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Behavior of osmium at the freshwater–saltwater interface based on Ganga derived sediments from the estuarine zone

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[1] Leaching experiments performed on several sediments of the Ganga river suggest that between 10 and 20% of the osmium is in an easily exchangeable position. Analyses of sediments from two estuarine rivers (the Pussur and the lower Meghna) reveal no enrichment of Os in the saltwater–freshwater mixing zone relative to Ganga sediments of similar $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, suggesting that osmium is not significantly trapped in this estuary. However, a significant decrease of the $^{187}\text{Os}/^{188}\text{Os}$ ratio is observed in the Pussur sediments relative to the Ganga composition. These latter are derived entirely from the Ganga or from erosion of the Ganga paleodelta, and thus would be expected to have similar Os isotopic compositions. Nd isotopic results from the Pussur are indistinguishable from those of the Ganga, while the Sr isotopic results are at the lower end of the Ganga range, confirming the absence of a major source difference between Ganga and Pussur sediments. It thus seems unlikely that the difference in Os isotopic signature can be entirely explained by a change in provenance, suggesting instead that the Os compositions have been modified. Our results show that the less radiogenic Os compositions of the Pussur sediments cannot result simply from desorption of radiogenic Os or from scavenging of river or seawater Os. Instead, the decrease of the $^{187}\text{Os}/^{188}\text{Os}$ ratio could imply a complex exchange between dissolved Os, derived partly from seawater, and Os in the leachable fraction of sediments. This mechanism could therefore constitute both a source and a sink for seawater osmium and may significantly influence the osmium marine budget.

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1. Introduction

[2] Chemical behavior in the freshwater–saltwater transition zone in estuaries may significantly influ-

ence the net effective contribution of trace metals carried by rivers to the ocean. Numerous studies have investigated this subject for various elements and have highlighted two different types of behav-

ior. Some elements (i.e., Ni, Cl [Karbassi *et al.*, 2008] and in most cases, Re [Anbar *et al.*, 1992; Singh *et al.*, 2011]) behave conservatively, thus no loss or gain is recorded relative to the concentrations expected from the salinity gradient. However, other elements behave nonconservatively (i.e., Mo, Zn, Cd, Pb and Cu [Karbassi *et al.*, 2008]) and addition or removal from the water column is observed during the mixture of river and seawater. This behavior is linked to possible changes of speciation and to the affinity of the trace metal for suspended or sedimented organic and inorganic particulate matter [Boyle *et al.*, 1977]. As a result, some elements may display behaviors that vary as a function of the specific environmental conditions [i.e., Carpenter and Smith, 1985; Boyle *et al.*, 1982] encountered in different estuaries.

[3] For osmium, the conclusions of previous studies of estuarine behavior are somewhat contradictory and remain subject to debate. Preliminary results obtained from acidic hydrogen peroxide leaching of sediments of diverse rivers [Pegram *et al.*, 1994] were interpreted to suggest a possible release of Os from sediments into the water column in the saltwater–freshwater transition zone. Nevertheless, these results indicate only that a fraction of Os in the river sediments is potentially mobilizable. Furthermore, these data were obtained essentially from river sediments without any influence from seawater. More recent, direct analyses of dissolved Os in estuarine waters provide contrasting information. Levasseur *et al.* [2000], in their study of the Lena estuary (Siberia), found that about 30% of the dissolved Os carried by rivers could be trapped, probably by adsorption on suspended particles, during the first stage of river water and seawater mixing. Based on their results from waters of the Fly River estuary of New Guinea, Martin *et al.* [2001] suggest that substantial amounts of seawater Os may also be trapped in the estuarine zone. This suggestion is supported by the results of Sharma *et al.* [2007] from the Godavari river estuary of India, which imply that Os may be removed onto particles in high salinity waters. Nevertheless these latter authors emphasize the complexity and the nonconservative nature of Os behavior inferred from their data, which indicate that both losses and gains of Os can occur in estuarine waters. It should also be noted that these studies were performed mainly on estuarine surface waters, which may bias the conclusions since estuaries have stratified waters.

[4] In order to reconcile results from solid phases with the dissolved phase data and to better under-

stand the behavior of osmium in the saltwater–freshwater transition, we have analyzed sediments from estuaries of the Bengal basin.

[5] For several reasons, the Ganga-Brahmaputra-Meghna (GBM) estuarine system is a particularly interesting region for investigating Os behavior at the river–seawater interface. First, it is now well-established that the Os isotopic composition of seawater has become markedly more radiogenic over the Cenozoic Era [Pegram *et al.*, 1992; Peucker-Ehrenbrink *et al.*, 1995], and some authors have attributed this increase to an enhanced continental contribution linked to Himalayan uplift and erosion [e.g., Pegram *et al.*, 1992]. However, it has been demonstrated that dissolved Os in Ganga river water, though unusually radiogenic relative to that of most rivers, is present in low concentrations and so has only a small influence on the marine Os budget [Levasseur *et al.*, 1999a]. It has also been shown that the flux of radiogenic Os carried by groundwater from the Bengal Basin is unlikely to have a substantial impact on seawater Os [Paul *et al.*, 2010]. On the other hand, the possible contribution of radiogenic Os from sediments derived from Himalayan erosion [Pierson-Wickmann *et al.*, 2000; Chakrapani *et al.*, 2002] and carried by the Ganga river has not yet been quantified. If this radiogenic Os can be preferentially removed, the Ganga could provide an important source of ^{187}Os , given the exceptionally large sedimentary discharge of this river (400–500 Mt/yr). Another motivation for studying Os behavior in the GBM estuary is provided by the strong isotopic contrast observed between Ganges sediments and waters ($^{187}\text{Os}/^{188}\text{Os}$ close to 2.5 [Pierson-Wickmann *et al.*, 2000; Paul, 2008; Levasseur *et al.*, 1999a]) and the seawater composition ($^{187}\text{Os}/^{188}\text{Os} \sim 1.06$ [Levasseur *et al.*, 1998]). This contrast could facilitate the tracing of the possibly complex mixture of Os derived from these end-members. In other contexts the osmium isotopic compositions of rivers are generally much closer to that of average upper continental crust ($^{187}\text{Os}/^{188}\text{Os} \sim 1.40$ [Peucker-Ehrenbrink and Jahn, 2001]) and are thus similar to the seawater isotopic composition, which impedes reliable isotopic tracing.

[6] To evaluate the behavior of Os from Himalayan sediments at the freshwater–saltwater mixing zone, we examined the Os isotopic composition of sediments from two estuarine rivers of the Ganga-Brahmaputra basin. Considering the large volume of Himalayan sediments and their radiogenic signatures [Pierson-Wickmann *et al.*, 2000, 2002a], this process could be an important factor in the

