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Evaluation of osmium isotopes and iridium as paleoflux tracers in pelagic carbonates

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Abstract

New osmium (Os) isotope and platinum group element (PGE) concentration data are used in conjunction with published ^{3}He and Th isotope data to determine the relative proportions of lithogenic, extraterrestrial and hydrogenous iridium (Ir) in a Pacific pelagic carbonate sequence from the Ocean Drilling Program (ODP) Site 806 on the Ontong Java Plateau (OJP). These calculations demonstrate that lithogenic and extraterrestrial contributions to sedimentary Ir budget are minor, while hydrogenous Ir accounts for roughly 85% of the total Ir. Application of analogous partitioning calculations to previously reported data from a North Pacific red clay sequence (LL44-GPC3) yields very similar results. Total Ir burial fluxes at Site 806 and LL44-GPC3 are also similar, 45 and 30 pg cm^{-2} kyr^{-1}, respectively. Average Ir/^{3}He and Ir/xs^{230}Th$_{initial}$ ratios calculated from the entire Site 806 data set are similar to those reported earlier for Pacific sites. In general, down-core profiles of Ir, ^{3}He and xs^{230}Th$_{initial}$, are not well correlated with one another. However, all three data sets show similar variance and yield sediment mass accumulation rate estimates that agree within a factor of two. While these results indicate that Ir concentration has potential as a point-paleoflux tracer in pelagic carbonates, Ir-based paleoflux estimates are likely subject to uncertainties that are similar to those associated with Co-based paleoflux estimates. Consequently, local calibration of Ir flux in space and time will be required to fully assess the potential of Ir as a point paleoflux tracer. Measured ^{187}Os/^{188}Os of the OJP sediments are systematically lower than the inferred ^{187}Os/^{188}Os of contemporaneous seawater and a clear glacial–interglacial ^{187}Os/^{188}Os variation is lacking. Mixing calculations suggest Os contributions from lithogenic sources are insufficient to explain the observed ^{187}Os/^{188}Os variations. The difference between the ^{187}Os/^{188}Os of bulk sediment and that of seawater is interpreted in terms of subtle contributions of unradiogenic Os carried by particulate extraterrestrial material. Down-core variations of ^{187}Os/^{188}Os with Pt/Ir and Os/Ir also point to contributions from extraterrestrial particles. Mixing calculations for each set of several triplicate analyses suggest that the unradiogenic Os end member cannot be characterized by primary extraterrestrial particles of chondritic composition. It is noteworthy that in efforts aimed at determining the effect of extraterrestrial contributions, ^{187}Os/^{188}Os of pelagic carbonates has greater potential compared to abundances of PGE. An attempt has been made for the first time to estimate sediment mass accumulation rates based on amount of extraterrestrial Os in the OJP samples and previously reported extraterrestrial Os flux. Throughout most of the OJP record, Os isotope-based paleoflux estimates are within a factor of two of those derived using other constant flux tracers. Meaningful flux estimates cannot be made during glacial maxima because the OJP sediments do not record the low ^{187}Os/^{188}Os reported previously. We speculate that this discrepancy may be related to focusing of extraterrestrial particles at the OJP, as has been suggested to explain down-core ^{3}He variations.

1. Introduction

In this study, we assess the sources of Ir to late Pleistocene pelagic carbonates from the Ontong-Java Plateau (OJP) and quantify total Ir burial flux at this western equatorial Pacific site. This effort is an essential step in evaluating the utility of Ir concentrations as a proxy of sediment

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accumulation rates. The first systematic study of Ir in marine sediment (Barker and Anders, 1968) demonstrated a general inverse relationship between Ir concentrations in pelagic clays and sediment accumulation rates. This relationship was interpreted in terms of a constant background flux of cosmic dust to the Earth superimposed on terrestrial Ir flux. Subsequently, variations of Ir concentrations in marine sediments received wide attention due to discovery of elevated Ir concentrations associated with the Cretaceous–Tertiary boundary (Alvarez et al., 1980). As a result of these and numerous later studies, Ir in marine sediments is widely considered to be either of extraterrestrial origin, or associated with terrigenous detrital material (cf. Bruns et al., 1996). In some of the recent studies, Ir in Precambrian sediments has been inferred to be extraterrestrial in origin, and has been used as an indicator of rapid sediment accumulation (Anbar et al., 2001) and as a proxy to determine the duration and intensity of Neoproterozoic glaciations (Bodiselitsch et al., 2005).

However, the most detailed studies of pelagic clay geochemistry to date (Zhou and Kyte, 1992; Kyte et al., 1993) demonstrated that Ir is strongly correlated with Co, an element that is primarily hydrogenous in origin. Consideration of the Os/Ir ratios and $^{187}Os/^{188}Os$ in these same sediment sequences requires that a substantial fraction of the Ir in these pelagic clays is hydrogenous (Peucker-Ehrenbrink, 1996). Similar studies of more rapidly accumulating biogenic sediments are lacking. This gap in our knowledge provided the impetus for the current study because better constraining accumulation rates of pelagic carbonates is of considerable paleoceanographic interest.

Regardless of the ultimate source of the Ir, hydrogenous or extraterrestrial, available data suggest that sediment Ir concentration has unexplored potential for estimation of sediment accumulation rates. Detailed investigation of ^{3}He flux to marine sediments has demonstrated a nearly constant flux of the small size fraction of extraterrestrial particles (Marcantonio et al., 1996, 1999), implying that the extraterrestrial Ir flux may be nearly constant as well. Similarly, there is evidence that concentrations of hydrogenous trace metals vary inversely with sediment accumulation rates (Krishnaswami, 1976). Kyte and co-workers (Zhou and Kyte, 1992; Kyte et al., 1993) extended this result and refined age models for Pacific pelagic clay sequences based on the assumption of constant flux of hydrogenous Co. These studies demonstrated that Ir behaved very similarly to Co. Thus, both the extraterrestrial and hydrogenous Ir components appear to accumulate at a nearly constant rate in slowly accumulating pelagic clay sequences. In this study, we present data that allow this result to be extended to pelagic carbonates that accumulate an order of magnitude more rapidly.

Reported here is a 200 kyr record of osmium isotope composition ($^{187}Os/^{188}Os$) and abundances of Os, Ir and Pt in a sediment core from the Ontong Java Plateau (OJP) in the equatorial Pacific (ODP Site 806). Site 806 was selected because detailed studies of ^{3}He (Patterson and Farley, 1998) and unsupported initial ^{230}Th excess ($xs^{230}Th_{initial}$) (Higgins et al., 2002) are available for the same site. This combination of data provides an opportunity to compare Ir concentrations with commonly used constant flux tracers (^{3}He and $xs^{230}Th_{initial}$) and to test whether Ir concentrations can be used effectively to determine sediment accumulation rates.

Although the influence of particulate extraterrestrial material on the $^{187}Os/^{188}Os$ of marine sediments has been inferred in several previous studies (Esser and Turekian, 1988; Ravizza and McMurtry, 1993; Peucker-Ehrenbrink, 1996; Peucker-Ehrenbrink and Ravizza, 2000a), it has not yet been evaluated as a paleoflux tracer. Existing data for ODP 806 sediments provide a means of estimating the concentration of extraterrestrial Os in bulk sediment. This, in conjunction with previous estimates of the flux of particulate extraterrestrial Os, allows calculation of sediment mass accumulation rates. The primary limitation of this approach is the need for independent constraints on the $^{187}Os/^{188}Os$ of the hydrogenous component, which dominates the Os budget of these sediments. Indeed, the Os isotope data reported here also have important implications for efforts to reconstruct the marine $^{187}Os/^{188}Os$ based on analogous ancient pelagic carbonate sequences. Data on platinum group elements (PGEs) also provide a means of quantitative assessment of hydrogenous component of Os, Ir and Pt.

2. Materials and methods

Samples analyzed in this study are from the ODP Site 806 (Hole C) on the OJP in the western equatorial Pacific (0°19′N, 159°E). The OJP sediments are predominantly foraminiferal nannofossil ooze with more than 90% biogenic materials, mainly calcium carbonate (Krissek and Janecek, 1993; Janecek, 1993). Well defined chronostratigraphy in the Quaternary exists for the Site 806 based on oxygen isotope studies (Berger et al., 1993, 1994). Owing to its shallow depth (ca. 1500 m), the OJP is characterized by better $CaCO_3$ preservation relative to sites in the deep Pacific Ocean. Extensive studies on the OJP have provided information on high resolution climate record in the Quaternary (Berger et al., 1993, 1994), sources of dust to the OJP (Krissek and Janecek, 1993; Patterson et al., 1999), variations in ^{3}He fluxes (Patterson and Farley, 1998) and sediment focusing (Higgins et al., 2002). Our sample depths were chosen to match those analyzed by Higgins et al. (2002). However, each sample in this study represents an average of 2 cm interval in the sediment sequence compared to 4 cm in Higgins et al. (2002). Age-depth relationships are based on oxygen isotope stratigraphy for the Hole B of the Site 806 (Berger et al., 1993, 1994). For the sections studied, depth corrections between Holes B and C were small enough to be ignored (Higgins et al., 2002).

We measured $^{187}Os/^{188}Os$ and concentrations of Os, Ir and Pt using a sector field ICPMS (Element 2). About

4–5 g of sample powders were accurately weighed and spiked with a mixed tracer solution enriched in ^{190}Os, ^{191}Ir and ^{198}Pt. PGE were concentrated from spiked samples by NiS fire assay using flux:sample ratio of ca. 2:1 (Ravizza and Pyle, 1997). Os isotopes were analyzed by sparging OsO_4 vapor from the sample solution into the plasma following the procedure of Hassler et al. (2000) with minor modifications that include introduction of an additional argon gas flow in the sample inlet chamber and use of a cyclonic spray chamber. Ir and Pt were analyzed by aspiration of the sample solution using a 100 μL/min self-aspirating nebulizer. One hundred picograms aliquots of an in-house Os standard were repeatedly analyzed yielding an average ^{187}Os/^{188}Os = 0.1092 ± 0.0017 (1 SD, $n = 53$). Mean and standard deviation (1 SD) of five sets of procedural blanks in the fusion flux mixture were 0.35 ± 0.02 pg/g for Os, 1.6 ± 0.5 pg/g for Ir and 2.8 ± 1.3 pg/g for Pt. The ^{187}Os/^{188}Os of procedural blank averaged at 0.80 ± 0.13 (1 SD). The speed and ease of analysis of Os isotopes and PGE by ID-ICPMS enabled us to process and analyze more than a third of the total number of samples in triplicates.

