An extraterrestrial trigger for the Early Cretaceous massive volcanism? Evidence from the paleo-Tethys Ocean

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The Early Cretaceous Greater Ontong Java Event in the Pacific Ocean may have covered ca. 1% of the Earth’s surface with volcanism. It has puzzled scientists trying to explain its origin by several mechanisms possible on Earth, leading others to propose an extraterrestrial trigger to explain this event. A large oceanic extraterrestrial impact causing such voluminous volcanism may have traces of its distal ejecta in sedimentary rocks around the basin, including the paleo-Tethys Ocean which was then contiguous with the Pacific Ocean. The contemporaneous marine sequence at central Italy, containing the sedimentary expression of a global oceanic anoxic event (OAE1a), may have recorded such occurrence as indicated by two stratigraphic intervals with 187Os/188Os indicative of meteoritic influence. Here we show, for the first time, that platinum group element abundances and inter-element ratios in this paleo-Tethyan marine sequence provide no evidence for an extraterrestrial trigger for the Early Cretaceous massive volcanism.

The contemporaneous emplacement of the Ontong Java Plateau (OJP), Manihiki Plateau, and Hikurangi Plateau marks the 118–125 Ma Greater Ontong Java Event (GOJE, Fig. 1)1–3 in the Pacific Ocean. The massive volcanism may have covered ca. 1% of the Earth’s surface4. However, the cause of the voluminous volcanism is still not understood. One of several possibilities is that the plateaus formed by decompression melting above a surfacing mantle plume head (plume impact4–7). Another idea is that rapidly upwelling mantle along ridges incorporates easily fusible recycled crust8 and that an enriched perisphere exists below the crust9–10 to explain the massive volcanism. These mechanisms, however, fail to explain both the geochemical composition of the lavas and the geophysical features of the oceanic plateaus resulting from the voluminous magma emplacement event.

An alternative mechanism proposed is that large-scale melting was caused by a bolide impact on the oceanic crust1,11–12. Although this model is disputed based on theoretical and geophysical grounds13, no strong geochemical evidence from contemporaneous sedimentary sequences is yet presented to test the bolide impact hypothesis. For example, Jones14 pointed out that with the likely size of the impactor required just to produce the OJP alone, a global record by glass-rich ash fallout now preserved as clay markers in Barremian-Aptian sequences in Europe or by environmental perturbations, such as an ocean-wide anoxia event (OAE), is expected. However, detailed chemical stratigraphy to specifically look for extraterrestrial signature within these Barremian-Aptian sequences has not been done yet to our knowledge. Indeed, five extraterrestrial impact events13–14 and one of the three major ocean wide anoxia events in the Cretaceous, known as OAE1a15–16, coincided with the GOJE, suggesting a potential linkage17–19. Furthermore, although the idea that oceanic plateaus are probable signatures of ancient meteorite impacts12 has been around for nearly thirty years now, the connection among these events, large volume volcanism and biotic perturbations is advocated only recently12,14. Thus, we examined the Gorgo a Cerbara section in Central, Italy, the type section identified to include the OAE1a marker20, for a potential geochemical record of the proposed bolide impact in Early Cretaceous oceans because this sequence was deposited in the Tethys Ocean at the time when it was largely connected with the Pacific Ocean (Fig. 1).

The Gorgo a Cerbara study section is a Barremian-Aptian (126-121 Ma) sequence deposited within 1–2 km depths in an open ocean environment isolated from inputs of clastic sediments20–21. It is composed mostly of pelagic limestones alternating with couplets of black shales, and including a 2-meter interval of organic-rich, black to greenish-gray shales with minor intercalation of chert and radiolarian sandstone, known as Selli Level (Fig. 2). This Selli Level horizon is believed to be the sedimentary expression of the OAE1a21, and records an interval of low seawater initial Os isotopic composition, [187Os/188Os]t ~0.2, previously interpreted as indicating a causal link between the global oceanic anoxia and massive volcanism22.
The Re-Os isotope system is an important tracer for mantle and extraterrestrial inputs into the ocean. The Os isotopic composition of seawater is recorded in marine sediments, which in turn reflects the changes in the relative mixture of inputs from the continents (through weathering), mantle (through hydrothermal and submarine volcanic activities) and extraterrestrial materials (through cosmic dust or bolide impacts) into the ocean through time.

