

# Nanodiamonds in the Younger Dryas Boundary Sediment Layer

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The Younger Dryas (YD) was a 1300-year-long interval during which deglacial warming in the Northern Hemisphere was interrupted by a return to cold conditions. Its cause remains unclear. Recently, it was hypothesized that multiple cometary airbursts barraged North America at the onset of the YD at  $\approx 12.9 \pm 0.1$  thousand calendar years before the present (cal. yr B.P.) (1), triggering massive environmental changes, abrupt Pleistocene megafaunal extinctions, and the disappearance of the Clovis cultural assemblage (2). The YD boundary (YDB) is a distinctive layer containing above-background amounts of magnetic microspherules, iridium, and other impact proxies found with evidence for intense wildfire (2). It often occurs immediately beneath an organic-rich layer reported in unconsolidated terrestrial deposits across North America (3). A YDB peak in the abundance of magnetic microspherules has been independently confirmed at Murray Springs, Arizona (3). Because traditional impact markers, such as high-pressure-modified (shocked) minerals, breccias, tektites, and visible craters appear to be absent from 12.9-thousand-cal.-yr-B.P. North American sediments, one explanation for the observed evidence is an impact by a previously fragmented body, for example, Comet LINEAR (4), that produced a cluster of widespread air shocks, each analogous to the Tunguska impact in 1908 (5).

We report that nanometer-sized impact diamonds are abundant at multiple locations across North America in YDB sediments dating to  $12.9 \pm 0.1$  thousand cal. yr B.P. Nanodiamonds (NDs) are associated with known impacts, during which they may arrive inside the impactor or form through shock metamorphism (6). We found subrounded, spherical, and octahedral crystallites, ranging in size from 2 to 300 nm, distributed within carbon spherules, suggesting crystallization from the amorphous carbon matrix. Selected area electron diffraction patterns (SADPs) display d-spacings typical of cubic diamonds (2.06, 1.26, and 1.08 Å) and often produce additional “forbidden” reflections indexed at 1.78, 1.04, and 0.796 Å, consistent with

the n-diamond polymorph (7) known to occur in meteorites (8). Diamonds within carbon spherules peaked in the YDB at glacial Lake Hind, MB, Canada (Fig. 1A) and other localities across North

America (Fig. 1 and fig. S1), estimated to range from  $\approx 10$  to 3700 parts per billion (ppb) by weight, amounting to  $>1$  billion diamonds per  $\text{cm}^3$ , with the highest concentrations overlapping the range for the Cretaceous-Tertiary impact (6).

We also have found NDs outside carbon spherules in bulk sediments at Murray Springs, Arizona, and Bull Creek, Oklahoma. Transmission electron microscopy (TEM) images and SADPs indicate that n-diamonds have abundances ranging from  $\approx 100$  to 200 ppb in YDB bulk sediments at both localities. In addition, we recovered typical cubic diamonds in samples from Bull Creek, Oklahoma, which are more angular and range in size from 1 to 50 nm. NDs were not detected above or below the YDB layer at any site tested.

Cubic diamonds form under high temperature-pressure regimes, whereas n-diamonds crystallize under lower temperature-pressure conditions (7). Both form outside the range of Earth’s surficial processes but may crystallize during cosmic impacts (6). These data support the hypothesis that a swarm of comets or carbonaceous chondrites produced multiple air shocks and possible surface impacts at  $\approx 12.9 \pm 0.1$  thousand cal. yr B.P. (2). Such a rare event would have had abrupt environmental consequences and severe repercussions for plants, animals, and humans in North America.

## References and Notes

- All ages expressed as thousands of calendar years before present. Atmospheric concentrations of radiocarbon are known to have varied unevenly across past millennia; accordingly, 10,900 radiocarbon years before present has been recalibrated and is equivalent to  $\approx 12.9$  thousand cal. yr B.P.
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## Supporting Online Material

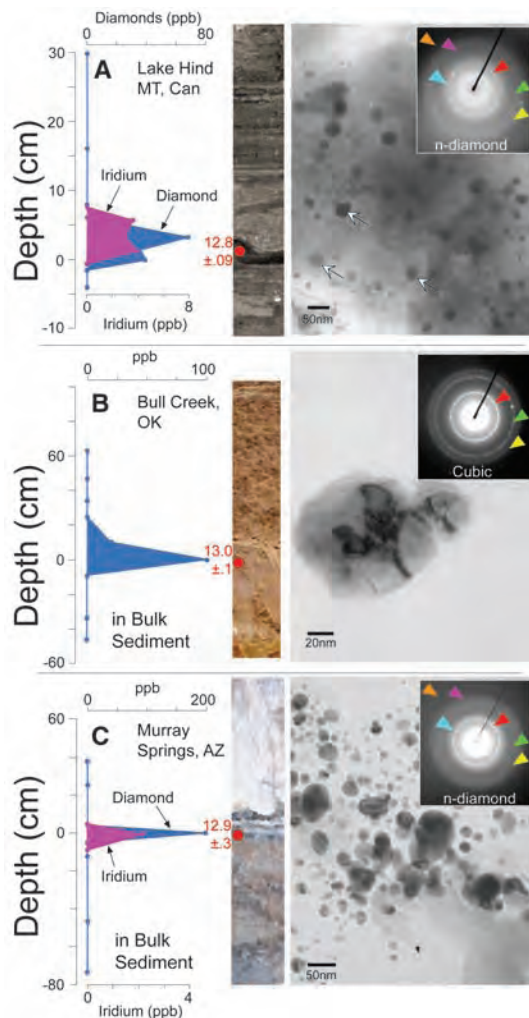
www.sciencemag.org/cgi/content/full/323/5910/94/DC1

Fig. S1

Reference

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**Fig. 1.** TEM photomicrographs and SADPs of YDB NDs from (A) Lake Hind, MB, Canada; (B) Bull Creek, Oklahoma; and (C) Murray Springs, Arizona. Stratigraphic profiles on left show NDs only in the YDB and peaking with above-background iridium amounts at Lake Hind and Murray Springs (1). Red dots on stratigraphic profiles (center) show age estimates based on available calibrated radiocarbon dates (thousand cal. yr B.P.). Arrows on the photomicrograph from Lake Hind highlight examples of diamonds within the amorphous carbon matrix of a spherule. Color-coded arrows on SADPs (upper right corners) are indexed d-spacings (Å): red indicates 2.06; blue, 1.78; green, 1.26; yellow, 1.08; purple, 1.04; and orange, 0.796.