The sections sampled in this study correspond to an average 'time–area product' of ca. 1 m^2 yr. This falls marginally short of the cut-off value for the 'unbiased' samples (2.5 m^2 yr) as suggested by the modeling of Peucker-Ehrenbrink and Ravizza (2000b).

3. Results and discussion

The concentrations of Os, Ir and Pt, and ^{187}Os/^{188}Os are presented in Table 1. The variation in concentrations are similar for Os and Ir, 42–87 and 18–37 pg/g respectively, whereas it was slightly higher for Pt, ranging from 266 to 784 pg/g (Table 1). These concentrations are generally higher than those reported for nannofossil oozes from DSDP Site 522 (Ravizza and Peucker-Ehrenbrink, 2003, Ravizza, unpublised data) but similar to those reported for the ODP Sites 1218 and 1219 (Dalai et al., 2006; Dalai, unpublised data). The measured ^{187}Os/^{188}Os are in the range of 0.92–1.00, significantly lower than the modern seawater value of ca. 1.06 (Sharma et al., 1997; Levasseur et al., 1998; Woodhouse et al., 1999). PGE abundance ratios at Site 806 are invariably non-chondritic (Table 1). This is evident from abundance ratios of Pt/Ir (mean = 21 ± 5, 1 SD), Pt/Os (mean = 7.3 ± 1.2, 1 SD) and Os/Ir (mean = 2.8 ± 0.5, 1 SD) compared to chondritic values of ca. 2.05, 2.0 and 1.03, respectively (Jochum, 1996).

3.1. Influence of lithogenic matter on the PGE budget of the OJP sediments

The OJP sediments at Site 806 are predominantly biogenic and the contributions from lithogenic sources are minor (Krissek and Janecek, 1993). Lithogenic fractions of Os, Ir and Pt in the OJP sediments were estimated using ^{232}Th activities reported at Site 806C (Higgins et al., 2002), from the following relation

$$[X]_{\text{lithogenic}} = ([X]_{\text{crust}}/[\text{Th}]_{\text{crust}}) \times [\text{Th}]_{\text{measured}}, \quad (1)$$

where [X] stands for [Ir], [Os] and [Pt]. Crustal concentrations of 22, 31 and 510 pg/g were assumed for Ir, Os and Pt, respectively (Peucker-Ehrenbrink and Jahn, 2001) and 10.7 μg/g for Th (McLennan, 1995; McLennan, 2001). The resulting average lithogenic contributions are: ca. 1 pg/g Ir (ca. 5% of bulk Ir), ca. 2 pg/g Os (ca. 3% of bulk Os) and ca. 29 pg/g Pt (ca. 6% of bulk Pt). The estimated fluxes of terrigenous materials for the last 1.9 Myr at Site 806B, 34–90 mg/cm^2/kyr (Krissek and Janecek, 1993), also yield similar lithogenic fractions, (2–5)% Ir, (1–2)% Os and (2–5)% Pt. It is likely that the estimate based on average Os concentration of upper crust is maximum for detrital fractions of Os in OJP sediments considering that volcanic dust is a relatively more significant source of lithogenic materials at the OJP compared to Asian dust (Krissek and Janecek, 1993) and that average Os concentrations of volcanics being transported to the OJP (4 ± 9 pg/g, based on averaging the data for arc-volcanics from Izu-Bonin, Philippines and Papua New Guinea; Alves et al., 2002) are significantly less than those for the Asian dust (ca. 30 pg/g Os, Peucker-Ehrenbrink and Jahn, 2001).

3.2. Contributions from cosmic dust

Extraterrestrial contributions of Os, Ir and Pt are estimated based on two independent approaches: (i) using Os/^{3}He, Ir/^{3}He and Pt/^{3}He in the cosmic dust and measured ^{3}He in the OJP sediments and (ii) mass balance considerations of the measured ^{187}Os/^{188}Os. Following the approach outlined in Marcantonio et al. (1999), contributions from the cosmic dust are calculated as

$$[X]_{\text{cosmic}} = [X]_{\text{chondrite}} \times ([^3\text{He}]_{\text{measured}}/[^3\text{He}]_{\text{IDP}}/0.005), \quad (2)$$

where [X] stands for [Os], [Ir] and [Pt]. $[^3\text{He}]_{\text{IDP}}$ is the average concentrations of ^{3}He in the interplanetary dust particles (1.9×10^{-5} cc STP/g, Nier and Schlutter, 1992). $[^3\text{He}]_{\text{measured}}$ is the average ^{3}He concentration at Site 806B for the last 240 kyr (Patterson and Farley, 1998). Average concentrations of Os, Ir and Pt in the chondrites: 492, 480 and 982 ng/g, respectively (Jochum, 1996) were assumed to be representative for the cosmic dust. The factor 0.005 in the equation accounts for the loss of ^{3}He from all but the smallest size fraction of cosmic duct due to frictional heating upon descent through the atmosphere (Farley et al., 1997). Calculations based on this approach suggest that average contributions from cosmic dust to the OJP sediments at Site 806 is 2.2 ± 0.4 pg/g Os (i.e. 3 ± 0.6% of bulk Os), 2.1 ± 0.4 pg/g Ir (i.e. 9 ± 1% of bulk Ir) and 4.3 ± 0.8 pg/g Pt (i.e. 1 ± 0.3% of bulk Pt). Note that ^{3}He and the PGE in cosmic dust are associated with different size fractions; small size extraterrestrial particles (<30 μm) are the major carriers

Table 1
Concentrations of Os, Ir, Pt and $^{187}Os/^{188}Os$ of Site 806 samples

Sample	Depth (cmbsf)	$^{187}Os/^{188}Os$	2 SD	Os (pg/g)	Ir (pg/g)	Pt (pg/g)	Os/Ir	Pt/Ir
806C-1H-1 28–30 cm	29	0.989	0.006	64	24.9	514	2.56	20.6
806C-1H-1 47–49 cm	48	0.996	0.007	71	25.2	535	2.83	21.2
806C-1H-1 53–55 cm	54	0.995	0.004	63	20.7	490	3.04	23.6
806C-1H-1 75–77 cm	76	0.999	0.004	75	21.8	501	3.45	22.9
806C-1H-1 98–100 cm	99	0.979	0.005	63	24.0	441	2.65	18.4
Rep1	99	0.975	0.005	63	21.2	455	2.99	21.5
806C-1H-1 118–120 cm	119	0.958	0.003	75	37.4	718	2.00	19.2
Rep1	119	0.993	0.004	71	26.7	550	2.65	20.6
Rep2	119	0.995	0.003	71	21.0	539	3.39	25.6
806C-1H-2 15–17 cm	162	0.935	0.007	59	21.2	335	2.80	15.8
Rep1	162	0.979	0.003	54	17.9	295	3.04	16.5
Rep2	162	0.967	0.003	56	18.8	306	3.00	16.3
806C-1H-2 32–34 cm	179	0.981	0.004	73	21.9	442	3.35	20.2
806C-1H-3 46–48 cm	193	0.986	0.006	70	19.7	411	3.54	20.9
806C-1H-2 58–60 cm	204	0.973	0.007	49	20.8	266	2.35	12.8
Rep1	204	0.968	0.005	52	18.1	278	2.87	15.4
806C-1H-2 79–81 cm	226	0.984	0.006	51	22.2	310	2.31	14.0
Rep1	226	0.950	0.009	51	27.8	336	1.85	12.1
Rep2	226	0.987	0.003	53	21.0	304	2.52	14.5
806C-1H-2 93–95 cm	240	0.982	0.005	43	19.6	288	2.21	14.7
806C-1H-2 103–105 cm	250	0.985	0.009	42	19.1	283	2.18	14.8
806C-1H-2 122–124 cm	269	0.998	0.005	87	26.6	653	3.29	24.5
806C-1H-2 133–135 cm	280	0.991	0.005	70	19.3	636	3.63	33.0
806C-1H-3 1–3 cm	298	0.981	0.004	65	28.6	568	2.26	19.9
806C-1H-3 16–18 cm	309	0.980	0.005	70	23.8	574	2.94	24.1
Rep1	309	0.968	0.004	74	25.9	605	2.86	23.4
Rep2	309	0.984	0.002	70	26.4	546	2.65	20.7
806C-1H-3 34–36 cm	327	0.943	0.005	73	21.7	466	3.35	21.5
Rep1	327	0.991	0.003	67	18.0	473	3.72	26.3
Rep2	327	0.992	0.004	67	20.4	471	3.29	23.1
806C-1H-3 53–55 cm	346	0.987	0.006	74	20.1	603	3.66	30.0
806C-1H-3 60–62 cm	353	0.966	0.007	63	23.8	584	2.64	24.6
806C-1H-3 73–75 cm	370	0.972	0.007	68	25.1	597	2.71	23.8
Rep1	370	0.943	0.008	71	24.9	625	2.85	25.1
Rep2	370	0.975	0.003	75	25.9	617	2.88	23.8
806C-1H-3 76–78 cm	373	0.988	0.004	78	25.0	784	3.14	31.4
Rep1	373	0.962	0.003	80	27.7	732	2.89	26.4
Rep2	373	0.979	0.004	79	27.5	758	2.87	27.6
806C-1H-3 88–90 cm	385	0.915	0.005	61	23.3	407	2.62	17.5
Rep1	385	0.984	0.004	60	19.7	418	3.06	21.2
Rep2	385	0.943	0.003	60	22.2	415	2.68	18.7
806C-1H-3 94–96 cm	391	0.931	0.006	55	21.5	357	2.57	16.6
Rep1	391	0.944	0.003	55	23.3	351	2.35	15.0
Rep2	391	0.979	0.004	54	21.2	337	2.54	15.9
806C-1H-3 103–105 cm	400	0.953	0.008	50	18.2	341	2.76	18.7
Rep1	400	0.972	0.002	48	20.1	327	2.40	16.3
Rep2	400	0.949	0.004	49	19.6	321	2.52	16.4
806C-1H-3 118–120 cm	415	0.990	0.005	81	22.9	685	3.52	29.9
Rep1	415	0.977	0.005	83	24.2	694	3.41	28.7
Rep2	415	0.954	0.002	86	27.2	685	3.17	25.2
806C-1H-3 124–126 cm	421	0.957	0.006	54	25.4	379	2.14	14.9
Rep1	421	0.956	0.003	56	24.0	389	2.32	16.2

Rep1, replicate 1; Rep2: replicate 2.

of ^{3}He (Farley et al., 1997; K.A. Farley, personal communication, 2005) whereas the PGE are carried by 100–200 μm size extraterrestrial particles (Peucker-Ehrenbrink and Ravizza, 2000b). Thus, this approach makes an implicit assumption that ^{3}He, Os, Ir and Pt in these different particle-size populations are not subject to systematic size fractionation.