Changes in the order of tens of thousands of years in the balance of the inputs are reflected in the sedimentary record because the Os residence time ranges from 10,000 to 50,000 years, an order of magnitude higher than the mixing time of the oceans (1–2 ka) today. Both extraterrestrial impact and large-scale mantle upwelling from the Earth’s interior can be inferred from a change in the Os isotope composition of seawater to very low values because continental crustal input results in significantly higher values (average 187Os/188Os of 1.0–1.52). Indeed, low 187Os/188Os values can be produced by the input of cosmic Os or mantle-derived Os in the ocean because Os from both sources is unradiogenic, with 187Os/188Os ca. 0.13.

Additional information on the concentration of platinum group elements (PGE) is required to discriminate whether upwelling mantle or extraterrestrial impact could have been responsible for the GOJE. The PGE concentrations in extraterrestrial materials are two to three orders of magnitude higher than the Earth’s mantle. Inter-element abundance ratios are also different between extraterrestrial and terrestrial materials, e.g. Os/Ir, Pd/Ir and Pt/Ir ratios are...
This approach may not rule out an impact hypothesis for the origin of the Early Cretaceous GOJE, and the contemporaneous OAE1a, using the PGE and Os isotope correlations recorded in a paleo-Tethyan marine sequence.

The Selli Level has been defined at depths of 0.4–2.3 m above the magnetic chron M0, with a long duration of 180–450 ka and another sharp and short drop, just above the base of the Selli Level, for a period of only 32–74 ka (duration based on 1.9–4.7 m/Ma rates). The Selli Level (Figs. 2 and 4) coincides with transient negative spike toward extraterrestrial Os isotopic values. For the Gorgo a Cerbara section, two negative excursions in initial Os isotopic values are observed (Fig. 2); one, just after magnetic chron M0, with a long duration of 180–450 ka and another sharp and short drop, just above the base of the Selli Level, for a period of only 32–74 ka (duration based on 1.9–4.7 m/Ma rates). The Selli Level has been defined at depths of 0.4–2.3 m above the Lower Critical Interval (LCI), where significant biotic changes are evident.