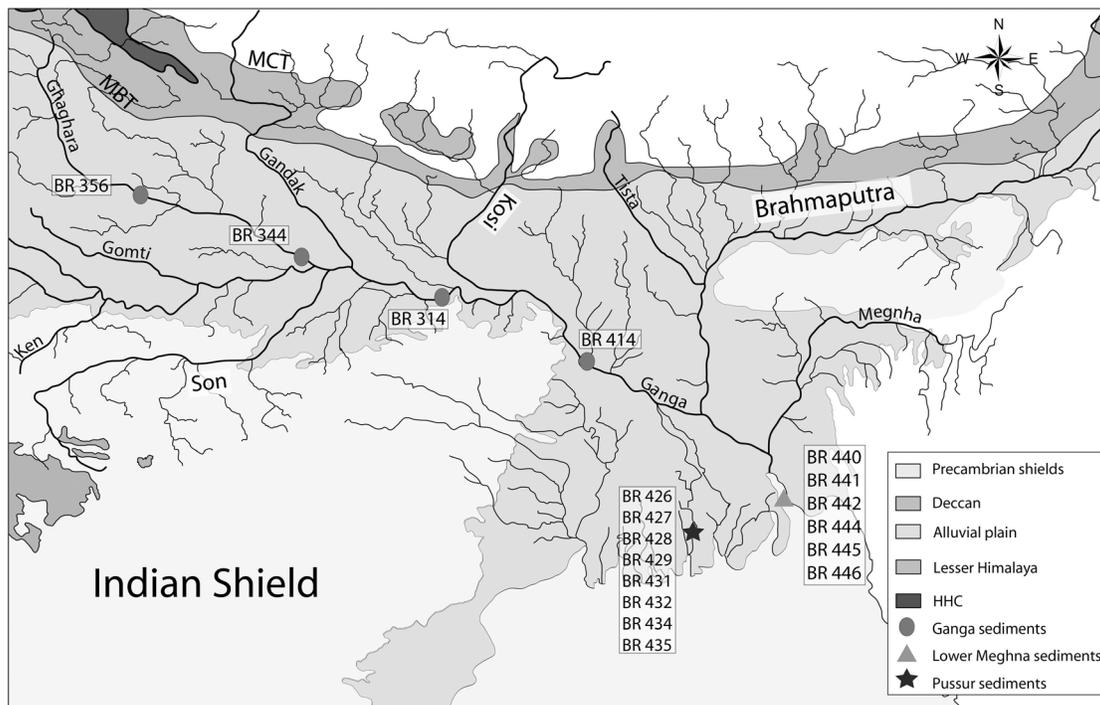


Figure 1. Map showing the different locations of analyzed sediment samples and the schematic geological context of the Himalaya and the Ganga floodplain.

osmium marine budget in the case of hypothesized osmium desorption. In order to quantify the amount of Os that could potentially be released from detrital matter on entry into the ocean, we also analyzed the leachable fraction of several Ganga sediments.

2. Study Area and Sampling

[7] The GBM estuary is the largest delta complex in the world, covering about 140 000 km² [Uddin and Lundberg, 1998]. This river system, fed by the physical erosion of the Himalaya (the world's largest orogenic system), annually carries almost 1000 tons of sediment to the ocean [Hay, 1998; Islam et al., 1999]. The delta is composed of numerous small distributaries, spread over the entire width of Bangladesh (Figure 1).

[8] For this study two estuarine rivers of the Bengal Delta were sampled, the Pussur and the Lower Meghna (Figure 1). The Pussur is located toward the eastern side of the great mangrove forest and represents a major distributary of the Ganga to the sea. This river is exclusively supplied by the Ganga [Goodbred and Kuehl, 2000]. The lower Meghna corresponds to the main discharge area of the GBM river system. Therefore the sediments and waters

of the lower Meghna represent a mixture of products carried by the Ganga, Brahmaputra and the Meghna rivers.

[9] Though the Pussur and the Lower Meghna rivers are both located in estuarine environments, the influence of seawater on these two rivers is different. Indeed, the dissolved load of the Pussur river has a chloride concentration of between 10 and 30 $\mu\text{mol/L}$, defining the Pussur water as brackish. On the other hand the water of the Lower Meghna river displays a lower chloride concentration (0.032 $\mu\text{mol/L}$) indicating an extremely limited influence of seawater. Sediments from both rivers were sampled in June, during the monsoon period. The six lower Meghna samples represent a profile of suspended sediments obtained at different water depths plus the bed load, while the eight Pussur samples include suspended load, bed load, and one bank sediment.

[10] Leaching experiments were performed on four bed load sediments of the Ganga river, sampled at different locations along its course (Figure 1). Sampling was performed in July 2004, before the monsoon, for the Ganga sediments except for sample BR421, which was collected during the monsoon period in June 2005. Sediments from the Pussur and Lower Meghna and Ganga sediment

Table 1. Os, Sr and Nd Isotopic Compositions and Os, Re Contents of Suspended Matter and Bed Loads From the Pussur and Lower Meghna Rivers

Sample	Location	Type	Depth (m)	Al ₂ O ₃ /SiO ₂	¹⁸⁷ Os/ ¹⁸⁸ Os	[Os] ppt	[Re] ppt	¹⁸⁷ Re/ ¹⁸⁸ Os	[Os] _{nonradio} ppt	εNd ^a	⁸⁷ Sr/ ⁸⁶ Sr ^a
<i>Lower Meghna</i>											
BR 441	Bhola	S. L.	0	0.33	1.37	57.3	215	21.0	49.2	-15.80 (±0.50)	0.74130
BR 444	Bhola	S. L.	2	0.29	0.97	59.1	257	23.3	53.1	n.a.	n.a.
BR 442	Bhola	S. L.	4	0.28	1.15	41	260	34.6	36.1	n.a.	n.a.
BR 440	Bhola	S. L.	6	0.22	1.32	28.9	123	23.7	25	-15.94	0.73762
BR 445	Bhola	S. L.	10	0.22	1.37	29.3	319	61.1	25.1	n.a.	n.a.
BR 446	Bhola	B. L.		0.13	0.82	10.6	33	16.5	9.7	-13.69 (±0.50)	0.72412
<i>Pussur</i>											
BR 427	B. L.			0.24	2.02	27.2	103	22.8	21.8	-17.8 (±0.50)	0.761630
BR 429	Silty			0.23	1.81	30.9	119	22.5	25.3	-18.2 (±0.50)	0.764697
BR 435	B. L.			0.19	1.76	24.3	99	23.8	20	-17.9 (±0.50)	0.763028
BR 434	B. L.			0.27	1.82	29.7			24.2	n.a.	0.761582
BR 426	B. L.			0.22	1.86	27.4	126	27.3	22.2	-18.3 (±0.50)	0.763215
BR 428	S. L.			0.29	0.96	61.1	127	11.1	54.9	-18.02 (±0.50)	0.76331
BR 431	S. L.	14		0.32	1.54	45			37.9	-17.40 (±0.50)	0.767715
BR 432	S. L.	5		0.29	1.78	37.3	124	19.5	30.6	-17.81 (±0.50)	0.76761

^aSr and Nd isotopic compositions obtained from detrital fractions after removal of the carbonate and organic fractions.

BR421 were sampled during the same field season. Both bulk and leachate Os data were collected from these samples.

3. Methods

[11] Sediments were crushed in an agate mortar prior to major element analysis (Al₂O₃/SiO₂ ratios, Table 1). Samples were digested by fusion with LiBO₂ and then analyzed by ICP-OES (Thermo Elemental IRIS radial) at the Service d'Analyse des Roches et des Minéraux (SARM) of CRPG (Vandoeuvre-lès-Nancy, France).

[12] In order to estimate the amount of exchangeable osmium, leaching experiments were performed on the four Ganga sediments. A large amount of sediment was used (~10 g) in order to reduce the relative analytical blank contribution. The leaching solution was similar in composition to that described by Pegrum *et al.* [1994]: Milli-Q water (120 mL), H₂O₂ 30% (30 mL) and H₂SO₄ 36 N (3mL). Fifty mL of this solution were placed in a pre-washed Teflon bottle with the sediments at room temperature until the end of the reaction (generally, after 48h). Solution and sediment were then separated by centrifugation. The separated solution was then spiked prior to Os extraction. Os was extracted using liquid bromine following the method of Levasseur *et al.* [1998]. However, because the leaching solution still remained oxidic and acidic after reaction with sediments, the use of Cr^{VI} as an oxidizing agent

proved to be unnecessary and was thus removed from the procedure.

[13] In addition to the standard leaching procedure described above, a preliminary experiment aimed at extracting the carbonate fraction was performed on the sample BR344. About 3.5 g of sediment were leached in HCl (2N). The supernatant, containing the dissolved carbonate phase, was separated by centrifugation and spiked. Os was extracted using the liquid bromine technique after adding a quantity of Cr^{VI} sufficient to oxidize both spike and sample.

[14] Re and Os bulk analyses were also performed for the four Ganga samples as well as for the Pussur and lower Meghna sediments. One to two grams of sediment were powdered in an agate mortar and digested with concentrated HCl:HNO₃ (1:2) using the Carius tube method [Shirey and Walker, 1995]. ¹⁸⁵Re and ¹⁹⁰Os spikes and 9 ml of the acidic solution (3 ml HCl: 6 ml HNO₃) were placed with the samples (~1g of powder) in frozen Carius tubes. After sealing, the tubes were placed in an oven at 230°C for at least 48 h. Os was then extracted into liquid bromine following a method adapted from that described by Birck *et al.* [1997]. After extraction the Os was purified by micro-distillation [Roy Barman, 1993]. Re was separated using columns of AG1X8 resin from the aqueous residues remaining after Os extraction.

