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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 ocurrence as indicated by two stratigraphic intervals with $^{187}Os/^{188}Os$ 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 surface[4]. 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 impact[4–7]). Another idea is that rapidly upwelling mantle along ridges incorporates easily fusible recycled crust[8] and that an enriched perisphere exists below the crust[9–10] 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 crust[1,11–12]. Although this model is disputed based on theoretical and geophysical grounds[8], no strong geochemical evidence from contemporaneous sedimentary sequences is yet presented to test the bolide impact hypothesis. For example, Jones[12] 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 events[13–14] and one of the three major ocean wide anoxia events in the Cretaceous, known as OAE1a[15–16], coincided with the GOJE, suggesting a potential linkage[17–19]. Furthermore, although the idea that oceanic plateaus are probable signatures of ancient meteorite impacts[11] has been around for nearly thirty years now, the connection among these events, large volume volcanism and biotic perturbations is advocated only recently[12,14]. Thus, we examined the Gorgo a Cerbara section in Central, Italy, the type section identified to include the OAE1a marker[20], 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 sediments[20–21]. 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 OAE1a[16], and records an interval of low seawater initial Os isotopic composition, $(^{187}Os/^{188}Os)_t \sim 0.2$, previously interpreted as indicating a causal link between the global oceanic anoxia and massive volcanism[22].

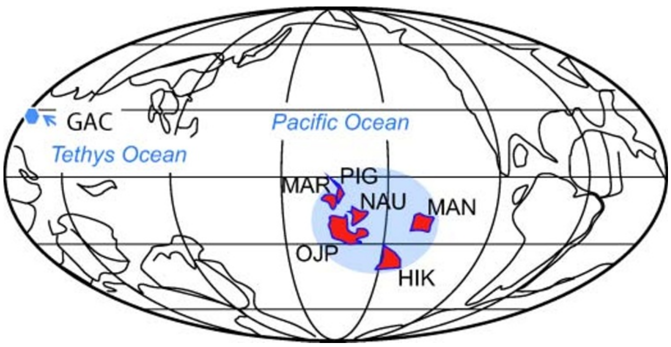

Figure 1 | Paleogeographic reconstruction at 118.7 Ma. The location of Gorgo a Cerbara section (GAC) relative to the Greater Ontong Java Event site (outlined by the ellipse) is shown. The Greater Ontong Java event includes Ontong Java Plateau (OJP), Manihiki Plateau (MAN), Hikurangi Plateau (HIK)[2–4] and the contemporaneous volcanism at Mariana (MAR), Nauru (NAU) and Pigafetta (PIG) basins[1]. Modified from Ingle and Coffin[1].

The Re-Os isotope system is an important tracer for mantle and extraterrestrial inputs into the ocean[23–24]. 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[23]. 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[25], 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 $^{187}Os/^{188}Os$ of 1.0–1.5[26]). Indeed, low $^{187}Os/^{188}Os$ values can be produced by the input of cosmic Os or mantle-derived Os[27] in the ocean because Os from both sources is unradiogenic, with $^{187}Os/^{188}Os$ ca. 0.13[28].

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[29]. Inter-element abundance ratios are also different between extraterrestrial and terrestrial materials, e.g. Os/Ir, Pd/Ir and Pt/Ir ratios are

