#### LETTER

# Reply to Blaauw et al., Boslough, Daulton, Gill et al., and Hardiman et al.: Younger Dryas impact proxies in Lake Cuitzeo, Mexico

#### Answer to Blaauw et al. (I.I.-A., J.L.B., R.B.F., J.P.K., A.W.)

Blaauw et al. (1) take issue with our age-depth model for the Cuitzeo core. They state that no offset for our accelerator mass spectrometry (AMS) <sup>14</sup>C dates was quantified, that our identification of the Cieneguillas tephra is doubtful, that we used an outdated calibration model, and they object to our rejection of six AMS dates in the anomalous zone.

Regarding the offset question, dissolved  $HCO_3$  in modern Lake Cuitzeo water precipitated in the laboratory as  $CaCO_3$ yielded a modern age (US Geological Service laboratory #WW 5645), so the offset is deemed to be zero.

Regarding the Cieneguillas tephra, it is the only Late Pleistocene tephra in the area (2, 3), and Guangoche Volcano, the source of the tephra, is located only approximately 30 km to the east of the lake. The tephra occurs roughly where predicted in the section, and its identification is confirmed by chemical composition, as shown in the accompanying triangular diagram (Fig. 1).

Four AMS dates from the uppermost 2 m are linear, with depth on a trend that projects from zero age for the lake bed at 0.6 m (0.6 m of fill) to 31.5 ka at the Cieneguillas tephra (figure 1 in ref. 4). Additional AMS dates below the tephra from 5 to 10 m plot smoothly on this linear trend. Only the six samples between these two levels yielded anomalous radiocarbon ages that are strikingly older than the linear trend, producing an 18-ka AMS reversal that is too large to reasonably be accepted, as Blaauw et al. propose. It is common practice in limnology to reject such dates (4). Additionally, a careful reading of our article shows that the organic matter in this interval is not normal lacustrine organic matter and is not extractable by conventional methods (4). Pyrolysis analysis (Rock/Eval, table S3 in ref. 4) suggests that much of the total organic carbon (TOC) at 2.75 m is allocthonous, unreactive carbon, whose nature and source remains enigmatic. Regardless of origin, the apparent linear decrease of ages up section in this interval is deemed to be a dilution curve caused by mixing of unreactive carbon with normal lacustrine organic matter. Consequently, it is reasonable to reject the six dates in this interval on the basis of the data. We consider that fitting all of the dates to a cubic spline, as Blaauw et al. suggest, is illogical.

Additionally, Blaauw et al. overstate the importance of our choice of AMS calibration curves. Comparison of the calibrations of  $10.9 \pm 0.1$  <sup>14</sup>C ka using IntCal09, IntCal04, and CalPal07 yields a maximum difference of <100 y, which is approximately equal to the AMS uncertainties. Regarding our location of the YD onset, it is common practice among limnologists to use secondary data to support an AMS-based age–depth model. We compared the pollen, diatom, and/or geochemical records from

Lake Cuitzeo with the biostratigraphic records from three regional lakes and the Cariaco Basin, as published by other authors, who also used biostratigraphy to constrain their age–depth models. Those four cores display a distinctive pattern of warming–cooling–warming, in which the cooling period represents the YD. For the 27-m Lake Cuitzeo core, only one interval of the core matches that pattern, as explained in our article. Thus, the proposal of Blaauw et al. to shift the age–depth model 2,000 y older is completely inconsistent with available regional biostratigraphic records.

## Answer to Boslough (J.L.B., P.S.D., T.E.B., R.B.F., A.W.)

We are puzzled by Dr. Boslough's comments (5). He complains that we have modified the hypothesis proposed in earlier papers, even though it is the nature of good scientific inquiry to modify hypotheses as they are tested with new data.

We proposed that the impactor striking near Cuitzeo was "greater than several hundred meters in diameter" (4), which Boslough erroneously took to mean "*exactly* several hundred meters." Additionally, we did not suggest that the Cuitzeo impactor was the only object impacting Earth. Boslough ignores the research of William Napier (6), who demonstrated that the Younger Dryas boundary (YDB) hypothesis is consistent with Earth's collision with the Taurid Complex debris field, which could have produced multiple airbursts capable of continentwide environmental and biotic degradation (7).

In their article on airbursts, Boslough and Crawford (8) assumed impacts were axisymmetric, arriving perpendicular to Earth's surface, whereas most scientists assume a  $45^{\circ}$  impact angle, and the Cretaceous-Paleogene (KPg) impact is postulated to have occurred at a 20–30° angle. We hypothesized that the modest-sized objects responsible for the inferred airshocks entered the Earth's atmosphere at a shallow angle. Boslough and Crawford's calculations thus do not prove that our scenario would have resulted in a crater.