It is well recognized that Os isotope composition of marine sediments is sensitive to contributions from extraterrestrial matter because of contrasting $^{187}Os/^{188}Os$ of terrestrial and extraterrestrial sources (Esser and Turekian, 1988; Esser and Turekian, 1993; Peucker-Ehrenbrink, 1996). The same is also true for ^{3}He (Farley et al., 1995). Thus, another approach for estimating contributions from cosmic dust is by assuming that measured $^{187}Os/^{188}Os$ in the OJP sediments are a result of mixing between hydrogenous Os and particulate extraterrestrial Os such that fraction of ^{188}Os derived from cosmic particles (fOs_{cosmic}) is given by

$$fOs_{cosmic} = [R_{sw} - R_{m}]/[R_{sw} - R_{cosmic}], \quad (3)$$

where R_{sw}, R_{cosmic} and R_{m} stand for $^{187}Os/^{188}Os$ values of seawater (1.06), cosmic dust (0.13) and measured (Table 1), respectively. Based on this approach, it is estimated that cosmic dust contributes ca. 6.0 ± 1.5 pg/g Os ($9 \pm 2\%$ of total Os). The estimate based on mass balance of hydrogenous and particulate extraterrestrial Os is higher compared to the one derived based on ^{3}He measurements by a factor of 2–3. This estimate is not free of uncertainties considering that $^{187}Os/^{188}Os$ of seawater is known to have changed during glacial–interglacial climate oscillations (Oxburgh, 1998; Peucker-Ehrenbrink and Ravizza, 2000a; Williams and Turekian, 2004; Dalai et al., 2005). The Os contributions from cosmic dust as calculated above translates to a much higher average extraterrestrial Os flux (ca. 12 pg/cm^{2}/kyr) compared to earlier estimates of 1–6 pg/cm^{2}/kyr (Esser and Turekian, 1988, 1993; Ravizza and McMurtry, 1993). An alternative estimate can be made using the average $^{187}Os/^{188}Os$ ($R_{sw} = 1.01$) of an approximately 200 kyr record from metalliferous carbonates (Oxburgh, 1998) in Eq. (3). The resulting estimate is that on an average 2.6 ± 1.4 pg/g Os ($4 \pm 2\%$ of total Os) at Site 806 comes from particulate cosmic dust. This estimate is similar to that arrived based on ^{3}He data and agrees reasonably well with estimates of particulate extraterrestrial Os fluxes reported earlier. This approach makes an implicit assumption that the metalliferous carbonate record itself is not biased to low $^{187}Os/^{188}Os$ by cosmic Os.

Assuming a chondritic Ir/Os ratio of 0.98 and Pt/Os ratio of 2.0 (Jochum, 1996) for the cosmic dust and using the lower of the two Os isotope based estimates of cosmic dust-associated Os made above (2.6 ± 1.4 pg/g), it is estimated that at Site 806 cosmic dust accounts for 2.6 ± 1.3 pg/g Ir (i.e. $11 \pm 6\%$ of total Ir) and 5.3 ± 2.7 pg/g Pt ($1.2 \pm 0.7\%$ of total Pt). These calculations also assume that PGE of the extraterrestrial particles do not undergo significant fractionation before reaching the seafloor. Brownlee et al. (1984) observed Os/Ir of ca. 1 in large extraterrestrial spherules, suggesting the chondritic composition, whereas non-chondritic Os/Ir was observed in some deep-sea cosmic spherules (Bonté et al., 1987). Interestingly, Kurat et al. (1996) reported Os/Ir that averaged at ca. 1, within errors, for both melted and unmelted Antarctic micrometeorites, indicating that Os and Ir undergo little fractionation during atmospheric heating. Nevertheless, above estimates based on two independent approaches suggest that extraterrestrial particles account for ca. 5% Os, ca. 10% Ir and ca. 1% Pt in the OJP sediments. Minor proportions of extraterrestrial PGE in the OJP sediments are consistent with the non-chondritic PGE ratios measured in this study (Table 1).

3.3. Importance of hydrogenous Ir

In this section, we determine the importance of Ir scavenged from seawater at Site 806 and compare these results to estimates from North Pacific pelagic clay sequence LL44-GPC3. Fractions of hydrogenous Ir are calculated from the following relation:

$$Ir_{total} = Ir_{lithogenic} + Ir_{cosmic} + Ir_{hydrogenous}. \quad (4)$$

From Eq. (4), hydrogenous Ir accounts, on average, 85% of bulk concentrations at Site 806. Relative importance of detrital, cosmic and hydrogenous fractions of Ir was also assessed in the Pacific pelagic clay core LL44-GPC3 following similar approaches to those described above. Using the Th concentrations reported for the last 1.5 Myr (Kyte et al., 1993) and crustal concentrations of Ir and Th as 22 pg/g and 10.7 μg/g, respectively (McLennan, 1995; McLennan, 2001; Peucker-Ehrenbrink and Jahn, 2001), it is estimated that detrital Ir in the LL44-GPC3 is 29 ± 1 pg/g, accounting for $13 \pm 2\%$ of total Ir. Similarly, using average ^{3}He concentration of 8 ± 2 pcc STP/g for the last 1.5 Myr at LL44-GPC3 (Farley et al., 1995) in Eq. (2), it is estimated that average extraterrestrial contributions to the core is $18 \pm 3\%$ of the total Ir (ranging from 15% to 28% using the upper and lower limits of mean ^{3}He concentration, 6 and 10 pcc STP/g, respectively). Thus, from Eq. (4), average hydrogenous contribution to total Ir in LL44-GPC3 is ca. 70% (Table 2). This agrees well with independent Os isotope based estimate of Peucker-Ehrenbrink (1996) that a maximum of one third of Ir in LL44-GPC3 is derived from the cosmic dust.

In the above discussion, the fraction of hydrogenous Ir supplied by dissolution of micrometeoritic particles has not been estimated. Estimates based on mass balance of Os isotopes in the oceans suggest that contribution of Os to the oceans via dissolution of cosmic dust constitutes a maximum of 20% of total extraterrestrial Os flux to the ocean sediments (Esser and Turekian, 1988), similar to the inference drawn by Sharma et al. (1997) that ca. 25% of Os evaporates during the atmospheric entry and heating of cosmic dust. Levasseur et al. (1999a), based on extraterrestrial mass flux at the top of the atmosphere and to the deep sea sediments, estimated only ca. 4% of total Os flux to the oceans is contributed by dissolution of cosmic dust. These studies, together with the knowledge that Ir, unlike Os, does not form a volatile compound upon oxidation, suggest that cosmic Ir is primarily associated with extraterrestrial particles. On the other hand, Gabrielli et al. (2004) suggest that a substantial fraction of meteoroids ablates completely on entering the Earth's atmosphere yielding nanometer-sized meteoritic smoke particles. A recent study by Lal and Jull (2002) suggests that ablation and fragmentation of larger extraterrestrial particles in the atmosphere contributes significantly to the flux of small particles at the Earth's surface, which would be largely undetected in the stratospheric collection. The approach used here only constrains the inventory of particulate extraterrestrial particles

Table 2
Average Ir contributions from lithogenic, cosmic and hydrogenous components, Ir/^{3}He and Ir burial fluxes at ODP Site 806 and LL44-GPC3

	Site 806	LL44-GPC3
$Ir_{lithogenic}$ (%)	5 ± 1[a], 2–5[b]	13 ± 2[f]
Ir_{cosmic} (%)	9 ± 1[c], 11 ± 6[d]	18 ± 3[g]
$Ir_{hydrogenous}$ (%)	85	70
Ir/^{3}He (pg/pcc)	55 ± 15[e]	27 ± 10[h]
Ir burial flux (pg/cm^{2}/kyr)	45 ± 7[i]	30 ± 7[j]

[a] Calculated using crustal Ir/Th ratio (22 pg Ir/10.7 μg Th) and average ^{232}Th activity reported for Site 806C (Higgins et al., 2002).
[b] Calculated using a terrigenous matter flux of 34–90 mg/cm^{2}/kyr at Site 806B (Krissek and Janecek, 1993), and average mass accumulation rates of 2 g/cm^{2}/kyr (Patterson and Farley, 1998).
[c] Based on chondritic Ir concentration of 480 ng/g (Jochum, 1996), IDP ^{3}He concentration of 1.9×10^{-5} cc STP/g (Nier and Schlutter, 1992) and average ^{3}He concentrations at Site 806B for the last 240 kyr (Patterson and Farley, 1998).
[d] Calculated from cosmic Os contributions based on Os isotope mass balance (see text) and a chondritic Os/Ir ratio of 1.03 (Jochum, 1996).
[e] Based on average Ir concentrations at Hole 806C (Table 1) and average ^{3}He concentrations at Hole 806B for the last 240 kyr (Patterson and Farley, 1998).
[f] Calculated using crustal Ir/Th ratio (22 pg Ir/10.7 μg Th), Ir and Th concentrations reported for core LL44-GPC3 for the last 1.5 Myr (Kyte et al., 1993).
[g] Based on chondritic Ir concentration of 480 ng/g (Jochum, 1996), IDP ^{3}He concentration of 1.9×10^{-5} cc STP/g (Nier and Schlutter, 1992) and average ^{3}He concentrations at LL44-GPC3 for the last 1.5 Myr (Farley et al., 1995).
[h] Based on average Ir concentrations (Kyte et al., 1993) and average ^{3}He concentrations (Farley et al., 1995) at at LL44-GPC3 for the last 2 Myr.
[i] Based on the average Ir concentration of Site 806 and average mass accumulation rate of 1.97 g/cm^{2}/kyr.
[j] Based on the average Ir concentrations and mass accumulation rates at LL44-GPC3 (Kyte et al., 1993) for the last 2 Myr.

in the sediment and makes comparison to similar marine sediment data. Thus, the above calculations are uninfluenced by uncertainties in estimates of total extraterrestrial flux. The conclusions of Lal and Jull (2002), if correct, would imply that a relatively larger fraction of extraterrestrial influx is lost to ablation or dissolution than suggested by Levasseur et al. (1999a).

