## **Supporting Information**

## **Paquay et al. 10.1073/pnas.0908874106**

## **SI Text**

Exposures of the YD black mats with reliable  $^{14}$ C dates were sampled and analyzed for PGE content and Os isotopic composition. For example, the Gainey Site that showed high concentrations of magnetic spherules and therefore high Ir concentration was not studied here because the age model from this section is poorly defined. Allen West provided samples of the black mat layer from Howard Bay, NC (level HB-11D2) and Blackwater Draw (NM) (levels BW-DT, D/C and BW-B/A) (1), similar to those measured in Firestone et al. (2). The Lommel, Maatheide section (Belgium), where the Usselo paleosoil horizon is well defined, yielded by far the highest Ir concentration [117 ng/g in the separated magnetic fraction (2)]. The sand and black mat layer at this site was resampled in detail.

The Lubbock Lake (TX), Topper section (SC) and a set of samples from Murray Springs from different trenches and profiles (Trench 22-Profile B1–B3) were also analyzed. Dolores Hill provided the Murray Springs samples that are splits of those used in the Firestone et al. study (2). The age model for these samples is constrained by multiple  $^{14}C$  dates (3). These sediments are mostly fine to coarse, fluvial to lacustrine sands, clays or muds with an organic rich black mat layer.

Two sets of samples from glacial Lake Hind (Flintstone Hill section, Manitoba, Canada) were also sampled on two separate occasions. Each set is from the same location and no lithological differences were observed between the two sets of samples. One of the sample sets yielded several elevated iridium concentrations ( $\approx$ 4 ng/g) (2, 4) distributed over a  $\approx$ 6-cm interval with a background level of  $\approx$  1 ng/g Ir. Such high background values are clear example of the analytical issues from (2), knowing that Ir concentration is (22 pg/g) for the average upper continental crust (5). The BA/YD transition at Lake Hind is derived by the linear extrapolation of the sedimentation rate from an AMS radiocarbon date of  $10,420 \pm 70$  years BP  $(12,677-11,991$  cal BP  $(6)$ . Additionally, this age estimate is supported by a radiocarbon date of 12.76 ka BP from the base of the peat, as reported in Firestone et al. (2). The BA/YD is thought to occur within the lithologic change from massive carbonate-rich clay to silty clay onto a peat with alternating silty clay and organic laminae, coinciding with a decrease in water level (6).

The two marine sediments records, DSDP 480 (Deep Sea Drilling Project) (Gulf of California,  $(27°54.10'N, 111°39.34'W)$ and ODP (Ocean Drilling Program) 1002C (Cariaco Basin,  $10^{\circ}40'$ N,  $65^{\circ}00'$ W) [\(Fig. S1\)](http://www.pnas.org/cgi/data/0908874106/DCSupplemental/Supplemental_PDF#nameddest=SF1) have high organic carbon content and high accumulation rate (7, 8) ideal to reconstruct the seawater Os isotopic composition at high resolution (9). The age control of the YD interval in DSDP Site 480-core 3H is well constrained by 14C dates [with a reservoir correction of 750 years (10)] on planktonic foraminifera at the onset, during and at the end of the YD (7, 11). At this site, the BA/YD transition shows a change in the oxygenation of the seafloor from laminated, biogenic silica-rich and carbonate-poor  $(2\%$  CaCO<sub>3</sub>) to nonlaminated and more carbonate-rich sediments ( $\approx$ 13% CaCO<sub>3</sub>). The YD/Holocene transition is marked by an abrupt return to laminated sediments. Sediments are organic-rich (2.2–4.9% TOC). The sedimentation accumulation rate throughout the YD averages 75 cm ka.

ODP Site 1002C sediments consist of anoxic and laminated organic-rich silts during the YD interval (4–5% TOC). The age model is derived from a correlation to the GISP2 core time scale (12). The sedimentation rate through the interval studied averages 35 cm ka. Each bulk sample  $(20 \text{ cm}^3)$  represents an integrated time of  $\approx$  20 years for Site 480 and  $\approx$  60 years for Site 1002C.

Each sample was oven-dried at 60 °C for several days until constant sample weight was obtained. Samples were carefully isolated to avoid any contamination between potentially highand low-iridium concentration samples. Sediments were disaggregated with a mortar and pestle. Homogenized powders were stored in a plastic beaker and isolated until further analysis. The determination of Os isotope ratios and Pt, Ir, and Os concentrations was carried out at the University of Hawaii. The same sediment powder was analyzed for all of the PGEs (Ir, Ru, Rh, Pt, Pd, Au) except Os at Ghent University.

