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Did Nanodiamonds Rain from the Sky as Woolly Mammoths Fell in their Tracks Across North America 12,900 Years Ago?

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The Younger Dryas (YD) Impact Hypothesis proposes that the Late Pleistocene megafauna extinctions, the YD stadial (a period at the end of the last glaciation marked by rapid climate change at its onset), and abrupt continent-wide disappearance of Clovis Paleoindian lithic technology from the sedimentary record were caused by a major cometary or meteoritic impact in North America roughly 12,900 years ago. While there are no known impact structures in North America that date to the onset of the YD stadial, physical evidence of one or more impact/bolide events is argued present in a stratigraphic horizon that is inferred to date to the Bølling-Ållerod/YD boundary (YDB) and span several continents (North America, South America, Greenland Ice Sheet, Europe, and the Middle East). While many of the proposed impact markers have been abandoned or rejected [1], reports of elevated concentrations of nanometer-sized diamonds, in particular the rare 2H polytype of diamond, lonsdaleite, in YDB sediments and Greenland ice, continue to be presented as the strongest evidence for an impact [2-8].

Nanodiamonds are reported to occur in YDB sediments and in millimeter-scale carbon forms (variously termed, 'glass-like', 'spherules', and 'elongates') in those sediments. The carbon forms are proposed to be products of the impact [2,7] and/or the resulting continent-wide wildfires [2,4]. Carbon spherules and their fragments were isolated from the same YDB sediments at Arlington Canyon, Santa Rosa Island, CA that are reported to host nanodiamond-containing C spherules [4]. Three different specimen sets were separately crushed between sapphire discs: (i) five spherules/fragments from SRI 09-28A; (ii) eight spherules/fragments from AC-003; and (iii) 13 acid-washed spherules/fragments from AC-003; see [9]. Carbon spherules from sediments predating the YD and from modern forest fire soils were also separately crushed; see [10]. In addition, YDB sediment from Lommel, Belgium was processed by acid-dissolution; see [9]. All specimens were characterized by transmission electron microscopy.

Diamond is chemically inert, highly resistant to weathering, 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 to distant alluvial deposits and sediments that bear little resemblance to the diamond source rocks. Thus, the mere presence of nano/microdiamonds in sediments is not an indicator of impact processes. However, nanodiamonds concentrated at the YDB (and their complete absence immediately above and below this level), as reported [3-8], would suggest a unique event occurred at the time the sediments were deposited. In regard to the nature of the event, much emphasis has been placed on the reported presence of lonsdaleite in YDB sediments because it has been traditionally associated with shock processing [4-7]. We found that polycrystalline aggregates of graphene and graphane occur in C spherules throughout sediments (including the YDB), and were misidentified as lonsdaleite in prior YDB studies (Fig. 1). Further, we determined that measurements of a nanodiamond abundance spike at the YDB reported by [7], and other impact proponents that used similar techniques, are critically flawed and are not credible [9]. Note, that the majority of the reported YDB nanodiamonds are not diamond, but rather are a controversial modified form of diamond termed 'n-diamond' [3-8]. Controversial 'i-carbon' is also reported at the YDB of many sites [6,7]. While neither are diamond polytypes, impact proponents describe them as nanodiamonds [3-8]. In YDB sediments, 'n-diamonds' are usually reported at higher abundances than diamond [6,7]. In fact at 14 out of 24 YDB sites studied, 'n-diamonds' but not diamonds are reported [7]. We did not observe diamond (or C phases consistent with 'n-diamond' and 'i-carbon') in the YDB sediments that we studied. Rather, we observed Cu (Fig. 1) and CuO_2 nanocrystals, which have identical diffraction lines as ascribed to 'n-diamonds' and 'i-carbon', respectively, with plane spacing differing by ≈1%. Thus, we find no nanodiamond-based evidence to support a YD impact. Our results are corroborated by recent studies of sediments at Bull Creek, Oklahoma [11]. At Bull Creek, YDB nanodiamonds were initially reported at a concentration of 102 p.p.b. [3]. Later, Bement *et al.* [8] reported a three order-of-magnitude larger 190 p.p.m. spike of nanodiamonds at the Bull Creek YDB, which is higher than that reported at all other YDB sites studied [7]. Yet, recent attempts by the Bement group to reproduce the observation of nanodiamonds at Bull Creek – in the exact same acid-dissolution isolate of YDB sediment previously reported to have the largest nanodiamond abundance of all YDB sites [8] – were unsuccessful [11].