### Table 1: Platinum Group Elements and present-day 187Os/188Os data for Gorgo a Cerbara, Central Italy

| SAMPLE NO. | Depth, cm | Pd (pg/g) | Ir (pg/g) | Pt (pg/g) | Os (pg/g) | S. E. 187Os/188Os | S. E. 187Os/188Os | Pt/Ir | Os/Ir |
|------------|-----------|-----------|-----------|-----------|------------|------------------|------------------|-------|-------|
| ASL1, 247–248 | 258 | 6734 | 142 | 6813 |
| SL27, 205–207 | 217 | 7667 | 220 | 8303 | 1 | 0.647 | 0.002 | 37.66 | 0.88 |
| SL28, 194–196 | 206 | 3855 | 49 | 3096 | 572 | 82 | 0.441 | 0.009 | 63.06 | 11.65 |
| SL16, 40–142 | 152 | 5343 | 66 | 1499 | 1080 | 147 | 0.290 | 0.006 | 22.84 | 16.46 |
| SL21, 98–100.5 | 110 | 3036 | 203 | 3286 | 187 | 1 | 0.204 | 0.001 | 16.19 | 0.92 |
| SL22, 82–83* | 95 | 8613 | 544 | 29852 | 0.621 | 0.002 | 54.88 |
| SL24, 53.5–55 | 65 | 2482 | 89 | 1391 | 309 | 11 | 0.293 | 0.003 | 15.68 | 3.48 |
| SL25, 41–41.5 | 51 | 5406 | 81 | 2141 | 689 | 2 | 1.024 | 0.001 | 25.29 | 8.15 |
| SLB1, 48–50 | 50 | 4888 | 82 | 1969 | 543 | 21 | 1.104 | 0.013 | 24.13 | 6.66 |
| SLB1, 39–40* | 40 | 5555 | 83 | 1969 |
| SLB4, 5–5.6 | 5 | 6977 | 86 | 2226 | 270 | 5 | 0.615 | 0.002 | 25.98 | 3.16 |
| SLB5, 0–0.3 | 0.3 | 6495 | 79 | 1859 | 71 | 1 | 0.502 | 0.052 | 23.51 | 3.43 |
| SLB1, 0–1 cm | –1 | 1693 | 35 | 608 | 104 | 3 | 0.695 | 0.011 | 18.14 | 3.09 |
| SLB2, 45–46 cm | –45 | 2871 | 34 | 608 | 104 | 3 | 0.695 | 0.011 | 18.14 | 3.09 |
| SLB1, 73–75 | –75 | 109 | 3309 | 1944 | 99 | 1 | 1.065 | 0.006 | 6.78 |
| SLB8, 104–105 | –105 | 77 | 1973 | 463 | 68 | 0.972 | 0.008 | 25.74 | 6.05 |
| SLB10, 166–167 | –166 | 49 | 919 | 97 | 0.708 | 0.005 | 18.72 |
| GCN 4, 244–245 | –245 | 9 | 113 | 13.1 | 0.822 | 0.011 | 12.36 | 1.43 | 15.3 |
| GCN 5, 253–255 | –255 | 133 | 1490 | 1443 | 99 | 1.337 | 0.007 | 31.11 | 10.81 |

Notes: Os stratigraphic depth is at the base of the lower critical interval, LCI, referring to biotic changes before the Selli Level highlighted by gray shade. Os, Pt, Ir, and Pd abundances and Os isotope measurements were done using Thermo-Finnigan 2 Element at the School of Ocean and Earth Science and Technology; present-day Os isotopes and Os concentration data from Teja et al. are presented for reference. Fusion blanks gave negligible values of 0.47–0.68 pg/g Os and replicate analysis of Johnson-Matthey standard solution yield an average value of 75 pg/g Os = 1.082; +/−0.0058 (n=8; 258) during the measurement. PGE measurements of TDB-1 standard in this laboratory gave average (n=8) values of Ir = 86.1+/−12.6; Os = 122.6+/−14.4, and Pt = 543.7+/−32.5 pg/g vs. published values of 75+/−10, 117+/−12, and 5010+/−180, respectively. Average Pd value of 32+/−3 ng/g measured from TDB-1 is systematically higher than the published value of 24.3 pg/g probably due to spike miscalibration. Samples marked with asterisk are way underspiked, giving large errors in Os concentrations. N-TIMS Os concentration data are used for those samples instead since Os data for both measurements are in good agreement for most samples.

### Results

Robinson et al. and Paquay et al. showed that for the KTB and Eocene impact-related sediments, respectively, Ir abundance peak coincides with transient negative spike toward extraterrestrial Os isotopic values. For the Gorgo a Cerbara section, two negative excursions in initial Os isotopic values are observed (Fig. 2); one, just after magnetic chron M0, with a long duration of 180–450 ka and another sharp and short drop, just above the base of the Selli Level, for a period of only 32–74 ka (duration based on 1.9–4.7 m/Ma rates). The Selli Level has been defined at depths of 0.4–2.3 m above the Lower Critical Interval (LCI), where significant biotic changes are evident.

This sequence was deposited in a moderately reducing to anoxic environment similar to that inferred for the Selli Level but without the influence of contemporaneous volcanism.

