The marine osmium isotope record

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ABSTRACT

Over the past decade the marine osmium isotope record has been developed into a new tracer in palaeoceanographic research. Several analytical developments, particularly in the past few years, have significantly increased our ability to study the behaviour of osmium in the surficial environment. The $^{187}Os/^{188}Os$ and osmium concentration of seawater, river water, rain, and hydrothermal vent fluids have been measured directly. Recently, the behaviour of osmium in estuaries–critical for estimating the marine residence time of osmium–has been studied. Our knowledge of the surficial osmium cycle has thus significantly improved. In addition, reconstructions of past variations in the marine $^{187}Os/^{188}Os$ recently have been extended back into the Mesozoic. This review attempts to summarize our current understanding of the marine osmium system–present and past.

The $^{187}Os/^{188}Os$ of seawater during the Cenozoic to first order mimics the marine $^{87}Sr/^{86}Sr$ record. It is therefore tempting to interpret both records as reflecting increased input of radiogenic osmium and strontium resulting from enhanced continental weathering regulated by climatic/tectonic processes. However, the marine osmium isotope system differs fundamentally from the marine strontium isotope system. This review emphasizes three important differences. First, large impacts are capable of resetting the $^{187}Os/^{188}Os$ to unradiogenic values without significantly affecting the marine strontium system. Second, organic-rich sediments are characterized by high $^{187}Re/^{188}Os$; resulting $^{187}Os/^{188}Os$ ingrowth-trajectories are similar to the average slope of the Cenozoic $^{187}Os/^{188}Os$ seawater record. Trends towards more radiogenic $^{187}Os/^{188}Os$ seawater therefore can be caused by weathering of organic-rich sediments at a constant rate. Third, the marine residence time of osmium is sufficiently short to capture short-periodic (glacial-interglacial) fluctuations that are inaccessible to the buffered marine strontium isotope system. This offers the opportunity to discriminate between high-frequency (climatic) and low-frequency (tectonic) forcing.

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Introduction

Spatial and temporal variations in the isotopic composition of seawater reflect the integrated effects of global processes on ocean chemistry. Among important global processes, silicate weathering has received special attention as it is believed to control the atmospheric CO_2 budget on geological time scales (e.g. Walker *et al.*, 1981; Berner *et al.*, 1983). Attempts to reconstruct past atmospheric CO_2 levels critically depend on a reliable proxy for past changes in silicate weathering intensity. The most widely used proxy is the marine Sr isotope record. Periods of increasing $^{87}Sr/^{86}Sr$ have been linked to intensified continental weathering caused by processes such as orogenesis (e.g. Raymo *et al.*, 1988) and glaciation (e.g. Armstrong, 1971). Recently, however, several studies (e.g. Palmer and Edmond, 1989; Krishnaswami *et al.*, 1992; Blum and Erel, 1995; Derry and France-Lanord, 1996; Quade *et al.*, 1997; Blum *et al.*, 1998) have questioned the validity of the marine $^{87}Sr/^{86}Sr$ as a proxy for silicate weathering intensity. The discovery of secular variations in the Os isotopic composition of seawater thus provides a promising new proxy for global processes affecting seawater chemistry (e.g. Pegram *et al.*, 1992; Ravizza, 1993; Peucker-Ehrenbrink *et al.*, 1995; Turekian and Pegram, 1997; Oxburgh, 1998; Reusch *et al.*, 1998; Pegram and Turekian, 1999). Much of the driving force for understanding the marine Os system is linked to the potential application of the marine Os isotope record as a proxy for climatic/tectonic processes in the geological past. In addition, its potential use as a stratigraphic tool in sediments devoid of useful calcareous or siliceous microfossils makes it a potentially useful addition to the well-established Sr-isotope record, particularly during periods of constant $^{87}Sr/^{86}Sr$.

In the following we first review our current understanding of Os in the modern ocean. We then discuss important sources and sinks of Os to seawater and finally review the current status of temporal variations in the isotopic composition of seawater by highlighting important differences to other, better established marine isotope tracers, specifically strontium.

Osmium in seawater

Osmium is among the least abundant elements in seawater. Early attempts to measure its isotopic composition therefore focused on chemical and/or biological precipitates (Fe–Mn nodules, organic matter) that preconcentrate hydrogenous (i.e. seawater-derived) Os (Turekian, 1982; Luck and Turekian, 1983; Turekian and Luck, 1984; Palmer and Turekian, 1986). Unaware of the existence of temporal variations in the isotopic composition of seawater, these authors interpreted the observed regional variations in Os isotopic composition as reflecting a marine residence time of Os shorter than the mixing time of the oceans. Thermodynamic calculations of the stability of Os in seawater led Palmer *et al.* (1988) to suggest that Os exists as an oxyanion in seawater with a residence time longer than the mixing time of the oceans. They re-interpreted the observed regional scatter in the isotopic composition of Fe–Mn nodules to be a result of incorporation of extraterrestrial particles and predicted a $^{187}Os/^{188}Os$ value for present-day seawater of ~1.11. This work was later complemented by a study of widely distributed, recent organic-rich sediments that provided the first analytical evidence for isotopic homogeneity of seawater (Ravizza and Turekian, 1992). The data, however, did not preclude the existence of subtle regional variations in $^{187}Os/^{188}Os$, because the uncertainty in the mean value

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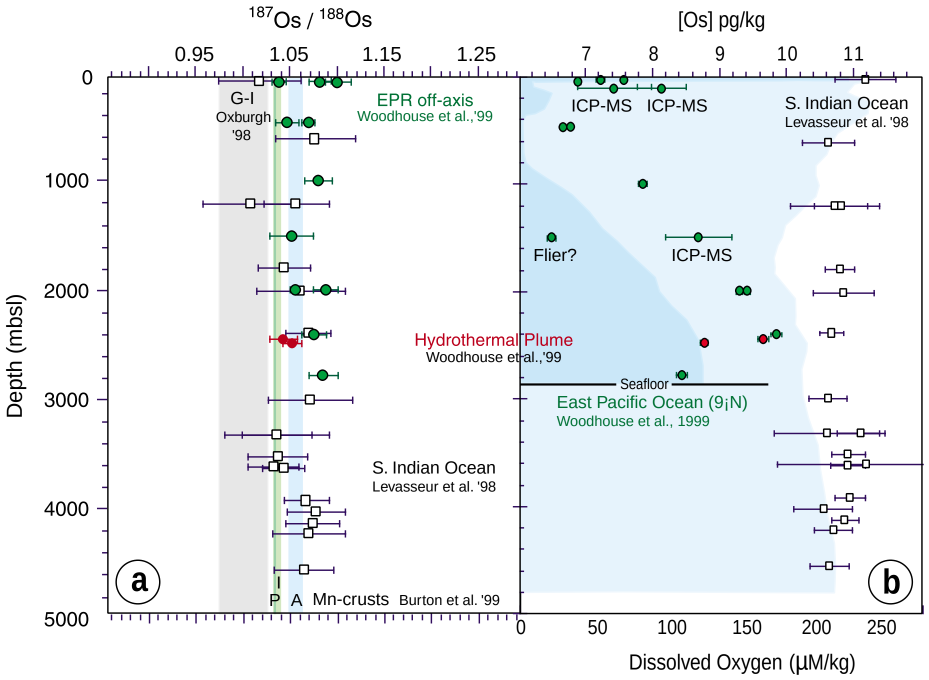

Fig. 1 (a) Depth profiles of $^{187}Os/^{188}Os$ in seawater. Data for SW Indian Ocean profiles (Levasseur *et al.*, 1998) are shown in open squares with error bars (2σ). Data from the East Pacific Rise profiles by Woodhouse *et al.* (1999) are shown in dark green circles with error bars (2σ). Hydrothermal plume (EPR 9°N) samples are shown in red. Also shown are the data for recent growth surfaces of hydrogenetic Fe–Mn crusts from the Atlantic (blue field), Indian (light green field) and Pacific (dark green line) oceans (Burton *et al.*, 1999). The range of glacial-interglacial variations in seawater (Oxburg, 1998) is shown in grey for comparison. (b) Depth profiles of Os concentration in seawater (same symbols as panel a). The dissolved oxygen contents are shown for both regions for comparison as blue fields. Whereas Woodhouse *et al.* (1999) measured dissolved oxygen *in situ* (9°46′N, 104°22′W: shown as dark blue field), the dissolved oxygen profile for the SW Indian Ocean (34°11′S, 55°37′E) is approximated by that of the closest GEOSECS station (Leg 5, St. 428: 37°45′S, 57°37E, shown as light blue field), because Levasseur *et al.* (1998) did not measure dissolved oxygen.

