can have different mineral modal
abundances than the TEM-accessible regions.

Kinzie et al. (2014) state in their supplemental materials that they analyzed between 16 and 92 (average of 28) random 350 x 350 nm² TEM field of views. Unfortunately, the sampling was not identical for each TEM grid, and it is unclear which sediment horizons received increased scrutiny (e.g., the horizons that were expected to contain nanodiamonds). A larger problem is that their mean sampling corresponds to ≈0.000017% of the viewable area of a TEM grid. Given the highly inhomogeneous grain dispersions on their TEM grids, this represents a statistically inadequate grain sampling that could account for the 0 ppb nanodiamond abundances they measured in sediments that bracketed the reported YDB layer. Of course, TEM can provide no measure of any grains dispersed on the TEM inaccessible grid bars.

The numerous experiment difficulties in using TEM to measure nanodiamond abundances in sediments render this approach infeasible. The only analytical method accepted to reasonably assess ~several to tens of ppm abundances of nanodiamonds within a matrix is a technique applied to meteoritic nanodiamonds that measures the amount of supernova-derived Xe-HL gases (see review by Daulton, 2006) released during stepped combustion of acid-dissolution residues. By measuring a tracer unique to the nanodiamonds, only the nanodiamonds are measured; this contrasts with the mass-balance approach that measures the combined mass all the different materials (including adsorbed moisture) present in the acid residue. Diamonds are thought to be the only carriers of the Xe-HL gases in the non-pure nanodiamond isolates, based on the smooth elemental abundance pattern of extracted noble gases relative to cosmic abundances, suggesting all HL noble gases are a single gas component trapped in a single mineral species (Huss and Lewis, 1994). This assumption is also based on the high release temperatures (1100-1600°C) of the HL gas component (Huss and Lewis, 1994). Furthermore, the release of HL gases is accompanied by release of CO₂ (Lewis, 1994), indicating that the HL component resides only in the most refractory carbonaceous minerals (see also Daulton, 2006). This method has the advantage that it can be used to monitor any decrease in the HL gas component (i.e., loss of the carrier phase) after each step of the acid-dissolution process, or following any post-processing. However, the method has the disadvantage that is does not directly measure nanodiamonds that lack Xe-HL gases.

A number of noble gas measurements have been performed on terrestrial diamonds (for a review, see Basu et al., 2013). For example, Verchovsky et al.
measured one diamond from the Popigai crater and reported unusually high concentrations of radiogenic $^{40}$Ar. Subsequent measurements of Popigai diamonds yielded a similar range of $^{40}$Ar/$^{36}$Ar ratios as in kimberlitic diamonds, however with significantly higher $^{40}$Ar concentrations (Shelkov et al., 1998). Metamorphic microdiamonds from the Kokchetav Massif have primary $^{40}$Ar concentrations that fall between the ranges exhibited by kimberlitic and Popigai impact diamonds (Verchovsky et al., 1993). Secondary processes, such as implantation of U and Th decay products, appear to have severely modified the primary isotopic compositions of the noble gases that were trapped during formation of the microdiamonds. Kokchetav microdiamonds contain $^4$He concentrations that are among the highest observed in any terrestrial diamonds (Verchovsky et al., 1993). Carbonado diamonds from Africa and Brazil also contain large amounts implanted radiogenic $^4$He in addition to nucleogenic Xe and Kr (Ozima et al., 1991). Unfortunately, there have been no measurements of trapped noble gases performed on nanodiamonds from the YDB boundary or the underlying/overlaying sediment layers. Therefore it is unclear if they carry any unique trapped gas component useful as a tracer for abundance measurements.