### Notes

1, 1–2, and 2 vs. a range from 1 to higher values for each of the ratios, respectively. PGE behavior in marine environment is still poorly known but their abundances in seawater are generally very low. Enrichment of PGE in marine sediments can be attributed to very slow sedimentation rate or anoxic conditions and from extraterrestrial or volcanic-hydrothermal source inputs. They can be incorporated either in detrital or in dissolved form and fractionation among them may be brought about by pre-depositional transport and post-depositional processes. Differential scavenging of Os and Ir from Pt and Pd from seawater contribute to the high Pd/Ir and Pt/Ir ratios recorded in pelagic sediments. Combined PGE abundances and Os isotope data provide an excellent tool to differentiate the effects of volcanism and meteorite impact at the Cretaceous-Tertiary boundary (KTB). Here we investigate the extraterrestrial impact hypothesis for the origin of the Early Cretaceous GOJE, and the contemporaneous OAE1a, using the PGE and Os isotope correlation recorded in a paleo-Tethyan marine sequence.

For ejecta products of oceanic impacts, an extraterrestrial contribution can be discriminated from purely volcanic input by anomalous enrichments and contrasting ratios of PGEs in contemporaneous sedimentary sequences. This approach may not rule out an impact by an achondrite body, as achondrites are not enriched in PGE. However, achondrite meteorites are uncommon and impacts identified so far form only up to 24 km-wide crater, much smaller than that postulated (≥200 km-wide crater) to produce the extent of melt volume required to form the OJP, the largest of the three plateaus representing the GOJE. Thus, we focus on the possibility of a chondritic bolide for the origin of the large-volume volcanism. We report here the PGE concentrations of the same sequence at Gorgo a Cerbara, central Italy that was analyzed previously for Os isotopes. Because PGE enrichments may also result from accumulation into organic-rich sediments, we compare the data with those of the normal Lower Miocene to Upper Paleocene organic-rich sedimentary sequence at Ocean Drilling Program (ODP) Site 959 in the Atlantic Ocean.
| Depth, mbsf | $^{187}$Os/$^{188}$Os | RSD | Os (pg/g) | RSD | S.D. % | Pt (pg/g) | S.D. % | Os/Ir S. D. % | Pt/Ir S. D. % |
|------------|----------------------|-----|-----------|-----|--------|-----------|--------|----------------|---------------|
| 374.9      | 1.180                | 0.010 | 128 | 15 | 380 | 8.0 | 25 |
| 384.4      | 1.145                | 0.002 | 229 | 24 | 550 | 9.0 | 22 |
| 386.2      | 1.246                | 0.004 | 225 | 19 | 440 | 12.0 | 24 |
| 386.2      | 1.214                | 0.005 | 233 | 44 | 810 | 5.0 | 18 |
| 386.2      | 1.231                | 0.002 | 215 | 27 | 709 | 8.0 | 26 |
| Average    | 386.2                | 1.230 | 1% | 224 | 4% | 653 | 29% | 8.3 | 42% |
| 394.2      | 1.061                | 0.005 | 277 | 17 | 662 | 17.0 | 40 |
| 403.6      | 1.194                | 0.019 | 158 | 15 | 326 | 11.0 | 22 |
| 403.6      | 1.240                | 0.005 | 175 | 14 | 324 | 12.0 | 23 |
| 403.6      | 1.218                | 0.003 | 137 | 37 | 525 | 4.0 | 14 |
| Average    | 403.6                | 1.217 | 2% | 157 | 12% | 392 | 29% | 9.0 | 48% |
| 404.0      | 1.053                | 0.002 | 256 | 30 | 972 | 9.0 | 32 |