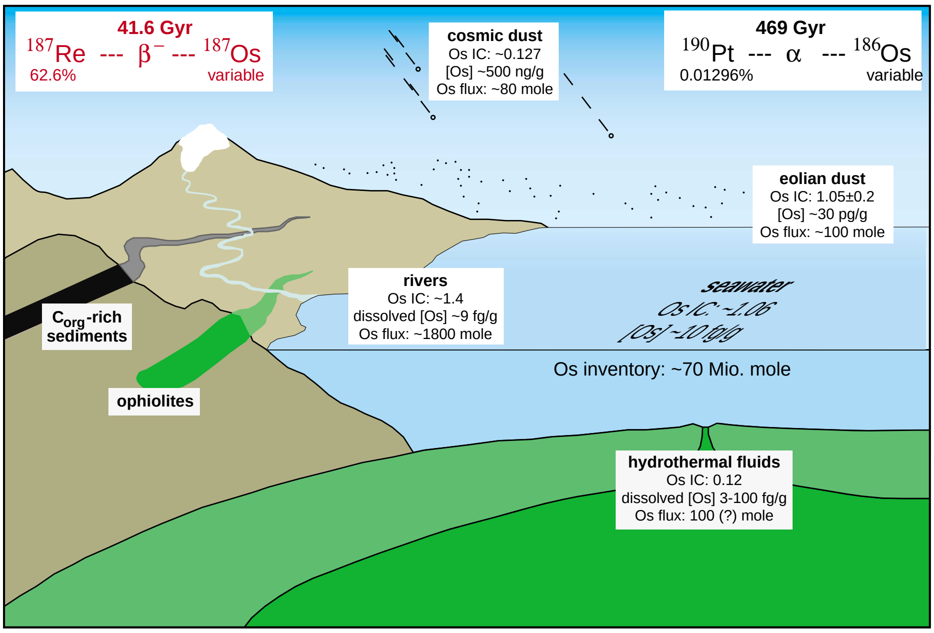

Fig. 2 The marine Os isotope system: Os concentration [Os], $^{187}Os/^{188}Os$ (IC) and estimated Os flux for various sources. Osmium flux from cosmic dust and aeolian dust are maximum estimates because–most likely–little Os from these sources will dissolve in seawater. Hydrothermal Os fluxes are highly uncertain at present. ^{190}Pt half-life and abundance from Begemann *et al.* (2001).

of 1.035 ± 0.036 was larger than the instrumental uncertainty. The existence of small regional variations was recently postulated by Burton *et al.* (1999) based on high-precision Os isotope analyses of hydrogenous Fe–Mn crusts from the Atlantic, Indian and Pacific oceans. The data are suggestive of a slightly more radiogenic North Atlantic relative to other ocean basins (Fig. 1a). The high Re/Os of seawater (^{187}Re/^{188}Os ~4200) suggests that subtle (60–70 ppm) increases in ^{187}Os/^{188}Os of seawater can occur on timescales similar to transit times for deep water from Atlantic to Pacific.

First attempts to analyse the concentration and isotopic composition of Os in seawater directly were plagued by difficulties in spike-sample equilibration, chemical yields, and very small amounts of analyte. The Os concentrations measured in Scripps Pier water (1.7 ± 0.85 pg Os L^{-1}) by Koide *et al.* (1996), and North Atlantic and Central Pacific seawater (~3.6 pg Os L^{-1}) by Sharma *et al.* (1997) are therefore probably too low. In contrast, the measured ^{187}Os/^{188}Os (0.76 ± 0.37, Koide *et al.*, 1996; 1.044 ± 0.36, Sharma *et al.*, 1997), although afflicted with large uncertainties, agree with the currently accepted value for open ocean water. Levasseur *et al.* (1998) reported the first fully successful seawater analyses on unfiltered seawater from two depth profiles at the south-west Indian Ridge (10.87 ± 0.34 [2σ] pg Os kg^{-1}, ^{187}Os/^{188}Os = 1.057 ± 0.038 [2σ]). The conservative depth profiles Levasseur and colleagues measured were later complemented by a profile at the East Pacific Rise (Woodhouse *et al.*, 1999) that shows a 30% decrease in Os concentration coinciding with the oxygen minimum at ~500 m depth (see Fig. 1a/b). The majority of Os in seawater appears to be either dissolved or associated with particles < 0.4 μm, because differences in Os concentration between filtered and unfiltered samples are small (Woodhouse *et al.*, 1999). While the Os isotopic composition of the two depth profiles agree within analytical uncertainty (East Pacific: 1.066 ± 0.038 [2σ] SW Indian: 1.057 ± 0.038 [2σ]), Os concentrations in the western Pacific are significantly lower (6.5–9.8 pg kg^{-1}) than in the south-west Indian Ocean. The EPR concentration profile therefore provides evidence for nonconservative behaviour of Os in seawater. It is important to point out that the two groups use different analytical techniques. Levasseur *et al.* (1998) achieve spike–sample equilibration and oxidation of Os to OsO_4 under hot (90 °C), strongly oxidizing conditions within about 48 h. In contrast, Woodhouse *et al.* (1999) use a large-scale (~1 L) conventional distillation to extract Os from seawater in about 4 h. The extended period of oxidation required to fully equilibrate spike and sample led Levasseur *et al.* (1998) to suggest that a significant fraction of Os is seawater is not, as suggested earlier based on thermodynamic modelling, present as oxyanions (H_2OsO_5 or $H_3OsO_6^-$), but organically complexed. It is therefore possible that concentration differences between the Indian and the Pacific Oceans reflect the existence of an Os species that resists mild oxidation. However, Sharma *et al.* (2000) recently reported an Os concentration of 10.1 pg kg^{-1} in unfiltered central Pacific seawater (2000 m depth) using a hot oxidizing spike–sample equilibration technique similar to that used by Levasseur and colleagues. The good agreement between deep central Pacific water and deep East Pacific water (9.8 pg kg^{-1}, Woodhouse *et al.*, 1999) indicates that differences in observed Os concentration may be real and unrelated to differences in analytical protocols used by the three groups. A methodological intercomparison is essential to confirm nonconservative behaviour of Os in seawater.

The present-day seawater ^{187}Os/^{188}Os of ~1.06 reflects the balance of input from unradiogenic mantle-derived and radiogenic continental sources of Os (Fig. 2 and Table 1). Dissolution of the background flux of extraterrestrial matter (~30 000 t yr^{-1}: Esser and Turekian, 1993b; Love and Brownlee, 1993; Peucker-Ehrenbrink, 1996; Peucker-Ehrenbrink and Ravizza, 2000) in seawater contributes, most likely, little to the unradiogenic sources of Os (see Sharma *et al.*, 2000, for a contrasting viewpoint). Osmium released by anthropogenic activities has been detected in coastal sediments. Sources include sewage sludge, catalytic converters and use as a staining reagent in biomedical research (Koide *et al.*, 1991; Esser and Turekian, 1993a; Ravizza and Bothner, 1996; Williams *et al.*, 1997; Tuit *et al.*, 2000). Anthropogenic sources are generally characterized by unradiogenic Os isotopic composition, because most commercial PGE are derived from mantle-derived deposits. Existing data for open ocean settings suggest that anthropogenic contamination does not significantly affect the marine Os system. We review the sources of Os to seawater and the processes that affect the transfer of Os from the sources to the ocean in more detail below.

Osmium in river water

The Os isotopic composition of seawater is currently dominated by input from the continents. Determining the isotopic composition and concentration of Os in river water is therefore of paramount importance. Analogous to the marine Os system freshwater Fe–Mn oxyhydroxides were initially used as proxies for the isotopic composition of river and lake water (Pegram *et al.*, 1994; Yin, 1995; Peucker-Ehrenbrink and Ravizza, 1996). Pegram and Turekian (1994) employed a reductive leaching technique developed for metalliferous marine sediments to separate hydrogenous Os associated with Fe–Mn oxyhydroxide coatings from river sediments. This study provided the first evidence that the isotopic composition of continental runoff is more radiogenic than the eroding continental crust. Peucker-Ehrenbrink and Ravizza (1996) used freshwater Fe–Mn nodules to estimate the isotopic composition of continental runoff into the Baltic Sea. The data not only provide evidence for significantly more radiogenic runoff from Precambrian shields (^{187}Os/^{188}Os ~4) compared to Phanerozoic sedimentary platforms (^{187}Os/^{188}Os ~1.2) but also indicate similar Os concentrations in rivers draining both terrains. This is in contrast to the relatively small flux of Sr from Precambrian shields that contribute little to the marine Sr budget (Wadleigh *et al.*, 1985). Continental runoff of radiogenic Os from Precambrian shields into the North Atlantic could therefore be the cause for the observed radiogenic nature of North Atlantic seawater.

Early estimates of the marine residence time of Os (Richter and Turekian, 1993: ~10^4 yr; Peucker-Ehrenbrink and Ravizza, 1996: ~16 000 yr) indicated that the concentration of Os in river water should be similar to that in seawater. Techniques developed for

Table 1 Re–Os–Pt data for important near-surface geochemical reservoirs.