Carbon Isotopic Compositions of Nanodiamonds

Nanodiamonds are a minor component (see Lewis et al., 1987; Rietmeijer and Mackinnon, 1987, Dai et al., 2002) of the $\sim 4 \times 10^7$ kg/yr interplanetary dust flux that is accreted by Earth (Love and Brownlee, 1993), with accretion rates in the last glacial period comparable to the present (Yada et al., 2004). In arguing against the fall of interplanetary dust as an explanation for nanodiamonds in YDB sediments, Israde-Alcántara et al. (2012a) incorrectly state that “Tian et al. (14) concluded that YDB NDs are not cosmic because they display $\delta^{13}$C abundances (−28.1 to −26.3‰) that are terrestrial.” van Hoesel et al. (2012) make a similar incorrect statement. Tian et al. (2011) actually stated, “carbon isotope measurements and C/N values were determined from the black material of the Lommel YDB layer. The nanodiamond particles in the present material could not be analyzed separately because of their small size.” Tian et al. (2011) performed these measurements to look for evidence of an impact event through the presence of C in the sediments that originated from the impactor and concluded that, “results obtained on the Lommel material do not
distinguish between terrestrial and extraterrestrial origins for the carbon.” Israde-Alcántara et al. (2012a) also incorrectly concluded that “Isotopic analyses of the carbon-rich YDB interval at Cuitzeo yielded values ranging from −23 to −19‰ for δ13C consistent with the formation of Cuitzeo NDs from terrestrial, not cosmic, carbon.” Similar to Tian et al. (2011), Israde-Alcántara et al. (2012a) measured sediment, not nanodiamond isolates. Neither of the bulk sediment δ13C measurements can provide direct information about the nanodiamonds, which make up only a tiny fraction of the C in the sediments. Kinzie et al. (2014) also invoke this erroneous evidence by citing both papers and stating, “(δ13C, δ15N, and C/N) in YDB NDs are consistent with a terrestrial origin.” They also incorrectly interpret the δ13C measurements of sediments by Tian et al. (2011) as ruling out a mantle origin of the nanodiamonds.

Measurement of the δ13C compositions of nanodiamonds isolated from sediments or matrix by acid dissolution is experimentally challenging. The non-diamond carbonaceous phases, which can comprise over half the residue, are potentially of different origin as the nanodiamonds and hence can have different C isotopic compositions. While δ13C values measured from C released at high temperature during stepped combustion of the acid residue will limit C contributions from the most labile (low-temperature released) components, it is not possible to correct for contributions from the non-diamond carbonaceous minerals that combust along with the nanodiamonds. Consequently, bulk C isotopic measurements of acid residues are highly suspect with respect to the true nanodiamond C isotopic composition. Therefore, bulk C isotopic measurements of acid dissolution isolates of terrestrial sediment nanodiamonds (Carlisle, 1992; Gilmour et al., 1992), impact diamonds (Hough et al., 1995; Gilmour et al., 2003), and meteoritic nanodiamonds (c.f., Swart et al., 1983, Russell et al., 1996) cannot provide information about their origins. Indeed, this point has driven recent attempts by two groups to pursue C isotopic measurements of individual meteoritic nanodiamonds using atom probe tomography (Heck et al., 2014).

Synchronous Chronologies and Stratigraphic YDB Markers

An important challenge for the YD Impact Hypothesis is that, in order to attribute the source of nanodiamonds in Late Pleistocene sediments to an impactor/bolide
event, it is necessary that all sediments reported to contain nanodiamonds date synchronous to the YD onset. However, nanodiamonds (and “n-diamond”) have been reported in sediments and in carbonaceous forms within sediments that do not date to the YDB (Firestone et al., 2007, 2010a; Yang et al., 2008; van Hoesel et al., 2012, 2013; Bement et al., 2014; Kinzie et al., 2014). Most importantly, and despite widespread claims of synchronicity by YD impact proponents (see, Kennett et al., 2015a,b), age control is poor or nonexistent at nearly all sites where nanodiamonds are reported “at” the YDB layer (e.g., see Blaauw et al., 2012; Ives and Froese, 2013; Wittke et al., 2013c; van Hoesel et al., 2013, 2014; Meltzer et al., 2014; Holliday et al., 2014). There are only two sites where nanodiamonds are reported at a layer that can be confidently dated to the YD onset: Daisy Cave and Sheridan Cave (Meltzer et al., 2014). However, Meltzer et al. (2014) cautions that at Sheridan Cave, “. . . the supposed YDB layer has the required age, but its age is inconsistent with the ages of the layers that encompass it.”

