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Osmium geochemistry of modern estuarine sediments from the Tama and Yasaka rivers in Japan

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ABSTRACT

Concentrations of Re and Os and $^{187}Os/^{188}Os$ ratios were obtained on the modern sediment samples from two estuarine areas: the Tama River in Tokyo and the Yasaka River in Oita, Japan. The shallow (<depth 25 cm) intervals of the Tama sediments contain Os of 29.0–36.7 ppt that are quite similar to that in the upper continental crust (UCC) of 30 ppt whereas the deep (>depth 25 cm) intervals are 99.2–105.5 ppt Os that are more than 3 times higher than UCC. However, all samples have $^{187}Os/^{188}Os$ ratios within a relatively narrow range of 0.3029–0.4035, much lower than that of UCC (1.0–1.3), indicating a similar source of Os in both parts. The lower $^{187}Os/^{188}Os$ ratios and high Os concentrations of the sediments in the Tama River suggest the impact from human activities. The sudden enrichment of Os at the deep interval may be related to the redox condition change. In addition, the Os concentration is vertically constant in either the upper and lower intervals of the sediment profile, suggesting constant burial fluxes of Os in the sediment.

The Os in the Yasaka River estuary sediments (9.22–29.4 ppt) are generally lower than that of the Tama River, either similar or much lower (~1/3) than the average UCC Os concentrations. The samples with high Os concentrations have lower $^{187}Os/^{188}Os$ ratios whereas the samples with lower Os concentrations have relatively higher $^{187}Os/^{188}Os$ ratios, probably indicating different Os sources. The relatively higher $^{187}Os/^{188}Os$ ratios and lower Os concentrations in some Yasaka River estuarine sediments than the Tama River may also suggest less pollution from human activity to the Yasaka River compared to the Tama River.

There is a large decrease of Re concentrations with depth in the Yasaka River estuarine sediment whereas less variations of Re in the Tama River estuarine sediments. The ratio of Re/Os is also sharply different between the two estuarine sediments, also indicating different sedimentary environments. The Tama River sediments may receive much more anthropogenic influence while the Yasaka River sediments get strong impact from modern volcanic activity due to their different geographical and geological surroundings: the Tama River flows through a heavily industrial metropolitan area whereas the Yasaka River flows through a volcanic active but less industrial area.

1. Introduction

The applications of rhenium–osmium (Re–Os) isotopic systematics have been rapidly expanding to various fields in Earth sciences during the last two decades such as cosmochemistry (Morgan et al., 1996; Shen et al., 1996), marine geochemistry (Peucker-Ehrenbrink and Ravizza, 2000), and environmental fields including continental erosion and climate change (Chesley et al., 2000; Cohen et al., 2004; Pegram et al., 1992), soils (Singh et al., 1999), desert sands (Hattori et al., 2003), loess and dust (Peucker-Ehrenbrink and Jahn, 2001). This is mostly due to the wide range signatures exhibited in $^{187}Os/^{188}Os$ ratios and variation among different kinds of geological and environmental materials. Natural osmium has variable isotopic ratios of $^{187}Os/^{188}Os$ because of the production of ^{187}Os by the beta-decay of ^{187}Re whereas ^{188}Os is a stable isotope that is constant in nature. Different origin of ^{187}Re in the starting materials will induce different isotopic composition of $^{187}Os/^{188}Os$ in the end materials, which can be used as a chemical tracer to the geological and environmental processes

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such as the anthropogenic osmium in coastal deposits (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Helz et al., 2000). In addition, recently developed techniques made the analysis of Re–Os isotopic systematics much easier to perform (Birck et al., 1997; Levasseur et al., 1998; Pierson-Wickmann et al., 2002; Suzuki et al., 2004). Particularly the detailed chemical procedures in extra clean laboratory followed by precise instrumental measurement have improved the analysis of Re and Os available even for siliceous rocks. The abundances of Re and Os in most siliceous rocks are extremely low, commonly in ppb to ppt level (e.g. Shirey and Walker, 1998), requiring special method to determine Re and Os concentrations in such materials.