	$^{187}Os/^{188}Os$ (2σ error)	[Os] (pg kg^{-1})	$^{187}Re/^{188}Os$	[Re] (pg kg^{-1})	$^{190}Pt/^{188}Os$	[Pt] (pg kg^{-1})	Os inventory (kg)	Os flux to ocean (kg yr^{-1})
Seawater	~ 1.06	~ 10	4270	$8240 \pm 70^{@}$	0.0058	$55 \pm 14^{@}$	1.37×10^{7}	
North Atlantic	$1.044 \pm 0.024^{*}$			$8170 \pm 110^{\$}$		$55 \pm 14^{@}$		
SW Indian	$1.057 \pm 0.038^{+}$	$10.87 \pm 0.34^{+}$						
Central Pacific	$1.044 \pm 0.036^{*}$			$8300 \pm 70^{\$}$				
			$7420 \pm 40^{\sim}$					
East Pacific	$1.066 \pm 0.038^{\#}$	$6.6–9.8^{\#}$						
Fe-Mn crusts/nodules		$10^{5}–10^{7}$			0.37	$10^{6}–10^{9\wedge}$		
North Atlantic	$1.059 \pm 0.008^{**}$							
Indian	$1.039 \pm 0.004^{**}$							
Pacific	$1.036 \pm 0.010^{**}$							
Cosmic dust	~ 0.127	$\sim 5 \times 10^{8++}$	~ 0.4	$\sim 3.7 \times 10^{7++}$	0.0019	$9.9 \times 10^{8++}$		< 15
HT hydrothermal	$0.129–0.388^{\#\#}$	$2.8–38^{\#\#}$						$0.07–7.6^{\$\$}$
LT hydrothermal	$0.11^{\#\#}$	$98^{\#\#}$						$\sim 20^{\&\&}$
Anthropogenic	$\sim 0.14^{***}$	$> 10^{5***}$						$< 71^{+++}$
Aeolian dust	$1.05 \pm 0.2^{\#\#\#}$	$3.1 \times 10^{4\#\#\#\#}$	$50^{\#\#\#}$	$3 \times 10^{5\#\#\#}$	0.013	$3.9 \times 10^{5\#\#\#}$		$28^{\$\$\$}$
Rivers (world mean)	~ 1.4	~ 9.1	227	$428^{\$}$				~ 350
		Os	Re	Pt				
Residence time in seawater (yr)		$\sim 10\,000^{\&\&\&}$ $\sim 16\,000^{****}$ $\geqslant 44\,000^{*}$ $< 12\,000^{++++}$ $2000–60\,000^{**}$ $25\,000–54\,000^{\#\#\#\#}$	$750\,000^{\$}$					

$^{@}$Colodner *et al.* (1993a); *Sharma *et al.* (1997); $^{+}$Levasseur *et al.* (1998); $^{\#}$Woodhouse *et al.* (1999); $^{\$}$Colodner *et al.* (1993b); $^{\sim}$Anbar *et al.* (1992); $^{\wedge}$Koide *et al.* (1991); **Burton *et al.* (1999); $^{++}$Anders and Grevesse (1989); $^{\#\#}$Sharma *et al.* (1999); $^{\$\$}$calculated using 0.13×10^{14} kg (Sleep *et al.*, 1983) and 2×10^{14} kg (Wolery and Sleep, 1976) HT hydrothermal flux annually as minimum and maximum estimates; $^{\&\&}$calculated using 2×10^{14} kg low-temperature water flux, ***Esser and Turekian (1993), Ravizza and Bothner (1997); $^{+++}$Hilliard (1998); US Imports only; $^{\#\#\#}$Peucker-Ehrenbrink and Jahn (1999); $^{\$\$\$}$calculated using the atmospheric flux of mineral aerosols to the World's ocean, estimated by Duce *et al.* (1991) at 910×10^{12} g yr^{-1}; $^{\&\&\&}$Richter and Turekian (1993); ****Peucker-Ehrenbrink and Ravizza (1996); $^{++++}$Oxburgh (1998); $^{\#\#\#\#}$Levasseur *et al.* (1999a).

analysing Os in seawater could thus be adapted for river water analysis. The first attempts (Sharma and Wasserburg, 1997; Porcelli *et al.*, 1998) were plagued by problems with spike-sample equilibration. Consequently, Os concentrations reported in these studies may be too low by a factor of up to 3. However, the isotopic composition is only indirectly affected by spike–sample equilibration and older data on Os isotopic composition are most likely accurate. The first comprehensive study of Os in rivers was undertaken by Levasseur *et al.* (1999a) and provides additional evidence for slightly more radiogenic continental runoff ($^{187}Os/^{188}Os$ 1.49–1.54) compared to average eroding continental crust (Esser and Turekian, 1993b: ~ 1.26; Peucker-Ehrenbrink and Jahn, 1999: $\sim 1.05 \pm 0.2$). There are several possible explanations for the slightly more radiogenic nature of Os in continental runoff. Preferential weathering of very radiogenic sediments, such as organic-rich sediments, tends to bias the isotopic composition of runoff towards more radiogenic values. Peucker-Ehrenbrink and Hannigan (2000) studied the effects of weathering of black shales on the Re and PGE budget. The data is indicative of significant (45–90%) loss of Re, PGE and organic carbon during surficial weathering. In a complementary study Peucker-Ehrenbrink and Blum (1998) investigated the release of Os upon weathering of moraine soils of granitic starting composition. Although the budget of Os is dominated by Os-rich trace phases such as magnetite, loss of radiogenic Os from young soils can be linked to preferential weathering of radiogenic biotite. Both weathering processes preferentially release radiogenic Os. The current data on Os in rivers are summarized in Fig. 3 (Levasseur *et al.*, 1999a; Sharma *et al.*, 1999; Martin *et al.* 2000). Although the data represent $\sim 36\%$ of the annual riverine water flux to the ocean, they represent only $\sim 22\%$ of the land area that drains into the oceans. Assuming that the average Os concentration of 9.1 pg kg^{-1} and the $^{187}Os/^{188}Os$ of 1.44 is representative for the global runoff, the total riverine flux of Os is calculated at ~ 350 kg yr^{-1}. This value has to be considered a minimum estimate, because analytical techniques used for some samples potentially underestimate the Os concentrations. As pointed out by Levasseur *et al.* (1999a) the present-day water flux for individual rivers is only know to within $\pm 20\%$, placing a lower limit on the uncertainty of the present-day riverine Os flux. Additional uncertainties arise from temporal variations in the concentration and isotopic composition of individual rivers, highlighted in Fig. 3 for the Ganges. Furthermore, it is possible that the estimate is biased because of the selection of rivers analysed. For instance, rivers draining recently glaciated Precambrian shields are underrepresented and no river draining the Baltic Shield, the Canadian Arctic, and Greenland has been analysed. Such rivers may be significantly more radiogenic than average continental

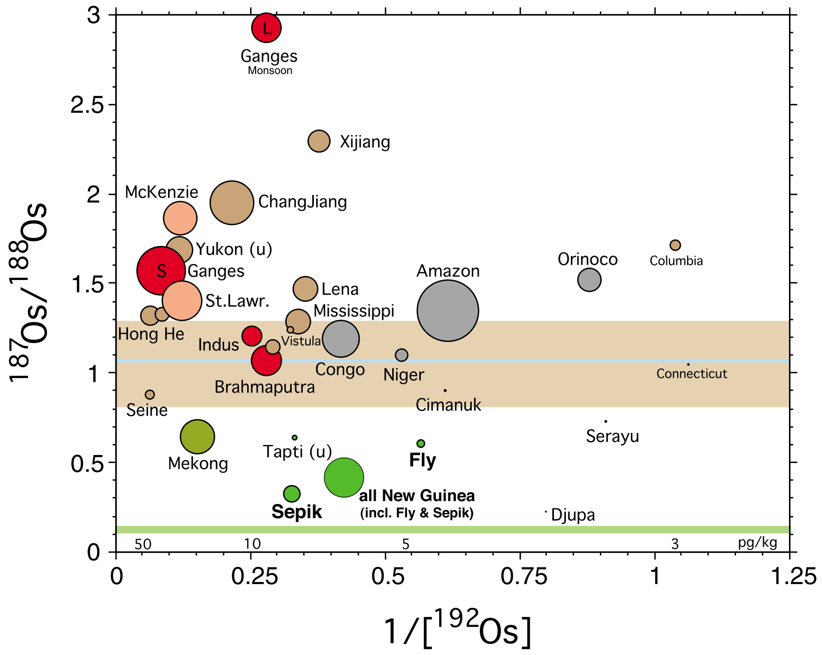

Fig. 3 Riverine ^{187}Os/^{188}Os, Os concentration (in pg kg^{-1}) and relative Os flux to the oceans. Data are from Levasseur *et al.* (1999a), Sharma and Wasserburg (1997)–data are shown in a smaller font to indicate uncertainties in the Os concentration due to spike-sample equilibration and yield–Sharma *et al.* (1999) and Martin *et al.* (2000). The surface area of the circles represents relative Os flux. (u): upstream sample: the Os isotopic composition and concentration does not necessarily represent that at the river mouth. Colour code: red: rivers draining the Himalaya (S, Sharma *et al.*, 1999; estimate for the post-Monsoon Ganges; L, Levasseur *et al.* (1999a) estimate for the Ganges during the Monsoon, annual Os flux was calculated using the measured Os concentration and isotopic ratio, but the same annual riverine flux. The average Ganges should therefore lie somewhere between the two circles labelled L and S depending on the relative impact of monsoonal runoff), brown: rivers draining a variety of sedimentary and igneous terrains, grey: rivers draining significant areas of Precambrian crust that was not recently glaciated, pink: rivers draining significant areas of recently glaciated Precambrian crust, green: rivers draining volcanic rocks and ophiolites. The big green circle labelled 'all New Guinea' represents total Os runoff from New Guinea calculated assuming the Sepik and Fly rivers are representative of runoff from New Guinea. The Os isotope composition of resent-day seawater is shown as blue line. The best estimate for the eroding upper continental crust is shown as the light brown field (average loess with 1σ uncertainties; Peucker-Ehrenbrink and Jahn, 1999). The present-day Os isotopic composition of the mantle is shown as a green line.

runoff (Peucker-Ehrenbrink and Ravizza, 1996). Small mountainous rivers draining young mantle-derived rocks are only represented by three rivers draining Java (Levasseur *et al.*, 1999a) and Papua New Guinea (Martin *et al.* 2000). Including the Fly and the Sepik Rivers draining Papua New Guinea in the average, for instance, decreases the average riverine ^{187}Os/^{188}Os from 1.46 to 1.42. If Os carried by the Fly river (drainage area 0.076×10^6 km^2, or 9.3% of New Guinea) and the Sepik river (drainage area 0.0793×10^6 km^2, or 9.7% of New Guinea) is representative of Os run off from New Guinea, runoff from New Guinea shifts the estimate of worldwide riverine ^{187}Os/^{188}Os from 1.46 to 1.38. This example indicates that a more representative coverage of young volcanic terrains may bias the average runoff toward less radiogenic values.