The YDB sediment layer is often described as being at the base of a dark-colored stratum termed by YD impact proponents as “the black mat” that is used as the primary stratigraphic marker for the YDB (Firestone et al., 2007, 2010a; Firestone 2009, Mahaney et al., 2010; Israde-Alcántara et al., 2012a; Wittke et al., 2013a). Nanodiamonds and other proposed impact markers are reported directly beneath the black mat (Firestone et al., 2007, 2010a). A distinct, dark colored stratum is present at the Murray Springs, Arizona archeological site, with sediments containing Clovis artifacts and megafaunal fossils below the horizon and sediments devoid of these materials above. Haynes (2008) identified 55 localities in the western United States and 2 in the eastern United States with " . . . a black organic-rich layer or 'black mat' in the form of mollic paleosols, aquolls, diatomites, or algal mats with radiocarbon ages suggesting they are stratigraphic manifestations of the Younger Dryas cooling episode." These and other similar deposits have been described as organic-rich, silty sediments (e.g., Brakenridge, 1981; Quade et al., 1998; Baker et al., 2008), however their total organic carbon content varies (most cases < 5 wt. %) and is not correlated with sediment texture and color (see Pinter et al., 2011; Harris-Parks, 2014, 2016). In fact, such deposits vary in color and white-colored diatomites have been described as “black mats” (Haynes, 2008). These deposits form in wet environments ranging from wet meadows to shallow ponds (Quade et al., 1998; Haynes, 2008; Harris-Parks, 2016). “Black mat” formation, at least in southern Nevada, peaked during the YD
from 11,200-10,000 $^{14}$C a BP (Quade et al., 1998). However, formation was time-transgressive across, rather than synchronous with, the YDB (Holliday and Meltzer, 2010; Harris-Parks, 2014, 2016). Such dark colored deposits are not unique to the western United States or to the YDB, but in fact are well recognized as paleo-wetland deposits found in similar settings around the world and at numerous time horizons through at least the late Quaternary (e.g., Quade et al., 1998; Rech et al., 2003; Mandel, 2008; Pinter et al., 2011; Pigati et al., 2012).

Black mats and the unreliable reports of spikes in the nanodiamond concentration, as discussed previously, cannot link chronologies at different sites. The reported concentration spikes of the other currently debated mineralogical and geochemical markers at the YDB have all been vigorously challenged. These markers include combustion products (charcoal/soot, glass-like carbon, carbon elongates, and carbon spherules), magnetic minerals (grains, spherules), and Ir (see, Firestone et al., 2007, 2010a; Firestone, 2009; Kennett et al., 2008, 2009b). In addition, Bunch et al. (2012) reported a correlation between elevated abundances of siliceous scoria-like objects and Fe/Si-rich microspherules at the YDB layer at three out of 18 sites studied (Abu Hureyra, Syria; Melrose, Pennsylvania; and Blackville, South Carolina). Of these materials, nanodiamonds have been reported within glass-like carbons (Firestone et al., 2007, 2010a; Firestone, 2009; Israde-Alcántara et al., 2012a supplemental materials; Kinzie et al., 2014), carbon elongates (Kennett et al., 2009b), and carbon spherules (Firestone, 2009, Firestone et al., 2010a; Kennett et al., 2009a; Israde-Alcántara et al., 2012a supplemental materials; Kinzie et al., 2014).

One aspect of most versions of the YD Impact Hypothesis is the assertion that intense, impact-ignited wildfire raged across North America and Europe (Kristan-Tollmann and Tollmann, 1992; Firestone et al., 2006). Charcoal/soot, glass-like carbon, carbon elongates, and carbon spherules reported in YDB sediments are interpreted as high-temperature combustion products and evidence of synchronous intercontinental wildfires (Firestone et al., 2007, 2010a; Firestone, 2009; Kennett et al., 2008, 2009a,b; Wittke et al., 2013a). For instance, Firestone et al. (2007) propose, “... glass-like carbon, carbon spherules, and nanodiamonds were produced in the YDB by high temperatures resulting from the impact and associated biomass burning.” Kennett et al. (2008) studied the wildfire evidence and wrote, “Intense wildfire evidence is also indicated by the presence of carbon spherules . . . spherules occur widely in the YDB layer in North America and have also been found in surficial
sediments associated with intense coniferous forest crown fires (Firestone et al., 2007).” In apparent contradiction, Israde-Alcántara et al. (2012a) state that the, “. . . indication that the YDB proxies [e.g., carbon spherules, nanodiamonds, magnetic spherules] are not wildfire-related is that marker peaks (2.80 to 2.75 m) were deposited earlier than the wildfire charcoal peak (2.70 to 2.65),” suggesting wildfires were not synchronous with (and immediately caused by) the impact event at their study site, Lake Cuitzeo. As for the nanodiamonds in the YDB spherules, Firestone et al. (2006) first speculated that they “. . . rode in with an asteroid or comet, or on the supernova debris cloud,” but later speculated they were formed during the impact event Firestone et al. (2007). Kinzie et al. (2014) conclude, “. . . the best explanation is that ND-rich carbon spherules derive from conifers that were incinerated by the impact event”, and cite Israde-Alcántara et al., 2012a who cite Kimbel et al. (2008), which report the formation of “n-diamonds” in charred coal, coconut shells, and wood; they state, “. . . [our] procedure is identical to the commercial process for producing activated charcoal . . . The process of forming n-diamonds requires conditions unlike any that are normal to the Earth's surface . . . [and] match the extreme conditions that exist during an ET impact or airburst.” Kinzie et al. (2014) stress that the nanodiamonds and their host carbon spherules must have been formed within the impact fireball itself, and provide several arguments against their formation by wildfire, stating, “. . . there is no evidence for and no known process for production of NDs in natural wildfires.” Millimeter-diameter, nanodiamond-containing carbon spherules that formed in an impact fireball should be localized to the immediate area of the impact site(s). However, despite the assertion by impact proponents that the primary YD impact site is in North America, nanodiamond-containing carbon spherules are reported widely distributed over several continents. For example, Kinzie et al. (2014) report the abundance of nanodiamonds in carbon spherules from YDB sediments in Ommen, the Netherlands are higher than at 12 out of 14 North American sites studied, and abundances in Lingen, Germany are higher than at 10 of those North American sites.