The Re–Os isotope systematics have been also applied to obtain information on the original source or precursor, transportation, and depositional processes of aquatic sediments, and even the early diagenesis processes, expanding the studies of Re–Os isotope systematics of aquatic sediments from terrestrial systems such as lakes, rivers (Pegram et al., 1992; Singh et al., 2003; Sharma and Wasserburg, 1997), to estuary areas (Williams et al., 1997), bay (Helz et al., 2000), and the sea coastal regions (Ravizza and Bothner, 1996). At the present, platinum group elements (PGEs) have been used as special materials in a wide range of industries such as vehicles and been released into the environment. Heinrich et al. (1996) observed clearly significant enrichment in PGEs in soils near the highway, which are mainly indicating anthropogenic sources. As one of the PGE, Os may have the similar characteristics of PGEs in materials which are contaminated by human activities. On the other hand, estuary areas are also favorable setting for biological activities that may contribute to the geochemical behaviors of various elements such as heavy metals, even radionuclides (Gleizon et al., 2003). However, only few studies have been conducted to investigate Re and Os in estuary areas including river water and sediments (Esser and Turekian, 1993). In this paper, Re and Os concentrations and Os isotopes of sediments from the estuary areas of the Tama River and Yasaka River were analyzed for their environmental implications (Zheng et al., 2003). In addition, the mechanism of Os fixation in estuary sediments, being important to understand the geochemistry of Os in relation to its geochemical behavior and the environmental impacts, is also discussed.

2. Study sites and samples

The Tama River is one of the major rivers flowing through the Tokyo metropolitan area into the Tokyo Bay (Fig. 1). The river flows 138 km eastward, and has a watershed area of 1240 km^2. This area has been heavily industrialized, and populated by 11.77 million people. A busy transportation network has been constructed within the urban area and connected with other regions on all directions since 1960s. The transportation network has been used by a huge amount of cars and trucks since 1950s. This geographical setting and commercial activities have resulted in heavy pollution with municipal sewage (Takii and Fukui, 1991), resulted in much interest from researchers and governments for this area during recent years (Zheng et al., 2002; Kuno et al., 1997, 1999). The sampling site for this study is located in a little inside of the riverbed, where the water column above the sediment surface varies with time during tidal cycles. The cored sediment samples for this study mainly consist of fine sand and silt, and small portion of broken shells. The samples studied here are the same as reported in Kuno et al. (1999).

The Yasaka River is located in the northern part of Oita Prefecture on the Kyushu Island, and is considered as one of the cleanest rivers without heavily human pollution in Japan. The watershed of Yasaka River consists of steep slopes and deep valleys, and the tributaries are characterized as short and steep grade of riverbed. Water flow in the Yasaka River and its tributaries is rapid in the raining season inducing relatively coarse sediment deposit on the riverbed. Another geological feature is that there are numerous hot springs in the watershed. A vertical sediment core of 48 cm in length was collected at the Station 1 (Y-1), about 1 km upstream from the river mouth and in the tidal flat region. The sediment of core Y1 is sandy in the upper section and slightly clayey in the lower part. The core collected with a handle plastic corer was sliced in situ at every 3 cm length of intervals, air-dried for more than 2 weeks, and then ground into powder using an agate mortar and pestle.

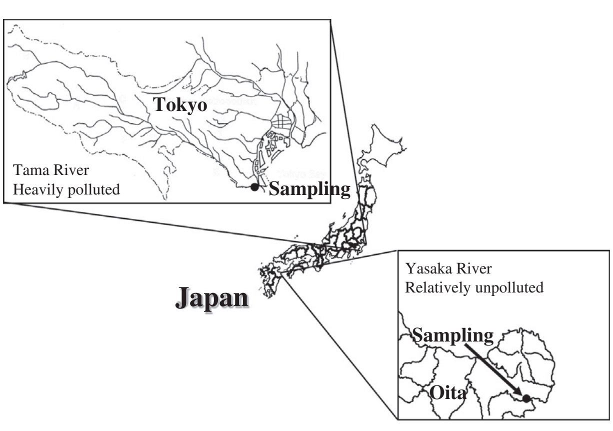

Fig. 1. A map showing the sampling stations for this study in the Tama River and Yasaka River estuaries. Sampling station in the Tama River is located at N 35°32′45″, E 139°45′08″, with altitude 0 m above sea level, and in the Yasaka River is at N 33°24′52″, E 131°37′46″ with altitude 0 m above sea level.