In order to reconstruct riverine input to seawater in the geological past, variations in the flux and isotopic composition of major rivers must be reconstructed. This area of research is at its infancy for all marine isotope tracers. Chesley *et al.* (2000) used Fe–Mn oxyhydroxides formed over the past 17 million years by pedogenetic processes in the upper Indu-Gangetic flood plains as recorders of the isotopic composition of shallow groundwater (i.e. river water). Os isotope ratios of pedogenic Fe–Mn oxyhydroxides from the Palaeo-Ganges were more radiogenic than contemporary seawater over the past 17 Myr, while those from the Palaeo-Indus were more radiogenic than palaeo-seawater only over the past 5 Myr. Although the data show a two-fold increase in the isotopic composition of both systems over the past 11 Myr, the significance of these regional changes for the global riverine input of Os to palaeo-seawater is poorly understood.

Osmium in the coastal ocean and estuaries

The total dissolved Os flux to the oceans need not match riverine flux because nonconservative mixing in estuaries can either liberate Os from particulate matter to solution, or visa-versa. Understanding estuarine mixing processes is therefore critical for estimating the continental flux, and thus the marine residence time, of Os to the oceans. For instance, Levasseur *et al.* (1999a) and Sharma *et al.* (1997) calculate marine residence times based on the riverine flux of Os at 25 000–54 000 yr and > 44 000 yr, respectively. Both estimates are significantly higher than previous estimates that were based on the response of the marine Os system to perturbations (~10 000 yr, Richter and Turekian, 1993; < 12 000 yrs, Oxburgh, 1998). Significant release of particulate terrestrial Os to seawater in near-shore environments could bridge this gap.

Our view of the behaviour of Os in estuaries and near-shore environments is heavily biased towards solid phase analyses. For example, data from contaminated coastal sediments provide evidence for removal of anthropogenic Os by organic matter (Koide *et al.*, 1991; Esser and Turekian, 1993a; Ravizza and Bothner, 1996; Williams *et al.*, 1997). Changing physico-chemical conditions in coastal sediments may lead to partial desorbtion of sediment-bound anthropogenic Os, a process that may enable some anthropogenic Os to escape the coastal environment (Pegram *et al.*, 1994; Ravizza and Bothner, 1996). Reisberg *et al.* (1997) argue for complete loss of the radiogenic continental isotope signature from sediments prior to deposition in the Bengal Fan to explain the surprisingly unradiogenic nature of Bengal Fan sediments. These studies indicate that both removal and release processes are operative, but insufficient data are available to determine the net effect of estuarine mixing on dissolved Os flux to the oceans.

Very little is currently known about the behaviour of dissolved Os in estuaries. Mixing of Os along a salinity gradient in the Columbia River estuary has been interpreted as conservative (Porcelli *et al.*, 1998), but the data are analytically problematic and not precise enough to rule out nonconservative behaviour. Data from the Lena estuary is suggestive of 28% removal of riverine Os within the estuary (Levasseur *et al.*, 1999a; Levasseur *et al.*, 2000) and provide no evidence for release of Os from estuarine sediments. A recent study of Os along the salinity gradient from the Fly River mouth into the Gulf of Papua clearly indicates that simple two-component mixing between Coral Sea water and Fly River water cannot explain the observed trend in Os concentration, thus providing further evidence for nonconservative behaviour (Martin *et al.*, 2000, 2001). Although the few existing data on the effects of estuarine mixing on riverine Os are suggestive of nonconservative behaviour of Os in estuaries, it is currently impossible to generalize the results and quantitatively assess the effects of estuarine processes on the marine Os budget.

Atmospheric deposition of osmium

Dissolution of aeolian dust in seawater as a source of Os in seawater has not been studied systematically. Assuming that Os concentrations in aeolian dust are similar to Os concentrations in loess (~ 30 pg g^{-1}, Peucker-Ehrenbrink and Jahn, 1999), the modern annual dust flux to the oceans (Duce *et al.*, 1991) carries only ~ 20 kg Os, too small to significantly affect Os in seawater. However, during periods of enhanced dust flux during peak glacial conditions this flux may have been more than an order of magnitude higher (Petit *et al.*, 1990) and thus significant for the marine Os budget.

Similarly, the role of rain in the global Os cycle has not been studied in detail. Levasseur *et al.* (1999a) analysed two rainwater samples from two ocean islands (Azores, Reunion). While the Os concentrations are similar to seawater (7.6 and 14.7 pg kg^{-1}), the isotopic composition (^{187}Os/^{188}Os ~ 0.175) is much less radiogenic than seawater and similar to ocean island basalts. Clearly, even over ocean islands seawater-derived Os does not dominate rainwater. The unradiogenic nature of ocean island rainwater requires either a local source (volcanic aerosols) or significant dissolution of cosmic dust in rainwater, possibly due to recondensation of material ablated from extraterrestrial particles during atmospheric entry heating. Annual precipitation on oceans has been estimated at 385 700 km^3 (Berner and Berner, 1987). If the average isotopic composition and concentration of Os in precipitation on the ocean is similar to the values measured by Levasseur *et al.* (1999a) the annual flux of unradiogenic Os is ~ 4300 kg, more than an order of magnitude higher than the riverine flux of Os. This indicates that the measured values cannot be representative for precipitation on oceans in general and likely reflect a local source. The isotopic composition and concentration of rain on continents has not been studied, and the contribution from anthropogenic sources of Os in rain, such as release of volatile OsO_4 through smelting processes, is unknown (Esser and Turekian, 1993a). Similarly, the input from volcanic aerosols cannot be quantified at present (Geissbühler, 1990), although the few existing data indicate high Os concentrations (~ 0.36 ng Os L^{-1} air) in volcanic aerosols during the spring 1984 eruption of Mauna Loa (Krähenbühl *et al.*, 1992).

Osmium in high- and low-temperature alteration of oceanic crust

The apparent constancy of the extraterrestrial matter flux throughout the Cenozoic stands in marked contrast to the dynamic nature of the marine Os isotope record. This implies that dissolution of extraterrestrial matter did not drive changes in the marine Os isotope system. Moreover, mass balance considerations limit the annual contribution of extraterrestrial Os to the marine Os budget to < 36 kg Os (Peucker-Ehrenbrink, 1996) or < 17.6 kg Os (Levasseur *et al.*, 1999a), corresponding to $< 11\%$ and $< 6\%$ of the riverine input, respectively. The most likely unradiogenic source of Os to seawater is therefore alteration of young, mantle-derived rocks. Alteration may occur through high- or low-temperature interaction of seawater with oceanic crust, or through weathering of young, mantle-derived rocks on ocean islands, island arcs and the continents. Palmer and Turekian (1986) and Palmer *et al.* (1988) emphasized the importance of alteration of ultramafic rocks as a source of unradiogenic Os. This mechanism is particularly appealing, because Os concentrations in abyssal peridotites are about two orders of magnitude higher than in oceanic basalts. Comparison of altered and unaltered abyssal peridotites and leaching experiments on altered peridotites provides evidence for incorporation of hydrogenous Os during peridotite alteration (Snow and Reisberg, 1995). Unequivocal evidence for systematic loss of Os during alteration of abyssal peridotites is lacking. Although this mechanism repeatedly has been invoked as a source of unradiogenic Os to seawater (Martin, 1991; Snow and Reisberg, 1995; Peucker-Ehrenbrink, 1996; Levasseur *et al.*, 1999a) this potentially important source awaits quantitative constraints.

Several studies have investigated the effect of hydrothermal circulation through oceanic crust on the mobility of Os (Ravizza *et al.*, 1996; Brügmann *et al.*, 1998; Sharma *et al.*, 1999). Both high- and low-temperature hydrothermal precipitates can be interpreted as two-component mixtures of hydrogenous and oceanic crustal Os (e.g. Ravizza *et al.*, 1996). Although the effects of unradiogenic, vent-derived Os can be traced to metalliferous sediments deposited in the vicinity of active hydrothermal vents (Ravizza *et al.*, 1996), neither the uptake of hydrogenous Os in altered oceanic crust nor the release of mantle-derived Os to seawater can be quantified. In analogy to other marine isotope traces with short marine residence times (e.g. Nd) lack of a mantle-like signature in hydrothermal plumes (Woodhouse *et al.*, 1999; see Fig. 1a) does not necessarily imply that hydrothermal sources are negligible for the marine Os budget. Direct analysis of hydrothermal vent water for Os is analytically and technologically challenging (contamination from Ti-samplers, *in-situ* filtration, precipitation upon cooling, etc.) The only attempt so far on samples from the Juan de Fuca Ridge (Sharma *et al.*, 1999) indicates that high- and low-temperature fluids are dominated by mantle-derived Os and characterized by Os concentrations ranging from 2.8 to 38 pg kg^{-1} in high-temperature fluids to 98 pg kg^{-1} in low-temperature hydrothermal fluids. Provided the present-day ocean is at steady state, the annual flux of hydrothermal fluid balances radiogenic riverine inputs if vent fluids analysed by Sharma *et al.* (1999) are representative for vent fluids in general.