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SUPPORTING ONLINE MATERIAL:

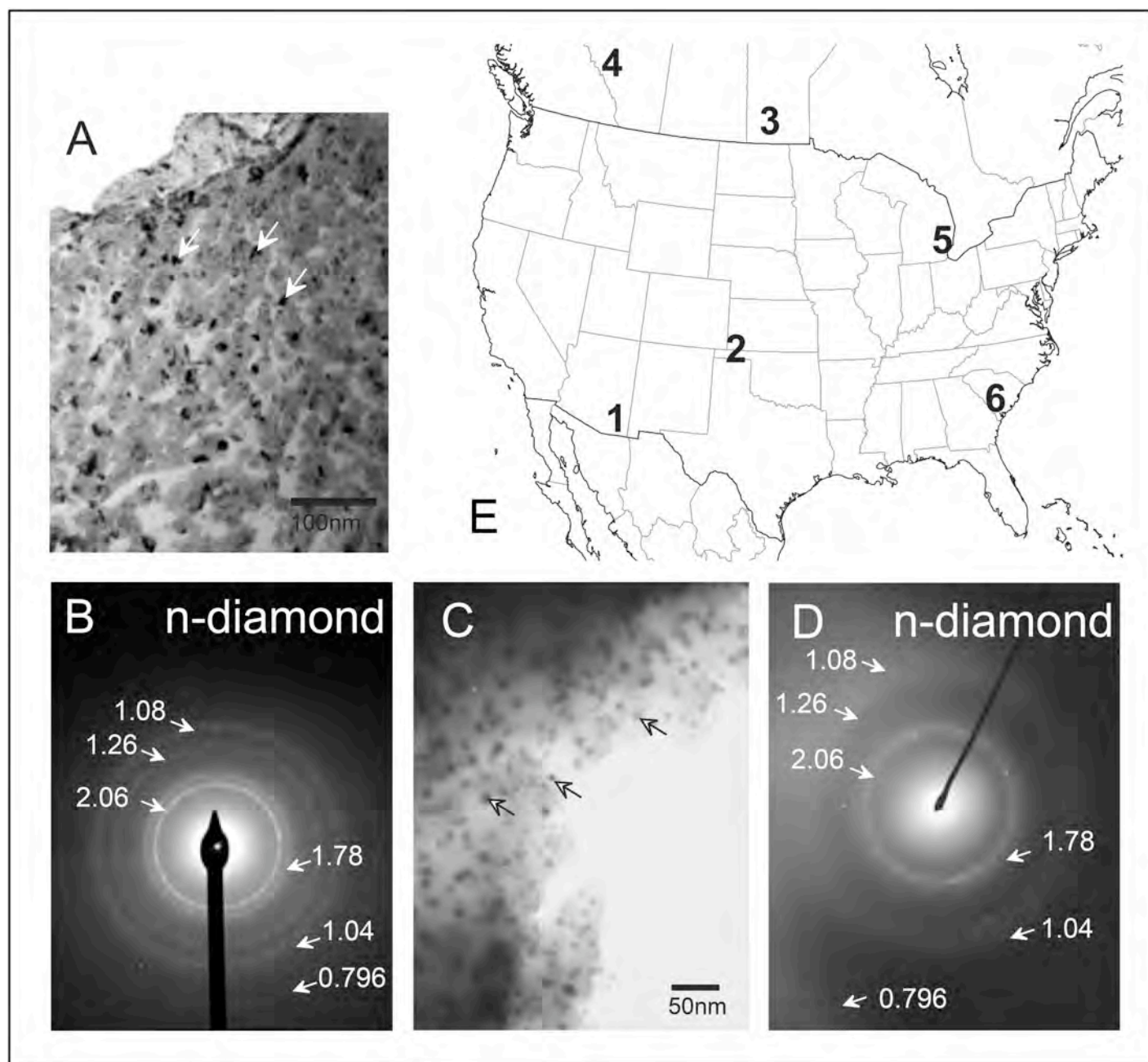


Fig. S1. Map showing currently known distribution of nanodiamonds in YDB sediments across North America: (1) Murray Springs, AZ: 200 ppb; (2) Bull Creek, OK: 100 ppb; (3) Lake Hind, MB, Canada: 70 ppb; (4) Chobot, AB, Canada: 10 ppb; (5) Gainey, MI: 3700 ppb; (6) Topper, SC: 108 ppb. In the TEM photomicrographs, diamonds inside carbon spherules are paired with associated SADPs from the Chobot (A and B) and Topper sites (C and D). Arrows on photomicrographs highlight examples of diamonds within the amorphous carbon matrices of spherules. Arrows on SADPs are indexed d-spacings (Å).

Established protocols were used to isolate diamonds from sediments (*SI*), except for eliminating use of perchloric and phosphoric acids, which were found to deplete n-diamonds. North American map by Jake Bartruff.

Reference:

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