3. Analytical procedures

The analytical procedures for the Os and Re concentrations and Os isotopes for this study have been described elsewhere (Kato et al., 2005; Zheng et al., 2012), which was based on Carius tube digestion (Shirey and Walker, 1995), combined with carbon tetrachloride extraction (Cohen and Waters, 1996; Pearson and Woodland, 2000) and microdistillation (Roy-Barman, 1993), with some modifications. The Carius tube method is an effective decomposition technique to achieve complete isotopic equilibration of sample-derived Os with the enriched spike in a wide range of geological materials (Suzuki et al., 1992; Suzuki and Tatsumi, 2001). About 2.0–2.5 grams (g) of sample powder were weighed and mixed together with ^{185}Re and ^{190}Os spike solutions and inverse aqua regia (ca. 10 ml) to Carius tubes. The Carius tubes were sealed and heated at 220 °C for at least 24 h. The digested sample was then transferred to a 30 ml PFA vessel. Osmium was extracted by carbon tetrachloride for three times. Then Os is back-extracted into 9N HBr. The Os-bearing HBr fraction was gently evaporated and then further purified by microdistillation. The purified Os was then ready for mass spectrometry. The Re-bearing solution was centrifuged to remove the residual precipitation. Rhenium was then separated from the aqueous phase using Muromac AG 1-X8 anion exchange resin (100–200 mesh).

All measurements presented here were performed on a Finnigan MAT^{R} 262 mass spectrometer at Kyoto University at Beppu or a ThermoFinnigan TRITON^{R} at JAMSTEC, in negative ion detection mode (Creaser et al., 1991; Volkening et al., 1991), equipped with an oxygen gas leak valve and an ion counting multiplier. The Os was loaded on high purity Pt filament (99.99%, 1 mm × 0.025 mm, Tanaka Precious Metal Co. Ltd. or 99.999%, 1 mm × 0.025 mm, H. Cross Co. Ltd.). The sample was covered with 10 μg Ba using a 10,000 ppm $Ba(NO_3)_2$ solution (CLARITAS, SPEX Inc.). Instrumental mass fractionation of Os was corrected by normalizing the measured $^{192}Os/^{188}Os$ ratio to 3.08271 (Nier, 1937). Rhenium isotopes were measured using a total evaporation technique (Suzuki et al., 2004). The key features of this method are evaporation of the entire sample and simultaneous integration of the signal from each isotope, which effectively eliminates isotope fractionation effects during the evaporation process. This technique allows one precisely to determine Re isotope ratios relative to conventional measurements for samples with very small mass. Oxygen subtraction for Os and Re used the ratios of $^{17}O/^{16}O = 0.00037$ and $^{18}O/^{16}O = 0.002047$ (Nier, 1950). Both Re and Os were corrected for blanks. Total blank levels were 7.1 ± 0.3 and 2.0 ± 0.4 pg for Re and Os (2 S.D., $n = 13$), respectively. The blank $^{187}Os/^{188}Os$ ratio was 0.298 ± 0.028 (2 S.D., $n = 13$).

4. Results and discussion

The concentrations of Re and Os and their isotopic compositions are listed in Table 1, in which the data show some distinguished differences in the rhenium and osmium concentrations between the two estuary sediments. In general, Tama River sediments contain relatively higher osmium and lower rhenium whereas the Yasaka River sediments contain relatively lower osmium and higher rhenium. This may reflect the different environmental processes because the Tama River flows through a heavily industrialized urban area in the main island, the Honshyu of Japan whereas Yasaka River originates from recently active volcanic mountainous area in the Kyushu Island of Japan. Naturally geological surroundings and human activities may contribute to the input of rhenium and osmium into the estuary sediments in these two rivers.