Reconstructing the marine Os isotope record

Marine sediments are mixtures of detrital, hydrogenous and extraterrestrial Os in varying proportions. As only the hydrogenous fraction serves as a proxy for the isotopic composition of seawater in the past this fraction has to be separated from the bulk sediment. Bulk sediment analyses can only be used if the hydrogenous fraction dominates the sedimentary Os budget, as for example in metalliferous carbonates (e.g. Ravizza and McMurtry, 1993; Ravizza, 1993; Peucker-Ehrenbrink *et al.*, 1995; Oxburgh, 1998; Reusch *et al.*, 1998). The generally low Re/Os of metalliferous sediments minimizes ingrowth corrections for Cenozoic samples. Recently Ravizza *et al.* (1999) used bulk analyses of umbers (i.e. obducted metalliferous sediments formed through accumulation of metal-rich hydrothermal precipitates) to extend the marine Os isotope record back into the Cretaceous. The similarity in major (Fe, Mn, Al) and trace element (e.g. V/Fe, REE pattern) signatures of umber and present-day metalliferous deposits or plume particles supports the notion that diagenetic processes did not compromise the usefulness of such deposits for reconstructing the marine Os isotope record.

The Os budget of organic-rich sediments is also dominated by hydrogenous Os, prompting Ravizza and Turekian (1992) to suggest that initial $^{187}Os/^{188}Os$ ratios from organic-rich sediments might allow reconstruction of past variations in the Os isotopic composition of seawater. There are potential problems with this approach that must be addressed in each specific setting where this method is applied. Deposition along continental margins makes these sediments susceptible to significant detrital inputs (e.g. Ravizza *et al.*, 1991; Ravizza, 1998). Consequently it must be demonstrated that the Os contribution from detrial material is a negligible fraction of the total Os inventory of the sediment. A second problem with the bulk analysis of old organic-rich sediments is the correction necessary for radiogenic ingrowth of ^{187}Os from ^{187}Re. $^{187}Re/^{188}Os$ values in organic-rich sediments of up to 2260 (Horan *et al.*, 1994) cause ingrowth trajectories whose slopes are similar to the average slope in the $^{187}Os/^{188}Os$ of seawater during the Cenozoic (e.g. Ravizza, 1998; see grey growth trajectory in Fig. 4 for comparison). It is therefore important for successful reconstructions of past $^{187}Os/^{188}Os$ seawater values from organic-rich sediment analysis that these sediments have remained as closed systems since deposition. Re–Os isochron relationships offer a means of testing whether old organic-rich sediments have experienced differential mobilization of Re and Os that may have compromised their integrity as a recorder of marine $^{187}Os/^{188}Os$ in the past (e.g. Ravizza and Turekian, 1989; Ravizza, 1998; Cohen and Coe, 1999; Cohen *et al.*, 1999). This technique is becoming increasingly important for reconstructing pre-Cenozoic seawater $^{187}Os/^{188}Os$, because older (obducted) sediments are susceptible to diagenetic overprint. Pioneered by Ravizza and Turekian (1989) this technique recently has been used with unprecedented precision by Cohen *et al.* (1999) to reconstruct Mesozoic seawater $^{187}Os/^{188}Os$ based on initial $^{187}Os/^{188}Os$ of isochrons for organic-rich Jurassic mudrocks. As the potential for secondary overprint increases with sample age, Re–Os isochrons is a very promising tool for extending the marine Os isotope record back in time.

For all other marine sediments in which the detrital and/or extraterrestrial Os fraction cannot be neglected, leaching procedures designed to selectively dissolve hydrogenous Os are used. Pegram *et al.* (1992) and Peucker-Ehrenbrink *et al.* (1995) have shown that dilute (0.6–6 Vol.%) H_2O_2–H_2SO_4 solutions are effective in reducing Fe–Mn oxyhydroxides and solubilizing their scavenged hydrogenous Os. However, Peucker-Ehrenbrink *et al.* (1995), Turekian and Pegram (1997) and Pegram and Turekian (1999) have also demonstrated that this leaching process is prone to artifacts as the leach also mobilizes unradiogenic Os associated with altered extraterrestrial matter in marine sediments. Leaches of slowly accumulating metalliferous pelagic clays with significant extraterrestrial Os thus tend to yield $^{187}Os/^{188}Os$ less radiogenic than contemporaneous seawater. These effects can be minimized if very dilute (0.15 Vol% H_2O_2) leaching solutions are used (Turekian and Pegram, 1997). Alternatively, Pegram and Turekian (1999) have used He isotope analyses on the same samples to correct the bulk Os for extraterrestrial contributions by assuming that extraterrestrial He is well correlated with extraterrestrial Os. This assumption is not necessarily valid. Extraterrestrial He is lost from larger ET particles during atmospheric entry heating (e.g. Nier and Schlutter, 1993; Farley *et al.*, 1997) and thus serves as a tracer for small ET particles only. In contrast, Os in extraterrestrial particles is largely unaffected by atmospheric entry processes and thus records the entire extraterrestrial particle size spectrum (Peucker-Ehrenbrink and Ravizza, 2000). Despite these differences the ^{3}He-corrected Os isotope compositions calculated by Pegram and Turekian (1999) agree well with results from very mild chemical leaches, except near the K–T boundary (Fig. 4c).

Although Os is enriched in hydrogenous Fe–Mn nodules and crusts, their usefulness as proxies for the marine Os isotope record is limited by two factors. First, slow accumulation rates (mm Myr^{-1}) limit temporal resolution and increase the likelihood that diffusion distorts the record. Both effects tend to dampen potential high-frequency variations in the Os isotopic composition of seawater reconstructed from such phases. Henderson and Burton (1999) estimate diffusivities of Os in a well-studied crust (Alv539) from the North Atlantic at 2×10^{-8} cm yr^{-1} (not 2×10^{-5} cm yr^{-1} as stated in their paper). This diffusivity is about an order of magnitude higher than diffusivities of Th, Nd, Pb, and Be, but about 3–4 orders of magnitude smaller than diffusivities of Li and Sr. These data indicate that diffusion of Os may slightly alter the original record of past