[15] Os isotopic measurements were performed at the CRPG by Negative Thermal Ionization Mass Spectrometry (NTIMS) [Creaser *et al.*, 1991;

[15] Volkening *et al.*, 1991] on a Finigann MAT262 instrument. For the Os analysis, the purified sample was loaded on a platinum filament previously outgassed in air. A small quantity of activator was added ($\text{Ba}(\text{OH})_2$ with minor NaOH) after complete evaporation of the sample following the method described by Birck *et al.* [1997]. All measurements (leaching and tidal sediments) were performed on an ETP electron multiplier by the peak jumping method. Instrumental mass fractionation was corrected by normalizing to a mass240/mass236 ratio of 3.092276 (corresponding to $^{192}\text{Os}/^{188}\text{Os} = 3.08271$) using an exponential law. Mass interferences caused by heavy oxygen isotopes were corrected assuming $^{18}\text{O}/^{16}\text{O} = 0.002045$ and $^{17}\text{O}/^{16}\text{O} = 0.0003708$ [Nier, 1950]. Possible mass interference caused by $^{187}\text{Re}^{16}\text{O}_3$ on the mass 235 ($^{187}\text{Os}^{16}\text{O}_3$), monitored by measuring mass 233 ($^{185}\text{Re}^{16}\text{O}_3$) throughout the analysis, were nearly always insignificant. In the rare cases where a problem was observed ($^{185}\text{Re}^{16}\text{O}_3/^{188}\text{Os}^{16}\text{O}_3 > 0.0005$) the measurements were rejected.

[16] During the period of analysis, our in-house osmium standard yielded a ratio of $^{187}\text{Os}/^{188}\text{Os}$ of 0.17371 ± 0.00076 (2σ , $n = 52$), which is consistent with the results obtained for this standard over the past 10 years. For the bulk sediment analyses total procedural blanks ($n = 8$) were 0.22 ± 0.13 pg of Os. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of the blank was difficult to characterize because of the low quantities, but generally blanks with low mass 233 contributions display $^{187}\text{Os}/^{188}\text{Os}$ ratios lower than 0.2. Because our blank Os isotopic composition is not well constrained, we did not correct sample $^{187}\text{Os}/^{188}\text{Os}$ for the procedural blank contribution. Nevertheless the Os blank contribution to the bulk sediments represents less than 3% in the worst case, and is usually less than 1%. For the leaching experiments the total analytical blank was difficult to quantify because of the presence of hydrogen peroxide in the leaching solution, which reacts with the liquid bromine in the absence of a sedimentary matrix, thus preventing Os extraction. However, all the reagents used for this study have provided low blanks (~ 50 fg [see Paul *et al.*, 2009]). In addition, as noted above, the use of 10g of sample powder (corresponding to more than 25 pg of osmium leached) reduced the relative importance of the analytical blank contribution to less than 1% of the total amount of osmium.

[17] Re concentrations were calculated by isotope dilution from $^{187}\text{Re}/^{185}\text{Re}$ ratios measured on an Elan 6000 ICP-MS at the SARM of CRPG. $^{187}\text{Re}/^{185}\text{Re}$ values of the standard ($^{187}\text{Re}/^{185}\text{Re} = 1.7008 \pm$

0.011 2σ , $n = 71$), remain fairly constant during a single session but could vary from day to day due to the variation of the mass fractionation effect. Sample $^{187}\text{Re}/^{185}\text{Re}$ ratios were corrected for these effects by normalizing the day's average standard ratio to $^{187}\text{Re}/^{185}\text{Re} = 1.6738$. Total Re procedural blanks were 0.5–5 pg. Owing to the blank variability, Re concentrations were not corrected for the blank contribution. Nevertheless, an uncertainty of 5 ppt should be attributed to the Re concentrations listed in Table 1 to reflect the blank variation.

[18] Strontium and neodymium analyses were performed on sediments previously leached with HCl (2,5 N) to remove carbonate phases. Residues were rinsed several times with Milli-Q water and then placed in an oven at 600°C in order to eliminate organic matter. Silicate phases were digested by a double passage in a mixture of HF, HNO_3 HClO_4 . After complete digestion the samples were dried down and redissolved in HCl. Standard chromatographic techniques were used to separate Sr and light rare earth elements using AG50X8 cationic exchange resin in quartz columns. Nd was then separated from the LREE fraction with AG1X8 anionic resin. Sr and Nd contents were measured by quadrupole ICP-MS (SARM-CRPG) and $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd isotopic measurements were performed by thermal ionization mass spectrometry on a Finnigan MAT262 (CRPG) in static mode. During the analytical period, the $^{87}\text{Sr}/^{86}\text{Sr}$ value obtained for the standard NBS987 was 0.710242 ± 0.000028 (2σ , 165 analyses). The $^{143}\text{Nd}/^{144}\text{Nd}$ value obtained for the La Jolla standard was 0.511850 ± 0.000032 (2σ , 25 analyses).

4. Results

4.1. Ganga Leachates

[19] Results of the leachate analyses are presented and compared with the corresponding bulk compositions in Table 2. As noted by Forstner and Kersten [1988], selective chemical extraction of specific phases often produces results with large external variability, and the degree of selectivity of different leaching procedures is the subject of debate. Our leaching procedure, similar to that of Pegram *et al.* [1994] is designed to optimize the dissolution of amorphous Fe and Mn oxy-hydroxides [Pegram *et al.*, 1992], though we cannot exclude some leaching of other phases as well (carbonate and possibly some magnetite, if present in the bulk sample). A slight yellow tint was observed in all H_2O_2 - $\text{H}_2\text{SO}_4^{2-}$ leaching solutions indicating the effective dissolution of the amorphous iron oxide.

Table 2. $^{187}\text{Os}/^{188}\text{Os}$ and Os Concentrations of Leachate and Bulk Sediments of Ganga Sediments

Sample	Type	Bulk		Exchangeable			Estimated Nonexchangeable Fraction	
		$^{187}\text{Os}/^{188}\text{Os}$	[Os] ppt	$^{187}\text{Os}/^{188}\text{Os}$	[Os] ppt ^a	%	$^{187}\text{Os}/^{188}\text{Os}$	[Os] ppt ^a
BR314	Clayey (bed load)	2.01	47	3.5	4.37	9	1.86	42.63
BR344	Clayey (bed load)	2.67	32.48	3.43	5.56	17	2.51	26.92
BR356	Clayey (bed load)	2.75	34.54	3.41	6.46	19	2.60	28.08
BR421	Silty (bed load)	2.34	17.58	3.15	2.31	13	2.22	15.27
BR344 carb ^b	Carb leach			1.95	0.56	2		

^aLeachable Os per gram of dry bulk sediment.

^bLeachable Os obtain on the carbonate fraction.

[20] The preliminary carbonate leaching test performed on sample BR 344 suggests that the carbonate fraction of Ganga sediments has a very low Os content (0.6 ppt) with an isotopic signature ($^{187}\text{Os}/^{188}\text{Os} = 1.95$) less radiogenic than the bulk sediment value (2.67; Table 2). This test must be interpreted with care because problems of spike/sample equilibration for carbonates have been reported in Os analyses of corals [Levasseur et al., 1999b]. However, the results are in agreement with those of Pierson-Wickmann et al. [2002a], who found that weak HCl leaching of a sediment from the Narayani basin released only small quantities of Os with an $^{187}\text{Os}/^{188}\text{Os}$ ratio lower than that of the bulk sediment. The less radiogenic compositions of the weak HCl leachates in both of these experiments might reflect a contribution from unradiogenic carbonates from the Tethyan Sedimentary Series of the northern Himalaya [Pierson-Wickmann et al., 2000].