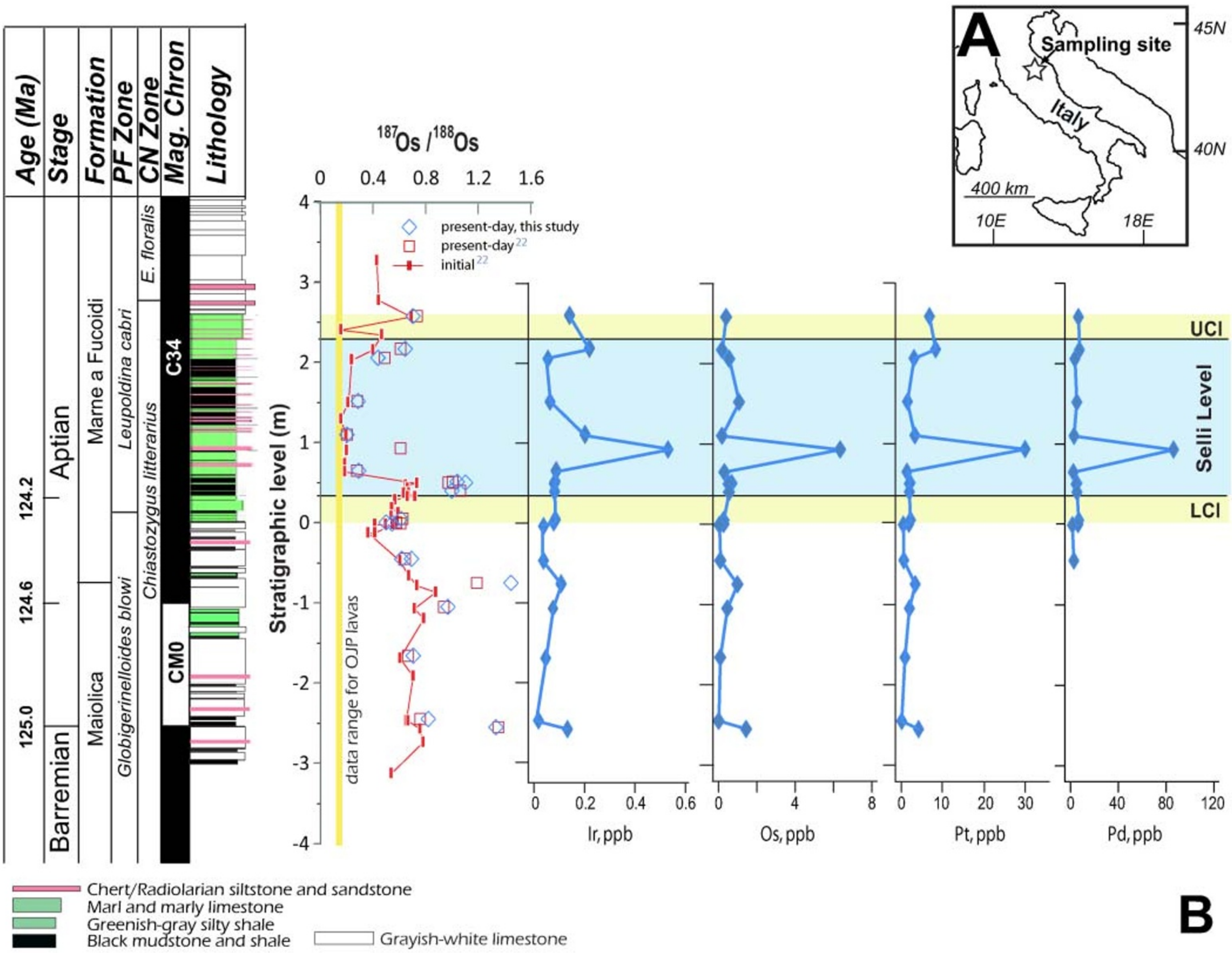

Figure 2 | Sampling site and PGE and Os isotope data. (A) Sampling location at the type locality of the Selli Level at Gorgo a Cerbara, central Italy, representing oceanic anoxic event OAE1a. (B) Variation of PGE and present-day and initial $^{187}Os/^{188}Os$ with stratigraphic depth. Initial Os isotope profile and lithology are adapted from Tejada et al.[22]. Note the very similar present-day $^{187}Os/^{188}Os$ values from previous work[22] and this study, except for one sample, suggesting consistency of results despite different analytical methods. LCI and UCI refer to lower and upper critical intervals, respectively, before and after the Selli Level horizon where significant biotic changes were detected[18,20].