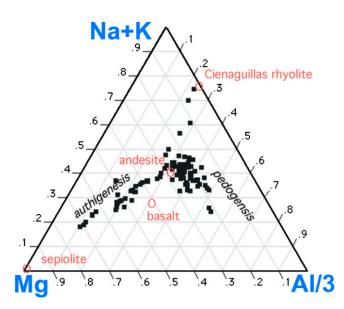
### Answer to Daulton (J.L.B., P.S.D., T.E.B., R.B.F., J.P.K., A.W.)

Daulton (9) questions the value of diamonds as an impact marker, mentions that no one has confirmed the presence of our lonsdaleite, and challenges our identification of lonsdaleite. First, we point out that Daulton makes several critical misstatements. Daulton asserts that when Tian et al. (10) found YDB nanodiamonds in Belgium, they did not examine sediment above or below the YDB, where nanodiamonds presumably would be found. Actually, Tian et al. wrote: "No such [diamondrich] particles are found in the overlying silt and clay or in the underlying fine sands." Daulton also ignores evidence that nanodiamonds are only found in the YDB at six documented North American sites, and not above or below (11). To our knowledge, no one has reported significant peak abundances of cubic nanodiamonds in any subsurface levels of Late Quaternary

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**Fig. 1.** Triangular diagram of Na+K, Mg, and Al content of bulk sediment samples from the entire 27-m section of the Lake Cuitzeo core. The sample that plots adjacent to the Cieneguillas rhyolite is from level 4.5–4.7 m in the core, establishing the correlation. Most sediments plot in andesitic/pedogenic region, reflecting the general andesitic regolith of the basin. The linear grouping of samples between the latter and the Cieneguillas rhyolite represent mixing between the two as the tephra that was initially deposited throughout the basin was subsequently washed into the lake. Data from ref. 3.

sediment other than the YDB and associated layers (e.g., due to reworking).

Daulton claims that the nanodiamonds found in forest soil in Germany by Rosler et al.\* cannot be impact-related. To the contrary, those authors stated that they "favor an impact related origin." Alternately, it is possible that surface nanodiamonds in modern European sediments were produced from detonation of WWI and WWII explosives, as shown by one of us (P.S.D.) who isolated pure detonation nanodiamonds in soil from the high-explosive test site of SRI International.

Daulton states that the "value of cubic diamonds as impact markers is suspect" and that lonsdaleite "in sediments can suggest (but not necessarily prove) shock processing of materials" by cosmic impact. We agree with these generalities, but that in no way precludes impacts as cause, as is documented (12). Some researchers have speculated that the YDB nanodiamonds were formed in wildfires (10), although there is no such published evidence. Additionally, the KPg impact event produced nanodiamonds that are morphologically indistinguishable from those in the YDB (13), suggesting a similar origin. Independent researchers have confirmed the identification of cubic nanodiamonds, settling the question of their presence in the YDB, as accepted by Daulton. We agree that the origin of YDB diamonds is uncertain, but considering their stratigraphy and association with other impact markers, a cosmic impact is the most likely source.

Daulton questions why others cannot independently confirm the presence of lonsdaleite. It is important to note that at Lake Cuitzeo we found lonsdaleite and other diamonds in acidresistant residue from bulk sediment. So far, no independent groups have used our diamond extraction technique for bulk sediment, which is derived from the proven protocol commonly used for extracting diamonds from meteorites. For example, Tian et al. (10) found YDB cubic diamonds and no lonsdaleite inside pieces of amorphous carbon but failed to examine the entire bulk sediment. In addition, Daulton et al. (14) failed to find cubic diamonds and lonsdaleite at Murray Springs, Arizona and claimed to refute previous results of nanodiamonds in bulk sediment (11), but they only examined charcoal, in which no one has reported finding YDB nanodiamonds. It is no surprise that researchers cannot find lonsdaleite if they look in the incorrect material and/or use the incorrect protocol.

Daulton's claims about the misidentification of lonsdaleite apply to different articles, each with a different mix of diamond researchers (11, 13). His complaints should properly be addressed to those articles. However, Daulton gives qualified acceptance to the lonsdaleite from Lake Cuitzeo.

For the nanodiamonds in the YDB and the KPg boundary, the problem is finding a mechanism for producing them. We agree with Daulton that formation of YDB lonsdaleite is unlikely to result from the solid–solid transition of graphite. Formation of diamonds by carbon vapor deposition (CVD) has been proposed as a mechanism (10), but that process requires a substrate. We now realize that, in the initial stages of condensation from a high-temperature hypoxic vapor, there would be a negligible energy difference between graphitic nuclei and diamond-like nuclei (including cubic diamonds, lonsdaleite, and possibly n- and i-forms of diamonds). Once graphite is nucleated, it continues to grow, explaining the presence of nanodiamonds at the center of carbon onions (e.g., graphite), consistent with Daulton's previous work (15).