Several lines of independent evidence support our conclusion that hydrogenous sources dominate the sedimentary PGE budgets at ODP Site 806. Measurements of Ir in river waters indicate that rivers supply more dissolved Ir to the oceans than extraterrestrial sources and that riverine Ir constitutes a significant fraction of Ir flux to the marine sediments (Anbar et al., 1996; Lee et al., 2003). Geochemical properties of Ir and PGE abundance ratios in the OJP sediments also suggest that the majority of Ir in these sediments is hydrogenous. Very low concentrations of Ir in the seawater suggest that this element is very particle reactive in seawater, particularly toward Fe–Mn oxyhydroxides (Goldberg et al., 1986; Anbar et al., 1996). Experimental studies suggest that in the oxic environments, tetravalent Ir is strongly scavenged on to the non-carbonate phases (Dai et al., 2000). Subchondritic values of Os/Ir in pelagic clays have been attributed to preferential scavenging of Ir from seawater (Peucker-Ehrenbrink, 1996). Pt/Ir ratios of the Site 806 samples (range: 12–31, mean: 21 ± 5) are much higher than the chondritic ratio of ca. 2.1 (Jochum, 1996) but much lower than the seawater ratio: >100 (Colodner et al., 1993; Anbar et al., 1996). This, together with the estimates made in the previous section indicating that extraterrestrial PGE fractions are minor compared to the hydrogenous PGE fractions of the OJP sediments, leads to the inference that Ir is preferentially scavenged over Pt in pelagic carbonates.

Contrasting Pt/Ir between chondrites and crustal phases (and seawater) suggest that this ratio should be sensitive to contributions of cosmic dust in marine sediments. In contrast, similarity of Os/Ir in the chondrites and terrestrial phases and susceptibility of Os burial to changes in redox condition makes this ratio less useful. The observation of chondritic Pt/Ir in the Holocene samples from the GRIP ice core, thought to be a result of contributions from extraterrestrial matter (Gabrielli et al., 2004), attests to the idea that Pt and Ir undergo negligible fractionation during the entry of extraterrestrial particles through the Earth's atmosphere. The Site 806 data also show a significant positive correlation between Os concentrations and Pt/Ir ($r = 0.82$, Fig. 1). However, mixing between cosmic and hydrogenous component is expected to yield a negative correlation between Pt/Ir and Os concentration. The positive correlation observed in Fig. 1 most likely results from mixing of a nearly constant amount of cosmic dust with either variable proportions of a hydrogenous component characterized by a constant Pt/Ir or with a hydrogenous end member having a variable Pt/Ir. The trend in Fig. 1 also suggests that Os concentrations increase with increasing hydrogenous fractions as indicated by higher Pt/Ir and are regulated mainly by scavenging of hydrogenous component. A similar albeit weaker positive correlation also exists between Ir and Pt/Os ($r = 0.59$) for the OJP samples.

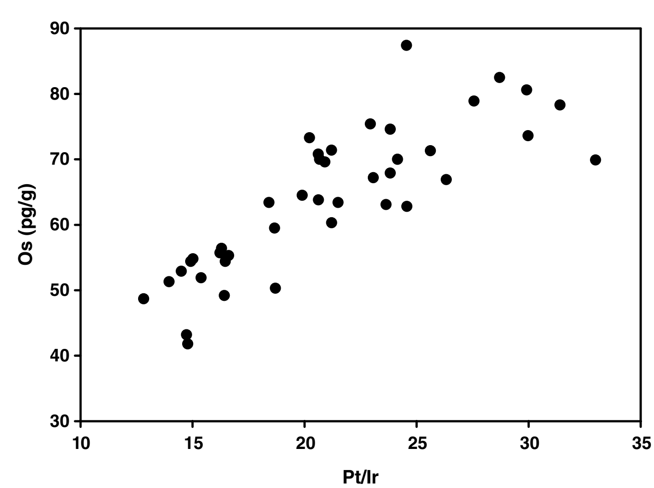

Fig. 1. Plot of Os concentrations vs. Pt/Ir in the OJP sediments. A significant positive correlation suggests that an increase in Os concentration is a result of higher proportion of hydrogenous component, superimposed on a nearly constant amount of extraterrestrial matter.

3.4. Iridium as a paleoflux tracer

In this section, we evaluate the utility of Ir concentration as a paleoflux tracer by comparing Ir data to published ^{3}He and xs^{230}Th$_{initial}$ data from Site 806 (Patterson and Farley, 1998; Higgins et al., 2002). Both of these isotopes have been utilized as paleoflux tracers in previous studies (Marcantonio et al., 1995; Marcantonio et al., 1996), and therefore provide a framework for assessing changes in the flux of Ir to late Quaternary OJP sediments. Variations in Ir flux are evaluated on different length scales in order to compare our Ir data to both ^{3}He and xs^{230}Th$_{initial}$. First, average Ir concentration of the full data set is used to calculate average down-core Ir/^{3}He and Ir/xs^{230}Th$_{initial}$ ratios for comparison to other published data. Second, we bin our Ir data to generate a depth profile from Hole 806C at approximately 50 cm resolution. This allows direct comparison to ^{3}He data that were measured in adjacent Hole 806B. Finally, we compare Ir to xs^{230}Th$_{initial}$ data from Hole 806C in which the core was sampled at approximately 20 cm depth resolution.

For the Ir concentrations to be used as a paleoflux tracer, it is required that the flux of Ir scavenged from seawater is constant. If this is the case, average Ir/^{3}He and Ir/xs^{230}Th$_{initial}$ ratios at various sites should be nearly constant in both time and space. It has been shown that xs^{230}Th$_{initial}$/^{3}He ratio varies only by approximately 30% (Marcantonio et al., 1995; Marcantonio et al., 1996) in the central equatorial Pacific. Here, we initiate a similar effort for Ir by calculating average Ir/^{3}He and Ir/xs^{230}Th$_{initial}$ ratios for Site 806 sediments. Based on average Ir concentrations at Site 806 Hole C (23.0 ± 3.6 pg/g, Table 1) and average ^{3}He concentrations at Hole B for the last 240 kyr (0.42 ± 0.08 pcc/g; Patterson and Farley, 1998), the mean Ir/^{3}He is 55 ± 15 (Table 2). This is higher than but within a factor of two of the value calculated for the Pacific core LL44-GPC3 based on abundances of Ir (Kyte et al., 1993) and ^{3}He (Farley et al., 1995) for the last 2 Myr (mean Ir/^{3}He $= 27 \pm 10$, Table 2). This offset in Ir/^{3}He between these two sites is also reflected in the average Ir burial fluxes at Site 806 (45 ± 7 pg cm^{-2} kyr^{-1}) and at LL44-GPC3 (30 ± 7 pg cm^{-2} kyr^{-1}, Table 2). We used Ir concentrations (Barker and Anders, 1968) and surface ^{230}Th concentrations (Goldberg and Koide, 1962) in pelagic clays from the western Pacific to calculate Ir/^{230}Th$_{surface}$. Average Ir/^{230}Th$_{surface}$ of four cores from the western Pacific (3.2 ± 1.4 pg/dpm), when compared with average Ir/xs^{230}Th$_{initial}$ at Site 806C (5.4 pg/dpm), shows agreement within a factor of ca. 2. These comparisons made for sites with contrasting lithology and an order of magnitude difference in the sediment accumulation rates would suggest that Ir flux has been likely constant within a factor of ca. 2 in the Pacific.

Independent data suggest that Ir burial fluxes in pelagic sediments vary over a relatively narrow range. For example, the Ir burial flux measured in a pelagic carbonate core from the NE Atlantic (25 pg cm^{-2} kyr^{-1} in Core 23#12: Cave et al., 2003) is roughly half that of Site 806 and is indistinguishable from that of LL44-GPC3 (Table 2). A south Pacific pelagic clay record spanning the Cenozoic yields an Ir burial flux of ca. 20 pg cm^{-2} kyr^{-1} (Zhou and Kyte, 1992). More generally, the strong correlation of Ir and Co in pelagic clays suggests that Ir burial fluxes may be similar over a wide range of pelagic settings as has been demonstrated for Co (Krishnaswami, 1976). It is also striking that estimated riverine flux of Ir (17.5 pg cm^{-2} kyr^{-1}, Anbar et al., 1996; Lee et al., 2003) agrees with the Ir burial fluxes in the Pacific and Atlantic carbonates to within a factor of 2–3, comparable to the likely uncertainty in these estimates. Cumulatively, these data suggest that Ir concentrations can, in principle, be used to identify variations in sediment accumulations rates in pelagic carbonates. The average Ir/^{3}He and Ir/xs^{230}Th$_{initial}$ ratios measured in Site 806 sediments provide a robust framework for evaluating this possibility in a more rigorous manner at other sites. Down core variations in these independent constant flux proxies at Site 806 can be used to make a first order assessment of the limits on the precision of Ir-based paleoflux estimates.

If Ir, ^{3}He and xs^{230}Th$_{initial}$ all behave as ideal point paleoflux tracers at Site 806, then the three depth profiles should be well correlated. Direct comparison of depth resolved profiles for each of these tracers is possible by comparing the Ir profile from Hole C to previously published ^{3}He data from Hole B and xs^{230}Th$_{initial}$ data from Holes B and C. To do this the Ir concentrations of Hole C were binned to match the depth scales for which data are available for Hole B. Down-core profiles of concentrations of Ir, ^{3}He and xs^{230}Th$_{initial}$, when averaged over 50 cm depth intervals, do not show correlated variations of Ir concentrations with either ^{3}He or xs^{230}Th$_{initial}$ (Fig. 2), but show similar variance in all three data sets. Moreover, the down core variation in sediment flux implied by any of the three records is modest. Higgins et al. (2002) argued that 100 kyr cycles of ^{3}He accumulation rates at the OJP were nearly eliminated when normalized to xs^{230}Th$_{initial}$ as this normalization corrected for sediment focusing. We examined down-core variations of Ir, xs^{230}Th$_{initial}$ and ^{3}He normalized to one another (Fig. 3). Coherent down-core variations between ^{3}He normalized Ir concentrations and xs^{230}Th$_{initial}$ is driven to a large extent by down-core variations of ^{3}He concentrations. It can be seen that the three normalized ratios show similar down-core profiles, each variable within a factor of two (Fig. 3). Down-core profiles shown in Figs. 2 and 3 suggest sediment flux estimates based on each of these tracers (^{3}He, Ir and xs^{230}Th$_{initial}$) should agree within a factor of two. Calculations of sediment flux suggest that this is indeed the case (Fig. 4). The Ir-based flux estimates are in between those based on ^{3}He and xs^{230}Th$_{initial}$.

