Absence of geochemical evidence for an impact event at the Bølling–Allerød/Younger Dryas transition

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High concentrations of iridium have been reported in terrestrial sediments dated at 12.9 ka and are interpreted to support an extraterrestrial impact event as the cause of the observed extinction in the Rancholabrean fauna, changes in the Paleoindian cultures, and the onset of the Younger Dryas cooling [Firestone RB, et al. (2007) *Proc Natl Acad Sci USA* 104:16016–16021]. Here, we report platinum group element (PGE: Os, Ir, Ru, Rh, Pt, Pd), gold (Au) concentrations, and $^{187}Os/^{188}Os$ ratios in time-equivalent terrestrial, lacustrine, and marine sections to seek robust evidence of an extraterrestrial contribution. First, our results do not reproduce the previously reported elevated Ir concentrations. Second, $^{187}Os/^{188}Os$ isotopic ratios in the sediment layers investigated are similar to average crustal values, indicating the absence of a significant meteoritic Os contribution to these sediments. Third, no PGE anomalies distinct from crustal signatures are present in the marine record in either the Gulf of California (DSDP 480, Guaymas Basin) or the Cariaco Basin (ODP 1002C). Our data show no evidence of an extraterrestrial (ET)-PGE enrichment anomaly in any of the investigated depositional settings investigated across North America and in one section in Belgium. The lack of a clear ET-PGE signature in this sample suite is inconsistent with the impact of a large chondritic projectile at the Bølling–Allerød/Younger Dryas transition.

Os isotopes | platinum group elements | Clovis | Pleistocene extinction | meteorite

Proxy records of millennial-scale climate variations during the most recent deglaciation from polar ice cores (1–3) as well as deep-sea and lacustrine sediments (4–10) display abrupt changes that are typically attributed to internal forcing of Earth's climate system. A striking example is the Younger Dryas (YD) cooling episode from 12.896 ± 0.138 thousand years (ka) to 11.703 ± 0.099 ka calendar years before AD 2000 (11) after the interstadial warming event Bølling–Allerød (BA) (14.692 ± 0.186–14.075 ± 0.169 ka). High-resolution stable $\delta^{18}O$ and δD in H_2O and the glaciochemical record from Greenland ice cores show that both the onset and the termination of the YD occurred abruptly, the former lasting slightly more than two centuries, whereas the latter transitioned into a new state in a few years (12). The most widely accepted interpretations of Earth's recent climate history place the origin and termination of the YD within Earth's complex network of feedback mechanisms (13–15). Proxies and model results favor a significant freshwater input into the North Atlantic reducing the formation of deep waters and weakening or shutting down of the meridional overturning circulation (16) as the primary cause of the YD cooling regardless of its source, timing, duration, volume, and path of melt water (17–21).

The view that the YD event originated from within Earth's climate system has recently been challenged by the proposition of an extraterrestrial trigger for the BA/YD transition (22–24).

The theory invokes either a large meteoritic impact or several violent airbursts of fragmented carbonaceous chondritic meteorites or (long period) comets (22–24) that are claimed to be the culprits for the sudden Rancholabrean termination, the trigger for the Northern hemisphere cooling of the YD, and the cause of the termination of the Clovis culture in North America. The alleged projectile(s) is/are supposed to have hit somewhere on the Laurentide Ice sheet, creating a melt water surge toward the North Atlantic through the Hudson and St Lawrence estuaries, subsequently slowing down the meridional overturning circulation and inducing a sustained cold interval for ±1,200 years. The other twist of this hypothesis claims that explosions of numerous projectiles in the atmosphere destabilized the Laurentian ice sheet and triggered the observed cooling. To provide support for this hypothesis, 14 markers, advocated to be of extraterrestrial origin, are documented as concentrated beneath a carbon-rich black layer (the black mat) at various sites across North America and Europe (22–24). Among the identified markers are magnetic grains and microspherules, charcoal, soot, carbon spherules containing nanodiamonds, fullerenes with extraterrestrial He, and elevated concentrations of iridium (Ir) (<0.1–117 ppb Ir).