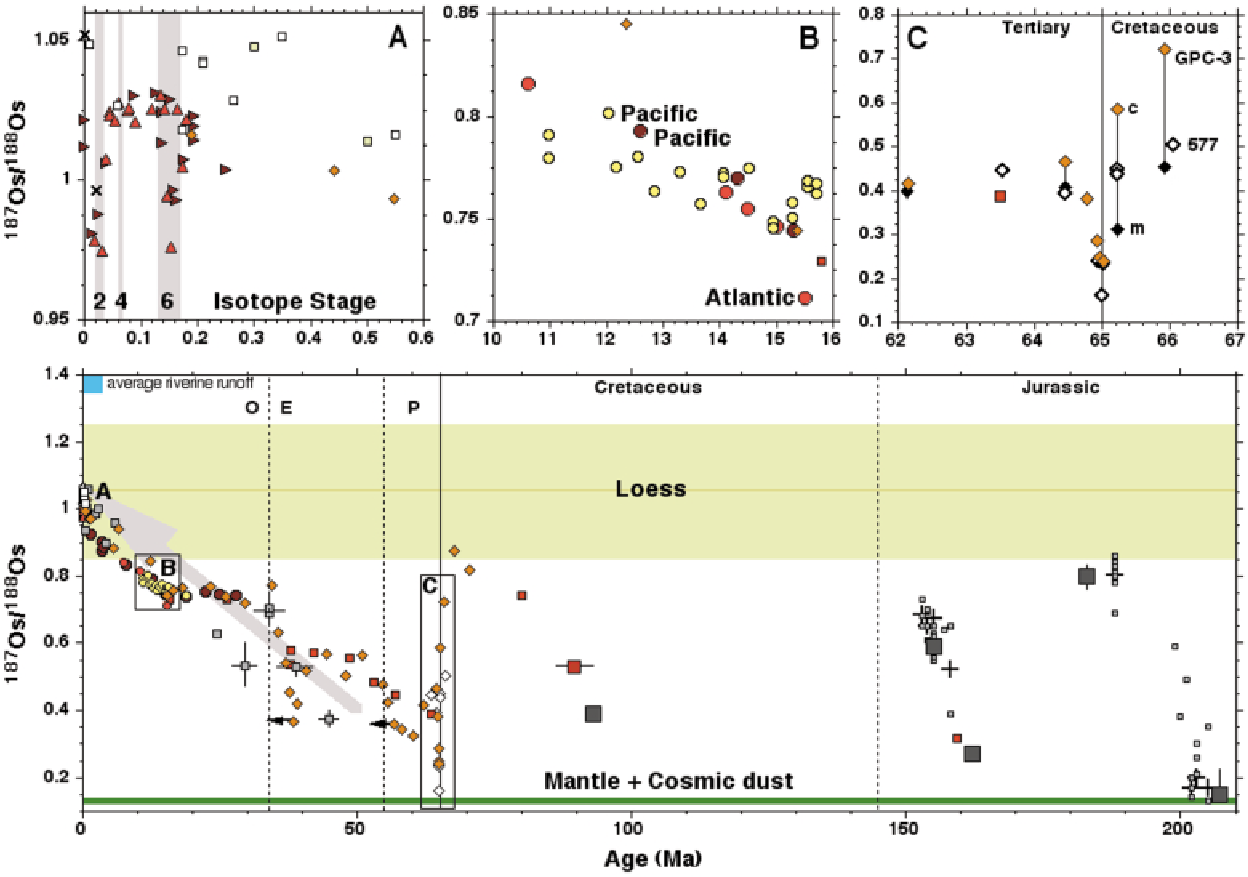

Fig. 4 The marine Os isotope record. Data for metalliferous pelagic clay are shown as orange diamonds (LL44 GPC-3, Pegram and Turekian, 1999; using a revised [K–T boundary at 65 Ma] chronology based on the constant hydrogenous Co accumulation model of Kyte *et al.*, 1993. The absolute chronology of this core, particularly between 25 Ma and 60 Ma, is poorly constrained. The arrows ponting left at the ^{187}Os/^{188}Os minimum in the late Eocene and the sharp rise in ^{187}Os/^{188}Os near the Palaeocene–Eocene boundary indicate by how much the age assigned to these events would shift if a chronology based on ichthyolith biostratigraphy for epic boundaries rather than constant hydrogenous Co accumulation were used). Metalliferous sediments from the Pacific (Peucker-Ehrenbrink *et al.*, 1995) are shown as small red squares, metalliferous carbonates from the Pacific (Leg 92, Ravizza, 1993) as dark brown circles, metalliferous carbonates from DSDP 597/8 (Reusch *et al.*, 1998) as yellow circles, metalliferous carbonates from the Atlantic (DSDP 521; Reusch *et al.*, 1998) as large red circles (see panel b), metalliferous carbonates from the Pacific (V19–54 brown triangles pointing right in panel a, and V19–55 red upright triangles; Oxburgh, 1998). Data from California basin core DSDP 480 are shown as black x's (panel a), Atlantic core 10400 (Peucker-Ehrenbrink and Ravizza, 2000 and unpubl. data) as open squares (see panel a), as well as initial ratios of organic-rich sediments from ODP 959 (Ravizza, 1998) as medium-sized grey squares plotted with uncertainties. K–T boundary sections from DSDP 577 carbonates are plotted as open diamonds (panel c), measured (filled black diamonds) and ^{3}He-corrected LL44-GPC3 metalliferous pelagic clays as orange diamonds (panel c). Margi umbers from Cyprus ($\sim$91 Ma, Ravizza *et al.*, 1999) are shown as large red square, initial ratios for Jurassic organic-rich mudstones from the U.K. (Cohen *et al.*, 1999) as large grey squares with 2σ uncertainties for the ^{187}Os/^{188}Os (age uncertainties based on biostratigraphic information), and initial ratios of individual organic-rich mudstones (Cohen *et al.*, 1999) as small grey squares, with averages for individual subzones plotted as crosses. Also shown are ^{187}Os/^{188}Os values for average riverine runoff (blue box near *y*-axis), average worldwide loess deposits as a proxy for the isotopic composition of average eroding continental crust (Peucker-Ehrenbrink and Jahn, 1999) as buff coloured band, indicating 1σ uncertainties, and high-and low-temperature hydrothermal alteration of mantle-derived rocks as green line. Panel a also shows glacial stages 2, 4, and 6 as grey bands. Some important stratigraphic boundaries are shown as solid and stippled lines. A typical ingrowth trajectory for average organic-rich sediments (Ravizza *et al.*, 1998, 1999) is shown as grey arrow. Ingrowth was calculated using a ^{187}Re/^{188}Os of 800, typical for organic-rich sediments, and an initial ^{187}Os/^{188}Os of 0.4 at 50 Ma.

variations in the Os isotopic composition of seawater. Secondly, sporadic occurrence of extraterrestrial particles with high Os concentration and unradiogenic isotope signature has been reported in Fe–Mn crusts (Finkelman, 1970; Jedwab, 1970). Peucker-Ehrenbrink *et al.* (1997) and Burton *et al.* (1999) provide evidence of mixing trends between hydrogenous and extraterrestrial Os in Fe–Mn crusts. This and difficulties in establishing a reliable chronology complicates interpretation of Os isotope records that are based on analyses of Fe–Mn nodules and crusts (e.g. Esser *et al.*, 1993).

Finally, Levasseur *et al.* (1999b) studied the use of corals as proxies for short-periodic variations in the isotopic composition of seawater. Corals are generally less radiogenic than present-day seawater, indicative of a complex mixture of hydrogenous and continental Os with additional unradiogenic Os. The surprisingly unradiogenic nature of corals resembles data from core-top carbonates (Oxburgh, 1996). This signature led Oxburgh (1996) to suggest that dissolution of extraterrestrial matter in seawater creates a less radiogenic surface layer compared to the deep ocean. Depth profiles in the Indian and the Pacific Oceans do not support this hypothesis (Levasseur *et al.*, 1998; Woodhouse *et al.*, 1999; see Fig. 1a). Corals and carbonate sediments do not appear to preserve a recognizable hydrogenous record and should not be used to reconstruct past variations in the Os isotopic composition of seawater.

The Cenozoic marine Os isotope record

The osmium isotopic composition of seawater has increased throughout the Cenozoic from a ^{187}Os/^{188}Os of ~0.2 at the K–T boundary to a ratio of ~1.06 at present (Pegram *et al.*, 1992; Ravizza, 1993; Peucker-Ehrenbrink *et al.*, 1995; Turekian and Pegram, 1997; Pegram and Turekian, 1999; see Fig. 4). At first glance this increase resembles the Cenozoic increase in the marine strontium isotope record. It is therefore tempting to interpret both records as proxies for increasing input of radiogenic continental material (average ^{187}Os/^{188}Os of upper continental crust ~1.2–1.3, Esser and Turekian, 1993b; average ^{187}Os/^{188}Os of worldwide loess 1.05 ± 0.2, Peucker-Ehrenbrink and Jahn, 1999; average ^{187}Os/^{188}Os of world-wide run-off ~1.5, Levasseur *et al.*, 1999b) caused by changes in the continental weathering intensity. However, the sources of osmium differ markedly from those dominating the marine strontium isotope system. Three properties unique to the marine Os isotope system are discussed in more detail below.

1 Impact events

The most prominent excursion to unradiogenic marine Os isotope values coincides with the K–T boundary (core DSDP 596, Peucker-Ehrenbrink *et al.*, 1995; core LL44-GPC3, Turekian and Pegram, 1997). Impact of a carbonaceous chondrite (Shukolyukov and Lugmair, 1998) delivered ~1×10^9 mole extraterrestrial Os [inferred from the globally integrated Ir-fluence of 40 ng cm^{-2} at the K–T boundary, Hildebrand, 1992 (this should be considered a lower estimate, as Kyte *et al.*, 1996; estimate the Ir-fluence over most of the Pacific plate at 90 ng cm^{-2})]. This is equivalent to ~600 000 yr of present-day riverine input of Os to the oceans, or ~15 times the Os inventory of the modern ocean. Dissolution of < 25% meteoritic Os in seawater would have been sufficient to decrease the ^{187}Os/^{188}Os of seawater at the K–T boundary from a pre-K–T value of ~0.45 to ~0.2. A drop in ^{187}Os/^{188}Os from 0.46 in the upper Maastrichtian to a value of 0.15 in the K–T boundary clay was reported by Geissbühler (1990). Slightly more radiogenic values were inferred for seawater at (^{187}Os/^{188}Os ~0.2) and shortly before (^{187}Os/^{188}Os ~0.5) the K–T boundary from DSDP Site 596 sediments by Peucker-Ehrenbrink *et al.* (1995). This illustrates that large impacts are capable of 'resetting' the marine Os isotope record to unradiogenic values characteristic of extraterrestrial matter (average meteoritic ^{187}Os/^{188}Os ~0.13, e.g. Meisel *et al.*, 1996). Osmium isotope data for K–T boundary in cores DSDP 577 and LL44-GPC3, shown in Fig. 4(c), indicate that the marine Os isotope system recovered quickly (within a few 100 kyr at most) from ^{187}Os/^{188}Os of > 0.16 at the K–T boundary to ^{187}Os/^{188}Os values of ~0.4 in the early Danian. Such a quick recovery is consistent with a short residence time of Os, estimated at < 12 000 kyr to ~60 000 kyr for the modern ocean (Richter and Turekian, 1993; Peucker-Ehrenbrink and Ravizza, 1996; Sharma and Wasserburg, 1997; Levasseur *et al.*, 1998; Oxburgh, 1998; Burton *et al.*, 1999; Levasseur *et al.*, 1999a). The ^{187}Os/^{188}Os of late Cretaceous seawater immediately before the K–T impact is difficult to determine in cores with a K–T boundary PGE anomaly, because diffusion and physical mixing of unradiogenic, impact-derived Os can distort the record. Data from DSDP 577 are suggestive of ^{187}Os/^{188}Os ~0.45. In contrast, ^{3}He-corrected values from LL44-GPC3 suggest more radiogenic values, but ^{3}He-corrections close to the K-T boundaries are afflicted with particularly large uncertainties (see Fig. 4c for details).