Table 1 | Platinum Group Elements and present-day $^{187}Os/^{188}Os$ data for Gorgo a Cerbara, Central Italy

		Bulk sediment, NiS Fire Assay, HR-ICPMS (this study)									*Chromic Acid digestion, N-TIMS[22]*				
SAMPLE NO.	Depth, cm	Pd (pg/g)	Ir (pg/g)	Pt (pg/g)	Os (pg/g)	S. E.	187Os/188 Os	S. E.	Pt/Ir	Os/Ir	Os (pg/g)	S. E.	187Os/188 Os	S. E.	Os/Ir
ASL1, 247–248	258	6734	142	6813							143	0.3	0.736	0.002	1.01
SL27, 205–207	217	7667	220	8303	194	1	0.647	0.002	37.66	0.88	317	2	0.611	0.003	1.44
SL28, 194–196	206	3855	49	3096	572	82	0.441	0.009	63.06	11.65	1102	5	0.493	0.003	22.46
replicate					*564*	*44*	*0.439*	*0.008*		*11.49*					
SL16, 140–142	152	5343	66	1499	1080	147	0.290	0.006	22.84	16.46	747	6	0.282	0.002	11.38
SL21, 98–100.5	110	3036	203	3286	187	1	0.204	0.001	16.19	0.92	330	3	0.204	0.003	1.62
SL22, 82–83*	93	86153	544	29852			0.621	0.002	54.88		6352	122	0.612	0.001	11.68
SL24, 53.5–55	65	2482	89	1391	309	11	0.293	0.003	15.68	3.48	343	1	0.281	0.001	3.87
SL25, 41–41.5	51	5406	85	2141	689	2	1.042	0.001	25.29	8.15	691	6	1.006	0.011	8.17
SLB1, 48–50	50	4888	82	1969	543	21	*1.104*	*0.013*	24.13	6.66	718	2	0.974	0.006	8.80
SLB1, 39–40*	40	5555	83	1969							560	2	1.065	0.006	6.78
SLB4, 5–5.6	5	6977	86	2226	270	5	0.615	0.002	25.98	3.16	321	1	0.627	0.005	3.75
SLB5, 0–0.3	0.3	6495	79	1859	271	111	0.502	0.052	23.51	3.43	157	1	0.580	0.007	1.99
BSL1, 0–1 cm	−1	1693	35	514	55.6	0.4	0.548	0.004	14.63	1.58	47.5	0.2	0.610	0.009	1.35
BSL2, 45–46 cm	−45	2871	34	608	104	3	0.695	0.019	18.14	3.09	135	0.3	0.647	0.003	4.02
BSL6, 73–75	−75		109	3386	994	5	1.450	0.001	31.11	9.14	1019	4	1.191	0.006	9.36
BSL8, 104–105	−105		77	1973	463	68	*0.972*	*0.008*	25.74	6.05	480	2	0.940	0.003	6.27
BSL10, 166–167	−166		49	919	97.0	0.7	0.708	0.005	18.72	1.97	78	0.2	0.668	0.006	1.58
GCN 4, 244–245	−245		9	113	13.1	0.1	0.822	0.011	12.36	1.43	15.3	0.1	0.762	0.018	1.67
GCN 5, 253–255	−255		133	4190	1443	99	1.337	0.007	31.39	10.81	1565	5	1.356	0.004	11.72

Notes: 0 stratigraphic depth is at the base of the lower critical interval, LCI, referring to biotic changes before the Selli Level[18,20] highlighted by gray shade. Os, Pd, Ir, and Pt abundance and Os isotope measurements were done using Thermo-Finnigan Element 2 at the School of Ocean and Earth Science and Technology; present-day Os isotope ratios and Os concentration data from Tejada et al.[22] 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 $^{187}Os/^{188}Os$ = 0.1082, +/− 0.0058 (n=8, 2SE) during the measurement. PGE measurements of TDB-1 standard in this laboratory gave average (n=6) values of Ir = 86.1+/−12.6, Os = 122.6 +/−14.4, and Pt = 5433.7 +/−32.5.5 pg/g vs. published values of 75+/−10, 117+/−12, and 5010+/− 180, respectively[49]. Average Pd value of 32 +/− 3 ng/g measured from TDB-1 is systematically higher than the published value of 24.3 ng/g probably due to spike miscalibration. Samples marked with asterisk are way underspiked, giving large errors in Os concentration. N-TIMS Os concentration data are used for these samples instead since Os data for both measurements are in good agreement for most samples.

1, 1–2, and 2 vs. a range from about 1 to higher values for each of the ratios, respectively[30–31]. PGE behavior in marine environment is still poorly known but their abundances in seawater are generally very low[31]. 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[31–33]. 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[31,33]. 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[34])). 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[12,34–35]. 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[36], much smaller than that postulated (≥200 km-wide crater[1,12]) 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[22]. Because PGE enrichments may also result from accumulation into organic-rich sediments[33], 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[37–38]. 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.