A study of 35 lake sediment cores across North America could neither confirm a charcoal peak associated with the YDB at any location nor find any indication of continent-wide wildfire (Marlon et al., 2009). Similar conclusions were drawn from subsequent studies (Gill et al., 2009; Daniau et al., 2010; Pinter et al., 2011). In fact, most YD-aged “black mats” in North America contain negligible amounts of charcoal
(Haynes et al., 2010a; Harris-Parks, 2014, 2016). As for as the other proposed impact-derived combustion products, Scott et al. (2010) report that glass-like carbon, carbon elongates, and carbon spherules are ubiquitous in sediments and occur throughout Late Pleistocene to Holocene sedimentary sequences. Further, sclerotia are morphologically identical to the reported YDB carbon spherules (Scott et al., 2010), and are commonly reported in sediments (e.g., see McWeeney, 1989; Shay and Kapinga, 1997; Deal, 2005).

The reported spikes in concentration at the YDB of magnetic spherules, siliceous scoria-like objects, and Ir are also strongly contested. These markers are not reported to be directly associated with nanodiamonds and, in fact, nanodiamonds are not reported at the three YDB sites where lechatelierite-containing magnetic spherules and scoria-like objects are reported. Therefore, these markers will not be discussed further, but reviews of the contested studies are found in Pinter et al. (2001), van Hosesel (2014), van Hoesel et al. (2014), and Holliday et al. (2014). The point is that there are no clear and undisputed concentration spikes for any mineral or geochemical signature that can be used identify the YDB and link chronologies at different sites.

Even if the reported concentration spikes in Late Pleistocene sediments are accepted, there are problems in interpreting them as indicators of impact/bolide event(s). Impact/bolide events should result in nearly simultaneous deposition of impact markers with respect to the mean sedimentary rates at a given site. Natural mixing processes (e.g., bioturbation, transport, and redeposition) should thoroughly mix the different mineralogical and geochemical markers within a sediment horizon and widen their distribution vertically in stratigraphic sequences. While some sorting might occur, the peaks in abundance with respect to stratigraphy should approximately overlap for all markers. Multiple abundance peaks for any given marker, and marker peaks that are vertically offset and distinct from one another, would not be expected. At several Carolina Bays (M31 and M33 of Myrtle Beach, South Carolina), two well-separated peaks in magnetic grain abundance are reported, with the peak at the higher stratigraphic level correlated with a peak in charcoal abundance (Firestone et al., 2010a). Firestone et al. (2007, 2010a) report at Chobot, Alberta Canada correlated abundance peaks in carbon spherules, glass-like carbon, and charcoal in sediments that lie below sediments with correlated abundance peaks in magnetic grains and magnetic spherules. At Topper, South Carolina, Firestone et al. (2007, 2010a) report that the abundance peaks in glass-like carbon and magnetic
grains do not overlap. At the Gainey, Michigan, Firestone et al. (2010a) report two peaks in magnetic grain abundance, with the peak at the lower stratigraphic level correlated with a peak in magnetic spherules abundance. At Arlington Canyon, two well separated sets of correlated peaks at ≈ 400 and ≈ 500 cm below surface (cmbs) for charcoal, carbon elongates, carbon spherules, and nanodiamonds are reported that bracket a horizon of gravel to coarse sand (Kennett et al., 2008, 2009b; Kinzie et al., 2014). Note that Kenneth et al. (2008, 2009b) report carbon spherules are absent between 95 to 416 cmbs and their abundance peaks near 500 cmbs, while the abundance of carbon elongates has two resolved peaks near 394 cmbs and 500 cmbs. Kinzie et al. (2014), with Kennett as a coauthor, provide no abundance measurements for carbon elongates and instead report two peaks in the abundance of carbon spherules at 394 cmbs and 500.5 cmbs at concentrations that are a sum of carbon spherule and carbon elongate concentrations reported by Kenneth et al. (2008, 2009b).