In impact-related studies, highly elevated concentrations of Ir together with enrichments of the other platinum group elements in nearly chondritic ratios are considered clear indicators of a meteoritic contribution delivered when an extraterrestrial object impacts the Earth (25). At the Cretaceous/Tertiary (KT) boundary, a positive Ir anomaly is documented at >112 sites worldwide (26). The elevated Ir concentrations reported in magnetic grains and in bulk sediments of YD age could then be considered as evidence of a chondritic or an iron meteoritic impact event at or close to the end at the onset YD. The other markers found (soot, charcoal, carbon spherules) are not direct indicators of a collision but could be generated by subsequent wildfires. Other claimed extraterrestrial (ET) markers such as fullerenes and their extraterrestrial He signature have been proposed as impact indicators, for example at the Permo–Triassic boundary (27). However, so far other laboratories have failed to duplicate these result (28, 29). Consequently, they cannot be reliably used as impact evidence. Nanodiamonds with cubic structures are also found within this black layer. However, their mode of formation is unclear, and their descriptions lack conclusive evidence of a meteoritic or shock origin (23, 24).

The postulated impact layer below the YD black mat layers and its interpretation as a distal ejecta layer are rather difficult to reconcile with the current knowledge of impact events because no other typical impact indicators characteristic of ejecta

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GEOLOGY

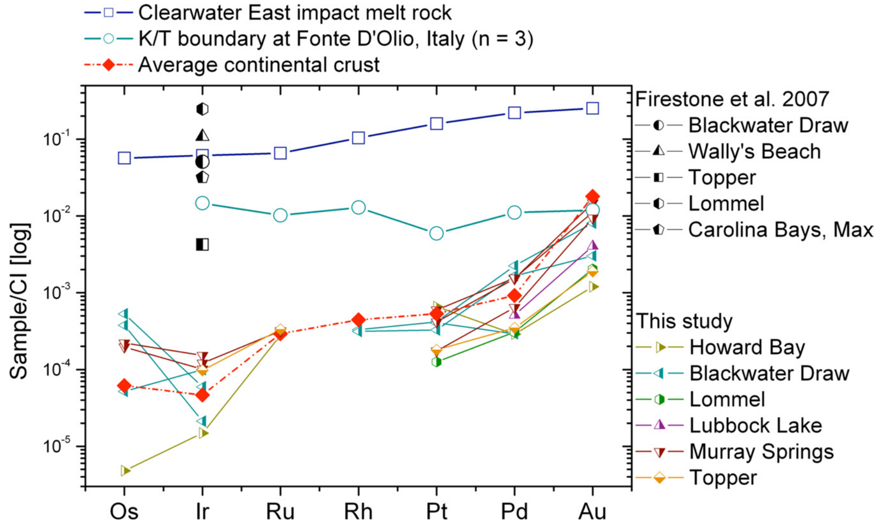

Fig. 1. Logarithmic scale plot of the PGE and Au concentrations in the black mat from the studied sections, normalized to CI-chondrite (39) and compared with the averaged values for the continental crust, the KT boundary at Fonte d'Olio section (Italy) and the melt rock from the Clearwater East impact structure. The PGEs are plotted from left to right in order of decreasing melting temperature. Os, Ir, Ru, Pt, and Pd values of the continental crust from (47), Rh and Au values from ref. 47; Os, Ir, Ru, Pt, and Pd values of the continental crust from ref. 48.

layers, such as shocked minerals, spherules composed of glass (or its alteration products), or Ni-rich spinels (30), have been reported. Therefore, the elevated Ir concentrations (measured in numerous locations containing this carbon-rich black layer (22) should be considered the most reliable indicator of a meteoritic component associated with the YD. However, elevated Ir concentrations alone are insufficient to demonstrate a significant extraterrestrial component. As described below, the relative abundances of platinum group elements and $^{187}Os/^{188}Os$ ratio provide a more robust test of the presence or absence of extraterrestrial matter in BA/YD samples.