| 404.7      | 1.232                | 0.009 | 153 | 14 | 499 | 11.0 | 35 |
| 422.2      | 1.147                | 0.005 | 272 | 45 | 957 | 6.0 | 21 |
| 422.2      | 1.207                | 0.003 | 254 | 32 | 864 | 8.0 | 27 |
| Average    | 404.0                | 1.136 | 1% | 263 | 5% | 30 | 43% | 8.3 | 42% |
| 434.0      | 0.981                | 0.006 | 277 | 29 | 1365 | 12.0 | 47 |
| 437.0      | 1.319                | 0.0045 | 271 | 34 | 994 | 8.0 | 29 |
| 439.6      | 1.187                | 0.036 | 217 | 10 | 509 | 23.0 | 53 |
| 439.6      | 1.474                | 0.003 | 559 | 29 | 2113 | 19.0 | 41 |
| Average    | 434.0                | 1.340 | 5% | 318 | 1% | 39 | 24% | 9.0 | 48% |
| 466.6      | 0.498                | 0.001 | 492 | 27 | 653 | 18.0 | 24 |
| 469.3      | 0.563                | 0.002 | 551 | 93 | 1082 | 6.0 | 12 |
| 475.8      | 1.205                | 0.013 | 330 | 11 | 545 | 29.0 | 48 |
| 475.8      | 1.122                | 0.003 | 306 | 25 | 1008 | 12.0 | 41 |
| Average    | 475.8                | 1.146 | 5% | 318 | 5% | 18 | 55% | 20.5 | 59% |
| 488.0      | 1.068                | 0.004 | 234 | 27 | 1314 | 13.0 | 49 |
| Average    | 488.0                | 1.100 | 1% | 307 | 1% | 25 | 11% | 13.0 | 49% |
| 495.3      | 1.211                | 0.005 | 210 | 9 | 490 | 24.0 | 55 |
| 495.5      | 1.481                | 0.002 | 552 | 17 | 1197 | 32.0 | 69 |
| 505.5      | 1.191                | 0.002 | 217 | 30 | 866 | 7.0 | 29 |
| Average    | 505.5                | 1.188 | 5% | 318 | 6% | 18 | 55% | 20.5 | 59% |
| 515.8      | 1.136                | 0.004 | 226 | 17 | 935 | 13.0 | 54 |
| 515.8      | 1.132                | 0.020 | 224 | 14 | 1017 | 16.0 | 72 |
| Average    | 515.8                | 1.134 | 5% | 318 | 1% | 16 | 14% | 14.5 | 63 |
| 517.6      | 1.062                | 0.003 | 191 | 27 | 1104 | 7.0 | 40 |
| 524.0      | 1.067                | 0.004 | 219 | 19 | 770 | 11.0 | 40 |
| 534.5      | 1.038                | 0.004 | 233 | 27 | 829 | 9.0 | 31 |
| 534.0      | 1.235                | 0.010 | 327 | 21 | 1262 | 15.0 | 59 |
| 552.4      | 1.010                | 0.004 | 299 | 36 | 1040 | 8.0 | 29 |
| 553.5      | 0.845                | 0.001 | 171 | 19 | 901 | 9.0 | 48 |
| 553.5      | 0.842                | 0.002 | 90 | 14 | 371 | 7.0 | 27 |
| 555.5      | 1.240                | 0.005 | 149 | 27 | 681 | 5.0 | 25 |
| 553.5      | 0.827                | 0.008 | 175 | 62 | 824 | 3.0 | 13 |
| Average    | 553.5                | 0.938 | 21.5% | 146 | 27% | 31 | 71% | 694 | 34% |
| 563.0      | 0.815                | 0.001 | 338 | 25 | 1244 | 14.0 | 50 |
| 563.0      | 0.817                | 0.008 | 351 | 28 | 1265 | 13.0 | 45 |
| Average    | 563.0                | 0.816 | 0% | 345 | 3% | 27 | 8% | 1255 | 1% |
| 592.0      | 0.895                | 0.006 | 196 | 8 | 152 | 24.0 | 19 |
| 592.0      | 0.886                | 0.004 | 198 | 11 | 320 | 17.0 | 28 |
| Average    | 592.0                | 0.900 | 1% | 197 | 1% | 10 | 22% | 236 | 50% |
| 623.7      | 0.820                | 0.009 | 105 | 8 | 224 | 13.0 | 28 |
| 626.0      | 1.157                | 0.097 | 131 | 13 | 266 | 10.0 | 21 |
| TDB-1 std  | measured             | published | |
| 123        | 12%                  | 86 | 15% | 5434 | 6% |
| 117        | 10%                  | 75 | 13% | 5010 | 4% |