The marine Os isotope record reconstructed from LL44-GPC3 shows another sharp excursion toward unradiogenic ^{187}Os/^{188}Os values of ~0.36 around 32–33 Ma (Turekian and Pegram, 1997; Pegram and Turekian, 1999), possibly indicative of another impact event (Fig. 4). Analyses of the abundance of oxidized Ni-rich spinel–indicators of the presence of extraterrestrial material–at 10 cm depth intervals demonstrate that the excursion at ~12 m depth is bracketed by major peaks in the abundance of Ni-rich spinel at 11.2 and 12.4 m (Robin *et al.*, 1999). While Robin *et al.* (1999) correlate the anomaly at 12.4 m with the late Eocene impact events around 35.6 Ma (Chesapeake Bay: 35.5 Ma, Popigai: 35.7 Ma; see Whitehead *et al.*, 2000), the major peak in Ni-rich spinel abundance at 11.2 m (~30 Ma) does not coincide with any known impact event and could be of local significance only. It is possible that the excursion toward unradiogenic ^{187}Os/^{188}Os at ~12 m depth had an extraterrestrial cause. Alternatively, the excursion to unradiogenic Os could be an artifact of the leaching process. Turekian and Pegram (1997) note that the excursion toward less radiogenic Os isotope composition coincides with high Th/Cr values of up to 0.7, characteristic of acidic volcanic ash. They interpret this signature as reflecting enhanced input from volcanism and ophiolite weathering at the suture between India and Eurasia formed at the site of the former Tethys. As this unradiogenic excursion so far has been documented only in core LL44-GPC3, analytical artifacts caused by preferential leaching of unradiogenic volcanic components cannot be excluded as an explanation for the observed feature. Documenting this excursion in additional cores with well-constrained chronologies is essential to discerning between these differing interpretations.

2 Organic matter

Although only a minor fraction (~5%) of the crustal Os is closely associated with organic matter, this fraction contributes disproportionately to the mobile Os inventory of the crust (Ravizza *et al.*, 1998). For instance, Peucker-Ehrenbrink and Hannigan (2000) show that weathered black shales have lost

45–90% of their initial Os budget. Simple mass balance considerations demonstrate that release of Os as a result of weathering of one volume unit black shale is equivalent to mobilization of Os from ~1000 volume units of typical granitoid upper crustal rocks (Peucker-Ehrenbrink and Blum, 1998). The Re/Os of organic-rich sediments is sufficiently large that weathering of organic-rich sediments at a constant rate can lead to a steady increase in the osmium isotopic composition of sea water with time (Ravizza *et al.*, 1998). The grey arrow in Fig. 4 shows an ingrowth trajectory for average organic-rich sediments (^{187}Re/^{188}Os ~800). Such facies develop ^{187}Os/^{188}Os identical to present-day seawater within 50 Myr from an initial ^{187}Os/^{188}Os of 0.4. In such a scenario trends towards more radiogenic Os isotope seawater values (e.g. the steady increase from a ^{187}Os/^{188}Os of ~0.7 at 16 Ma to a ^{187}Os/^{188}Os of ~0.95 at 2 Ma) are unrelated to increases in continental weathering intensity. We emphasized that weathering of Ca–Mg silicates and net oxidation of sedimentary organic matter have opposing effects on the atmospheric CO_2 budget. Whereas weathering of Ca–Mg silicates and release of Ca^{2+} and Mg^{2+} consumes atmospheric CO_2 through deposition of Ca–Mg carbonates in the ocean, net oxidation of organic matter consumes atmospheric O_2 and releases CO_2. In the above scenario towards more radiogenic ^{187}Os/^{188}Os values are therefore linked to constant release of CO_2, the opposite effect of what the classic interpretation of the marine Sr isotope record predicts. Ravizza and Esser (1993) suggested that the negative correlation between the marine ^{187}Os/^{188}Os and δ^{13}C during the Neogene support the notion that accelerated oxidation of organic matter on the continents led to the observed increase in the marine ^{187}Os/^{188}Os and decrease in the marine δ^{13}C records. Recently, Ravizza *et al.* (1998) suggested testing this hypothesis by reconstructing the marine ^{186}Os/^{188}Os record. ^{186}Os is produced by α-decay of ^{190}Pt with a half-life of ~469 Gyr (Begemann *et al.*, 2001). The rationale behind this suggestion is based on the observed fractionation of Re–Os–Pt in the surficial environment, shown in Fig. 4 (see also Table 1). While most organic-rich sediments are characterized by ^{190}Pt/^{188}Os significantly lower (~0.004) than average eroding continental crust (~0.013), metalliferous sediments and umbers (~0.06) and Fe–Mn nodules (~0.35), their ^{187}Re/^{188}Os is one to two orders of magnitude higher than that of average crustal material or metalliferous sediments. If weathering of organic-rich sediments has been the driving force towards more radiogenic marine ^{187}Os/^{188}Os in the Neogene, the marine ^{186}Os/^{188}Os is expected to be decoupled from the ^{187}Os/^{188}Os record. The few preliminary data for Fe–Mn nodules is suggestive of chondritic ^{186}Os/^{188}Os values (Walker *et al.*, 1999), whereas values for recent marine sediments seem to be biased towards supra-chondritic values. If the more precise values for Fe–Mn nodule are representative for present-day seawater, weathering of average continental crust–characterized by an order of magnitude higher ^{190}Os/^{188}Os relative to chondrite–cannot be the main source of Os in seawater. However, the analytical uncertainties associated with these preliminary measurements are large and do not preclude a supra-chondritic composition of present-day seawater. The combined study of ^{186}Os/^{188}Os –^{187}Os/^{188}Os variations has great potential as source indicators of Os in the surficial environment, because the dynamic range is at least an order of magnitude larger than in high-temperature systems. Consequently, the low-temperature ^{186}Os/^{188}Os isotope system may be studied by somewhat less precise, but less laborious multicollector ICP-MS analysis rather than by conventional N-TIMS analysis (e.g. Walker *et al.*, 1997). Results from such studies may also have important implications for modelling isotope signatures in mantle-derived melts. Supra-chondritic ^{186}Os/^{188}Os observed in a variety of plume-related basalts have been inferred as resulting from core–mantle interaction (e.g. Walker *et al.*, 1997; Brandon *et al.*, 1998). It should be noted that Fe–Mn nodules, characterized by high Os concentrations, rapidly develop radiogenic ^{186}Os/^{188}Os due to their high ^{190}Pt/^{188}Os of ~0.35 (Koide *et al.*, 1991; see Fig. 5). Such a Fe–Mn nodule, isolated in the mantle for 2 billion years, will develop a ^{186}Os/^{188}Os anomaly relative to the chondritic reservoir of ~1%, without developing radiogenic ^{187}Os/^{188}Os. This indicates that reconstructing marine ^{186}Os/^{188}Os variations from samples with high Pt/Os is problematic because of the necessary ingrowth corrections.

3 Short-periodic variations

The marine residence time of osmium is short enough to capture short-periodic (glacial–interglacial) fluctuations that are inaccessible to the buffered marine strontium isotope system. This offers the opportunity to discriminate between high-frequency (climatic) and low-frequency (tectonic) forcing. It also increases the likelihood of the system reaching steady state. Oxburgh (1998) reconstructed glacial–interglacial variations in the isotopic composition of seawater for the past 250 kyr, documenting for the first time climatic forcing of the marine Os isotope record (Fig. 4a). In general, seawater values fluctuate from less radiogenic ^{187}Os/^{188}Os values of ~0.97 in times of enhanced atmospheric dust input during glacial periods to more radiogenic ^{187}Os/^{188}Os values of ~1.03 during interglacial periods (Fig. 4a). We complement this dataset with new analysis from DSDP 480 for the past glacial and the current interglacial period. While the new data confirm the existence of glacial–interglacial differences in the Os isotope composition of seawater, the absolute values are more radiogenic than those reported by Oxburgh (1998). Most likely this is caused by differences in sedimentation rates and bioturbation depth between both cores. Lower sediment mass accumulation rates and deeper depth of bioturbation tend to dampen the amplitude of high-frequency variations reconstructed from marine sediments. The cause for such glacial-interglacial fluctuations is still a matter of debate. Oxburgh (1998) favours reduced riverine flux during periods of enhanced dust flux (aridity) as the main cause for less radiogenic seawater during glacial periods. Peucker-Ehrenbrink and Blum (1998) argue that preferential release of radiogenic Os in the early stages of weathering following deglaciation leads to an ‘extra delivery’ of radiogenic Os to seawater, speeding up recovery to more radiogenic Os isotope values. Rapid recovery from less radiogenic glacial to more radiogenic interglacial seawater isotopic compositions has been used by Oxburgh (1998) to place constraints on the marine resi-