Results

Robinson et al.[34] and Paquay et al.[35] showed that for the KTB and Eocene impact-related sediments, respectively, Ir abundance peak coincides with transient negative spike toward extraterrestrial Os isotope values. For the Gorgo a Cerbara section, two negative excursions in initial Os isotope 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[39–41]). 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[18,20] (Fig. 2). A sharp decline in initial or age-corrected Os isotope value, $(^{187}Os/^{188}Os)_t$, from 0.75 to 0.19 and steady, low values of ~0.2 for a protracted period coincide with the Selli Level[22]. Except for a prominent spike in Os, Ir, Pt, and Pd (~6000, 544, 29852, and 86153 ppt, respectively) about 50 cm above the base, samples within this interval have concentrations of Os (187–1080 ppt), Ir (49–220 ppt), Pt (1391–8303 ppt), and Pd (2482–7667 ppt) that are low, although much higher than continental crustal abundances (average Os =31 ppt; Ir = 22 ppt; Pt = 510; and Pd = 520 ppt[26]) (Table 1; Fig. 3). There are no marked changes in the range of PGE concentrations (Os =13–1443 ppt; Ir = 9–142 ppt; Pt = 113–6813 ppt; Pd = 1693–6977 ppt) as well as in the Os/Ir = 1.4–11 and Pt/Ir = 12–31 in sedimentary beds above and below the Selli Level (Figs. 2 and 4). In contrast, the first gradual decline in Os isotopic values from 0.87 to 0.39 just after the magnetic chron M0 is accompanied by decreasing abundances of Ir, Os and Pt from maximum concentrations of 109, 994, and 3386 ppt to 35, 56, and 514 ppt, respectively (Fig. 2, Table 1).

Table 2 | Platinum group element and present-day $^{187}Os/^{188}Os$ data for ODP Site 959, Atlantic Ocean

	Depth, mbsf	$^{187}Os/^{188}Os$	RSD	Os (pg/g)	RSD	Ir (pg/g)	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%	30	43%	653	29%	8.3	42%	23	18%
	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%	22	59%	392	29%	9.0	48%	20	25%
	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	422.2	1.177	4%	263	5%	39	24%	911	7%	7.0	20%	24	18%
	432.1	1.308	0.005	325		15		624		22.0		43	
	434.0	*1.480*	*0.017*	*335*		*29*		*1365*		*12.0*		*47*	
	434.0	*1.421*	*0.002*	*329*		*24*		*1319*		*14.0*		*56*	
Average	434.0	1.450	3%	332	1%	27	13%	1342	2%	13.0	11%	52	12%
	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*		*73*	
Average	439.6	1.330	15%	388	62%	20	69%	1311	87%	21.0	13%	63	22%
	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	1.164	5%	318	5%	18	55%	777	42%	20.5	59%	45	11%
	476.2	1.236	0.006	113		10		503		12.0		52	
	486.0	1.109		463		40				12.0			
	486.3	1.866	0.005	348		13		711		27.0		54	
	488.0	*1.072*	*0.003*	*345*		*23*		*1206*		*15.0*		*52*	
	488.0	*1.068*	*0.004*	*349*		*27*		*1314*		*13.0*		*49*	
Average	488.0	1.070	0%	347	1%	25	11%	1260	6%	14.0	10%	51	4%
	495.3	1.191	0.004	403		35		1444		11.0		42	
	496.1	1.201	0.005	210		9		490		24.0		55	
	505.5	*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	1.336	15%	385	62%	24	39%	1032	23%	19.5	91%	49	58%
	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	0%	225	1%	16	14%	976	6%	14.5	15%	63	20%
	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*	
	553.5	*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%	6.0	43%	28	51%
	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%	13.5	5%	48	7%
	577.4	0.883	0.004	413		35		1625		12.0		46	
	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	0.890	1%	197	1%	10	22%	236	50%	20.5	24%	24	27%
	623.7	0.820	0.009	105		8		224		13.0		28	
	651.2	1.157	0.097	131		13		266		10.0		21	
TDB-1 std	*measured*			123	12%	86	15%	5434	6%				
	published			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[49]. Os isotope compositions are measured present-day values.