While the constancy of Ir burial fluxes and agreement among flux estimates based on independent tracers within a factor of two is encouraging, it should be emphasized that the mode of supply of Ir to the oceans and its deposi-

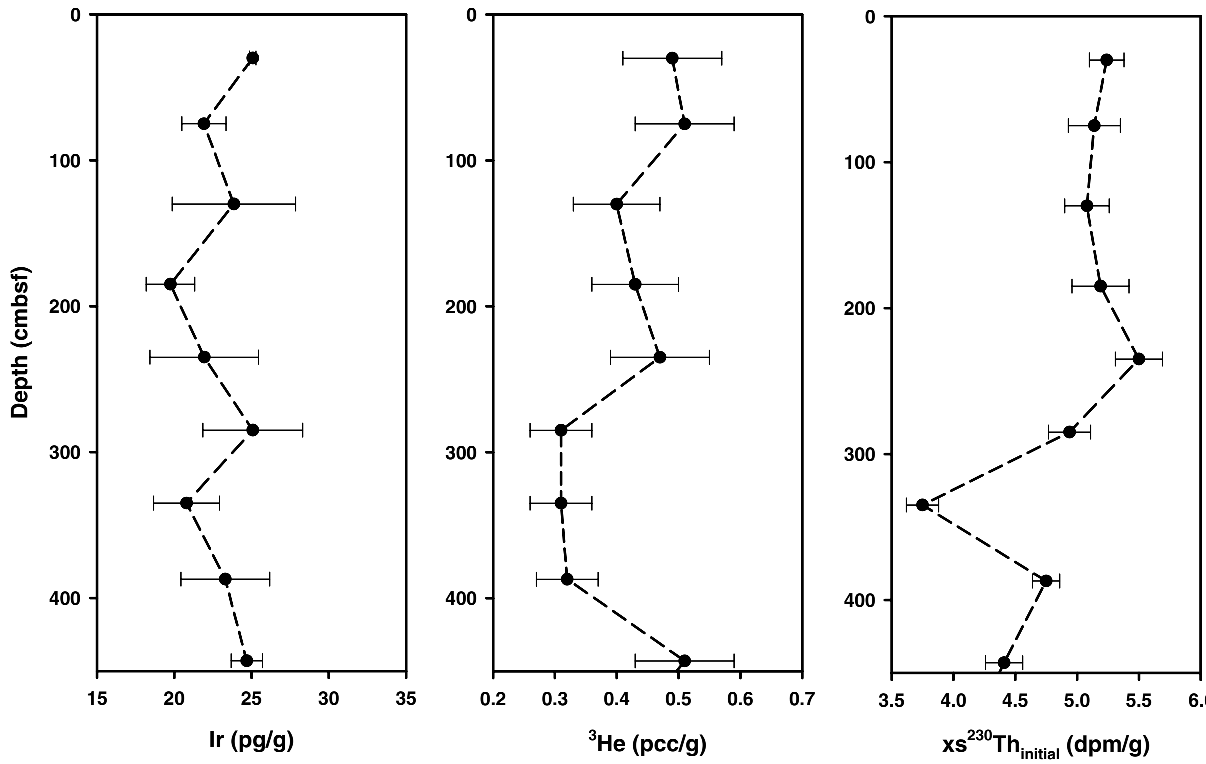

Fig. 2. Comparison of down-core variations of Ir of Hole 806C with ^{3}He (Patterson and Farley, 1998) and xs^{230}Th$_{initial}$ (Higgins et al., 2002) of Hole 806B. Ir data were binned over depth of ca. 50 cm to match the sampling intervals of Hole 806B. Down-core variations of these parameters are not correlated but show similar variance. Error bars represent 1 SD of the mean concentration/activity over the binned interval.

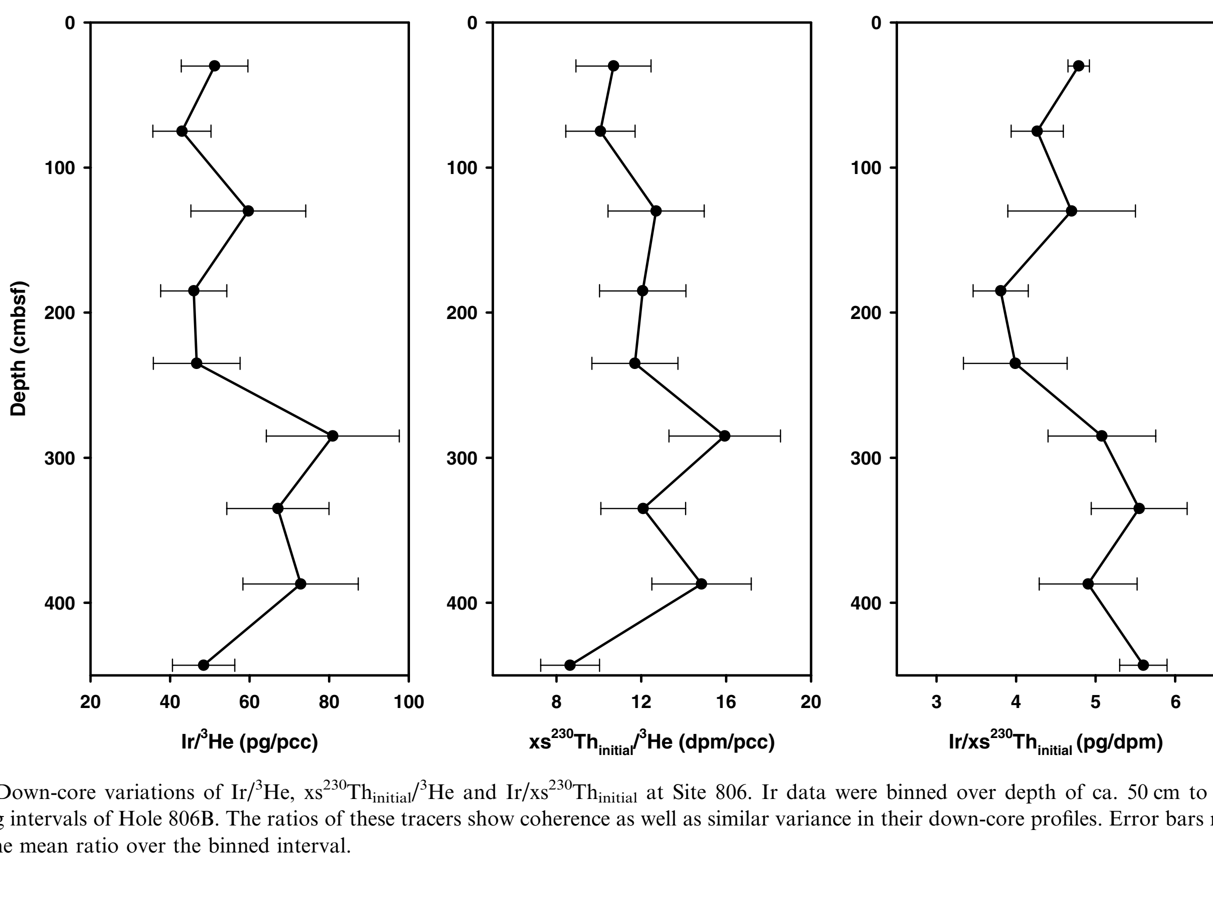

Fig. 3. Down-core variations of Ir/^{3}He, xs^{230}Th$_{initial}$/^{3}He and Ir/xs^{230}Th$_{initial}$ at Site 806. Ir data were binned over depth of ca. 50 cm to match the sampling intervals of Hole 806B. The ratios of these tracers show coherence as well as similar variance in their down-core profiles. Error bars represent 1 SD of the mean ratio over the binned interval.

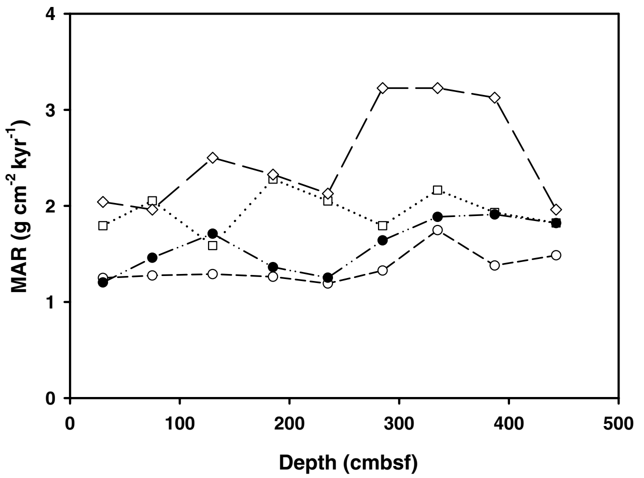

Fig. 4. Comparison of estimates of sediment mass accumulation rates (MAR) at the OJP based on Ir concentrations of Hole C (open squares), ^{3}He of Hole B (open diamonds) and $xs^{230}Th_{initial}$ of Hole C (filled circles) and Hole B (open circles). The data of Ir and $xs^{230}Th_{initial}$ of Hole 806C were binned over ca. 50 cm depth intervals to match the sampling intervals of ^{3}He data of Hole B. The results show that MAR estimates agree with one another within a factor of about two.