4.1. Tama River

The concentrations of Os range from 29 to 105 ppt in the sediment samples collected from the Tama River estuary. The vertical distribution of Os in the sediments showed the upper part contained relatively lower Os and the lower part contained much higher Os (Fig. 2). For the upper part, Os concentrations are in the range of 29.0–36.7 ppt, being very close to the average concentration of the upper continental crust (UCC), 30 ppt Os, as proposed by Hattori et al. (2003), based mainly on the desert sands, moraines and river sediments around the Taklimakan desert and Tibetan soils in West China. However, Os concentrations of the lower part sediments are ranging from 99.2 to 105.5 ppt, about 3 times higher than that of the upper part of the sediments and also much higher than the average Os of the UCC. The sudden increase in Os concentrations occurs at depth around 25 cm. In addition, the concentrations of Os are quite consistent either in the upper or lower intervals. The consistent Os concentrations may strongly indicate the homogenesis of the sediment for both the upper and lower parts of the sedimentary column in the Tama River estuarine.

Therefore, the sediment samples can be classified into two groups based on their Os concentrations, the upper part with 29–36.7 ppt Os and the lower parts 99.2–105.5 ppt Os, respectively. However, the $^{187}Os/^{188}Os$ ratios for all samples of these two groups distribute in a narrow range from 0.3029 to 0.4035 (Fig. 3). These ratios are quite lower than the present UCC, of which the $^{187}Os/^{188}Os$ ratios are about 1.2–1.3 (Hattori et al., 2003), and higher than that of the upper mantle with Os isotopic ratios of 0.1198 (Brandon et al., 2000). These $^{187}Os/^{188}Os$ ratios of the sediments may indicate a mixing of two sources, including both more radiogenetic natural origin and less radiogenetic anthropogenic source of osmium. At present, osmium used in industry, medicine and commerce is mainly mined from ore deposits associated with ultramafic rocks that normally have relatively low $^{187}Os/^{188}Os$ ratios. The metal osmium is used largely for the production of hard alloys for use in fountain pen points, phonograph needles, and instrument bearings. Some portion of the osmium then could be released into the environment during its usages. The Tama River flows throughout the metropolitan area of Tokyo with large amounts of industries and transportation systems, and the estuarine area of the Tama River itself has become an urban part of the huge Tokyo metropolis area. Human activities along the Tama River resulted in heavy pollutions to the river water and also higher rate deposition.

Rhenium concentrations of Tama River estuarine sediments are ranging from 0.0216 to 0.584 ppb. The less concentrations and large variation of rhenium may also suggest that osmium in the Tama River estuary sediments might be derived in a bigger portion from artificial sources. Rhenium is used as catalysis widely in vehicles and industries, whose releasing into the environment has been investigated along highways (Heinrich et al., 1996). Surface washing drainage of road may be mostly contributed to this kind of enrichment of Re in the catchments of rivers.

4.2. Yasaka River

The concentrations of Os in the sediments of Yasaka River estuary range from 9.22 to 29.4 ppt, generally lower than that of the Tama River estuarine sediments, and also lower or equal to the Os concentration of UCC (Hattori et al., 2003). The variation in Os concentrations in the Yasaka River sediments is also much narrow than that of Tama River as shown in Fig. 2. This may indicate there is less input of osmium into the Yasaka River estuarine sediments from human activities. The Yasaka River flows through a relatively remote area and is considered as the cleanest river in Japan (Kuno et al., 1999). These Os concentrations of the Yasaka River estuarine sediments may represent the natural sources of Os in the river sediments in Japan.

The $^{187}Os/^{188}Os$ ratios of the Yasaka River estuarine sediments range from 0.250 to 0.726, which has a much wider range than that of Tama River, showing different sources and variable ratios of mixing. As shown in Fig 3, two groups of sediments can be

Table 1
Concentrations and isotopic ratios of Re and Os in estuary sediments from Tama River and Yasaka River in Japan.