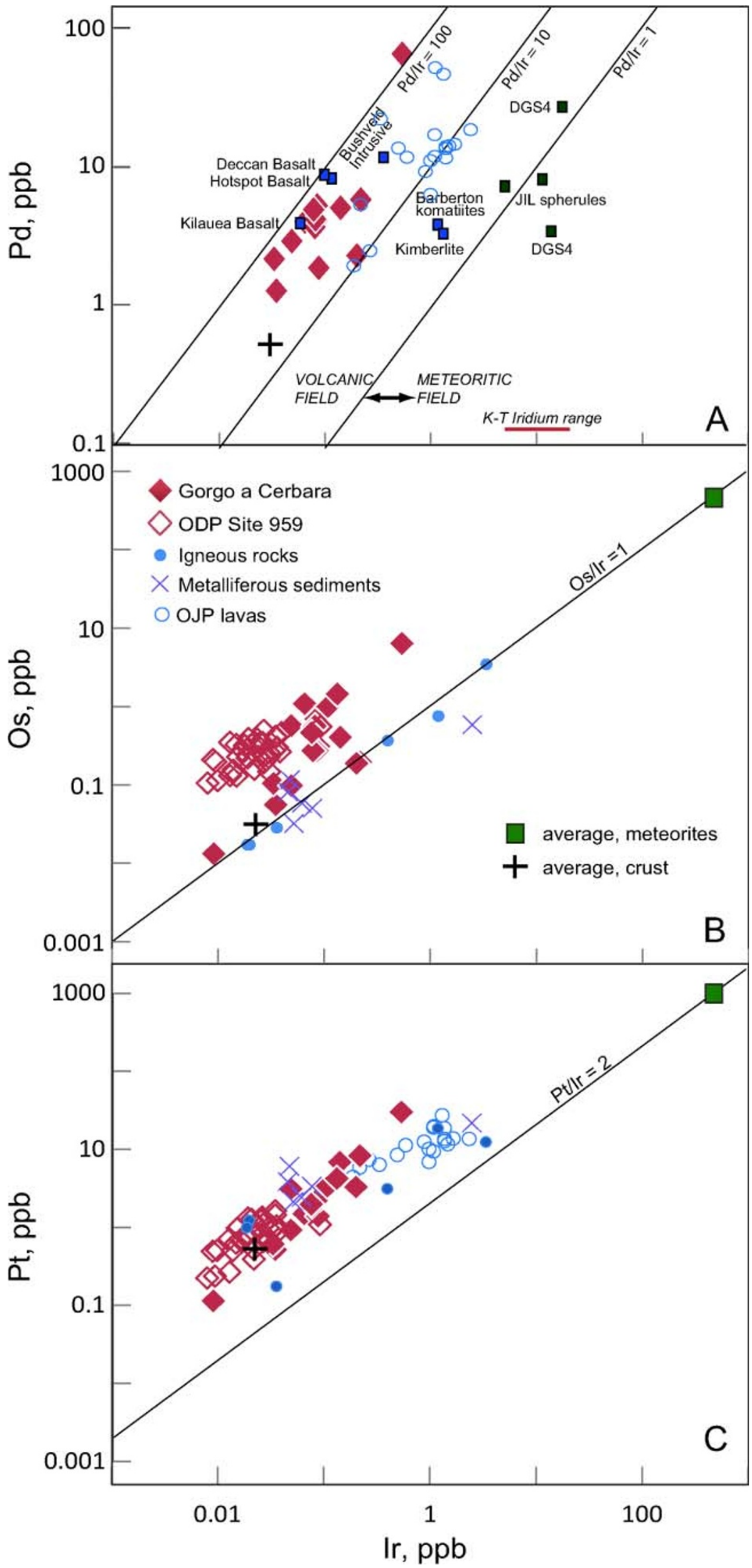

Figure 3 | Plots of Pd, Os and Pt vs. Ir for Gorgo a Cerbara and ODP Site 959 samples. Data show mostly non-chondritic Pd/Ir, Os/Ir and Pt/Ir ratios. No Pd data were obtained for ODP Site 959. Data for OJP[42–43] and a range of LIP and hotspot samples[31], impactites[14], igneous rocks, and metalliferous sediments[30] are plotted, together with average crustal (cross) and meteoritic (square) compositions from Peucker-Ehrenbrink and Jahn[26] and Palme and O'Neill[44], respectively. The range for K-T Ir abundances are from Glikson[14] and Frei and Frei[45]. Chondritic lines for Os/Ir =1 and Pt/Ir = 2 are shown for reference.