**Analytical Methodology for PGE (Ghent University).** The PGEs (except for Os that volatilizes during the applied procedure) and Au concentrations were determined by using a nickel-sulfide fireassay preconcentration method in combination with subsequent analysis using an ELAN DRC*plus* quadrupole-based ICP-MS instrument following the procedure described by Plessen and Erzinger (13) and Tagle and Claeys (14). A flux of 30 g of sodium carbonate, 60 g of sodium tetraborate, 5 g of calcium fluoride, 5 g of sulfur, and 5 g of nickel powder was added to the powdered samples, weighing between 13 and 70 g (pure  $SiO<sub>2</sub>$  powder was added when necessary). All reagents were of analytical grade and have been tested for PGE content. These mixtures were homogenized with an agate pestle, transferred into clay crucibles, and heated in a furnace at 1,150 °C for 1 h. After cooling, the nickel sulfide beads were separated from the slag by breaking the crucibles, subsequently ground, and dissolved in concentrated HCl in a hot water bath at 90 °C for 14 h. The residues were separated by filtration through glass micro filter devices (Schott, porosity 4), dissolved with a mixture of 2 parts of HCl (32 vol %, doubly distilled) and one part of  $H_2O_2$  (30 vol %, analytical grade) in two subsequent steps, passed through a filter paper, and evaporated on a hotplate to a volume of 1–2 mL. After adding a final 5 mL of HCl and 2 mL of  $H_2O_2$ , the solution was evaporated to 1–2 mL, cooled, and diluted with 2 vol % HCl to a volume of 10 mL. Once In and Tl had been added as internal monitors, each solution was measured twice on separate measuring days for their <sup>99</sup>Ru, <sup>101</sup>Ru, <sup>102</sup>Ru, <sup>103</sup>Rh, <sup>105</sup>Pd, <sup>106</sup>Pd, <sup>108</sup>Pd, <sup>108</sup>Pd, <sup>104</sup>Pt, <sup>195</sup>Pt, <sup>195</sup>Pt, <sup>196</sup>Pt, and <sup>197</sup>Au concentrations by using external calibration solutions. Mathematical corrections were applied for isobaric interferences where necessary. The results obtained for international reference materials, a diabase TDB-1 with low PGE abundances and an altered peridotite WPR-1 with high PGE concentrations (Canadian Certified Reference Materials Project, CCRMP), are consistent with the certified data (15) and the recommended values of Meisel and Moser (16) [\(Table S1\)](http://www.pnas.org/cgi/data/0908874106/DCSupplemental/Supplemental_PDF#nameddest=ST1). These authors propose to compare new PGE data not only with the original certified values, but also with their compiled literature values until the certified values are up to date. Additionally, the precision and accuracy of the method are regularly tested by the analyses of a set of laboratory working standards (Popigai impact melt material, KT boundary clays, and meteorites). To determine the procedural detection limits (the instrumental detection limits are significantly lower), procedural PGE blank are determined by substituting the real samples with  $SiO<sub>2</sub>$  powder; omission of such a PGE-low substitute would result in a destruction of the clay crucibles by the aggressive fire assay flux. In this work, limit of detection (LOD) and limit of quantification (LOQ) are calculated as respectively 3 and 10 times the standard deviation (3 SD and 10 SD  $\sigma$ ) on 10 reagent blanks. The measured values below the LOD are reported as ND, not detected, whereas concentrations below the LOQ are indicated as  $\leq$ numeral value of the LOQ in [Table S1.](http://www.pnas.org/cgi/data/0908874106/DCSupplemental/Supplemental_PDF#nameddest=ST1)

**Analytical Methodology for 187Os/188Os Ratio, Ir, Pt, and Os Concentrations (University of Hawaii).** Os, Pt, and Ir were preconcentrated from bulk sediment samples by using a NiS fire assay. The amount of chemical fluxes was adjusted as a function of organic matter content. Each sample powder was accurately weighted  $(6-10 \text{ g})$  and spiked with a tracer solution enriched in  $^{105}$ Pd,  $^{190}Os$ ,  $^{191}Ir$ , and  $^{198}Pt$  before fusion for concentration determination by isotope dilution. Isotope ratio measurements were made by using a magnetic-sector inductively coupled plasma mass spectrometer (ELEMENT2) according to a procedure slightly modified from that of Hassler et al.  $(17)$  where the  $\mathrm{OsO}_4$ becomes volatile after gassing into the vial by an argon stream into a torch and then transferred directly into the plasma.