[21] Though admittedly imperfect, these procedures provide rough estimates of the mobile and immobile fractions present in sediments and are commonly used for studying the behavior of metallic trace elements. Assuming that our results are representative of the mobilizable fraction, they suggest that between 10 and 20% of the osmium carried by sediments could potentially be released to the ocean. In addition, the $^{187}\text{Os}/^{188}\text{Os}$ ratios of the mobilizable fractions, which range between 3.15 and 3.5, are systematically more radiogenic than the corresponding bulk analyses (Table 2).

4.2. Estuarine Sediments

[22] The Os concentrations of the sediments from the Pussur river range between 24.3 and 61.1 ppt (corresponding to 20 and 54.9 ppt of non-radiogenic osmium, Table 1 and Figure 2), while their $^{187}\text{Os}/^{188}\text{Os}$ ratios vary from 0.96 to 2.02 (Table 1 and Figure 3). Excluding the two extreme values the isotopic compositions are clustered

around a mean $^{187}\text{Os}/^{188}\text{Os}$ ratio of $\sim 1.76 \pm 0.2$. This value is significantly less radiogenic than the mean isotopic signature reported in the Ganga after the influx of its principal tributaries, where nearly all $^{187}\text{Os}/^{188}\text{Os}$ ratios are comprised between 2.20 and 2.60 [Pierson-Wickmann et al., 2000; Chakrapani et al., 2002; Paul, 2008]. The Os contents of the lower Meghna sediments vary from 11 in the bed load to 59 ppt near the surface. Their isotopic ratios range from 0.82 to 1.37, and are thus similar to those of Brahmaputra sediments, which have $^{187}\text{Os}/^{188}\text{Os}$ between 0.6 and 1.6, with most values less than 1 [Singh et al., 2003], though some contribution from Ganga sediments is likely.

[23] Strontium isotopic compositions from the lower Meghna depth profile vary greatly with depth, ranging from 0.72412 for the bed load (BR 446) to

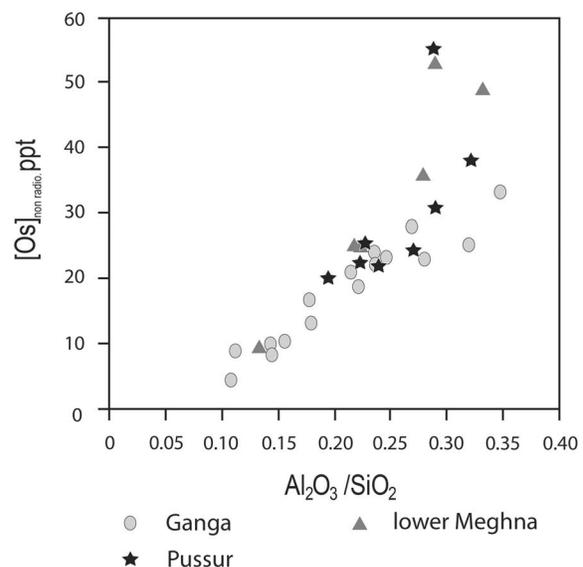


Figure 2. Nonradiogenic osmium contents of Ganga, Pussur and lower Meghna sediments as a function of their $\text{Al}_2\text{O}_3/\text{SiO}_2$ compositions. Data for Ganga sediments are from Paul [2008].

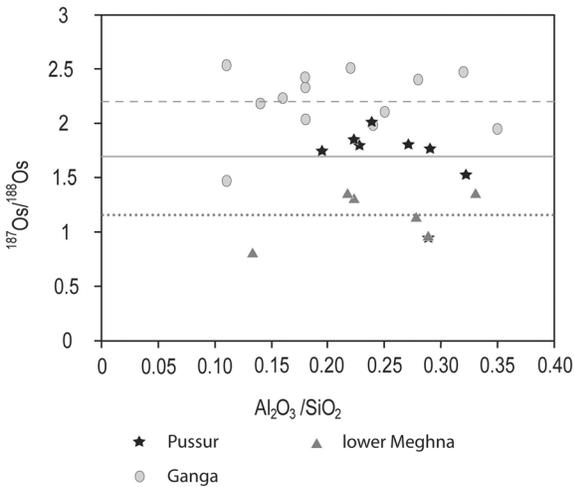


Figure 3. Comparisons of $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions of Ganga, Pussur and Lower Meghna sediments versus their $\text{Al}_2\text{O}_3/\text{SiO}_2$ compositions (wt %). Dashed, gray and dotted lines indicate the mean $^{187}\text{Os}/^{188}\text{Os}$ compositions of Ganga, Pussur and Lower Meghna sediments, respectively.

0.74130 for the surface sample (BR 441). This large variation is also recorded by the neodymium system showing ϵNd of -13.69 for BR 446 and -15.80 for BR 441. Results from both isotopic systems are consistent with mixing between pre-Cambrian crustal sediment from the Ganga ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.748$ to 0.782 ; $\epsilon\text{Nd} \sim -15.6$ to -21.4 [Galy and France-Lanord, 2001; Singh et al., 2008]) and a younger, and/or more mantle-like contribution from the Brahmaputra ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.721$ to 0.734 ; $\epsilon\text{Nd} \sim -12.4$ – -16.9 [Singh et al., 2008; Singh and France-Lanord, 2002]).

[24] Isotopic results from the Pussur river show less variation, ranging between 0.761582 and 0.76761 and between -17.4 and -18.3 for $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd respectively. Nd isotopic compositions from the Pussur are indistinguishable from those of the Ganga, while Sr isotopic ratios plot at the unradiogenic end of the Ganga sediment field obtained from previous studies (Figure 4; data from Galy and France-Lanord [2001] and Singh et al. [2008]).

5. Discussion: Potential Release of Osmium From Sediments

5.1. Transport of Osmium in the Himalayan Context: Implications of the Leachate Data

[25] The behavior of osmium during weathering of the continental crust and its transport by rivers has

been the subject of a relatively limited number of studies [e.g., Esser and Turekian, 1993; Peucker-Ehrenbrink and Ravizza, 1996; Peucker-Ehrenbrink and Blum, 1998; Pierson-Wickmann et al., 2002b; Levasseur et al., 1999a; Huh et al., 2004; Chen et al., 2006]. Fortunately, many of these studies concern the Ganga-Brahmaputra basin, providing a substantial amount of Os data for this region [e.g., Levasseur et al., 1999a; Sharma et al., 1999; Pierson-Wickmann et al., 2000; Chakrapani et al., 2002; Paul, 2008]. Though only a few data exist for Ganga river water [Levasseur et al., 1999a; Sharma et al., 1999], these suggest that Ganga sediments and river water have similar Os isotopic compositions, which would argue for congruent behavior during chemical erosion. This observation is surprising, as much of the radiogenic Os in Himalayan sediments is thought to be derived from black shales [Pierson-Wickmann et al., 2000]. In a study of the Mackenzie River basin of Canada, Huh et al. [2004] found that the dissolved loads of rivers draining basins containing black shales are substantially more radiogenic than the detrital loads. This seems logical, as previous studies have shown that Os, particularly ^{187}Os , is easily mobilized during black shale weathering [Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002]. This behavior seems to be confirmed in the Himalayan case, where Pierson-Wickmann et al. [2002b] have found evidence for likely Os loss and possible preferential mobility of

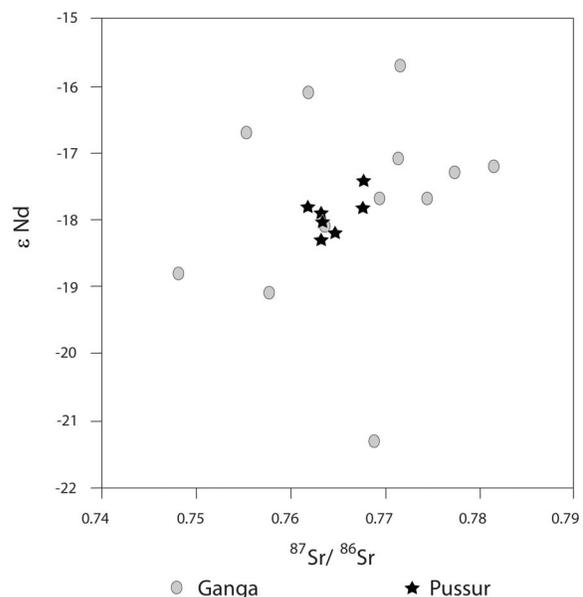


Figure 4. ϵNd compositions of Ganga and Pussur sediments as a function of their $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. Ganga sediment data are from Galy and France-Lanord [2001] and Singh et al. [2008].