To further explore claims of an impact at the BA/YD transition, we present detailed PGEs (Os, Ir, Ru, Rh, Pt, Pd) and gold (Au) analyses from continental YD sections (the "black mat"), including some of the same sites where Firestone et al. (22) reported anomalously high Ir values and two additional continental margin cores spanning the YD. PGE concentration data are complemented with new Os isotope data on the same suite of samples using a different analytical approach (ICP-MS, Ni fire assay) than Firestone et al. (22). This isotope system is a sensitive indicator of an extraterrestrial component (except for basaltic achondrites that lack high PGE concentrations) in terrestrial and marine sediments (31–33). The Os isotopic tracer is valuable provided that the target lithology does not contain recently mantle-derived or ultramafic components (34) a prerequisite that is certainly fulfilled by all terrestrial sections investigated here. Two marine cores with high accumulation rates were analyzed for Os isotopes, accompanied by Ir concentrations measured on the same powder split. In both cores, the BA/YD transition was clearly defined by excellent age control and confirmed by changes in several other proxies (35, 36).

Results

Platinum Group Elements and $^{187}Os/^{188}Os$ in the Continental Sections. The PGE abundances for Murray Springs (AZ), Blackwater Draw (NM), Howard Bay (NC), Lake Lubbock (TX), Topper (SC), and Lommel (Belgium) sections are presented in Table S1. From these same sections, but on a different powder split, a comparison of $^{187}Os/^{188}Os$, Os concentrations and Os/Ir ratios in different depositional settings is also given (Table S1).

Firestone et al. (22) have reported 169 measurements of Ir at 14 sites up to ≈9,200 km apart in the ^{14}C-dated BA/YD (see Fig. S1) bulk sediments, magnetic fraction, and beneath the black mat, but not in the over- and underlying layers. In 5 of the 12 sites reported in table 1 of ref. 22, the Ir concentrations in the bulk sediment are >0.5 ng/g, and the concentrations in four sites (Murray Springs, Blackwater Draw, Lake Hind, and Carolina Bays, Max) reach 2.3–3.8 ng/g Ir. These values are comparable to those obtained at a number of KT boundary sites (e.g., 3.7 ng/g in Petriccio, Italy; 0.85 ng/g in Brazos River, TX; 5.7 ng/g in Beloc, Haiti; 2.9 ng/g in Frenchman River, Canada; and 1.4 ng/g in Hell Creek, MT (37). The Ir concentrations in the magnetic fractions of four samples (22) (Blackwater Draw, Wally's Beach, Lommel, and Carolina Bay, Max) show concentrations between 15 and 117 ng/g [i.e., ≈25% of CI chondrites, Ir = 460–472 ng/g; (38, 39)].

The data presented by Firestone et al. (22) also show a clear inverse correlation between Ni and Ir (Fig. S2*A*). This is rather unusual as Ni and Ir are both siderophile elements, enriched in meteorites compared to the terrestrial crust. Both elements typically show the same geochemical behavior during a meteorite impact on the terrestrial crust. In numerous crater impactites such as Popigai (40) Lapparjävi (41), Morokweng (42), Clearwater East (43) and at the KT boundary (25), Ir and Ni display a positive correlation (Fig. S2*B*).

Table S1 shows that the new analyses do not to confirm the elevated Ir values published by Firestone et al. (22). The PGE concentrations measured in bulk sediments are lower by at least an order of magnitude. Nugget effects, which cause small-scale inhomogeneities in PGE distribution and account for a variability of concentrations in geological samples (44–46), can be fully discarded here. The use of samples >10 g precludes any nugget effect and has been demonstrated to lead to good sample reproducibility (40), confirmed by repeated analyses in this study. Table S2 presents the Ir and Pt concentration data for Rock Standard TDB-1 between different laboratories.

