LETTER

Reply to Bunch et al.: Younger Dryas impact proponents challenge new platinum group elements and osmium data unsupportive of their hypothesis

Bunch et al. (1) attempt to distort the significance of our results by referring to percentage variations rather than absolute concentrations in platinum group elements (PGE). Table 1 shows that the highest Ir concentrations we measured within the intervals highlighted by Bunch et al. (1) are roughly 30 times lower than those they previously reported (2). Readers should note that Ir data from the University of Hawaii and Belgian laboratories compare well with those from other laboratories using different analytic methods, and that our data from the Younger Dryas (YD) sections do not remotely resemble analyses of sediments from known impact horizons. Bunch et al. (1) implicitly acknowledge that the original data (2) are erroneous by selectively replotting our data to argue that small variations in Ir concentrations, $3-5\times$ crustal average, ≈ 22 pg/g (3), suggest an extraterrestrial (ET) component. However, it has been known for nearly 2 decades that Ir enrichments of this magnitude can easily result from diagenetic redistribution of Ir and are not indicative of the presence of a meteoritic component (4). Additionally, the radiogenic ¹⁸⁷Os/¹⁸⁸Os ratios preclude a significant extraterrestrial Os component (Table 1).

The fact that we did not attempt to isolate magnetic spherules for analysis does not undermine our interpretations. The important and irrefutable point of this study is that two independent laboratories with an established experience in PGE analyses failed to reproduce the previously reported Ir data (2). If indeed a magnetic, Ir-rich material is present, its abundance is so very low that it could easily be attributed to non-ET sources. Additionally, the use alone of magnetic grains as impact marker, that cannot be corroborated (5), does not provide diagnostic evidence of an impact event.

Bunch et al. (1) claim that an unpublished Os isotope record from a slowly accumulating Mn crust lends support for the notion of a YD impact event. However, our marine records show no indication of strong Ir enrichments and yield ¹⁸⁷Os/¹⁸⁸Os ratios very close to that of modern seawater. Mn crusts accumulate slowly ($\approx 1-10$ mm/Ma), and this material can never yield the centennial resolution of our sediment records. Moreover, the slow accumulation of these crusts is likely to lead to the incorporation of small micrometeorite fragments. Previous work has demonstrated that isolated instances of low ¹⁸⁷Os/¹⁸⁸Os ratios in Mn crust surfaces are common (6), thus low ¹⁸⁷Os/¹⁸⁸Os in this single crust will never constitute compelling evidence of an impact.

We are not experts in nanodiamond formation and have clearly identified our comments about nanodiamonds as speculative. Given that definitive evidence for either an impact crater or impact ejecta are lacking, it seems prudent to assume that not all possible routes to nanodiamond synthesis are known at this time.

In closing we wish to thank Bunch et al. (1) for their comment because it brought to our attention a typographical error in our supplemental material (7). Specifically, the results of our TDB-1 reference material analyses should read 0.086 ± 0.012 , not $0.086 \pm$ 0.12 (Table 2 shows the result of individual analyses for clarity).

François S. Paquay^{a,1}, Steven Goderis^{b,c}, Greg Ravizza^a, and Philippe Claeys^b

^aDepartment of Geology and Geophysics, University of Hawaii at Manoa, Honolulu, HI 96822; ^bEarth System Sciences and Department of Geology, Vrije Universiteit Brussel, 1050 Brussels, Belgium; and ^cDepartment of Analytical Chemistry, Universiteit Ghent, 9000 Ghent, Belgium

- 1. Bunch TE, et al. (2010) Geochemical data reported by Paquay et al. do not refute Younger Dryas impact event. *Proc Natl Acad Sci USA* 107:E58.
- 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.
- Peucker-Ehrenbrink B, Jahn B-M (2001) Rhenium–osmium isotope systematics and platinum-group element concentrations: Loess and the upper continental crust. Geochem Geophys Geosyst 2:10.1029/2001GC000172.
- Colodner DC, Boyle EA, Edmond JM, Thomson J (1992) Post-depositional mobility of platinum, iridium and rhenium in marine sediments. *Nature* 358:402–404.
- Surovell T, et al. (2009) An independent evaluation of the Younger Dryas extraterrestrial impact hypothesis. Proc Natl Acad Sci USA 106:18155–18158.
- Burton KW, Bourdon B, Birck J-L, Allegre C, Hein JR (1999) Osmium isotope variations in the oceans recorded by Fe-Mn crusts. *Earth Planet Sci Lett* 171:185–197.
- 7. Paquay FS, et al. (2009) Absence of geochemical evidence for an impact event at the Bølling-Allerød/Younger Dryas transition. *Proc Natl Acad Sci USA* 104:21505–21510.

The authors declare no conflict of interest.

Author contributions: F.S.P. and S.G. designed research; F.S.P. and S.G. performed research; F.S.P., S.G., G.R., and P.C. contributed new reagents/analytic tools; F.S.P. and S.G. analyzed data; and F.S.P. and S.G. wrote the paper.

¹To whom correspondence should be addressed. E-mail: paquay@hawaii.edu.

Table 1. Ir concentration from Firestone et al., our reported Ir and ¹⁸⁷ Os/ ¹⁸⁸ Os, and a comparison with the ¹⁸⁷ Os/ ¹⁸⁸ Os of average
continental crust, chondrites, and known impact events (K/Pg-Late Eocene)

Sections	Ir (pg/g) Firestone et al. (2)	Ir (pg/g) Paquay et al. (7)	¹⁸⁷ Os/ ¹⁸⁸ Os measured	¹⁸⁷ Os/ ¹⁸⁸ Os average continental crust*	¹⁸⁷ Os/ ¹⁸⁸ Os chondrites	¹⁸⁷ Os/ ¹⁸⁸ Os K/Pg-Late Eocene [†]
Murray Springs	2,300	77	1.54	1.4	0.13	0.15–0.28
Lake Hind	3,800	114 (29–31 cm) 75 (30–32 cm) 49 (30–32 cm)	1.91 [‡]			

PNAS PNAS

*See ref. 48 in Paquay et al. (7). [†]See ref. 33 in Paquay et al. (7). [‡]Average of three samples from the same depth interval.

Table 2. Ir, Os, and Pt concentrations for five replicates of the diabase international reference						
standard TDB-1 (prepared by the Canadian Certified Reference Materials Project)						

TDB-1 (<i>n</i> = 6)	lr (pg/g)	Os (pg/g)	Pt (pg/g)	
	96.6	101.1	5,557.5	
	90.5	137.3	6,014.9	
	73.5	112.3	5,079.0	
	73.9	119.6	5,245.0	
	78.7	128.5	5,321.1	
	103.4	136.7	5,384.8	
Average	86.1	122.6	5,433.7	
SD	12.6	14.4	325.5	