Sample ID	Depth/cm	Re conc. (ppb)	2 sigma	Os conc. (ppt)	2 sigma	$^{187}Re/^{188}Os$	2 Sigma	$^{187}Os/^{188}Os$	2 Sigma
Tama River									
T2-15	1.5	0.464	0.019	33.4	0.77	52.6	2.2	0.3658	0.0051
T2-14	4.5	0.256	0.011	31.3	0.38	31.5	1.3	0.3678	0.0039
T2-12	10.5	0.193	0.008	29.0	0.19	25.6	1.1	0.3733	0.0013
T2-09	19.5	0.263	0.011	36.7	0.86	29.9	1.2	0.3569	0.0066
T2-07	25.5	0.584	0.024	99.2	2.7	21.98	0.92	0.3029	0.0047
T2-04	34.5			100.2	2.8			0.3521	0.0041
T2-01	43.5	0.0216	0.0009	105.5	5.4	0.886	0.037	0.4035	0.008
Yasaka River									
Y1-16k	1.5	2.175	0.091	29.4	4.7	2038	85	0.413	0.048
Y1-13k	19.5	1.435	0.06	11.6	0.19	1689	70	0.7263	0.0096
Y1-07k	37.5	0.581	0.024	9.22	1.08	2167	90	0.67	0.029
Y1-01k	46.5	0.241	0.01	23.2	15.9	352	15	0.25	0.1

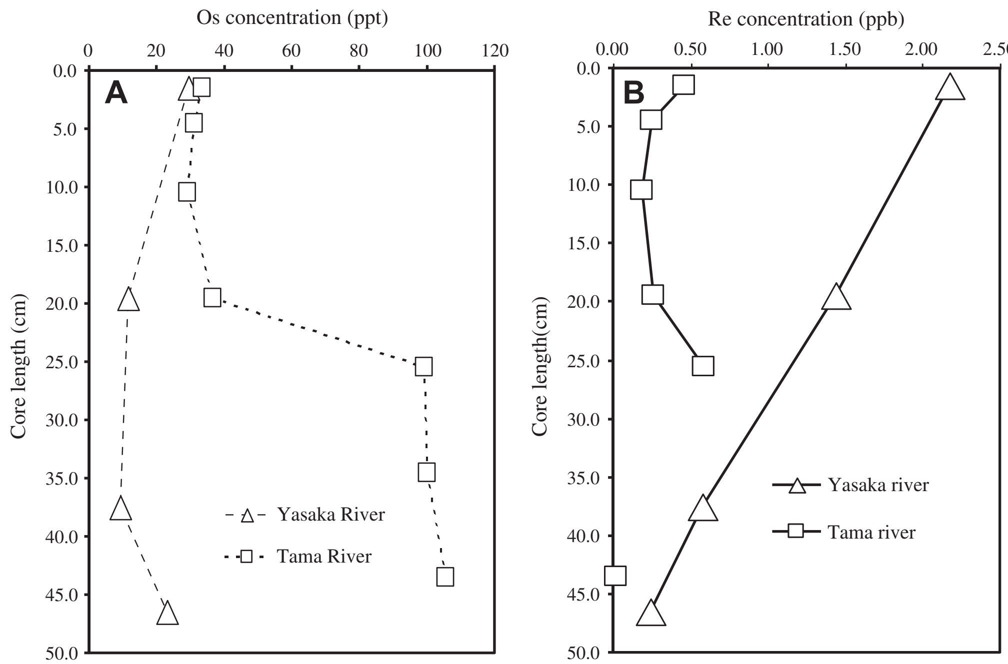

Fig. 2. Vertical distribution of Re and Os in the estuary sediment from the Tama River and Yasaka River estuarine sediments.

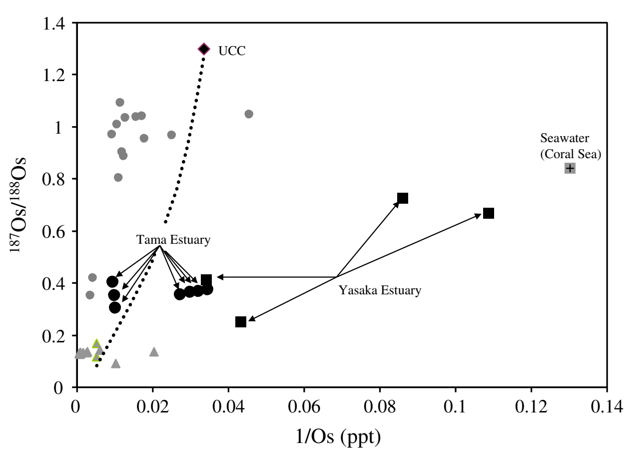

Fig. 3. Osmium isotopic composition vs. 1/Os concentration of the estuarine sediments from the Tama River and Yasaka River, Japan. Data for both Tama and Yasaka rivers were obtained from this study. The data of Boston Harbor cored sediments (gray filled circle) are referenced from Ravizza and Bothner, (1996), the Coral Sea seawater from Martin et al. (2001), and the basalt (triangle) from Schaefer et al. (2000).