The PGEs concentrations obtained in this study are similar to or only slightly higher than the average continental crust (Table S1; Os = 0.031 ng/g; Ir = 0.022 ng/g, Ru = 0.210 ng/g, Rh = 0.060 ng/g, Pt = 0.510 ng/g, Pd = 0.520 ng/g, and Au = 2.500 ng/g; Rh and Au values from ref. 47; other PGEs from ref. 48). In Fig. 1 we show the CI-normalized, PGE patterns on a logarithmic scale for each section analyzed compared with the almost flat patterns obtained for KT boundary samples and impactites from the

Clearwater East crater, used as representative of terrestrial material clearly contaminated by a meteoritic component. The sloping patterns obtained for all samples of the YD black layer strongly resemble the pattern typical of average continental crust (42, 48–51). The Blackwater Draw and Murray Springs sections display slightly elevated values of Os and Ir concentrations compared with average crustal values (48). The widely distributed depositions of the carbon-rich black mat in North America in some of these sections have been interpreted as the result of reducing conditions and a shallower water table (52). It is therefore possible that variations in the reduction–oxidation (redox) conditions during the black mat formation played a role in moderately concentrating these trace metals, especially if the black mat layer is of algal origin (53). We suggest that as the redoxcline formed, sulfide and organometallic complexes concentrated chalcophile elements and PGEs. The high concentrations of U reported in Firestone et al. (22) can also be explained in a similar manner.

Black mat samples from the Murray Springs and Blackwater sections yield bulk $^{187}Os/^{188}Os$ ratios slightly more radiogenic than the eroding continental crust [1.26; (48, 54, 55)]. Although the purpose of this study was not to leach the black mat samples, the data agree well with previous leachates on rivers sediments (54, 56) that have shown that the soluble river load delivered to the world ocean is more radiogenic than the currently eroding continental crust. The $^{187}Os/^{188}Os$ data presented here show very radiogenic values, typical for continental runoff (57) and do not allow for a significant extraterrestrial component in these samples. The black mat may indicate the averaged Os isotopic composition of freshwater because the Os hydrogenous budget likely dominates the bulk sediment.

Sediments from Lake Hind (Manitoba, Canada) were reanalyzed because this site yielded high Ir concentration in the bulk (3.8 ng/g) (22). For the two samples batches, the upper end of the range of measured Os (15–104 pg/g) and Ir concentrations (25–117 pg/g) exceed the average continental crustal values of respectively 31 and 22 pg/g (48) (Table S3, Fig. S3). However, these slightly elevated values are not outside the range known to result from natural authigenic enrichment of Os and Ir, and can be attributed to processes like those described above. The high $^{187}Os/^{188}Os$ precludes any significant extraterrestrial contribution to these sediments, and demonstrates a terrestrial origin for the Os in Lake Hind sediments (Fig. S3). In summary, the PGE and Os isotope values obtained from samples of the carbon rich black layer associated with the YD do not confirm the presence of an elevated meteoritic contribution. Terrestrial sequences could fail to record an impact event if sedimentation is discontinuous. However, we show below that this possibility is unlikely based on results from the marine $^{187}0s/^{188}0s$ record.

Marine $^{187}Os/^{188}Os$ Record. The present-day seawater $^{187}Os/^{188}Os$ ratios of 1.05–1.06 (58–61) reflect a flux weighed average of soluble Os inputs to the world ocean, dominated by radiogenic Os from continental sources ($^{187}Os/^{188}Os \approx 1.2$ to 1.4) (54, 55) and unradiogenic Os inputs from extraterrestrial and mantle sources ($^{187}Os/^{188}Os \approx 0.13$) (62). Large chondritic impact events (33, 63) such as Chicxulub at the KT boundary (64) and Popigai at the Late Eocene (40) added significant quantities of soluble ET Os to seawater shifting the Os isotopic composition to lower $^{187}Os/^{188}Os$ (33). If a sizeable chondritic impact occurred at the onset of the YD, it is reasonable to expect that seawater $^{187}Os/^{188}Os$ would also shift to lower values after vaporization of the incoming projectile and subsequent incorporation of unradiogenic Os to the marine sediments. We have investigated the possibility of a marine $^{187}Os/^{188}Os$ excursion across the YD in two high-resolution records, DSDP 480 and 1002C (Fig. 2, Table S4).