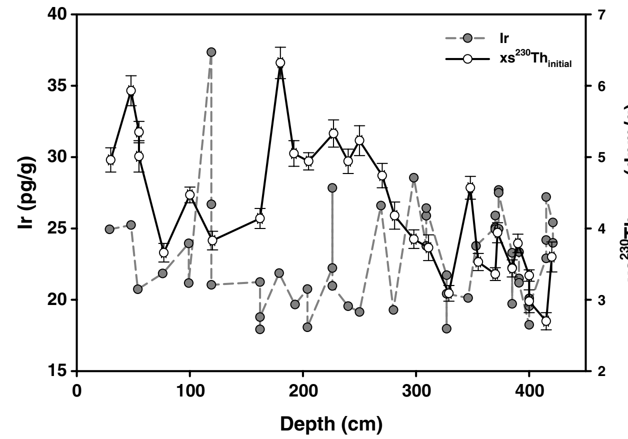

Fig. 5. Comparison of high resolution records (ca. 20 cm) of Ir concentrations with $xs^{230}Th_{initial}$ at ODP Hole 806C. Ir does not show correlated variation with $xs^{230}Th_{initial}$ on this scale. The vertical error bars represent 1 SD of $xs^{230}Th_{initial}$ data (Higgins et al., 2002), whereas the horizontal error bars indicate the sampling intervals for $xs^{230}Th_{initial}$ data (4 cm, Higgins et al., 2002).

tion in sediments are different compared to the delivery of ^{3}He and $xs^{230}Th_{initial}$ to marine sediments. For example, rate of supply of Ir to the oceans, analogous to Co, would respond to processes influencing the degree and intensity of weathering in the continents whereas delivery of ^{3}He and $xs^{230}Th_{initial}$ should not be affected by these processes. In addition, it has been demonstrated previously that enhanced Ir burial rates can be associated with deposition of hydrothermally influenced sediments (Cave et al., 2003). Similarly, flux estimates based on ^{3}He and $xs^{230}Th_{initial}$ are not without problems, either. Oceanographic processes such as sediment focusing, redistribution and size fractionation can limit the utility of all these constant flux tracers: ^{3}He, $xs^{230}Th_{initial}$ and Ir. It is likely that ^{3}He being associated with small particles is more readily redistributed than Ir. In addition, $xs^{230}Th_{initial}$ in the sediments are influenced by boundary scavenging. Nevertheless, burial fluxes of Ir are likely to vary in space and time, and Ir concentrations in marine sediments are unlikely to fit a simple universal constant flux model. This underscores the necessity of local calibration of Ir burial flux in space and time for Ir-based paleoflux estimates. The preliminary assessment in this study based on available data should be confirmed by further studies to determine if burial fluxes of Ir have been constant in the past and vary regionally or among lithologies (e.g. pelagic clays and carbonates).

Results from the higher resolution profiles (Fig. 5) show that down-core variations between Ir concentrations and $xs^{230}Th_{initial}$ are not correlated. The lack of correlation indicates that fractionation of Ir from ^{230}Th occurs during and/or after deposition of sediments. The specific processes responsible for Ir–Th fractionation are not known. While there is a substantial body of data vindicating the use of $xs^{230}Th_{initial}$ as a paleoflux tracer (Krishnaswami, 1976; Bacon, 1984; Yu et al., 2001; Marcantonio et al., 2001; Higgins et al., 2002; Francois et al., 2004), this application has recently been challenged (Lyle et al., 2005). Relatively less is known about the behavior of Ir in the water column and during sediment diagenesis. Experimental studies, albeit limited, suggest that adsorption of Ir is essentially irreversible at seawater pH (Dai et al., 2000) and continuous sequences of oxic pelagic clays record nearly constant Ir burial fluxes (Zhou and Kyte, 1992; Kyte et al., 1993). However, mobilization of Ir during sediment diagenesis is evident in pelagic sequences influenced by turbidite deposition (Colodner et al., 1992). Regardless of the cause of the variation in $Ir/xs^{230}Th_{initial}$ ratios, more coherent variation between these tracers result from sampling strategies that average over larger depth/time intervals.

3.5. Os isotopic record: implications for records of seawater composition

In the context of studying climate-weathering feedbacks (Walker et al., 1981; Raymo et al., 1992), marine Os isotope records serve as a valuable tool. Reconstructing seawater $^{187}Os/^{188}Os$ relies on measurements of Os isotopes in marine sediment records such as pelagic clays (Pegram et al., 1992), metalliferrous carbonates and calcareous oozes (Ravizza, 1993; Ravizza and McMurtry, 1993; Peucker-Ehrenbrink, 1996; Reusch et al., 1998; Oxburgh, 1998; Ravizza and Peucker-Ehrenbrink, 2003; Dalai et al., 2006), reducing sediments (Peucker-Ehrenbrink and Ravizza, 2000a; Cohen et al., 1999, Williams and Turekian, 2004; Dalai et al., 2005) and ferromanganese crusts (Burton et al., 1999; Klemm et al., 2005). Down-core variations of $^{187}Os/^{188}Os$ and $\delta^{18}O$ of benthic foraminifer *C. wuellerstorfi* (Bickert et al., 1993) at Site 806 are shown in Fig. 6. The plot also shows $^{187}Os/^{188}Os$–$\delta^{18}O$ data from East Pacific

Rise (EPR) reported by Oxburgh (1998). The results show that a clear glacial–interglacial difference in $^{187}Os/^{188}Os$, as was observed at EPR, is either lacking or too small to be resolved in the OJP records.

One of the characteristic features of the OJP pelagic carbonates is that their bulk $^{187}Os/^{188}Os$ (Table 1) is significantly lower compared to the modern seawater value of ca. 1.06 (Sharma et al., 1997; Levasseur et al., 1998; Woodhouse et al., 1999). Similar observations are also evident from data earlier reported for pelagic carbonates (Ravizza and McMurtry, 1993; Oxburgh, 1998) and corals (Levasseur et al., 1999b). Contributions from unradiogenic Os from ultramafics and/or cosmic dust have been suggested as a cause for the above discrepancy (Sharma et al., 1997; Burton et al., 1999). However, experimental results unequivocally documenting the influence of either of these sources are still lacking.

To test if Os contributions from lithogenic sources are important, we made calculations for mixing between hydrogenous and lithogenic components (volcanic and Asian dust) using the detrital Os fraction in OJP sediments as estimated earlier using ^{232}Th activities. The $^{187}Os/^{188}Os$ values used for the end members are: seawater = 1.06 (Levasseur et al., 1998; Woodhouse et al., 1999), Asian dust = 1.05 (Peucker-Ehrenbrink and Jahn, 2001), volcanic dust = 0.15. This low value of $^{187}Os/^{188}Os$ for volcanic materials was chosen to determine the maximum impact of volcanics on $^{187}Os/^{188}Os$ of the mixture. Using a value of 5% of Os in the OJP sediments as lithogenic, it is observed that even for a detrital component of 100% volcanic dust, the expected $^{187}Os/^{188}Os$ resulting from mixing of hydrogenous–lithogenic components is 1.024 (Fig. 6). The $^{187}Os/^{188}Os$ for the arc-volcanics from

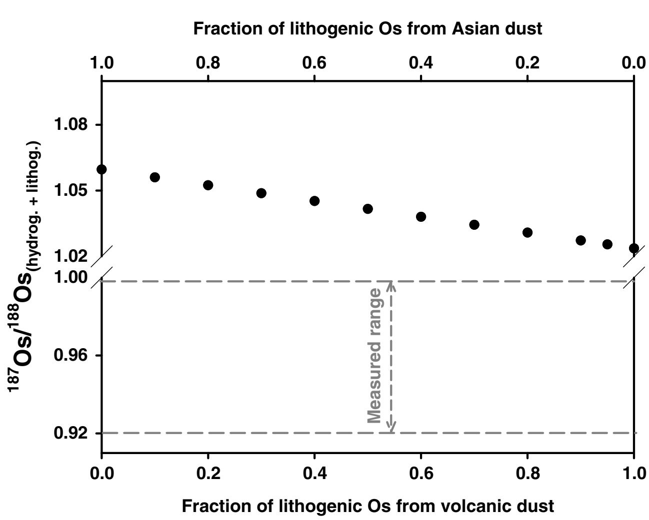

Fig. 6. Calculated $^{187}Os/^{188}Os$ (filled circles) for the mixture of lithogenic Os (volcanic dust and Asian dust) hydrogenous Os. The results show the measured $^{187}Os/^{188}Os$ at the OJP cannot be accounted for even with an assumption that all lithogenic Os at are derived from volcanic dust. Mixing calculations were done by using $^{187}Os/^{188}Os$ of seawater = 1.06, $^{187}Os/^{188}Os$ of volcanic dust = 0.15, $^{187}Os/^{188}Os$ of currently eroding crust = 1.05 and fraction of terrigenous Os = 5% (see text).

the volcanoes around the OJP range from 0.13 to 1.18 with a mean of 0.31 ± 0.27 (Alves et al., 2002). If $^{187}Os/^{188}Os$ value >0.15 is used for the volcanic dust end member, mixing of hydrogenous and lithogenic component with 100% volcanic dust will yield $^{187}Os/^{188}Os$ even higher than 1.024. Thus, mixing of seawater with a mixture of Asian and volcanic dust will yield $^{187}Os/^{188}Os$ that is significantly higher than the measured values (0.92–1.00, Table 1). The possibility of local inputs of dissolved unradiogenic Os from hydrothermal sources or weathering of ultramafics is difficult to assess. However, a prolonged supply of unradiogenic Os from such sources can be ruled out based on the observation of higher interglacial $^{187}Os/^{188}Os$ recorded in EPR sediments (Oxburgh, 1998). In addition, anoxic sediments from the Japan Sea, a site relatively close to the OJP, recorded a $^{187}Os/^{188}Os$ value of 1.04 during the interglacial (Dalai et al., 2005). Thus, the observed lower values of $^{187}Os/^{188}Os$ are likely to be a result of mixing between hydrogenous Os and non-lithogenic Os (e.g. extraterrestrial particulate Os).