**Discussion and Conclusions**

The YDB nanodiamond data are considered by some as the strongest physical evidence for an YD impact/bolide event. We have analyzed the nanodiamond data used to provide evidence for the YD Impact Hypothesis and have identified critical problems with the collection of those data and/or the data interpretation. In evaluating the evidence we arrived at four main conclusions.

1) The presence of lonsdaleite in sedimentary deposits can suggest – but cannot on its own demonstrate – that an impact event occurred. In YDB sediment, however, there is no credible evidence of the presence of lonsdaleite. In previous studies, graphene/graphane aggregates have been misidentified as lonsdaleite, diffraction patterns have been incorrectly indexed to lonsdaleite, and FFT transforms of single high-resolution lattice images used to identify lonsdaleite are known to yield misleading results.

2) While there is evidence of cubic nanodiamonds in Late Pleistocene sediments, their presence does not provide evidence of an impact because they have not been linked with impact processes. To do so would require correlating the nanodiamonds to an established and recognized impact marker. There are no established reports in YDB sediments of any of the accepted and recognized shock minerals found at known
impact structures (c.f., French and Koeberl, 2010; van Hoesel et al., 2014). Carbon spherules, carbon elongates, and glass-like carbon reported associated with the nanodiamonds are not recognized as impact markers. Furthermore, these associations are reported to occur in sediments that are not limited to the YDB and therefore cannot provide evidence of processes unique to the YD onset.

3) The use of the controversial “n-diamond” as an impact marker, which constitutes the majority of the nanodiamond evidence for the YD Impact Hypothesis, is problematic due to the presence of native Cu nanocrystals in sediments that can be easily confused for “n-diamond”. Further, “n-diamond” is reported in sediments that do not date to the YD onset, and more importantly, formation of these nanocrystals have not been linked exclusively to shock formation processes.

4) The presence of a single spike in nanodiamond concentration within Pleistocene to Holocene sediments at the YDB layer would strongly suggest that a unique event – but not necessarily an impact – occurred at the YD onset. Nanodiamond abundances from bulk sediments processed by acid dissolution, for crushed carbon spherules, and for ice by Kinzie et al. (2014) and those previously published by several of its coauthors in other studies (e.g., Kennett et al., 2009a,b; Kurbatov et al., 2010; Israde-Alcántara et al., 2012a), as well as by a coauthor of Kennett et al. (2009a) (Bement et al., 2014) are all based on TEM studies. However, the TEM measurements by Kinzie et al. (2014) and others using similar methodologies are not of nanodiamonds, but are of “rounded particles.” More importantly, the many experiment difficulties inherent in using TEM to measure nanodiamond abundances lead to large unconstrained error, rendering this approach infeasible. We find there is no evidence to suggest a unique spike in the nanodiamond concentration at the YDB layer. The distribution of nanodiamonds in Pleistocene to Holocene sediments (and in ice, if present, which has yet to be confirmed by independent groups, see Boslough, 2013b) remains unclear. Therefore, considering conclusions 1-4, the reports of nanodiamonds in Late Pleistocene sediments cannot provide evidence for an YD impact.