There is a clear offset in the $^{187}Os/^{188}Os$ between both sites,

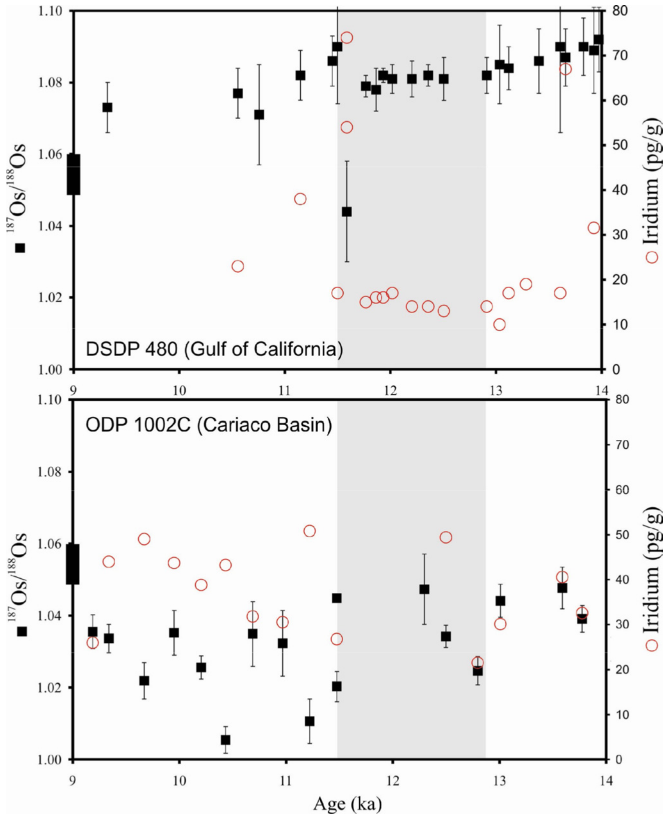

Fig. 2. $^{187}Os/^{188}Os$ ratios (black squares) and Ir concentrations (open red circles) in DSDP 480 (Gulf of California) and 1002C (Cariaco Basin) compared with the present seawater $^{187}Os/^{188}Os$ ratio (black vertical line on the *y* axis) (58–61). These age data are expressed as thousands of calendar years before present. The gray area represents the YD interval.

with the Gulf of California consistently displaying higher $^{187}Os/^{188}Os$ ($\approx$1.08) compared with Cariaco Basin (1.01–1.05). Although this offset is suggestive of regional variations in the $^{187}Os/^{188}Os$ of dissolved Os in the ocean, for the purposes of this work it is sufficient to note the overall similarity of both records to present-day seawater $^{187}Os/^{188}Os$ (1.05–1.06). The single point to lower $^{187}Os/^{188}Os$ in DSDP 480 does not coincide with the onset of the YD and most likely represents the influence of unradiogenic Os derived from weathering of mantle-derived rocks or a particle of cosmic dust (not plotted for clarity purposes). It does not constitute evidence of an impact.

We interpret our bulk data from both sites as records of seawater $^{187}Os/^{188}Os$ variations for the following reasons. First, the measured $^{187}Os/^{188}Os$ is close to the modern value of 1.05–1.06. Second, reducing sediments efficiently scavenge hydrogenous Os (seawater-derived). This is supported by the elevated Os burial fluxes in each of these sections (average 4,440 pg cm^{-3} ka^{-1}), allowing us to neglect the influence of ET cosmic dust flux that typically has an average Os burial flux of 4 pg cm^{-3} ka^{-1} (54). Third, the Os and Pt concentrations are above average eroding crustal values (48), typical of organic-rich sediments from other continental margin settings (65, 66). Fourth, the range in the Os/Ir ratios (1.6–12.8) indicates a minimal terrigenous influence (Os/Ir $\approx$ 1) supporting authigenic enrichment of Os relative to Ir.

These two high-resolution marine Os isotope and PGEs records lack a spike of soluble or particulate unradiogenic extraterrestrial Os and Ir at the onset of the YD and across the whole interval studied.