Notes: Relative standard deviation, RSD, and standard deviation (S.D.) as % of average of replicates; published values for TDB-1 are from Meisel and Moser. Os isotope compositions are measured present day values.
Figure 3 | Plots of Pd, Os and Pt vs. Ir for Gorgo a Cerbara and ODP Site 959 samples. Data show mostly non-chondritic Pd/Ir, Os/Ir and Pt/Ir ratios. No Pd data were obtained for ODP Site 959. Data for OJP42–43 and a range of LIP and hotspot samples31, impactites14, igneous rocks, and metalliferous sediments30 are plotted, together with average crustal (cross) and meteoritic (square) compositions from Peucker-Ehrenbrink and Jahn26 and Palme and O’Neill44, respectively. The range for K-T Ir abundances are from Glikson14 and Frei and Frei15. Chondritic lines for Os/Ir = 1 and Pt/Ir = 2 are shown for reference.
Figure 4 | Age vs. $^{187}$Os/$^{188}$Os, Ir, Os/Ir and Pt/Ir plots for Gorgo a Cerbara and ODP Site 959. Estimated initial and present-day Os isotope and PGE data for Gorgo a Cerbara (this study) are compared with those of organic-rich sedimentary sequence at ODP Site 959 to show the contrast between deposition with and without contemporaneous volcanism. Volcanism induced by extraterrestrial impact on oceanic crust should leave meteoritic signature on distal ejecta sediments like that of the Gorgo a Cerbara section if it happened in the Pacific Ocean around 125 to 118 Ma. The Gorgo a Cerbara data show characteristics in between those of normal organic-rich sedimentary sequence at ODP Site 959 and OJP lavas and unlike the extreme values characteristic of extraterrestrial materials. Dashed line marks the PGE spike that does not correspond to negative shifts in ($^{187}$Os/$^{188}$Os)$_t$, Os/Ir, and Pt/Ir values as expected for a bolide impact signature. Values for chondritic meteorite abundances are from Palme and O’Neill44. Reference data for meteorite impacted sediments and for OJP lavas are from Frei and Frei46, Paquay et al.35, Robinson et al.34, Ely and Neal42, Chazey and Neal43. Ages were calculated based on published sedimentation rates38–41 and Re data used for age-correction of present-day $^{187}$Os/$^{188}$Os to initial values are from Tejada et al.22, Ravizza37, and Ravizza and Paquay38.
In general, the levels of abundance of Pd and Ir in the Selli interval fall within the range of data for the OJP3–41, other LIPs and hotspot basalts30–31 (Fig. 3A) but the Ir concentrations are much lower than values of ≥10000 ppt determined for impactites and chondrites42,43 and for a similarly reducing, organic-rich KTB sedimentary section at Stevens Klint, Denmark (9–35 ppb)44. In addition, Os/Ir and Pt/Ir values within the Selli Level are mostly non-chondritic (Fig. 3B–C, Fig. 4), including the bed that yielded the highest concentration of Re and other PGE (Os/Ir = 12 and Pt/Ir = 55; Fig. 4). Significantly, the Pd, Pt, and Ir concentrations of the whole sedimentary section are slightly lower than, but overlap with, those of OJP lavas (Figs. 3–4). The Pd/Ir ratios also fall between those of plateau lavas and seawater (Fig. 3A).

The Lower Miocene to Upper Paleocene sedimentary sequence (375–651 mbsf) at ODP Site 959 in the Atlantic is composed mostly of diatomites interbedded with nanofossil chalk and clay, grading into Upper Cretaceous chert and claystone with depth45. Sedimentary sequence cored at this site records an anoxic to moderately reducing environment in a restricted basin, resulting in deposition of organic-rich sediments37–38,46, and thus provides baseline data for comparison with those of the Selli Level interval. Sedimentary beds at ODP Site 959 contain up to 4.7% TOC and are carbonate poor to siliceous with elevated proportions of marine organic matter, similar to the Selli Level. PGE concentrations range from 90–551 ppt for Os, 8–93 ppt for Ir, and 152–1625 ppt for Pt (Table 2; Figs. 3–4); Os/Ir and Pt/Ir values range from 3–32 and 12–73, respectively (Fig. 4), similar to that of seawater today46.