classified based on their Os concentrations and $^{187}Os/^{188}Os$ ratios. The samples of Group I contain much higher osmium with lower $^{187}Os/^{188}Os$ ratios whereas the samples of Group II contain lower osmium with elevated $^{187}Os/^{188}Os$ ratios. The $^{187}Os/^{188}Os$ ratios of Group I samples are much closer to the $^{187}Os/^{188}Os$ ratio of UCC. This may indicate the source of osmium is most likely from natural source of surrounding rocks, in which ^{187}Os has been accumulated with geological history and is quite similar to the continental crust rocks. The relatively lower concentration of Os in these samples may be contributed from some weathered rocks in the watershed. A relatively much higher $^{187}Os/^{188}Os$ ratio and lower Os concentration in the middle part of the Yasaka River estuarine sediments strongly suggest that there is less anthropogenic pollution in the Yasaka River than that in the Tama River. Another potential process for the lower concentration of osmium in these sediments may be the washing effect of water that transferred osmium from the sediments into the aquatic phase. Considering the vertical distribution of osmium concentrations and their isotopic ratios, washing effect may play an important role in lowering Os concentration of the Yasaka River estuary sediments than the Tama River estuary because of their different interaction with ocean water. The Yasaka River flows into the open sea directly to the Pacific Ocean with much stronger tidal circulation of seawater from the ocean whereas the Tama River flows into the Tokyo Bay. Tokyo bay is a semi-closed bay with relatively weak influence from the open ocean than the Yasaka estuary area. This should be one of the reasons inducing lower Os concentrations in the Yasaka River estuarine sediment. Another potential influence may be the sediment particle sizes. The cored samples from the Yasaka River estuary consist of fine sands and silts whereas the cored samples from the Tama River estuary mainly consist of silt and clay materials. Clay minerals in the estuarine sediments may play an important role in trapping and absorbing osmium into the sediments (Esser and Turekian, 1988).

Although osmium released from human activity is most likely much less to the Yasaka River than the Tama River, the samples from the uppermost and lowermost intervals of the profile have relatively higher concentration of Os than the middle part, indicating these two layers receive much more Os from human activity because their $^{187}Os/^{188}Os$ ratios are relatively lower, 0.250–0.413, compared with the middle part of the sediments profile. These relatively lower $^{187}Os/^{188}Os$ ratios are also very similar to the upper layer of the Tama River estuarine sediments, indicating relatively more Os from less radiogenetic anthropogenic sources.

Rhenium concentrations in the Yasaka River estuarine sediments range from 0.241–2.18 ppb, much higher than that in the Tama River estuarine sediments. Relatively high concentrations of Re with lower Os concentrations in the sediments may be resulted from the volcanic source because the Yasaka River originates from recently active volcanic mountains that may contain richer rhenium and less osmium (Schaefer et al., 2000).

4.3. Sources of osmium

The ratio of $^{187}Os/^{188}Os$ is changing up on the rocks types because of the production of ^{187}Os by the beta-decay of ^{187}Re whereas ^{188}Os as a stable isotope and constant in nature. Natural osmium has a variable isotopic ratio of $^{187}Os/^{188}Os$ in different geological sittings so that the $^{187}Os/^{188}Os$ ratio can be used as an isotopic chemical tracer to many kinds of geological processes and also some environmental issues such as the anthropogenic osmium in coastal deposits (Esser and Turekian, 1993). For the Tama River estuarine sediments, a sharp increase of Os concentrations in depth around 25 cm and then a constant enrichment of Os kept in the sediments below 25 cm were observed in this study. However, their isotopic ratios, $^{187}Os/^{188}Os$, are within a narrow range for all samples from either the upper part or the lower part of the cored sediments. These factors may indicate that Os in both the lower and upper parts of the cored sediments were derived from the similar source, probably including both natural source and anthropogenic source considering their $^{187}Os/^{188}Os$ ratios. As shown in Fig. 3, the Os in the Tama River estuarine sediments may be mixed mainly from two kinds of sources, less radiogenetic natural source as released from weathered rocks and more radiogenetic anthropogenic source from human activity. It would be similar to the situation around New Haven Harbor (Esser and Turekian, 1993) and Chesapeake Bay (Helz et al., 2000).