¹⁸⁷Os in two black shale soil profiles, though these authors stress the complexity of the process. Thus the approximate agreement between Os isotopic compositions of waters [Levasseur *et al.*, 1999a] and sediments [Pierson-Wickmann *et al.*, 2000] collected at the same locality in the Ganga river is difficult to explain.

[26] Our leachates of Ghaghara and Ganga sediments display Os isotopic signatures significantly more radiogenic than the corresponding bulk analyses (Table 2), in agreement with results from most previous leaching experiments of Ganga and Himalayan sediments [Pegram *et al.*, 1994; Pierson-Wickmann *et al.*, 2000]. The high ¹⁸⁷Os/¹⁸⁸Os ratios of the leached fractions, relative to those of bulk sediments, could indicate that osmium ultimately derived from chemical weathering of black shales is preferentially concentrated in the exchangeable fraction, probably in the form of Fe oxides. Amorphous iron oxides, very rich in highly radiogenic Os (¹⁸⁷Os/¹⁸⁸Os ~18), have been observed on altered black shales [Pierson-Wickmann *et al.*, 2002b]. Such phases can also be observed optically on coarse sediments, notably on quartz; moreover as noted above, during leaching the solutions develop a slight yellow tint, indicating the dissolution of amorphous iron oxide. Some well crystallized magnetites are also present in Ganga and Brahmaputra sediments but these are only slightly attacked by the leaching solution. Despite being significantly more radiogenic than the bulk sediments, the ¹⁸⁷Os/¹⁸⁸Os ratios of the leachates are still lower than those of most Himalayan black shales (ranging up to ~20 [Pierson-Wickman *et al.*, 2000, 2002b; Singh *et al.*, 1999]). This probably indicates that the leaching process dissolves not only amorphous iron oxides formed directly on black shales, but also those carried by other detrital phases. Thus the leached Os represents a mixture of osmium adsorbed from the dissolved load, which as noted above is not much more radiogenic than typical Ganga sediment, with highly radiogenic osmium derived from Fe oxides formed by the weathering of black shales [Pierson-Wickmann *et al.*, 2002b]. Continuous exchange of Os between the leachable and the dissolved loads could buffer the isotopic signatures of sediments and dissolved load, conferring to the osmium an apparent conservative isotopic signature during the sedimentary transport (assuming that the residence time of osmium in the exchangeable position is relatively short compared to the residence times of sediments and dissolved load in the basin).

[27] Though the leaching procedure is selective, it cannot exclusively target a single mineralogical

phase, so we cannot exclude the possibility that phases other than amorphous iron oxide have also contributed to the leachates. Nevertheless, the fact that both clayey and silty sediments display similar fractions of exchangeable Os with comparable isotopic compositions (Table 2) suggests that extensive leaching of phases other than Fe oxide is probably minor, as a larger leaching fraction might be expected in the clayey sediments if this were the case. Regardless of their mineralogical nature, the phases attacked by the leaching procedure cannot represent solely the weathering products of radiogenic black shales (which have a mean ¹⁸⁷Os/¹⁸⁸Os of $9.17 \pm 3.20(1\sigma)$ [Pierson-Wickmann *et al.*, 2000]) and must instead have equilibrated isotopically to some extent with the less radiogenic dissolved load during sedimentary transport.

[28] The amount of radiogenic Os available for exchange in the Ganga basin can be evaluated from the leachates of clayey and silty sediments from the Ghaghara and Ganga rivers. Assuming that the Os released during leaching represents the exchangeable fraction, the osmium that could be liberated to the ocean represents as much as 10 to 20% of the total osmium carried by the sediments (Table 2), corresponding to between 0.5 and 1 kg of ¹⁸⁷Os (~1.5–3 kg of total Os) per year for the Ganga basin (assuming an annual discharge of 500 millions tons of sediments per year). This is comparable to the ~1.6 kg of ¹⁸⁷Os (~5.8 kg of total Os, calculated from the data of Levasseur *et al.* [1999a]) that is carried in dissolved form by Ganga river water. Mobilization of Os in the freshwater–saltwater transition zone could thus potentially constitute a nonnegligible flux of radiogenic osmium to the ocean, though as discussed below the tidal river sediments do not show evidence for a simple release mechanism. If the leachable Os is indeed carried by amorphous iron oxides, dissolution of these phases under reducing conditions in estuaries might provide a mechanism for Os release. As the possible processes and the time scale of osmium release are still unknown the current estimate of Os available for desorption or exchange is admittedly speculative. Nevertheless, it is possible that the quantities of Os delivered to the ocean by this process are comparable to those provided by the river flux [Levasseur *et al.*, 1999a] and the groundwater flux [Paul *et al.*, 2010].

5.2. Possible Exchange Processes in the Saltwater–Freshwater Transition Zone

[29] The results of our leaching experiments suggest that up to 20% of the Os carried by detrital sediments

is potentially available for exchange. We now consider what happens to this Os in the saltwater–freshwater mixing area by comparing Ganga and tidal river sediments. Simple comparison of the nonradiogenic Os concentrations of tidal river sediments (9–55 ppt, Table 1) with those of Ganga basin sediments (4–38 ppt [Paul, 2008]) suggests that the former have generally higher Os contents. However, this difference is primarily caused by mineralogical sorting (mostly due to the quartz dilution effect), as shown by the fact that the tidal rivers and the Ganga define overlapping trends in a plot (Figure 2) of Os content versus $\text{Al}_2\text{O}_3/\text{SiO}_2$, an indicator of the degree of sorting. When this effect is taken into account by comparing samples of equivalent $\text{Al}_2\text{O}_3/\text{SiO}_2$, the Ganga and the tidal rivers show similar concentrations. On the other hand, the $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Pussur (0.96–2.02) and Lower Meghna (0.97–1.37) river sediments are significantly lower than those of the Ganga (Figure 3). In the case of the Lower Meghna, the less radiogenic osmium isotopic signature can be easily explained by a mixture between Ganga and Brahmaputra sediments, since the latter are known to have relatively low $^{187}\text{Os}/^{188}\text{Os}$ ratios reflecting a substantial ultramafic component [Singh et al., 2003]. A large contribution from Brahmaputra sediments in the lower Meghna is also consistent with the higher Re concentrations of the lower Meghna sediments (123–319 ppt excluding the quartz-rich bed load, compared to 99–127 ppt in the Pussur sediments; Table 1), since Brahmaputra sediments have higher Re contents at a given $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio than Ganga sediments [Paul, 2008]. In addition, the present and previous Sr and Nd isotopic results argue for extensive sediment input from the Brahmaputra (Table 1) [also Galy and France-Lanord, 2001; Singh et al., 2008].

[30] The difference observed between the Ganga and Pussur sediments is more enigmatic since the Pussur derives all of its sediments directly from the Ganga or from erosion of the former Ganga delta [Goodbred and Kuehl, 2000]. Thus the Pussur sediments would be expected to have $^{187}\text{Os}/^{188}\text{Os}$ ratios greater than ~ 2 , as do nearly all of the Ganga sediments from this region [Pierson-Wickmann et al., 2000; Paul, 2008]. However, most of the Pussur sediments have $^{187}\text{Os}/^{188}\text{Os}$ ratios substantially lower than 2 (Table 1). Plotting $^{187}\text{Os}/^{188}\text{Os}$ as a function of $\text{Al}_2\text{O}_3/\text{SiO}_2$ (Figure 3) shows that the significant difference between the Os isotopic compositions of Ganga and Pussur sediments cannot be attributed to mineralogical sorting.