The PGE concentrations obtained from the Selli Level interval are comparable to those in organic-rich sediments at ODP Site 959 but approach the values for OJP lavas42–43. Selli Level Pt and Ir values are intermediate between those of the plateau lavas and those of the normal organic-rich sedimentary section at ODP Site 959 (Figs. 3–4). The fractionation between Ir vs. Os in the Selli Level sediments is only slightly lower than seen for ODP Site 959 (chondrite-normalized Os/Ir, Os/Ir = 0.8–16 vs. 5–25). Fractionation of Os from Ir is common in pelagic sediments and has been suggested to be controlled by variation in the redox condition in the oceans37,38. High Os/Ir values reflect Os uptake from seawater by organic-rich sediment35,37.

**Discussion**

During the period marked by the first Os isotope excursion just after magnetic chron M0 and before OAE1 event, a decline in abundance in nannococonids and nannofossil paleoloxues was observed40–49, which is attributed to the initiation of volcanogenic CO₂ input into the ocean. Based on 187Os/188Os, values (0.54–0.89) and Ir contents (9–133 ppt) prior to this interval (Figs. 2 and 4), no extraterrestrial influence is apparent before the inferred initiation of volcanism. It is the sharp drop in 187Os/188Os values to 0.19 and the spikes in PGE abundances within the Selli Level interval that signals a probable meteoritic input within the sequence. This Os isotopic shift can be attributed to the OJP’s submarine eruption22, but could it be that the volcanism itself was initiated by a bolide impact22,23?

To answer this question, the timing of the Os isotope shift and the Ir or PGE spike is important. These two observations are coincident in both the Late Eocene and the KTB impact sites34–35. However, peak Ir concentration is found 30 cm above the sharp drop in 187Os/188Os, and associated large (>2 per mil) shift toward lighter carbon isotope compositions at Gorgo a Cerbara35. This depth interval is equivalent to a 64–138 thousand years lag based on sedimentation rates of 1.9–4.7 m/Ma determined within the Selli Level34–35. Thus, even if one ignores the fact that the measured PGE ratios are distinctly different from those of other known impact horizons, the fact that maximum Ir concentration lags behind the onset of sharp decrease in 187Os/188Os values cannot be reconciled with the hypothesis that an extraterrestrial impact triggered volcanism. Rather, it seems more likely that highly elevated concentrations of Ir and other trace metals, including Re and Os, within this narrow interval are a consequence of the lithology and the high organic carbon content. This interval is entirely composed of black shale, with one of the highest organic content (total organic carbon, TOC = 3.76%). It is sandwiched by green marl above and radiolarian sandstone beds below it, indicating that the PGE enrichment is controlled by the amount of organic matter in this black shale bed. If the PGE peaks were of meteoritic origin, a transient spike of 187Os/188Os ~0.13 should have also registered over the already low ~0.2 steady-state level within this interval, akin to the KTB44, where a 50% shift to lower value was observed. Instead, the Os isotope composition before, during, and after the PGE spikes remained at 0.2 in these sediments. This value approaches those of the OJP lavas (Fig. 4), pointing to the voluminous mantle input during the plateau’s emplacement as the source of the low (187Os/188Os), values in this interval.

The PGE concentrations across the Selli Level at Gorgo a Cerbara also do not show a systematic enrichment with the drop in Os isotope ratio (Figs. 2 and 4). There is no clear difference in Pd, Pt, and Ir concentrations within the Selli relative to intervals below and above it. Although Pt, Os, and Ir values are much higher than in the normal organic-rich sediments at ODP Site 959, the ratios of Pt/Ir and Os/Ir are mostly higher than both chondritic and continental crust values (Figs. 3–4). The black shale bed with the PGE spikes has a high Os/Ir value of 11, similar to values of the organic-rich sediments at ODP Site 959 (Fig. 4). These findings are not consistent with the results expected for impact events, as exemplified by the KTB and Late Eocene examples34–35, data for which show an antithetical relationship between Ir/Os contents and the 187Os/188Os, of the sediments, and Os/Ir values of 2 or lower. The duration of both the Os isotope and Ir spikes is also the same in both impact sites. This is not the case for the Selli Level interval at Gorgo a Cerbara.