3.6. *Influence of extraterrestrial particles on $^{187}Os/^{188}Os$ records at the OJP*

The Os isotope data for the 11 sets of triplicate analyses demonstrate that the sample powders are not homogeneous. The results for most of the samples analyzed in triplicates (9 out of 11) show that out of three analyses, two of them agree well with each other while the third is characterized by the lowest $^{187}Os/^{188}Os$. This common observation, together with consistent amount and composition of procedural Os blank in our laboratory, leads to the inference that mismatch among the triplicate analyses is not due to analytical artifacts. Within a given set of triplicate data, the analysis yielding the lowest $^{187}Os/^{188}Os$ ratio commonly displays relatively lower Pt/Ir ratios and lower Os/Ir ratios. Qualitatively, such elemental associations are consistent with extraterrestrial particles as the underlying source of sample heterogeneity. Given that the 'area–time products' of the samples are marginally lower than that required for unbiased samples, it is likely that undersampling of extraterrestrial particles also contributes to the observed sample heterogeneity. Thus, it is necessary to assess the mixing relationship between various components. We carried out this exercise by plotting $^{187}Os/^{188}Os$ vs. $1/^{188}Os$ for data of each of the 11 sets of triplicate analyses (Fig. 7). This indicates that the sample powders behave as two component mixtures of a radiogenic end member and a higher concentration unradiogenic end member. Mixing between hydrogenous Os and chondritic Os is expected to result in trends that should project toward a y-intercept with a nearly chondritic $^{187}Os/^{188}Os$. Instead, a wide range of y-intercept values, characterized by much higher than the chondritic $^{187}Os/^{188}Os$, are observed (Fig. 7). This requires that the mixing end members that we are assessing within a given sample vial varies among

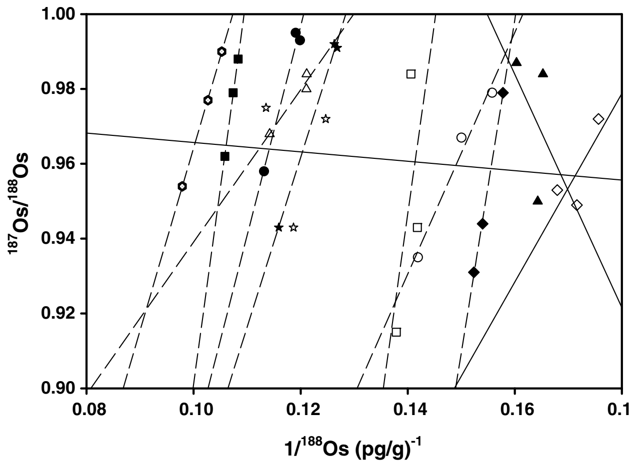

Fig. 7. Plot of $^{187}Os/^{188}Os$ vs. $1/^{188}Os$ for 11 triplicate sets of analyses, with each set shown by different symbols. For most of the triplicate analyses, the data points for each set define a two component mixing line (dashed). However, the $^{187}Os/^{188}Os$ of unradiogenic Os end members defined by the *y*-intercepts of the mixing lines have a large range and are higher than the chondritic $^{187}Os/^{188}Os$.

different samples, and that the unradiogenic Os end member is not similar to primary extraterrestrial particles.

The settling rate of a 100–200 μm extraterrestrial particle (Love and Brownlee, 1993) in the ocean would be on the order of 1 m/day while most of the mass flux of sinking particles in the ocean is composed of much larger particles (Stemmann et al., 2004 and references therein). We suspect that the variable end members implied by our triplicate analyses reflect incorporation of extraterrestrial particles into larger sinking particles and/or feeding by marine biota. These processes may effectively create a sedimentary component that is an admixture of primary extraterrestrial Os and hydrogenous Os. It is noteworthy that if extraterrestrial particles are biologically processed, they may loose their chemical integrity and be subject to elemental fractionation.

The evidence of general influence of extraterrestrial particles on $^{187}Os/^{188}Os$ records at OJP, however, can be seen in the down-core variations of $^{187}Os/^{188}Os$ with Pt/Ir and Os/Ir. Low $^{187}Os/^{188}Os$ are generally associated with low values of Pt/Ir and Os/Ir (Fig. 8), consistent with contributions from cosmic dust. Regression analysis suggests a weak positive correlation between Pt/Ir and $^{187}Os/^{188}Os$ ($r = 0.38$, Fig. 9). Mixing calculations, however, show that $^{187}Os/^{188}Os$ and Pt/Ir data of the OJP samples cannot be explained by a simple mixing of extraterrestrial particles with hydrogenous component of fixed Pt/Ir. The spread of the OJP data points in Fig. 9 requires presence of a hydrogenous end member with variable Pt/Ir which can be met if Pt and Ir are not scavenged from seawater in a constant proportion owing to their variable scavenging efficiency, and/or if processes other than mixing of hydrogenous and cosmic components contribute to the observed variations in $^{187}Os/^{188}Os$ and Pt/Ir. It is unclear as to whether or not climate oscillations and associated changes in oceanographic processes influence Pt/Ir in marine sediments. In addition, alteration of extraterrestrial particles via biological processes may also contribute to variable abundances of Pt and Ir, and Pt/Ir.

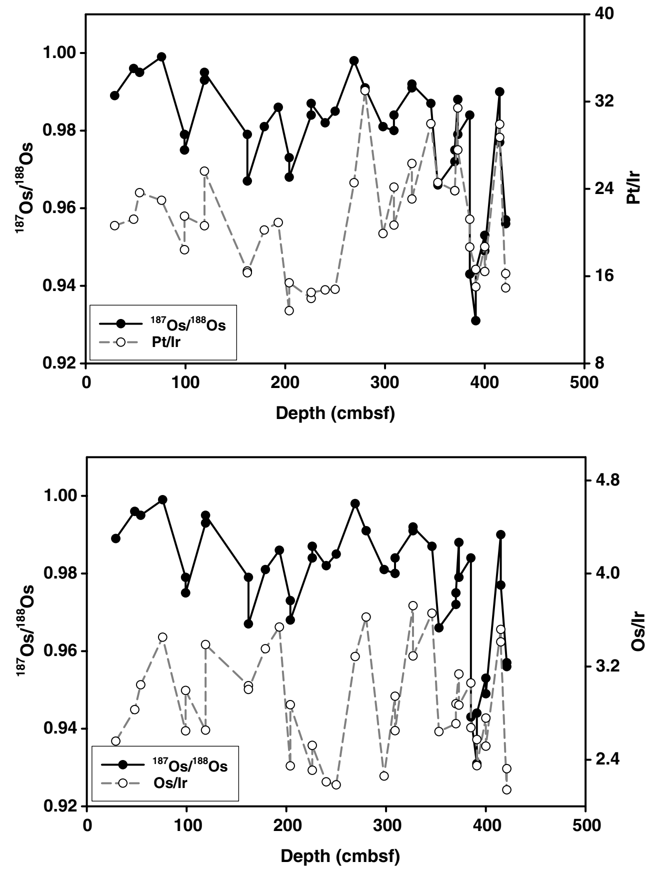

Fig. 8. Down-core variations of Pt/Ir, Os/Ir and $^{187}Os/^{188}Os$ at Site 806. Low Os/Ir and Pt/Ir are generally associated with low $^{187}Os/^{188}Os$ indicating contributions from particulate extraterrestrial matter.

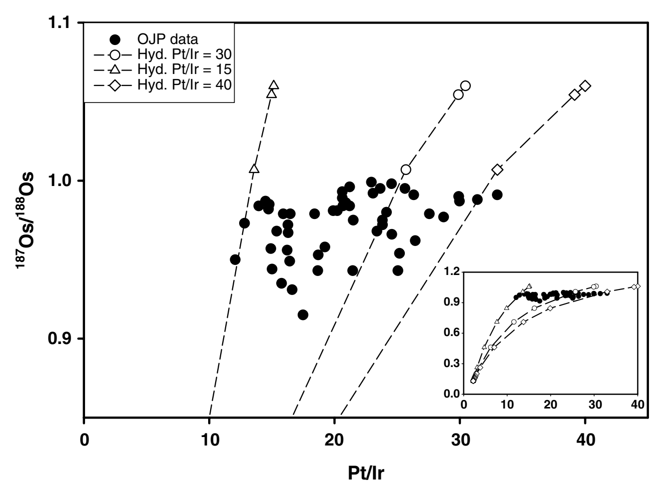

Fig. 9. Scatter plot of $^{187}Os/^{188}Os$ vs. Pt/Ir at Site 806. The data show a weak positive correlation ($r = 0.38$). Calculations suggest the spread of the data can be explained by mixing of minor extraterrestrial component with predominantly hydrogenous component characterized by variable Pt/Ir. A part of the whole plot (inset) is blown up for clarity.

An important implication of the above discussions is that at oceanic sites characterized by low burial fluxes of Os, contributions from cosmic dust significantly influence the bulk $^{187}Os/^{188}Os$. Comparison of $^{187}Os/^{188}Os$ data of this study (Table 1) as well as for modern and Quaternary pelagic carbonates reported earlier (Oxburgh, 1998) with those for modern organic rich sediments (Ravizza and Turekian, 1992) also supports this contention. Organic rich sediments characterized by about an order of magnitude higher Os burial fluxes than the pelagic carbonates record $^{187}Os/^{188}Os$ that are higher relative to those measured in pelagic carbonates and are closer to the seawater value. Mass balance calculations suggest that for an Os burial flux of $100\ pg\ cm^{-2}\ kyr^{-1}$, glacial-interglacial shifts in $^{187}Os/^{188}Os$ of the order of 5% can be obscured by extraterrestrial contributions. Based on the above discussions, we suggest that the most likely cause for the reduced amplitude between glacial–interglacial variations of $^{187}Os/^{188}Os$ at Site 806 is supply of unradiogenic Os by cosmic dust. Patterson and Farley (1998) reported that ^{3}He fluxes at Site 806 are well correlated with records of oxygen isotopes such that high ^{3}He fluxes are associated with the interglacials. Existing studies suggest that flux of ^{3}He to the Earth's surface has been nearly constant since the early Pleistocene (Marcantonio et al., 1995, 2001; Winckler et al., 2004). Coupled ^{3}He-$xs^{230}Th_{initial}$ studies on the OJP records (Higgins et al., 2002) suggest that high ^{3}He fluxes during the interglacials are a result of climate related changes in the sediment redistribution and do not imply an increase in flux of extraterrestrial particles. Thus, if particulate extraterrestrial mater was a relatively more important source of Os to the OJP sediments during the interglacials, then higher $^{187}Os/^{188}Os$ characteristic of seawater during this time (Oxburgh, 1998; Peucker-Ehrenbrink and Ravizza, 2000a; Williams and Turekian, 2004; Dalai et al., 2005) must have been diluted by extraterrestrial unradiogenic Os. This may explain the observation that $^{187}Os/^{188}Os$ is ca. 1.0 during the interglacials in the OJP sediments. Mixing calculations suggest that amount of extraterrestrial matter required to result in a decrease of $^{187}Os/^{188}Os$ from an interglacial value of 1.02 (Oxburgh, 1998) to 1.00 would account for ca. 2% of total Os in the OJP sediments (ca. 1.5 pg/g Os based on average Os concentration of 65 ppt). Assumption of a chondritic Os/Ir yields ca. 1.5 pg/g Ir in the interglacials sediments to be extraterrestrial in origin. It is noteworthy that given the procedural blanks and the analytical uncertainty, a 1.5 pg/g change in Os and Ir is difficult to be resolved, whereas variation of $^{187}Os/^{188}Os$ of 0.03 units can be clearly differentiated. Thus, $^{187}Os/^{188}Os$ in marine sediments are more sensitive indicators of contributions from extraterrestrial particles than PGE abundances and their ratios at least for two reasons. First, subtle variations in $^{187}Os/^{188}Os$ due to contributions from the cosmic dust can be easily resolved with our current analytical precision whereas this is not always possible for PGE abundances. Second, PGE abundances and their ratios are likely influenced by varying degrees of scavenging efficiency and under different lithology and depositional conditions that result in changes of the relative proportions hydrogenous PGE.