[31] Part of the explanation for the less radiogenic Os signature of the Pussur may be a subtle change in source between current Ganga sediments and those of the former Ganga delta present in the Pussur. This issue can be addressed by comparing the Sr and Nd isotopic compositions of the Pussur and Ganga rivers, though we recognize that the provenance of these lithophile elements may not be identical to that of Os, which is often concentrated in trace phases. As shown in Figure 4 while ϵNd signatures of Pussur sediments are indistinguishable from those of the nearby Ganga, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios fall at the low end of the Ganga range. (Ganga isotopic signatures between Rajmahal and Rajshahi typically vary between 0.755 and 0.770 for $^{87}\text{Sr}/^{86}\text{Sr}$ and between -16.1 and -21.3 for ϵNd [see Galy and France-Lanord, 2001; Singh et al., 2008].) This difference becomes more evident when the mineralogical sorting effect is considered. For a given $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, Pussur sediments have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those of the nearby Ganga (Figure 5). Nevertheless, it seems unlikely that the small difference in source suggested by the Sr isotopes could fully explain the systematically lower $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Pussur. Moreover the recent Os results from Bengal groundwater [Paul et al., 2010] do not show any decrease of $^{187}\text{Os}/^{188}\text{Os}$ in the Pussur area, suggesting that the Os isotopic compositions of sediments present in the Pussur catchment probably do not strongly differ from those of modern Ganga sediments.

[32] An alternative, or possibly additional, explanation of the low $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Pussur sediments might be interaction with the dissolved load, which can be considered as a mixture between seawater and Ganga river water. Several types of interaction are possible. Os might simply be adsorbed by sediments or trapped by biological processes in the tidal zone, as suggested by the results of Levasseur et al. [2000], which document a loss of 30% of dissolved osmium at relatively low salinities in the Lena estuary. Sediment adsorption of Os at higher salinities is supported by the studies of Martin et al. [2000, 2001] on the Fly river estuary of New Guinea and of Sharma et al. [2007] on the Godavari estuary of India. This behavior could be favored by precipitation/flocculation of iron oxides and/or of organic matter in the estuary as reported by Boyle et al. [1977]. Indeed, considering the affinity of osmium for iron oxide, we can assume that precipitation of iron with organic and inorganic particles could constitute a trap for dissolved osmium from fresh water and seawater.

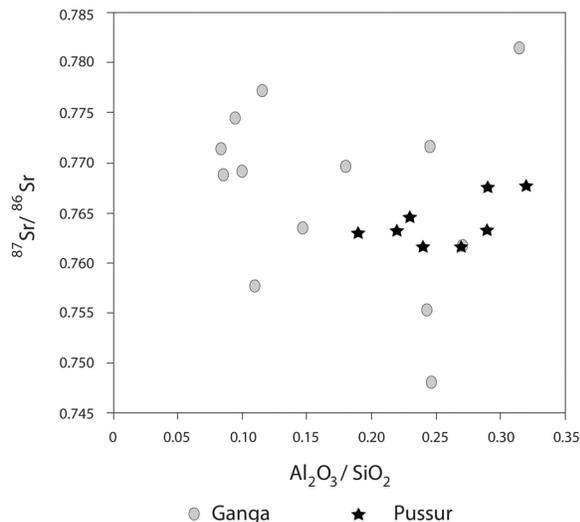


Figure 5. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions versus $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio (wt % of oxides) for Ganga and Pussur sediments (bank and suspended matter). Ganga sediment data are from *Galy and France-Lanord [2001]* and *Singh et al. [2008]*.

To test this possibility, we have plotted the amount of seawater Os that would have to be added to Ganga sediments to explain the observed Os isotopic compositions of the Pussur sediments (Figure 6). While the Os isotopic composition of Pussur river water is not known, use of a seawater composition ($^{187}\text{Os}/^{188}\text{Os} \sim 1.06$ [*Levasseur et al., 1998*]) produces minimum estimates of the amount of adsorbed Os required. At least 10 to 30 ppt of seawater Os would be needed to explain the Pussur sediment compositions. This seems unrealistic, as it would imply a strong enrichment in osmium contents relative to those of Ganga sediments of similar $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, which is not observed (Figure 2).

[33] Alternatively, we consider the hypothesis that the Pussur sediments have lost the fraction of their Os that is both exchangeable and radiogenic, as documented by the leaching studies. The Os concentrations and isotopic compositions of the residues remaining after removal of the leachable Os were calculated and are shown in Table 2. In the most extreme case (BR356), $\sim 20\%$ of the osmium is exchangeable, while the most radiogenic leachate $^{187}\text{Os}/^{188}\text{Os}$ ratio is 3.5 (sample BR314). We use these extreme values to estimate the maximum likely effect of removal of the exchangeable Os fraction. Total loss of such Os from typical Ganga sediments ($^{187}\text{Os}/^{188}\text{Os} = 2.3$ and Os content = 20 ppt) would lead to an Os concentration of 16 ppt and a $^{187}\text{Os}/^{188}\text{Os}$ composition of 2. This also does not seem to be an acceptable

scenario, since it would imply a decrease of osmium content that is not observed, and dissolution of iron hydroxide which is in discordance with the reported behavior of iron in estuaries [*Boyle et al., 1977*]. Moreover, this mechanism does not decrease the $^{187}\text{Os}/^{188}\text{Os}$ ratios sufficiently to fully explain the isotopic signature of Pussur sediments.

[34] Finally, we consider the possibility that the Os in the leachable sediment fraction is not lost but is instead exchanged with dissolved Os in the tidal zone. This behavior could produce a significant decrease of the $^{187}\text{Os}/^{188}\text{Os}$ ratio without affecting the Os concentrations. Such a process might be roughly analogous to Nd boundary exchange processes that are thought to imprint the Nd isotopic composition of seawater [*Lacan and Jeandel, 2005*],

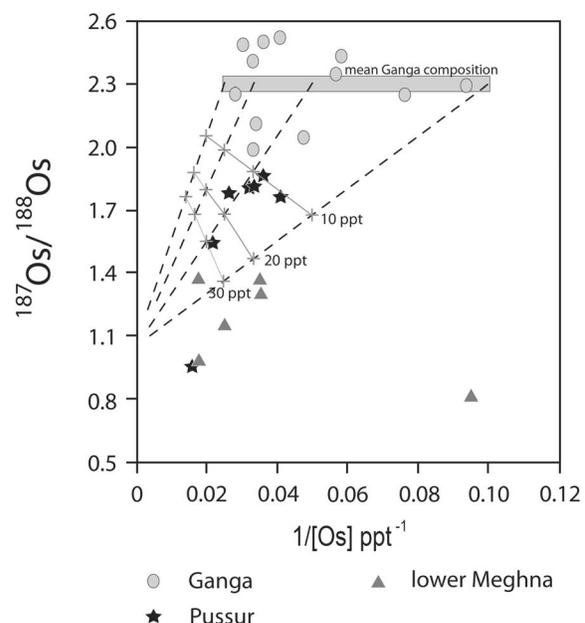


Figure 6. Comparison of Os compositions from Pussur and lower Meghna sediments against a simulation of the effects of seawater adsorption ($^{187}\text{Os}/^{188}\text{Os} = 1.06$ [*Levasseur et al., 1998*]) on Ganga sediments (characterized by an $^{187}\text{Os}/^{188}\text{Os}$ composition of 2.3 and concentrations of 40, 30, 20 and 10 ppt). Grey bar defines the mean range of Ganga sediments based on data from *Paul [2008]*. Dotted lines represent the theoretical evolution of sediment compositions resulting from increasing osmium adsorption from seawater on Ganga sediments. Grey lines indicate the effect of absorption of 10, 20, 30, 40 ppt of seawater osmium on Ganga sediments. Greater amounts of Os adsorption in the estuary would likely be required to explain the Os compositions of Pussur sediments, since the $^{187}\text{Os}/^{188}\text{Os}$ ratio of Pussur river water is probably higher than that of seawater.

though these occur in offshore rather than estuarine settings. Isotopic exchange could reasonably explain the Os compositions of most of the Pussur samples. Nevertheless, it may not adequately explain the $^{187}\text{Os}/^{188}\text{Os}$ ratio (0.96) of sample BR428, which is lower than most determinations of the seawater value (~ 1.06 [Levasseur et al., 1998; Sharma et al., 2007; Woodhouse et al., 1999]). The unradiogenic isotopic composition of this sample, coupled with its relatively high Os concentration (55 ppt) which deviates from the Ganga trend in Figure 2, might suggest the inclusion of a small amount of ultramafic material. Such material, which contains high concentrations of unradiogenic Os but little Sr or Nd, could strongly affect the Os isotopic signature while having little effect on the Sr or Nd isotopes, which do not differ from those of the other Pussur sediments. Pierson-Wickmann et al. [2000] found a few examples of sediments with surprisingly unradiogenic Os isotopic compositions and high Os concentrations in the catchment of the Narayani river, which flows into the Ganga. Assuming it can survive transport without excessive dilution by more typical Ganga sediments, incorporation of such material could explain the unusual Os signature of sample BR428. Alternatively, this sample may have adsorbed large quantities of Os from unusually unradiogenic nearshore waters, analogous to those analyzed by Martin et al. [2001] in the Coral Sea.