For the Yasaka River estuarine sediments, two groups of samples can be distinguished with distinct variations of both Os contents and the $^{187}Os/^{188}Os$ ratios, and their variation is much larger than that of the Tama River (Fig. 3). The vertical distribution of osmium content showed the middle part of the sediment column contained less Os content whereas the topmost and the bottom sediments contained relatively higher Os (Fig. 2). Considering their osmium isotopic ratios, the middle part of the sediments may have more input of Os from natural sources because of their high $^{187}Os/^{188}Os$ ratios (0.670–0.726) whereas the top and the bottom sediments may receive relatively larger portion of osmium from human activity because of the lower $^{187}Os/^{188}Os$ ratios (0.250–0.413). These samples (Group I) are quite similar in both their osmium contents (Os: 23.2–29.4 ppt) and isotopic ratios ($^{187}Os/^{188}Os$: 0.250–0.413) to the upper part of the Tama River estuarine sediments (Os: 29.6–36.7 ppt; $^{187}Os/^{188}Os$: 0.357–0.373). The Yasaka River is considered as one of the cleanest rivers in Japan based on some other geochemical investigations (Kuno et al., 1999). However, this investigation on the osmium concentrations and their isotopic ratios indicates some level of osmium pollution occurred even in the Yasaka River. Input of osmium to estuarine sediments should be popular in river sediments in Japan, especially the coastal areas since most population are located in such coastal areas with intensive industry and transport systems.

Geothermal activity, including volcanic actions and hot springs, may supply extra input of rhenium to the Yasaka River estuarine sediments. The vertical decrease of Re in the sedimentary profile may indicate a more active geothermal activity in the Yasaka River area, where the Aso volcano has been still active. At the same time, numerous hot springs in the river area may also supply more rhenium than river water from normal meteoric precipitation. Fumarolic gas condensates are normally characterized by the high Re content (Tessaline et al., 2008). In addition, pollution from motor engine is another potential source for rhenium in the environment. There is no other heavy metals such as Cu, showed top pollution in the Yasaka River sediments (Kuno et al., 1999), but there is shown distinct enrichment of Re on the top layer in this study, being probably due to modern human activities such as motor engines. Road washing may play an important role for the transportation of Re to the river and the estuary sediments.

There is a large decrease of Re contents with depth in the Yasaka River estuarine sediments whereas less variation of Re is found in the Tama River sediments. The ratio of Re/Os is also sharply different between the Tama River and Yasaka River estuarine sediments, being 22–53 and 352–2167, respectively. Such a big difference is most likely due to the different sedimentary environments, the Tama River sediments may receive much more relatively old rocks and anthropogenic influence while the Yasaka River sediments get strong impact from volcanic activity and relatively younger rocks regarding to their different geographical and geological surroundings: the Tama river flows through a heavily industrialized metropolitan area whereas the Yasaka River flows through a volcanic active district. Relative lower ratio of Re/Os in Tama River estuarine sediments than the Yasaka River may also confirm a larger portion of osmium in the Tama River sediments derived from human activity. These facts may imply that the Re content along with the Re/Os ratios of estuarine sediments may be used as an indicator of the sedimentation and very early diagenetic conditions.

4.4. Fixation of Os in estuary sediment

Osmium can possess seven oxidation states (+1 $\sim$ +8) depending on oxidation–reduction circumstances, thus osmium is one kind of redox sensitive element. Vertical migrations with pore water circulation and bacteria activity during sedimentation and early diagenetic processes may induce the accumulation of Os in the deep sediments. River is the pathway of dissolved elements, and also particles, from continental source areas to the sea; estuarine sediments are normally rich in organic matter with both the continental and aquatic sources. The rapid deposition and accumulation of organic matters in estuary area are largely due to the sharp variation of water salty. Clay minerals are also easily deposited in association with organic matters in estuarine environments. Such a sedimentary environment is very favorable to many kinds of living beings, especially microbes under a warm climate. Thus, biological activity is generally strong in the estuaries, especially the industrialized estuaries of larger rivers such as the Tama River through Tokyo. Human activities supply extra input of organic matters and other nutrients, even extra energy such as warmer water, inducing much more activity of microbes. The estuarine environment is also favorable to keeping the redox condition as relatively much more reducing, under which sulfate reducing bacteria will be active in all the time.