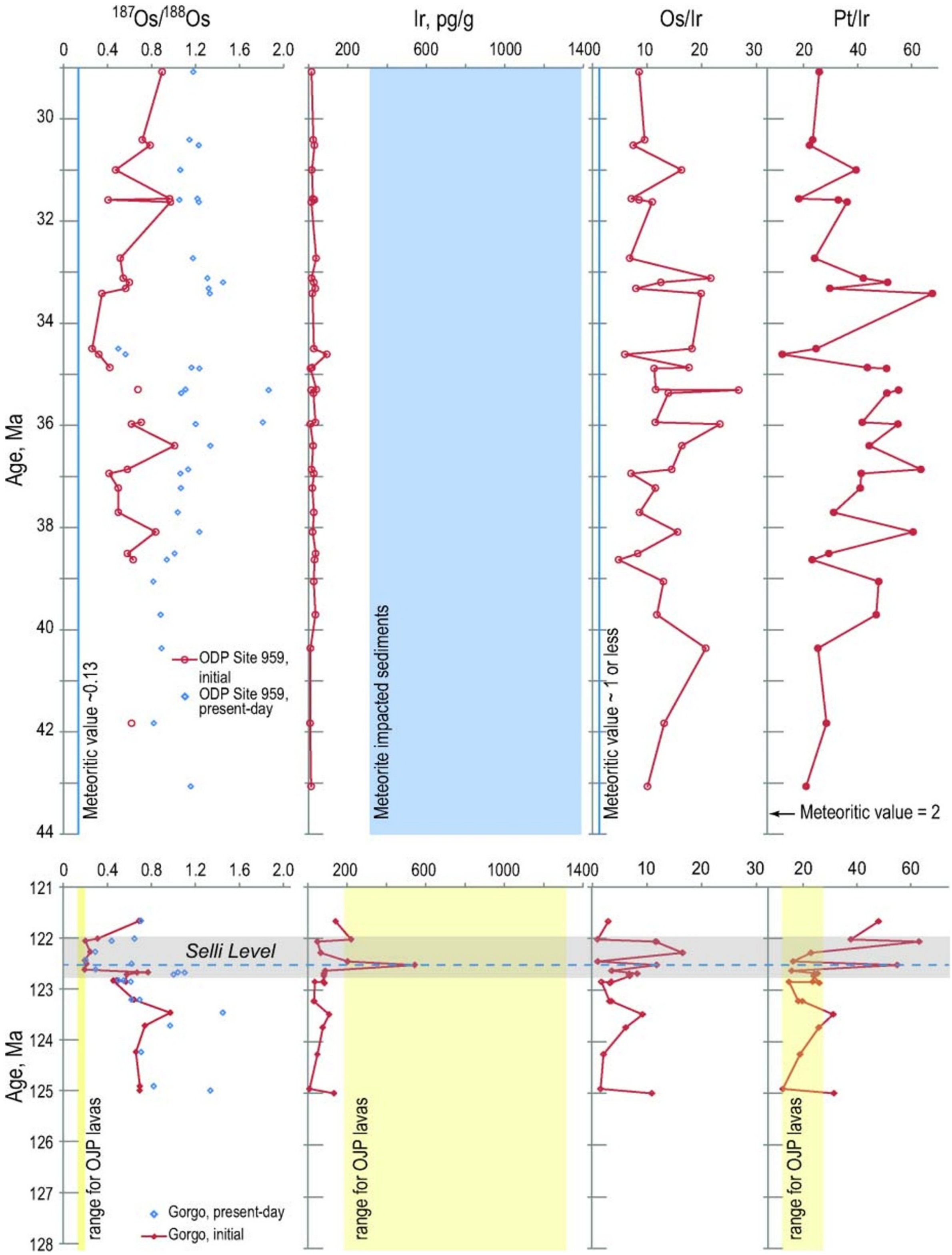

Figure 4 | Age vs. $^{187}Os/^{188}Os$, Ir, Os/Ir and Pt/Ir plots for Gorgo a Cerbara and ODP Site 959. Estimated initial and present-day Os isotope and PGE data for Gorgo a Cerbara (this study) are compared with those of organic-rich sedimentary sequence at ODP Site 959 to show the contrast between 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'Neill[44]. Reference data for meteorite impacted sediments and for OJP lavas are from Frei and Frei[45], Paquay et al.[35], Robinson et al.[34], Ely and Neal[42], Chazey and Neal[43]. Ages were calculated based on published sedimentation rates[38–41] and Re data used for age-correction of present-day $^{187}Os/^{188}Os$ to initial values are from Tejada et al.[22], Ravizza[37], and Ravizza and Paquay[38].

In general, the levels of abundance of Pd and Ir in the Selli interval fall within the range of data for the OJP[42–43], other LIPs and hotspot basalts[30–31] (Fig. 3A) but the Ir concentrations are much lower than values of ≥10000 ppt determined for impactites and chondrites[14,31,44] and for a similarly reducing, organic-rich KTB sedimentary section at Stevens Klint, Denmark (9–35 ppb[45]). 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 nannofossil chalk and clay, grading into Upper Cretaceous chert and claystone with depth[46]. Sedimentary sequence cored at this site records an anoxic to moderately reducing environment in a restricted basin, resulting in deposition of organic-rich sediments[37–38,46], 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 today[31].

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 lavas[42–43]. 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_n =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 oceans[31,33]. High Os/Ir values reflect Os uptake from seawater by organic-rich sediments[33,37].

Discussion

During the period marked by the first Os isotope excursion just after magnetic chron M0 and before OAE1a event, a decline in abundance in nannoconids and nannofossil paleofluxes was observed[18–19,47], which is attributed to the initiation of volcanogenic CO_2 input into the ocean. Based on $(^{187}Os/^{188}Os)_t$ 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 $^{187}Os/^{188}Os$ 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 eruption[22], but could it be that the volcanism itself was initiated by a bolide impact[1,11–12]?