References:
[1] Pinter N. *et al.*, Earth-Science Reviews **106** (2011), pp. 247-264.
[2] Firestone R. B. *et al.*, Proc. of the Nat. Acad. of Sci. USA **104** (2007), pp. 16016-16021.
[3] Kennett D. J. *et al.*, Science **323** (2009), p. 94.
[4] Kennett D. J. *et al.*, Proc. of the Nat. Acad. of Sci. USA **106** (2009), pp. 12623-12628.
[5] Kurbatov A. V. *et al.*, Journal of Glaciology **56** (2010), pp. 749-759.
[6] Israde-Alcantara I. *et al.*, Proc. of the Nat. Acad. of Sci. USA **109** (2012), pp. E738-E747.
[7] Kinzie C. R. *et al.*, Journal of Geology **122** (2014), pp. 475-505.
[8] Bement L. C. *et al.*, Proc. of the Nat. Acad. of Sci. USA **111** (2014), pp. 1726-1731.
[9] Daulton T. L. *et al.*, Journal of Quaternary Science **32** (2017), pp. 7-34.
[10] Daulton T. L. *et al.*, Proc. of the Nat. Acad. of Sci. USA **107** (2010), pp. 16043-16047.
[11] Sexton M. R., MS Thesis, University of Oklahoma (2016).

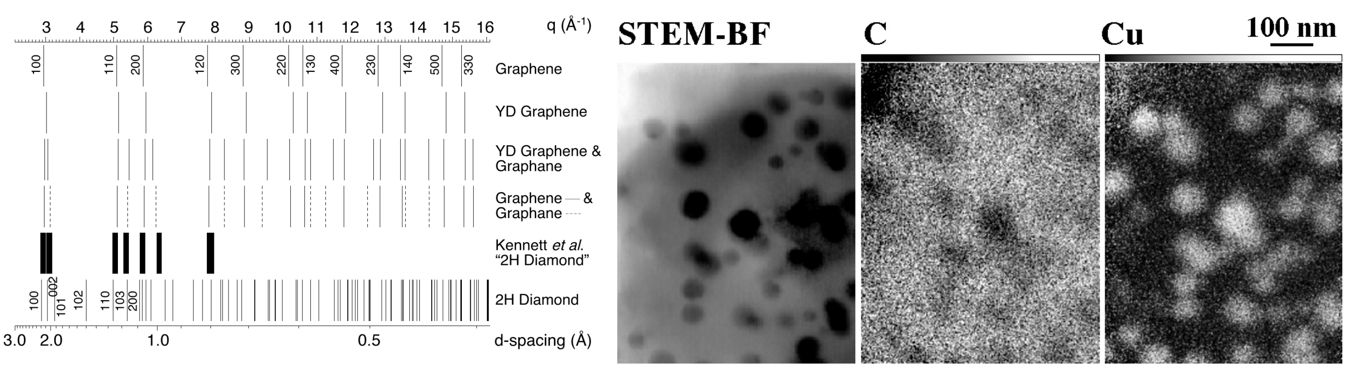

Figure 1. Left: Predicted electron diffraction of 2H diamond (with both general and special extinctions), graphene, and graphene/graphane mixture. Shown also are those from graphene and graphene/graphane aggregates in YDB carbon spherules as well as those identified as 2H diamond (line widths represent error in our measurement of diffraction patterns reported in [3]), all from Santa Rosa Island, CA. Right: Native Cu nanocrystals in YDB carbon spherules (i.e., sclerotia [9]) from Santa Rosa Island, CA (gray scale LUT of STEM-EDXS elemental maps: black = minimum, white = maximum).

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