Various criticisms have been raised on both sides of the debate regarding the identification, analysis, and interpretation of proposed YD impact markers. To advance this field, it would be advantageous for working groups to develop and standardize techniques for collection, splitting/distribution, and analysis of specimens
from key YDB sites, in order to try to reconcile conflicting results and prevent the use of inappropriate approaches that lead to erroneous results. To perform the highly challenging measurement of nanodiamond abundance in sediments/ice, methods other than TEM will need to be explored and developed. Any method must be tested/calibrated against control specimens (sediments/ice initially devoid of nanodiamonds, that are spiked with measured ppb amounts of nanodiamonds). Furthermore, unlike previous abundance measurements, future measurements must be conducted as blind studies to preclude unconscious bias.
Acknowledgements. This research was partially supported by the McDonnell Center for the Space Sciences and Institute for Material Science and Engineering (TLD) as well as grants from the National Geographic Society (8321-07) to NP and from the National Science Foundation (EAR-0746015) to NP and RSA. ACS undertook the completion of this research while in receipt of a Leverhulme Emeritus Fellowship (EM-2012-054), which is gratefully acknowledged. We thank Ph. Claeys (Vrije Universiteit Brussel) for providing YDB sediment specimens from Lommel Belgium. We thank M. Watanabe (Tokyo Metropolitan University, Graduate School of Urban Environmental Sciences) for valuable discussions. We thank the numerous staff at the Channel Islands. ACS thanks Sharon Gibbons and Neil Holloway for technical support. We thank reviewers C. Koeberl and B. Alloway for valuable comments.

Abbreviations: DF, dark field; BF, bright field; EDXS, energy dispersive X-ray spectroscopy; EELS, electron energy loss spectroscopy; FFT, fast Fourier transformation; GIF, Gatan imaging filter; NMR, nuclear magnetic resonance; ppb, parts per billion; ppm, parts per million; SDD, silicon drifted detector; HR-TEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy; TEM, transmission electron microscopy; YD, Younger Dryas; YDB, Younger Dryas Boundary
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THE NANODIAMOND EVIDENCE


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Figure Captions

Figure 1: (a) A HR-TEM lattice image of a nanocrystal from the Allende meteorite acid-dissolution residue. The nanocrystal exhibits a homoeptixial interface between two crystal lattices that is consistent with the (b) 3C cubic diamond and 2H lonsdaleite atomic structure (figure adapted from Daulton et al., 1996). The grain displays one domain with close packed tetrahedral planes stacked in the \((A^b)(B^c)(C^a)\)... sequence defining the 3C structure and a second domain stacked in the \((A^b)(B^a)\)... sequence defining the 2H structure. Through-focus HR-TEM imaging (not shown) is consistent with these atomic structures. Furthermore, since this grain exhibits a homoeptixial interface of two crystal structures, the possible pairs of candidate phases that comprise the grain are significantly limited. (c) Atomic models of the six unique (fundamental) bilayer planes \((A^b, A^c, B^a, B^c, C^a, and C^b)\) in diamond (top), that comprise stacked tetrahedral planes (depicted normal to stacking direction shown at bottom). The two basic stacking arrangements, \((X^a)(Y^a)\) and \((X^b)(Y^b)\) where \(X, Y,\) and \(Z\) are all different, form planes of vertex-sharing antiparallel and parallel tetrahedra, respectively.

Figure 2: HR-TEM images of well-ordered (a) [01\(\bar{1}\)] zone of cubic diamond and (b) [010] zone of lonsdaleite from products of thermobaric high-pressure, high-temperature treatment of graphite. (c) Calculated HR-TEM image of lonsdaleite for [010] zone axis (figure adapted from Kulnitskiy et al., 2013). (d) HR-TEM image of diamond grown on (100)-oriented Si held at 600 or 700\(^{\circ}\) C by bombardment with 80 or 200 eV ions from a \((\text{CH}_4\text{ or C}_2\text{H}_2)/\text{Ar}/\text{H}_2\)-fed Kaufmann source (figure adapted from Lifshitz et al., 2001). (e) Schematic atomic model of lonsdaleite projected along the [010] zone axis.

Figure 3: Shown in top row Fig. 6 part b and part d of Kurbatov et al. (2010); its figure caption states, “Lonsdaleite analyses. (b) HR-TEM image showing characteristic lonsdaleite lattice spacings. (d) Fast Fourier transform (FFT) of lonsdaleite ND crystal. All values (Miller indices) are consistent with each other and with the published lattice spacings for lonsdaleite as shown in Table 3. Sample numbers, as referenced in Table 2, are shown in the lower left of
each image.” Shown at bottom is a schematic of the atomic structure of lonsdaleite. In diamond, C atoms covalently bond to four other C atoms in a tetrahedral geometry. The \{002\} planes in the lonsdaleite structure contain the base of the C tetrahedra that are stacked in the structure. The set of \{002\} planes are oriented edge-on only in \([hk0]\) zone axes projections, and high-resolution lattice images of \([hk0]\) zone axes display only one set of \{002\} planes, contrary to the nanocrystal shown by Kurbatov et al. (2010).