Discussion

For an extraterrestrial body to produce continent-wide ecologic and climatologic consequences, recorded in a myriad of depositional settings in North America and Europe, the projectile size must have been at least a few kilometers in diameter. However, our data fails to detect an impact signature. Therefore, the sensitivity of the marine Os isotope record is further discussed below to argue that a prominent ET signature is unlikely to have been missed.

One of the fundamental uncertainties in using Os isotopes to detect meteorite impact events in marine sediments and to estimate their sizes is to constrain the fraction of projectile-derived Os that is dissolved in seawater and removed to sediments (33). The data documenting seawater Os isotope variation across the YD do not allow for an excursion larger than 0.05 $^{187}Os/^{188}Os$ units. Therefore, we have adopted an excursion of 0.05 as means of calculating an upper limit on the size of a chondritic projectile, which could have potentially impacted Earth at the BA/YD transition. Considering that a large fraction of meteoritic Os is soluble in seawater, chondritic projectiles 1 km and larger should be easily detectable in the marine Os isotope record. To illustrate the sensitivity of the Os isotope system, we have chosen a wide range in fractional dissolution (1–5-50–100%) of projectile-derived Os in seawater. We show the potential influence of the alleged YD projectile on the Os isotope composition of seawater for a complete (100%) to a partial (1–5-50%) dissolution of Os carried by a carbonaceous chondritic projectile (Fig. S4). The calculations show that if 50–100% of a 1-km projectile-derived Os dissolved in seawater, the $^{187}Os/^{188}Os$ ratio should decrease by ≈0.05. Second, if only 1–5% of a 2.5- to 4.5-km projectile is dissolved, a similar ≈0.05 decrease is expected. If this latter scenario is representative of the BA/YD situation, this would imply that a remaining 95–99% of undissolved PGE-rich ET matter is unrecognized in Earth's crust and missed in analyses. This is unlikely because no well-dated crater, no impact-melts, nor particle-rich layers have been described in any of the Greenland and Antarctica ice cores dated at the YD onset (67), and none of the YD black mat layers show significantly enriched quantities of this extraterrestrial matter based on our results. In other words, if 50% of the projectile dissolves in seawater, our record is likely to detect an excursion, but if 50% remains insoluble in seawater, terrestrial YD sections are expected to record ET PGE enrichment. Finally, applying simple model calculations (see supporting text in ref. 33, the modern $^{187}Os/^{188}Os$ of seawater should still be recovering from a soluble extraterrestrial Os–Ir spike because the residence time of Os in seawater (10–50 ka) (62) is comparable with the time between the YD and the present day. Complete flushing of a pulse of ET Os from the global ocean would require several residence times before a complete recovery. Therefore combined data from proximal marine and terrestrial sections reported here and Ir data from Greenland ice cores (67) provide no evidence of a sizable chondritic impact at the BA/YD transition. An alternative impactor type could be a carbon-rich, nickel/iron-poor impactor, most likely a comet (22, 24). It is inferred that the best candidates for cometary meteorites are now thought to be the type-1 (and maybe type-2) carbonaceous chondrites (68). Type-1 chondrites include the members of the CI group, whereas type-2 chondrites encompass all CM and CR chondrites (and some ungrouped carbonaceous chondrites). In terms of siderophile element content, these groups do not differ strongly [CI: Ir = 472 ng/g, Ni = 10,863 μg/g, Cr = 2,796 μg/g; CM: Ir = 605 ng/g, Ni = 12,396 μg/g, Cr = 3,059 μg/g; CR: Ir = 622 ng/g, Ni = 13,794 μg/g, Cr = 3,810 μg/g; (38)]. The Chicxulub impact structure was formed by an asteroidal CM carbonaceous chondrite, compositionally similar to comets without an icy component (64, 69). It is also worth mentioning that comets have never been analyzed for their PGE-composition, but cometary interplanetary dust particles thought to have originated from comets lack nanodiamonds (70).

There is now a situation where the BA/YD horizon is greatly enriched in nanodiamonds but depleted in PGEs. Indeed, if the origin of the nanodiamonds is extraterrestrial, then the projectile that delivered this material must be unlike any known meteoritic material because all meteorites known to contain nanodiamonds are also enriched in PGEs.