## Answer to Gill et al. (I.-I.A., J.L.B., G.D.-V., R.B.F., A.W.)

This group's main point (16) seems to be that they prefer another interpretation to ours. They challenge our purported claim that the Lake Cuitzeo black mat was caused solely by fire. However, they misread our article, in which we clearly state that carbon in the black mat is "enigmatic and not the normal plantderived kerogenous organic matter" (4), as would be expected in wildfires. In their complaint about incomparable data among sites, they misunderstood our stated purpose, which is to compare the response of various proxies (e.g., charcoal and pollen) to climatic change before, during, and after the YD cooling episode. We did not state that these data are comparable to each other, but rather that they show the same trend with respect to climate. Because comparable lake core data spanning the YD are lacking in central Mexico, sometimes owing to hiatuses, we maintain it is reasonable to compare different proxies at regional and interhemispheric sites that display a similar climate record.

#### Answer to Hardiman et al. (R.B.F., J.P.K., A.W.)

We agree with Hardiman et al. (17) that the carbon spherules previously reported (7) appear similar in some respects to charred fungal sclerotia (18), but they are different in other aspects (4). Using SEM imaging, we have conclusively shown that

<sup>\*</sup>Rosler W, et al. (2006) Carbon spherules with diamonds in soils. European Space Agency, First International Conference on Impact Cratering in the Solar System, European Space Research and Technology Centre, May 8–12, 2006, Noordwijk, The Netherlands.

Lake Cuitzeo carbon spherules have "smooth, glassy, highly reflective interiors with no evidence of filamentous structure observed in fungal sclerotia" (4), consistent with previous

observations (7). Although some carbon spherules at some YDB sites may be charred sclerotia, it is clear that not all are, because they can also be produced from the burning of resinous wood, as in wildfires (4).

Hardiman et al. also complain that some proxies (glass-like carbon, aciniform soot, and elongates) are not discussed for Lake Cuitzeo. All proxies are not present or preserved at every YDB site, and we chose to focus on the evidence we found.

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 Blaauw M, Holliday VT, Gill JL, Nicoll K (2012) Age models and the Younger Dryas Impact Hypothesis. Proc Natl Acad Sci USA 109:E2240.

- Arce JL, et al. (2012) Late Pleistocene rhyolitic explosive volcanism at Los Azufres Volcanic Field, central Mexico. The Southern Cordillera and Beyond: Geological Society of America Field Guide 25, eds Aranda-Gómez JJ, Tolson G, Molina-Garza RS (The Geological Society of America, Boulder, CO), pp 45–82.
- Pradal E, Robin C (1994) Long-lived magmatic phases at Los Azufres volcanic center. Mexico J Volcan Geotherm Res 63:201–215.
- Israde-Alcántara I, et al. (2012) Evidence from central Mexico supporting the Younger Dryas extraterrestrial impact hypothesis. Proc Natl Acad Sci USA 109:E738–E747.
- Boslough M (2012) Inconsistent impact hypotheses for the Younger Dryas. Proc Natl Acad Sci USA 109:E2241.
- Napier WM (2010) Palaeolithic extinctions and the Taurid Complex. Mon Not R Astron Soc 405:1901–1906.
- 7. Firestone RB, et al. (2007) Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. *Proc Natl Acad Sci USA* 104:16016–16021.
- 8. Boslough MBE, Crawford DA (2008) Low-altitude airbursts and the impact threat. Int J Impact Eng 35:1441–1448.
- Daulton TL (2012) Suspect cubic diamond "impact" proxy and a suspect lonsdaleite identification. Proc Natl Acad Sci USA 109:E2242.
- Tian H, Schryvers D, Claeys P (2011) Nanodiamonds do not provide unique evidence for a Younger Dryas impact. Proc Natl Acad Sci USA 108:40–44.
- Kennett DJ, et al. (2009) Shock-synthesized hexagonal diamonds in Younger Dryas boundary sediments. Proc Natl Acad Sci USA 106:12623–12628.
- Gilmour I, et al. (1992) Terrestrial carbon and nitrogen isotopic ratios from Cretaceous-Tertiary boundary nanodiamonds. Science 258:1624–1626.
- Kurbatov AV, et al. (2010) Discovery of a nanodiamond-rich layer in the Greenland ice sheet. J Glaciol 56:749–759.
- Daulton TL, Pinter N, Scott AC (2010) No evidence of nanodiamonds in Younger-Dryas sediments to support an impact event. Proc Natl Acad Sci USA 107:16043–16047.
- Daulton TL (2006) Extraterrestrial nanodiamonds in the cosmos. Ultrananocrystalline Diamond, eds Shenderova O, Gruen D (William Andrew Publishing, Norwich, NY), pp 23–78.
- Gill JL, et al. (2012) Paleoecological changes at Lake Cuitzeo were not consistent with an extraterrestrial impact. Proc Natl Acad Sci USA 109:E2243.
- Hardiman M, Scott AC, Collinson ME, Anderson RS (2012) Inconsistent redefining of the carbon spherule "impact" Proxy. Proc Natl Acad Sci USA 109:E2244.
- Scott AC, et al. (2010) Fungus, not comet or catastrophe, accounts for carbonaceous spherules in the Younger Dryas "impact layer." *Geophys Res Lett* 37:L14302.