6. Conclusion

[35] We find that the low $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Pussur tidal sediments, relative to those of the Ganga, cannot result simply from desorption of the radiogenic, exchangeable Os fraction. We also find that scavenging of river or of seawater Os at the river–ocean interface, which has been observed in other estuaries [Levasseur et al., 2000; Martin et al., 2000, 2001; Sharma et al., 2007], also cannot explain this isotopic difference. Though we cannot rule out the possibility that a minor change in source has contributed to the lower Os isotopic values of the Pussur, our data suggest that effective exchange occurs between dissolved Os and the leachable Os fraction of sediments at the saltwater–seawater transition. Our leaching study suggests that up to 20% of the Os carried by detrital sediment is potentially exchangeable. Thus this mechanism, which constitutes both a source and a sink for seawater osmium, could significantly influence the osmium marine budget. On the other hand, our results suggest that systematic scavenging of

osmium in estuaries, leading to a large decrease of the osmium river flux to the ocean, probably does not occur.

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References

- Anbar, A. D., R. A. Creaser, D. A. Papanastassiou, and G. J. Wasserburg (1992), Rhenium in seawater: Confirmation of generally conservative behavior, *Geochim. Cosmochim. Acta*, *56*(11), 4099–4103, doi:10.1016/0016-7037(92)90021-A.
- Birck, J. L., M. Roy Barman, and F. Capmas (1997), Re–Os isotopic measurements at the femtomole level in natural samples, *Geostand. Newsl.*, *21*(1), 19–27, doi:10.1111/j.1751-908X.1997.tb00528.x.
- Boyle, E. A., J. M. Edmond, and E. R. Sholkovitz (1977), Mechanism of iron removal in estuaries, *Geochim. Cosmochim. Acta*, *41*(9), 1313–1324, doi:10.1016/0016-7037(77)90075-8.
- Boyle, E. A., S. S. Husted, and B. Grant (1982), The chemical mass balance of the amazon plume–II. Copper, nickel, and cadmium, *Deep Sea Res., Part A*, *29*(11), 1355–1364, doi:10.1016/0198-0149(82)90013-9.
- Carpenter, P. D., and J. D. Smith (1985), Effect of pH, iron and humic acid on the estuarine behaviour of phosphate, *Environ. Technol. Lett.*, *6*(1), 65–72, doi:10.1080/09593338509384319.
- Chakrapani, G. J., J. Gaillardet, B. Dupre, and C. J. Allegre (2002), Osmium isotopic compositions in Ganga river sediments, *Curr. Sci.*, *83*(10), 1253–1255.
- Chen, C., M. Sharma, and B. C. Bostick (2006), Lithologic controls on osmium isotopes in the Rio Orinoco, *Earth Planet. Sci. Lett.*, *252*(1–2), 138–151, doi:10.1016/j.epsl.2006.09.035.
- Creaser, R. A., D. A. Papanastassiou, and G. J. Wasserburg (1991), Negative thermal ion mass spectrometry of osmium, rhenium and iridium, *Geochim. Cosmochim. Acta*, *55*(1), 397–401, doi:10.1016/0016-7037(91)90427-7.
- Esser, B. K., and K. K. Turekian (1993), The osmium isotopic composition of the continental crust, *Geochim. Cosmochim. Acta*, *57*(13), 3093–3104, doi:10.1016/0016-7037(93)90296-9.
- Forstner, U., and M. Kersten (1988), Assessment of metal mobility in dredged material and mine waste by pore water chemistry and solid speciation, in *Chemistry and Biology of Solid Waste: Dredged Material and Mine Tailings*, edited by W. Salomons and U. Forstner, pp. 214–237, Springer, Berlin.
- Galy, A., and C. France-Lanord (2001), Higher erosion rates in the Himalaya: Geochemical constraints on riverine fluxes, *Geology*, *29*, 23–26, doi:10.1130/0091-7613(2001)029<0023:HERITH>2.0.CO;2.
- Goodbred, S. L., and S. A. Kuehl (2000), The significance of large sediment supply, active tectonism, and eustasy on margin sequence development: Late Quaternary stratigraphy and