There are three known diamond allotropes: n-diamonds, cubic diamonds, and hexagonal diamonds (lonsdaleite). Diamonds found in impact melts and breccias are predominately cubic diamonds, likely produced by shock metamorphism of preexisting graphite (71, 72). Cubic diamonds have also been found in some KTB horizons (73) and are the most common type of diamonds found in meteoritic material (74). Lonsdaleite occurrences in meteoritic material are rare and limited to a few chondritic meteorites (74), but its occurrence in any know impact craters is open to debate (74). Consequently, we consider the presence of the lonsdaleite diamond polymorph at Arlington to be enigmatic and not readily attributable to formation by shock metamorphism.

Results presented here suggest that it is unlikely that the nanodiamonds were derived from any known meteoritic projectile, in contrast to suggestions of a swarm of comets or carbonaceous chondrite (24). Specifically, mass balance calculations show that if all of the nanodiamonds in the BA/YD sections are primary meteoritic material (1,500 ppm of the bulk; (74) (covering a fluence of ≈30% of Earth's surface) (Fig. S1), and were not formed upon surface impact, a chondritic projectile of 1.2 km in diameter should produce an Ir fluence of ≈1 ng/cm^2 that is clearly missing based on our results. For clarity, we emphasize that PGE and Os isotope data are sensitive indicators of undifferentiated meteoritic material. Alternatively, to avoid PGE enrichment, it is possible to invoke the impact of one or several differentiated, PGEs-poor, possibly still unknown type of achondritic meteorites that vaporized in Earth's atmosphere at the BA/YD transition is one possibility. However, the probabilities of the arrival of this type of projectile to Earth is low (www.unb.ca/passc/ImpactDatabase/), and this type of bolide lacks all allotropes of nanodiamonds. In the case of one or several surface impact(s) of achondritic projectile(s), which could explain the absence of PGEs in the studied BA/YD sections, it becomes difficult to explain the formation of nanodiamonds without a well-dated surface expression of one or several craters. So far, no BA/YD craters are yet known. Based on the existing distribution of terrestrial craters (75), one or several large craters of this very young age cannot be eroded, filled with younger sediments or erased by subduction. Most likely such fresh impact crater(s) would have been found and confirmed many years ago. In the scenario of a 1- to 2-km-diameter achondritic, PGEs-poor projectile exploding into the atmosphere or hitting only the Laurentide Ice Sheet, a crater would possibly not have been formed. However, in this case, a source of carbon is required to form the recovered lonsdaleite crystals, and the concentration of carbon in this type of meteorites is extremely low. It is possible that the nanodiamonds were formed during an airburst, but it does not explain the absence of a geochemical anomaly.

Therefore, a strong decoupling of PGEs and nanodiamonds exists which differs from other known impact events. The occurrence of high concentrations of cubic diamonds and n-diamonds (≈1,340 ppb) (24) in multiple BA/YD sections, found within carbon spherules without an associated defined geochemical anomaly, is therefore not a robust diagnostic of an impact event.

Cubic and n-diamonds have been reported to occur in the inner structures of similar carbon spherules, found in upper soils in Belgium and Germany (76). The n-diamonds allotrope requires high temperatures, low oxygen levels and a source of carbon. Such conditions can also be found in wildfires, in topsoils, once the oxygen required fueling the fire has been exhausted. This leads us to speculate that the n-diamonds observed at multiple BA/YD sections were formed in situ after intense wildfires. The association of cubic diamonds and lonsdaleite remains enigmatic. Clearly more work is needed to the understanding of the presence of the nanodiamonds at 12.9-ka sections, and it seems to us equally likely that there may be mechanisms for nanodiamond formation that are wholly terrestrial and do not require an impact.

Materials and Methods

Samples from ^{14}C-dated terrestrial (the black mat horizon) and marine sections (DSDP-ODP sites) known to recover the onset of the YD cooling were measured for their PGEs concentrations and osmium isotopes. Our methods (ICP-MS) of measuring the PGEs concentration differ significantly from Firestone et al. (22) and are described in further detail in *SI Text*.

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