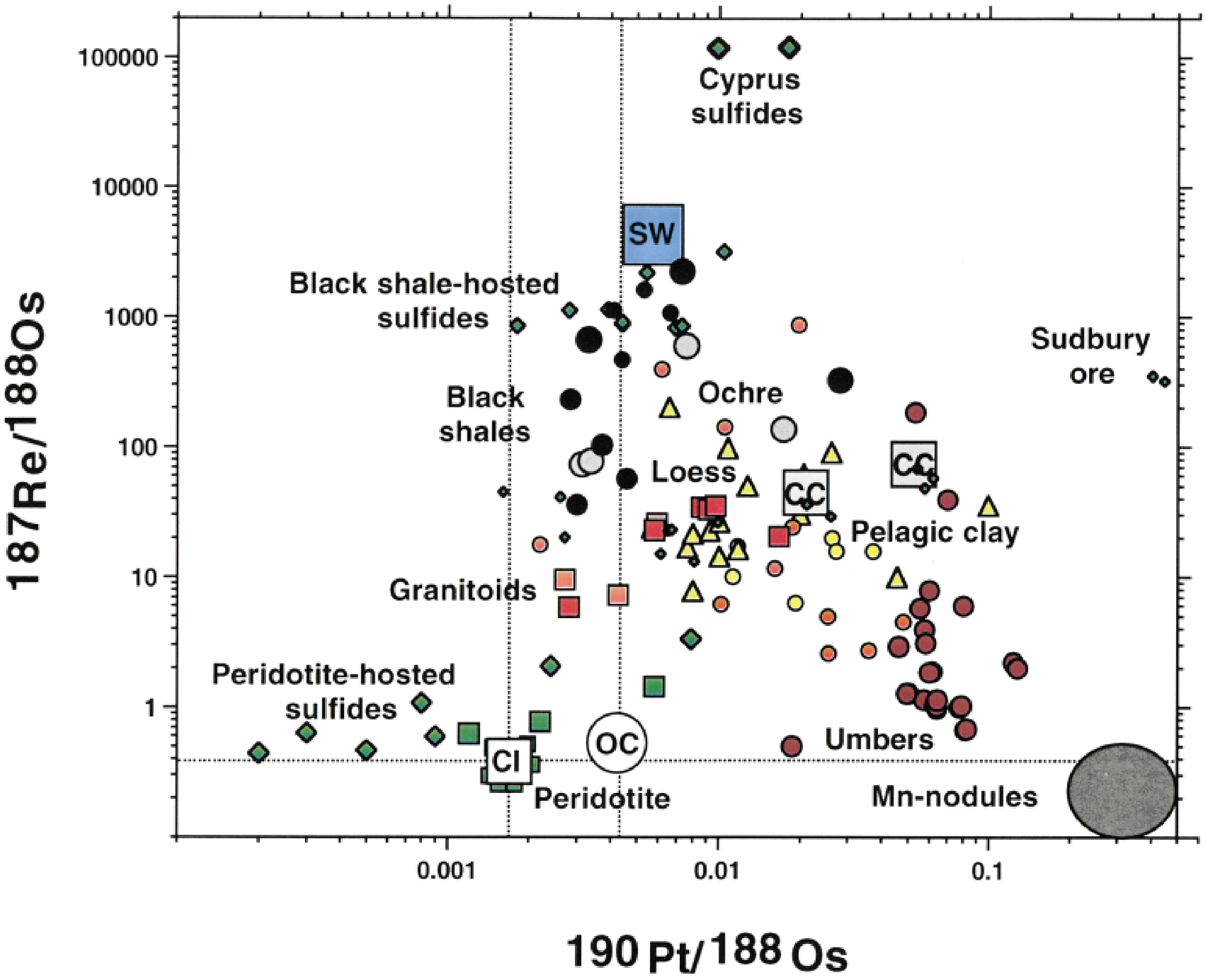

Fig. 5 ^{187}Re/^{188}Os–^{190}Pt/^{188}Os data. SW, present-day seawater (Anbar *et al*., 1992; Colodner *et al*., 1993a,b; Levasseur *et al*., 1998; Woodhouse *et al*., 1999). CI, present-day chondritic reservoir (Walker *et al*., 1997; Brandon *et al*., 1998). OC, estimate for the present-day composition of the outer core (Walker *et al*., 1997; Brandon *et al*., 1998. Note that this estimate is strongly model-dependent). Mn-nodules, the large grey circle approximates the composition of Mn-nodules, because to our knowledge Re–Os–Pt concentrations have not been reported for the same Mn nodule (Os data from Burton *et al*., 1999; Re and Pt data from Koide *et al*., 1986). CC: upper continental crust (grey squares) of Schmidt *et al*. (1998) (higher ^{187}Re/^{188}Os and ^{190}Os/^{188}Os) and Peucker-Ehrenbrink and Jahn (1999) (lower ^{187}Re/^{188}Os and ^{190}Os/^{188}Os). Loess: worldwide loess deposits (upright buff-coloured triangles, Peucker-Ehrenbrink and Jahn, 1999). Granitoids: Precambrian granitoids (red squares) and related soils (orange squares) from the western Wind River Range, Wyoming (Peucker-Ehrenbrink and Blum, 1998; unpublished data). Black shales: unweathered (black circles) and weathered (grey circles) black shales and organic-rich sediments (Horan *et al*., 1994; Ravizza and Pyle, 1997; Peucker-Ehrenbrink and Hannigan, 2000). Black-shale-hosted sulphides (intermediate-sized green diamonds at high ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os, Horan *et al*., 1994). Peridotite-hosted sulphides (large green diamonds at low ^{187}Re/^{188}Os; Hulbert and Grégoire, 1993) and sulphides from Cyprus (large green diamonds at very high ^{187}Re/^{188}Os, Ravizza *et al*., 1999). Sudbury ore: ores with variable ^{187}Re/^{188}Os (13–352) and ^{190}Pt/^{188}Os (0.0016–234, values > 0.5 not shown) (small dark green diamonds, Walker *et al*., 1991); Peridotite: abyssal peridotites (small green squares near CI composition, Brandon *et al*. 2000) and Archean ultramafic rocks (large green squares, Hulbert and Grégoire, 1993). Ochres: Cyprus ochres and other metalliferous sediments (orange circles, Ravizza and Pyle, 1997; Ravizza *et al*., 1999; unpubl. data). Umbers: late Mesozoic umbers from Cyprus (brown circles, Ravizza *et al*., 1999; unpubl. data). Pelagic clay: clays from DSDP 386 (yellow circles, unpubl. data).

dence time of Os. Assuming a constant residence time the data is consistent with the shortest residence time inferred for Os so far: $< 12\,000$ yr. It should be noted, however, that the assumption of a constant residence time may be violated if the areal extent of anoxic marine sediments underwent significant fluctuations on glacial–interglacial timescales (e.g. Rosenthal *et al*., 1995; Morford and Emerson, 1999). Such sediments are important sinks for Os in seawater (Ravizza and Turekian, 1992) and temporal changes may affect the marine Os budget.

It is worth noting that short periodic fluctuations in the marine Os isotopic composition may not be unique to the late Pleistocene. Reusch *et al.* (1998) have reconstructed oscillations in the marine Os isotope record during the middle Miocene with $^{187}Os/^{188}Os$ amplitudes of 0.01–0.02 and over time intervals of $= 1$ Myr (Fig. 4b). These oscillations appear to be negatively correlated with the bulk carbonate $\delta^{13}C$ and the benthic foraminiferal $\delta^{18}O$ records. While the data provide evidence for Os isotopic homogeneity between the Atlantic (large red circles in Fig. 4b) and the Pacific (small yellow circles in Fig. 4b) during the middle Miocene, additional analyses are needed to confirm the global nature of the observed oscillations. It should also be noted that the temporal sampling density (~ 1 Myr^{-1}) for most of the marine Os isotope record is up to two orders of magnitude lower than the theoretical sampling density (~ 0.01 Myr^{-1}) necessary to capture potential variability in the Os isotope system that is caused by its short residence time. This is in contrast to the marine Sr isotope record for which the actual temporal sampling density is sufficiently high that missing high-frequency oscillation in the marine Sr isotope record is extremely unlikely. Thus far Os data from the two periods that have been sampled at higher resolution (i.e. middle Neogene, late Quaternary) imply that the amplitude of short-periodic fluctuations most likely will not exceed a few percent. We therefore suspect that the main features of the Cenozoic marine Os isotope record have been properly reconstructed, however, brief large amplitude excursions cannot be precluded given the available data.

The Mesozoic marine Os isotope record

It is of particular interest to investigate the correlation of the marine Os and Sr isotope records further back in time to test if periods of radiogenic marine $^{87}Sr/^{86}Sr$ coincide with periods of radiogenic $^{187}Os/^{188}Os$. Such a correlation is to be expected if both isotope systems are useful proxies for the intensity of continental weathering, orogenesis, and global climate. Reconstructing the Mesozoic marine Os isotope record is currently at its infancy (Cohen and Coe, 1999; Cohen *et al.*, 1999; Ravizza *et al.*, 1999). Existing data are shown in Fig. 4 and indicate $^{187}Os/^{188}Os$ fluctuations from unradiogenic values of ~ 0.2 during the Hettangian (~ 206 Ma) to radiogenic values of ~ 0.8 during the Toarcian (~ 183 Ma). Cohen and Coe (1999) also report a rapid drop in the isotopic composition of seawater following an anoxic event in the Toarcian. As noted above, the residence time of Os in seawater may be sensitive to the areal extent of anoxic sediments, allowing rapid fluctuations in the isotopic composition of sea water during and shortly after prominent anoxic events, potentially accompanied by regional contrasts in the Os isotopic composition between ocean basins. The Mesozoic and pre-Mesozoic marine Os isotope record can be reconstructed using carefully selected metalliferous sediments (e.g. Ravizza *et al.*, 1999) and high-precision Re–Os isochron data for organic-rich sediments (e.g. Cohen *et al.*, 1999). Ravizza *et al.* (1999) have taken the first step in establishing geochemical criteria for the integrity of obducted metalliferous sediments as recorders of past variation in the marine Os isotopic composition. An improved understanding of the geochemistry of metalliferous sediments, their diagenesis and susceptibility to weathering (Re mobility) would significantly enhance our ability to extend the marine Os isotope record back into the geological past.

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