Figure 4: Shown in top row is Fig. S2 (part B) of Kennett et al. (2009b); its figure caption states, “(B) cluster of lonsdaleite crystals and associated diffraction pattern from 4.59-4.64m(AC#348).” We modified the diffraction pattern from the original published by Kennett et al. (2009b) by inverting its contrast to aid in visual clarity and by superimposing additional annotations on the pattern. In right of top row, ovals were superimposed to demonstrate the azimuthal asymmetry of the diffraction pattern and the presence of additional partial diffraction rings. Half circles were superimposed to illustrate the predicted reflections for lonsdaleite. The scale of the diffraction pattern was calibrated assuming that the ring labeled (110) by Kennett et al. (2009b) corresponds to the (110) reflection of lonsdaleite. Notice, there are many missing lonsdaleite reflections. Left of bottom row is Fig. 15 (part B) of Kinzie et al. (2014); its figure caption states, “Younger Dryas Boundary lonsdaleite-like crystal”. This is the same grain shown in Kennett et al. (2009b). Shown at right of the bottom row is the diffraction pattern of Kennett et al. (2009b) with half circles superimposed to illustrate the predicted reflections for a homogeneous mixture of graphene and graphane where the <100> \(d\)-spacing in graphane is contracted by a factor of 1.054 from that of graphene (Daulton et al., 2010). The scale of the diffraction pattern was calibrated assuming the ring labeled (110) by Kennett et al. (2009b) corresponds to the (100) reflection of graphene. Consistent with this diffraction pattern, disordered graphite could be present and predominantly oriented with its [001] crystallographic axis in the electron beam direction. As such, the high-resolution lattice image published for this grain (see Fig. 16, Kinzie et al., 2014) is consistent with a [001] zone axis of graphitic/graphene structure. Similarly, the diffraction pattern identified as lonsdaleite by Redmond and Tankersley (2011) is
consistent with [001] graphite.

Figure 5: Typical electron diffraction pattern from aggregates of polycrystalline graphene/graphane recovered from sediments exhibits a) azimuthally asymmetric electron diffraction rings indicative of texturing of two phases (Daulton et al., 2010). Different regions within the same aggregate exhibit diffraction rings from b) only graphene (solid triangles), c) both graphene and graphane, or d) only graphane (open triangles). To aid in visual clarity, the diffraction patterns are displayed in reverse contrast.

Figure 6: SEM images of carbon spherules from Arlington Canyon YDB sediments (AC-003): a) Fig. 1 (part A), b) Fig. S6 (part E), and c) Fig. S6 (part F) of Kennett et al. (2009b). Their figure captions state, “SEM images represent carbon spherules (A)” and “(E) [relabeled B here] Bisected carbon spherule showing typical internal reticulate (honeycomb) structure and thin, nonreticulate crust. (F) [relabeled C here] Close-up of carbon spherule interior shown in E [relabeled B here] with well-organized reticulate (honeycomb) structure and thin, nonreticulate crust.” d) Light microscope image of fungal sclerotia charred at 350°C for 5 mins. e) SEM image of broken fungal sclerotia from charcoal residue of a low-temperature surface fire, Thursley, Common, Surrey, England. f) SEM image of broken fungal sclerotia charred at 350°C for 5 mins showing mesh-like internal structure comprising fused fungal hyphae.

Figure 7: Left column is Fig. 5 of the supplemental materials of Israde-Alcántara et al. (2012a). Their figure caption states, “CARBON SPHERULES from the 2.8-m layer. A) The upper inset show a whole CSp in reflected light. B) SEM image of a crushed CSp; C) Photomicrograph of the same crushed CSp. D) Closeup of bottom of crushed CSp, illustrating the lack of filamentous texture, as typical of fungal sclerotia, and indicating that these objects are not sclerotia, as speculated by Scott et al. (2010).” Right column or panel e) SEM image of the interior of cross-sectioned C. geophilum sclerotia displaying a hollow center with smooth interior walls (image courtesy of M. Watanabe).
Figure 8: a) SEM image of the interior of cross-sectioned *C. geophilum* sclerotia displaying micron-sized holes (septal pores), which are morphological features characteristic of sclerotia (image courtesy of M. Watanabe). b) SEM image of the interior of a carbon spherule from Arlington Canyon YDB sediments (AC-003) from Fig. S6 (part F) of Kennett *et al.* (2009b). The originally published image (shown in Fig. 6c of this paper with a modified panel label) has been cropped with circles overlaid to denote several of the submicron-sized holes present in the cell-like walls. Their figure caption states, “(F) Close-up of carbon spherule interior shown in E with well-organized reticulate (honeycomb) structure and thin, nonreticulate crust.” The presence of the holes provides a conclusive identification of the spherule as a sclerotium (private communication M. Watanabe). Both images are reproduced at the same spatial scale.