The absence of a positive correlation between enrichment of PGE and chondritic Os isotopic ratios in the Selli Level horizon nor in the time interval prior to the inferred initiation of the Early Cretaceous GOJE does not support an extraterrestrial input. Highly variable Os/Ir ratios that are uncorrelated with 187Os/188Os, can only be reconciled with an extraterrestrial impact hypothesis in the case of a PGE-poor (achondritic) impactor. Thus, conclusive geochemical evidence supporting an oceanic bolide impact as a cause of Early Cretaceous GOJE remains elusive and calls for further work in contemporaneous sedimentary sequences elsewhere.

**Methods**

**Sample collection and preparation.** The ~1.9-m-thick Selli Level in the type section at Gorgo a Cerbara, central Italy, is composed of alternating olive-green mudstones and organic-rich black shales, with minor intercalations of radiolarites18,20 (Fig. 1). Underlying this horizon is an organic-rich interval, ~40 cm thick, known as the Lower Critical Interval (LCI). Samples of the organic-rich sedimentary sequences were taken from ~3.5 m below to ~1 m above the Selli Level were previously analyzed for Re and Os concentrations, 187Os/188Os, total organic carbon (TOC) content, and stable C isotopic ratios of organic carbon (δ13Corg). We picked samples for PGE analysis at the locations where we expect the Ir enrichment based on the Os isotope results, that is, the interval between and during the two negative spikes in 187Os/188Os. Our Os isotope results indicate that these intervals are 1.3 m below the Selli Level and 50 cm above the Selli Level where we did a similar sampling resolution as that for Os isotope determination. It is ideal to have a higher resolution sampling but is not required to test our hypothesis, considering limited time and resources.

Splits of these samples were washed in deionized water to remove fines and loose materials. Then they were cleaned with ultrapure water (3–5 times) and reagent grade ethanol. The chips were then dried in the oven at 80°C overnight prior to crushing in agate (for shales) and iron mortar (for limestones and silty samples, but wrapped in thick, clean paper). The crushed fragments were finally ground in alumina ceramic mill.

**Analytical methods.** Os isotopic compositions and PGE concentrations were measured by isotope dilution combined with nickel sulfide (NiS) fire assay preconcentration procedure30,48. Five to ten grams of sample powders were mixed with fusion flux made up of 10 g NaBO₃, 0.2 g S, and 0.3 g Ni. The mixtures were fused in an oven for one to one and a half hours at 1000°C to separate the PGEs from the matrix. During fusion, the PGEs were collected into a sulfide bead, which was then separated from the enclosing glass and subsequently dissolved in 6N distilled HCl on a hotplate at 200°C. The solutions were then filtered to collect the PGEs, which stick to
the filter paper. The filter papers were then dissolved in 20 ml Teflon beakers with concentrated ultrapure HNO3 and heated up to 110 °C to release the PGEs. Os isotopes and concentrations were measured first by sparging method84, after which the concentrated HNO3 solutions containing PGEs were then diluted 20 times and the PGE concentrations were measured by Thermo-Finnigan’s Element 2 High Resolution Inductively-Coupled Plasma Mass Spectrometry (HR-ICPMS) at the School of Ocean and Earth Sciences, University of Hawaii.

Approximately 1 fusion blank was analyzed for about 7 analyses performed. Gas blanks and standard solutions were analyzed between every 6 samples. Gas blanks were used to monitor the amount of Os cross contamination between successive samples. Where gas blanks have 33Os intensities that are more than 10% of that of the sample, the results are not used.

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Author contributions
M.L.G.T and G.R. contributed equally to design the study. M.L.G.T. wrote the manuscript, but with significant contribution and refinements from G.R., K.S., and F.P. G.R. and F.P. contributed their ODP Site 959 data for comparison with Gorgo a Cerbara data.

Additional information
Competing financial interests: The authors declare no competing financial interests.

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