To answer this question, the timing of the Os isotopic shift and the Ir or PGE spike is important. These two observations are coincident in both the Late Eocene and the KTB impact sites[34–35]. However, peak Ir concentration is found 30 cm above the sharp drop in $(^{187}Os/^{188}Os)_t$ and associated large (>2 per mil) shift toward lighter carbon isotope compositions at Gorgo a Cerbara[22]. This depth interval is equivalent to a 64–158 thousand years lag based on sedimentation rates of 1.9–4.7 m/Ma determined within the Selli Level[39–41]. 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 $(^{187}Os/^{188}Os)_t$ 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 $^{187}Os/^{188}Os$ ~0.13 should have also registered over the already low ~0.2 steady-state level within this interval, akin to the KTB[34], 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 $(^{187}Os/^{188}Os)_t$ 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 examples[34–35], data for which show an antithetical relationship between Ir contents and the $(^{187}Os/^{188}Os)_t$ 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 $(^{187}Os/^{188}Os)_t$ 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 radiolarites[18,20] (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 taken from ~3.5 m below to ~1 m above the Selli Level were previously analyzed for Re and Os concentrations, $^{187}Os/^{188}Os$, total organic carbon (TOC) content, and stable C isotopic ratios of organic carbon ($\delta^{13}C_{org}$)[22]. 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 before and during the two negative spikes in $^{187}Os/^{188}Os$. 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 (2 times), and rinsed once with analytical 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 isotope compositions and PGE concentrations were measured by isotope dilution combined with nickel sulfide (NiS) fire assay preconcentration procedure[30,48]. Five to ten grams of sample powders were mixed with fusion flux made up of 10 g $NaBO_3$, 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 segregate 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 HNO_3 and heated up to 110°C to release the PGEs. Os isotope and concentrations were measured first by sparging method[48], after which the concentrated HNO_3 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 ^{188}Os 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

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