Figure 9: High-resolution TEM lattice images (top row) and bright-field (BF) TEM image of nanocrystals embedded within amorphous fragments (middle row) obtained from finely crushed carbon spherules collected from Arlington Canyon YDB sediments (AC-003). Many of the nanocrystals exhibit twining, particularly $\Sigma=3$ twin boundaries or occasionally $\Sigma=9$ twin boundaries when successive $\Sigma=3$ twin domains impinge on one another (e.g., see Luyten *et al.*, 1992; Daulton *et al.*, 2003), characteristic of face centered cubic structures. Shown in the bottom row are Figure 13 (part A) and Figure 6 (part C) from Kinzie *et al.* (2014); their respective figure captions states, “carbon spherules from Gainey, Michigan (Younger Dryas Boundary [YDB]: 3933 ppb at 30 cm below surface [cmbs])” and “nanodiamonds (NDs) in carbon spherules (CS) . . . n-Diamond from Topper, South Carolina (YDB: 108 ppb at 60 cmbs).”

Figure 10: Representative diffraction pattern from amorphous grains obtained from finely crushed carbon spherules collected from Arlington Canyon YDB sediments (AC-003) that contain nanocrystals (see, Fig. 6, middle row). The diffraction pattern is displayed in reversed contrast and three different electron exposures are superimposed to cover the large dynamic range of the Bragg
intensities. The diffraction lines of cubic diamond (along with the kinematically forbidden diamond reflections denoted by *) are shown.

Figure 11: Top: Bright-field (BF) and Dark-field (DF) STEM images of nanocrystals embedded within an amorphous grain from finely crushed carbon spherules collected from Arlington Canyon YDB sediments (AC-003). Below are STEM Energy Dispersive X-ray Spectroscopy (EDXS) and Electron Energy Loss Spectroscopy (EELS) maps (in dashed rectangle) of relative elemental composition normalized to the sum of all measured elements. Areas in the maps that exhibit a deficit of C and Fe correlate to areas that show an excess of Cu. For nanocrystals on the surface of the amorphous C-rich and Fe-containing grain, this is a result of the normalization of the compositions. For nanocrystals within the grain, this results from the nanoparticles displacing the amorphous C-rich and Fe-containing matrix. The 256 grey scale look-up table (LUT) is linearly mapped between the minimum and maximum element composition for each map. (The elemental maps are published online in false color with a dynamic range of 1786 colors.) As described in the text, the amorphous matrix had an elemental composition, as determined by EDXS, of 82.49 at.% (70.56 wt.%) C, 13.40 at.% (15.27 wt.%) O, 2.87 at.% (11.41 wt.%) Fe, 0.39 at.% (0.89 wt.%) S, 0.35 at.% (0.70 wt.%) Si, 0.17 at.% (0.47 wt.%) K, 0.12 at.% (0.21 wt.%) Mg, 0.10 at.% (0.29 wt.%) Ca, 0.05 at.% (0.11 wt.%) P, 0.05 at.% (0.10 wt.%) Al.

Figure 12: Top: Bright-field (BF) image of nanocrystals from finely crushed carbon spherules collected from Arlington Canyon YDB sediments (AC-003). Below are STEM Energy Dispersive X-ray Spectroscopy (EDXS) maps of relative elemental composition normalized to the sum of C, O, Cu, and S contributions. Carbon and O is associated with the support film and deficits in those elements occur in the maps where the nanocrystals are located due to the normalization of the elemental compositions to the sum of C, O, Cu, and S contributions. If the nanocrystals contained C, excesses in C would be observed at the locations of the nanocrystals. The 256 grey scale look-up table (LUT) is linearly mapped between the minimum and maximum element composition for each map. (The elemental maps are published online in false
color with a dynamic range of 1786 colors.)
### Table 1: Lonsdaleite Bragg Reflections

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† lattice parameters: $a = 2.52$ Å and $c = 4.12$ Å.
Table 2: Comparison of Cu and Cu$_2$O Bragg Reflections to those of “n-diamond” and “i-carbon”.

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† lattice parameter: $a = 3.6149$ Å
‡ lattice parameter: $a = 4.2696$ Å
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12