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An in-house standard is analyzed every five to six samples in each run to monitor the reproducibility. The average  $187Os/188Os$ of these standards is  $0.1082 \pm 0.0028$  (2 SD;  $n = 20$ ). Ten procedural fusion blanks are carried out during the course of this study. The fusion blanks yielded an average of  $0.64 \pm 0.20$  pg/g of reagents for Os and  $1.5 \pm 0.05$  pg/g for Ir for a total weight of 31.5 g. Argon gas blanks are measured every set of five to six Os isotope analyses to monitor potential carryover of osmium between analyses. Iridium and platinum analyses are carried out on the same aliquot of powder split after  $187Os/188Os$  analysis. Analytical uncertainties in Os concentration from the terrestrial sections are based on counting's statistics and are all  $\leq 2\%$ .

We estimate that the  $^{187}$ Re in situ decay into  $^{187}$ Os is unimportant because the sediments studied are recent. Therefore, no age correction was applied to the sediments.

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**Fig. S1.** Locations of the terrestrial and marine BA/YD sections analyzed in this study (red stars). The shaded area represents the approximated geographical extent of the nanodiamond fluence based on the report of nanodiamonds findings (4, 18).

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**Fig. S2.** (*A*) Ni-Ir concentrations in the black mat layer according to (2). (*B*) Positive Ni–Ir correlation in impact crater materials and KT ejecta layer. Note that the inverse Ni–Ir correlation in data from ref. 2 are uncharacteristic of impact products.

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**Fig. S3.** 187Os/188Os ratios (open squares: batch 1 and filled squares: batch 2) and Ir concentrations (open circles: batch 1 and filled circles: batch 2) from the Lake Hind section. The 12.4-ka age is derived from ref. 6, whereas the 12.76-ka age datum is based on bulk <sup>14</sup>C (represented by arrows) reported in refs. 2 and 4. The depth scale (in centimeters) is derived from ref. 6. The horizontal bar represents the approximate depth interval where high Ir concentrations were previously reported (2).

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Fig. S4. Sensitivity of the marine <sup>187</sup>Os/<sup>188</sup>Os record (Gulf of California dataset) to an alleged carbonaceous chondritic impactor (<sup>187</sup>Os/<sup>188</sup>Os  $\approx 0.13$ ; averaged Os concentration of 650 ng/g (19) and density of 3.0 g cm<sup>-3</sup> (http://meteorites.wustl.edu/id/density.htm), as a function of varying projectile diameters and varying fraction of Os vaporized (1–5-50–100% of projectile Os inventory) and soluble in seawater. These averaged concentrations and density values are based on the type of suggested projectiles (2). The calculations assume a global distribution of the extraterrestrial PGE fallout subsequently mixed to deep-sea sediments. Dissolution of projectile-derived Os over only a restricted region of the ocean would amplify the magnitude of the Os isotope excursion.

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**Table S1. 187Os/188Os ratios, and PGE's concentrations from the sections studied here (Howard Bay, Blackwater Draw, Murray Springs, Lubbock Lake, Topper, Lommel) compared with the averaged crustal material, the KT boundary at Fonte D'Olio (Italy) and the Clearwater East impact**



ND, not determined.

SVNG SVNG

\*Murray Springs section (AZ). The symbols associated to each sample stand for the following: from Murray Springs, Profile B1 (North of Area 1); From Murray Springs Profile B3 (3 m West of Profile B1), from bottom to top: F1 (arkosic sand); F1a (grayish brown sandy clay); F2 (black mat); F2b (white marl). From Murray Springs Profile B1, from bottom to top: F1 (arkosic sand); F2a1a: black clay; F1a1: sandy clay; F2b2: white marl from Murray Springs right bank at Curry Draw at North end Trench 22: F2/D, Lower YD Boundary/olive green sandy mudstone.

†Os, Ir, Ru, Pt, and Pd values of the continental crust are from ref. 1; Rh and Au values are from ref. 2.

‡To cover the entire suite of PGEs and Au in the Clearwater East impact melt, the values reported here are those of sample DWC-2-63-1045 analyzed by ref. 3 This is the only PGE enriched impact melt sample of the Clearwater East impact structure that was measured for Pt. To obtain a workable value for the Os concentration, the Os/Ir ratio obtained by ref. 4 was multiplied with the corresponding Ir concentration.

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**Table S2. Comparison of Ir and Pt concentration from International Rock Standard Reference material (TDB-1) between UH, VUB, and WHOI**

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## **Table S3. 187Os/188Os, Ir, and Pt concentrations from two samples batches, Lake Hind, Manitoba, Canada**



ND, not determined.

\*Batch 1.

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†Batch 2 .





The sample in italic type is from ref. 1. mbsf, meters below sea floor; ND, not determined.

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