- evolution of the Ganges-Brahmaputra delta, *Sediment. Geol.*, *133*(3–4), 227–248, doi:10.1016/S0037-0738(00)00041-5.
- Hay, W. W. (1998), Detrital sediment fluxes from continents to oceans, *Chem. Geol.*, *145*(3–4), 287–323, doi:10.1016/S0009-2541(97)00149-6.
- Huh, Y., J.-L. Birck, and C. J. Allègre (2004), Osmium isotope geochemistry in the Mackenzie River basin, *Earth Planet. Sci. Lett.*, *222*(1), 115–129, doi:10.1016/j.epsl.2004.02.026.
- Islam, M. R., S. F. Begum, Y. Yamaguchi, and K. Ogawa (1999), The Ganges and Brahmaputra rivers in Bangladesh: Basin denudation and sedimentation, *Hydrol. Processes*, *13*(17), 2907–2923, doi:10.1002/(SICI)1099-1085(19991215)13:17<2907::AID-HYP906>3.0.CO;2-E.
- Jaffe, L. A., B. Peucker-Ehrenbrink, and S. T. Petsch (2002), Mobility of rhenium, platinum group elements and organic carbon during black shale weathering, *Earth Planet. Sci. Lett.*, *198*(3–4), 339–353, doi:10.1016/S0012-821X(02)00526-5.
- Karbassi, A. R., J. Nouri, Gh. R. Nabi Bidhendi, and G. O. Ayaz (2008), Behavior of Cu, Zn, Pb, Ni and Mn during mixing of freshwater with the Caspian Sea water, *Desalination*, *229*(1–3), 118–124, doi:10.1016/j.desal.2007.06.035.
- Lacan, F., and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface, *Earth Planet. Sci. Lett.*, *232*, 245–257, doi:10.1016/j.epsl.2005.01.004.
- Levasseur, S., J.-L. Birck, and C. J. Allègre (1998), Direct measurement of femtomoles of osmium and the $^{187}\text{Os}/^{186}\text{Os}$ ratio in seawater, *Science*, *282*(5387), 272–274, doi:10.1126/science.282.5387.272.
- Levasseur, S., J.-L. Birck, and C. J. Allègre (1999a), The osmium riverine flux and the oceanic mass balance of osmium, *Earth Planet. Sci. Lett.*, *174*(1–2), 7–23, doi:10.1016/S0012-821X(99)00259-9.
- Levasseur, S., J.-L. Birck, and C. J. Allègre (1999b), Osmium isotopic composition of corals: Evidences for multiple sources, *Geochim. Cosmochim. Acta*, *63*(9), 1335–1343, doi:10.1016/S0016-7037(99)00017-4.
- Levasseur, S., V. Rachold, J.-L. Birck, and C. J. Allègre (2000), Osmium behavior in estuaries: The Lena River example, *Earth Planet. Sci. Lett.*, *177*(3–4), 227–235, doi:10.1016/S0012-821X(00)00049-2.
- Martin, C. E., B. Peucker-Ehrenbrink, G. J. Brunskill, and R. Szymczak (2000), Sources and sinks of unradiogenic osmium runoff from Papua New Guinea, *Earth Planet. Sci. Lett.*, *183*(1–2), 261–274, doi:10.1016/S0012-821X(00)00281-8.
- Martin, C. E., B. Peucker-Ehrenbrink, G. Brunskill, and R. Szymczak (2001), Osmium isotope geochemistry of a tropical estuary, *Geochim. Cosmochim. Acta*, *65*(19), 3193–3200, doi:10.1016/S0016-7037(01)00654-8.
- Nier, A. O. (1950), A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium, *Phys. Rev.*, *77*, 789–793, doi:10.1103/PhysRev.77.789.
- Paul, M. (2008), Étude des isotopes de l’osmium dans les eaux souterraines du Bangladesh et les sédiments himalayens: Implications et rôle de l’érosion himalayenne sur le budget océanique de l’osmium, thesis, 251 pp., Inst. Natl. Polytech. de Lorraine, Nancy, France.
- Paul, M., L. Reisberg, and N. Vigier (2009), A new method for analysis of osmium isotopes and concentrations in surface and subsurface water samples, *Chem. Geol.*, *258*(3–4), 136–144, doi:10.1016/j.chemgeo.2008.09.018.
- Paul, M., L. Reisberg, N. Vigier, Y. Zheng, K. Matin Ahmed, L. Charlet, and M. R. Huq (2010), Dissolved osmium in Bengal plain groundwater: Implications for the marine Os budget, *Geochim. Cosmochim. Acta*, *74*, 3432–3448, doi:10.1016/j.gca.2010.02.034.
- Pegram, W. J., et al. (1992), The record of sea water $^{187}\text{Os}/^{186}\text{Os}$ variation through the Cenozoic, *Earth Planet. Sci. Lett.*, *113*(4), 569–576, doi:10.1016/0012-821X(92)90132-F.
- Pegram, W. J., B. K. Esser, S. Krishnaswami, and K. K. Turekian (1994), The isotopic composition of leachable osmium from river sediments, *Earth Planet. Sci. Lett.*, *128*(3–4), 591–599, doi:10.1016/0012-821X(94)90172-4.
- Peucker-Ehrenbrink, B., and J. D. Blum (1998), Re–Os isotope systematics and weathering of Precambrian crustal rocks: Implications for the marine osmium isotope record, *Geochim. Cosmochim. Acta*, *62*(19–20), 3193–3203, doi:10.1016/S0016-7037(98)00227-0.
- Peucker-Ehrenbrink, B., and R. E. Hannigan (2000), Effects of black shale weathering on the mobility of rhenium and platinum group elements, *Geology*, *28*(5), 475–478, doi:10.1130/0091-7613(2000)28<475:EOBSWO>2.0.CO;2.
- Peucker-Ehrenbrink, B., and B. Jahn (2001), Rhenium–osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust, *Geochim. Geophys. Geosyst.*, *2*(10), 1061, doi:10.1029/2001GC000172.
- Peucker-Ehrenbrink, B., and G. Ravizza (1996), Continental runoff of osmium into the Baltic Sea, *Geology*, *24*(4), 327–330, doi:10.1130/0091-7613(1996)024<0327:CROOIT>2.3.CO;2.
- Peucker-Ehrenbrink, B., G. Ravizza, and A. W. Hofmann (1995), The marine $^{187}\text{Os}/^{186}\text{Os}$ record of the past 80 million years, *Earth Planet. Sci. Lett.*, *130*(1–4), 155–167, doi:10.1016/0012-821X(95)00003-U.
- Pierson-Wickmann, A.-C., L. Reisberg, and C. France-Lanord (2000), The Os isotopic composition of Himalayan river bedloads and bedrocks: Importance of black shales, *Earth Planet. Sci. Lett.*, *176*(2), 203–218, doi:10.1016/S0012-821X(00)00003-0.
- Pierson-Wickmann, A.-C., L. Reisberg, and C. France-Lanord (2002a), Impure marbles of the Lesser Himalaya: Another source of continental radiogenic osmium, *Earth Planet. Sci. Lett.*, *204*(1–2), 203–214, doi:10.1016/S0012-821X(02)00962-7.
- Pierson-Wickmann, A.-C., L. Reisberg, and C. France-Lanord (2002b), Behavior of Re and Os during low-temperature alteration: Results from Himalayan soils and altered black shales, *Geochim. Cosmochim. Acta*, *66*(9), 1539–1548, doi:10.1016/S0016-7037(01)00865-1.
- Roy Barman, M. (1993), Mesure du rapport $^{187}\text{Os}/^{186}\text{Os}$ dans les basaltes et les péridotites: Contribution à la systématique ^{187}Re – ^{187}Os dans le manteau, thesis, Univ. Paris VII, Paris.
- Sharma, M., G. J. Wasserburg, A. W. Hofmann, and G. J. Chakrapani (1999), Himalayan uplift and osmium isotopes in oceans and rivers, *Geochim. Cosmochim. Acta*, *63*(23–24), 4005–4012, doi:10.1016/S0016-7037(99)00305-1.
- Sharma, M., K. Balakrishna, A. W. Hofmann, and R. Shankar (2007), The transport of Osmium and Strontium isotopes through a tropical estuary, *Geochim. Cosmochim. Acta*, *71*(20), 4856–4867, doi:10.1016/j.gca.2007.08.004.
- Shirey, S. B., and R. J. Walker (1995), Carius tube digestion for low-blank rhenium–osmium analysis, *Anal. Chem.*, *67*(13), 2136–2141, doi:10.1021/ac00109a036.
- Singh, S. K., and C. France-Lanord (2002), Tracing the distribution of erosion in the Brahmaputra watershed from isotopic compositions of stream sediments, *Earth Planet. Sci. Lett.*, *202*(3–4), 645–662, doi:10.1016/S0012-821X(02)00822-1.

- Singh, S. K., J. R. Trivedi, and S. Krishnaswami (1999), Re-Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in the $^{187}\text{Os}/^{188}\text{Os}$ evolution of seawater, *Geochim. Cosmochim. Acta*, *63*(16), 2381–2392, doi:10.1016/S0016-7037(99)00201-X.
- Singh, S. K., L. Reisberg, and C. France-Lanord (2003), Re-Os isotope systematics of sediments of the Brahmaputra River system, *Geochim. Cosmochim. Acta*, *67*(21), 4101–4111, doi:10.1016/S0016-7037(03)00201-1.
- Singh, S. K., S. K. Rai, and S. Krishnaswami (2008), Sr and Nd isotopes in river sediments from the Ganga basin: Sediment provenance and hotspots of physical erosion, *J. Geophys. Res.*, *113*, F03006, doi:10.1029/2007JF000909.
- Singh, S. P., S. K. Singh, and R. Bhushan (2011), Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal, *Mar. Chem.*, *126*(1–4), 76–88, doi:10.1016/j.marchem.2011.04.001.
- Uddin, A., and N. Lundberg (1998), Cenozoic history of the Himalayan-Bengal system: Sand composition in the Bengal Basin, Bangladesh, *GSA Bulletin*, *110*(4), 497–511, doi:10.1130/0016-7606(1998)110<0497:CHOTHB>2.3.CO;2.
- Volkening, J., T. Walczyk, and K. G. Heumann (1991), Osmium isotope ratio measurements by negative thermal ionization mass spectrometry, *Int. J. Mass Spectrom. Ion Processes*, *105*(2), 147–159, doi:10.1007/BF00328491.
- Woodhouse, O. B., G. Ravizza, K. Kenison Falkner, P. J. Statham, and B. Peucker-Ehrenbrink (1999), Osmium in seawater: Vertical profiles of concentration and isotopic composition in the eastern Pacific Ocean, *Earth Planet. Sci. Lett.*, *173*(3), 223–233, doi:10.1016/S0012-821X(99)00233-2.