3.7. Os isotopes as paleoflux tracers

Finally, we initiate estimates of sediment mass accumulation rates (MAR) using Os isotope results of this study. Sediment MAR is calculated from the following relation:

$$\mathrm{MAR} = (\mathrm{Os\ flux})_{cos}/[\mathrm{Os}]_{cos}, \tag{5}$$

where $[Os]_{cos}$ is Os concentration in the OJP sediments contributed by cosmic dust and $(Os\ flux)_{cos}$ is the reported extraterrestrial Os flux (ca. $4\ pg\ cm^{-2}\ kyr^{-1}$, Esser and Turekian, 1993; Peucker-Ehrenbrink, 1996). $[Os]_{cos}$ is calculated from the product of total Os concentration and fraction of Os in the OJP sediments contributed by cosmic dust (F_{cos}). F_{cos} is estimated using a three component mixing equation:

$$R_{sed} = F_{hy} \times R_{hy} + F_{cos} \times R_{cos} + F_{lith} \times R_{lith}. \tag{6}$$

Substitution of the relation $F_{hy} + F_{cos} + F_{det} = 1$ in Eq. (6) yields

$$F_{cos} = [R_{sed} - R_{hy} + F_{lith}(R_{hy} - R_{lith})]/[R_{cos} - R_{hy}], \tag{7}$$

where R and F stand for $^{187}Os/^{188}Os$ and fraction of ^{188}Os in the mixing components respectively. Subscripts 'hy,' 'cos,' 'lith' and 'sed' refer to hydrogenous, cosmic, lithogenic and bulk sediment, respectively. R_{sed} is measured $^{187}Os/^{188}Os$, R_{cos} = ca. 0.13 (Walker and Morgan, 1989), $R_{lith} = 1.05$ (Peucker-Ehrenbrink and Jahn, 2001), F_{lith} is estimated based on reported ^{232}Th concentrations (Higgins et al., 2002) using the Eq. (1). The value of R_{hy} was chosen as 1.02 for the interglacials and 0.98 for the glacial period (Fig. 10) based on results of Oxburgh (1998). Slightly lower 'area–time products' of samples of this study than that required for the unbiased samples can, in principle, result in underestimation of extraterrestrial Os in the OJP samples and thus overestimation MAR values based on Eq. (5). However, the MAR values derived from Eq. (5) agree within a factor of two with the estimates based on $xs^{230}Th_{initial}$ and Ir for most of the studied interval (Fig. 10). In addition, MAR values based on Os isotopes of triplicate analyses should bracket the 'true' MAR that is unaffected by the sample bias, and yet the results are either similar to or lower than Ir-based flux estimates. Together, these observations suggest that overestimation Os isotope-based paleoflux estimates at the OJP arising from undersampling of extraterrestrial particles is likely to be very small. In the glacial sections, where the $^{187}Os/^{188}Os$ of bulk sediments are substantially higher than assumed hydrogenous end member, Eq. (5) yields unrealistic values for MAR. Based on observations of low ^{3}He burial fluxes during the glacials (Patterson and Farley, 1998) and sediment focusing at the OJP (Higgins et al., 2002), it is speculated that this discrepancy in Os isotope-based MAR during the glacial is linked to focusing of extraterrestrial particles. General agreement

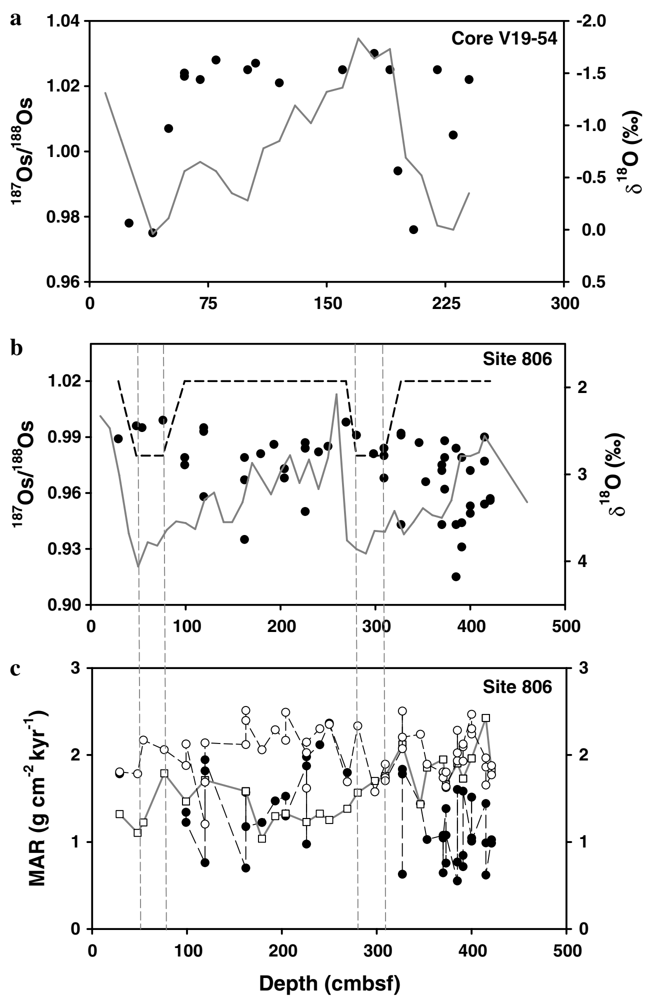

Fig. 10. (a) Down-core variation of benthic $\delta^{18}O$ (grey line) and $^{187}Os/^{188}Os$ (filled circles) for East Pacific Rise (core V19-54, Oxburgh, 1998). (b) Similar plots for $\delta^{18}O$ (grey line) and $^{187}Os/^{188}Os$ (filled circles) at Site 806C. $^{187}Os/^{188}Os$ of hydrogenous fraction, based on the data of Oxburgh (1998) and indicated by the dashed black line, is used in the model to calculate the sediment mass accumulation rates (MAR) (see text for detailed discussion). (c) Comparison of Os isotope-based sediment MAR (filled circles) with those derived using Ir concentrations (open circles) and $xs^{230}Th_{initial}$ (open squares). This shows that Os isotope-based MAR values agree within a factor of ca. 2 with other estimates except in the glacial intervals bound by vertical dashed grey lines.

of Os isotope-based MAR values with estimates based on independent approaches underscores the potential of marine $^{187}Os/^{188}Os$ records in paleoflux estimations, provided there are independent constraints on $^{187}Os/^{188}Os$ and Os concentrations of hydrogenous and lithogenic components.

4. Summary and conclusions

This study provides some of the first estimates for the relative PGE contributions from various sources to pelagic carbonates. Based on independent approaches, it is estimated that terrigenous matter contributes, on an average, ca. 5% of total Ir, Os and Pt, whereas particulate extraterrestrial mater supplies ca. 1% Pt, ca. 5% Os and ca. 10% Ir to the OJP sediments. Thus, the majority of these PGE are hydrogenous. Comparison of Ir/^{3}He and Ir/$xs^{230}Th_{initial}$ at Site 806 with those reported for pelagic clay sequences from the Pacific suggests that Ir flux is constant within a factor of ca. 2. Available information also suggests that Ir accumulation rate is likely constant within a factor of ca. 2 between the Pacific and the Atlantic. All this leads to the inference that Ir concentrations, in principle, can be used as a constant paleoflux tracer. Concentrations of Ir, ^{3}He and $xs^{230}Th_{initial}$, when normalized to one another, show similar down-core variations, with each of the ratios varying within factor of two. In addition, down-core records of Ir, ^{3}He and $xs^{230}Th_{initial}$, when averaged over ca. 50 cm depth intervals, are not well correlated but show variability that is similar in magnitude. Calculated sediment MAR based on these independent tracers yield similar values when averaged over a 50 cm depth scale. However, high resolution records of Ir concentrations (ca. 20 cm interval) do not show coherent down-core variation with $xs^{230}Th_{initial}$. This observation presumably results from fractionation of Ir and ^{230}Th during/or after sediment deposition. Thus, the estimates and results of this study suggest that Ir concentrations, on scale of several tens of centimeter, can be used a constant flux tracer. However, consideration of mode and nature of supply of Ir to the oceans suggest that application of Ir as a constant paleoflux tracer would require calibration both in space and time.

Data on $^{187}Os/^{188}Os$ and concentrations of Os, Ir and Pt in the OJP sediments indicate contributions from particulate extraterrestrial material. Correlated down-core variations of $^{187}Os/^{188}Os$ with Pt/Ir and Os/Ir point to unradiogenic Os contributions from the cosmic dust. However, assessing the mixing relationship for each of triplicate analyses indicate that the unradiogenic Os end member cannot characterized by an unaltered chondritic composition. Comparison of oxygen isotope records with $^{187}Os/^{188}Os$ does not show a clear glacial–interglacial variation in $^{187}Os/^{188}Os$. The interglacial $^{187}Os/^{188}Os$ values recorded in the OJP sediments are ca. 1.00 and lower compared to the value of 1.02–1.04 reported earlier at other sites. This observation results most likely from cosmic dust contributions considering that at Site 806, ^{3}He fluxes were higher during the interglacials. This inference is also supported by the observation that calculated cosmic Os contributions yield estimates of sediment accumulation rates that agree within a factor of ca. 2 with estimates based on Ir and $xs^{230}Th_{initial}$. Mixing calculations suggest that subtle contributions from particulate extraterrestrial matter can be resolved analytically with $^{187}Os/^{188}Os$, whereas PGE abundances and ratios are of limited utility for this purpose.

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