The previous studies showed that there was a significant zone in depth around 25 cm in Tama River estuary for iron sulfide and pyrite precipitation and accumulation, mainly regarding to sulfur reducing bacteria activity (Kuno et al., 1999). The sulfur contents in the Yasaka River estuarine sediments increased with increasing depth, which was the same trend as that in the Tama River estuarine sediments. Hence this trend would be common to estuarine sediments. The increase in the S content with increasing depth is attributable to accumulation of sulfides. In estuarine sediments, sulfate ion from seawater is reduced to hydrogen sulfide through bacterial oxidation of organic matter under anaerobic environments such as a deeper section of sediments; this explains the accumulation of sulfides in the deeper section. Based on such reference, we may explain the osmium distribution in both the sedimentary profiles of the Tama River and the Yasaka River estuaries as follows: sulfide accumulation is likely favorable to an enrichment of Os in the deeper parts of the Tama River sediments where sulfur reducing bacteria is very active.

In addition, vertical profiles of Co, Cr, and Zn in the Tama River estuarine sediments also showed these heavy metals intended to combine with sulfides as shown in Table 2 (Kuno et al., 1999). Increases in the Co and Zn contents with increasing depth in the Tama River estuarine sediments may also be attributable to accumulation of sulfides. A possible source of excess Co and Zn would be also industrial and municipal effluents. However, the Co and

Table 2
Osmium and other elements content in the Tama estuarine sediment samples (data for elements other than Os from Kuno et al., 1997).

Sample ID	Os ppt	Si %	Ti %	Al %	Fe %	Mn %	Ca %	Na %	K %	H %	B ppm	Cl ppm	Eu ppm	Gd ppm	La ppm	S ppm	Sc ppm	Sm ppm	V ppm
T2-15	33.4	28.8	0.332	7.68	3.21	0.042	0.88	1.64	1.81	0.49	39	1690	0.68	2.7	16.4	2100	6.7	3.3	91
T2-14	31.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
T2-12	29.0	28.3	0.33	7.43	3	0.042	0.87	1.63	1.75	0.44	36	1170	0.66	2.3	19.4	1810	11.9	3.6	94
T2-09	36.7	29.4	0.289	7.32	2.95	0.043	0.81	1.62	1.65	0.43	39	1210	0.72	2.7	12.4	2700	12.8	3.2	88
T2-07	99.2	25.1	0.393	8.23	3.5	0.043	0.65	1.56	1.76	0.7	44	1900	0.82	3.2	22.9	5800	18.4	4.5	105
T2-04	100.2	24.1	0.379	8.81	4.14	0.044	0.78	1.46	1.69	1.0	50	2350	0.39	4.1	19.3	10,300	17.6	4.6	124
T2-01	105.5	23	0.464	9.17	4.34	0.048	0.88	1.48	1.62	1.15	51	2750	0.98	4.2	24.7	11,900	16.1	4.8	132

Zn contents in the Yasaka River estuarine sediments are almost constant throughout the cores in spite of sulfide accumulation similar to the Tama River. Vertical distribution of osmium concentration in the Tama River estuarine sediments agrees with sulfide distribution, but not for the Yasaka River. This evidence may indicate that Os in the Tama River estuarine sediments is supplied from industrial and municipal effluents and that its distribution is dependent on fixation as sulfides. The lowest osmium content in the middle part of the core from the Yasaka River may be likely as the natural background level in non-polluted and/or less polluted estuarine sediments in Japan.

Once osmium is fixed in the sediment, it will be stable under anaerobic conditions with less or without remobilization (Yamashita et al., 2007). Reworks of bacteria and reduction by organic matters may be considered as important factors in the environmental applications. Remobilization of bacteria in treatment of radio nuclides is possible (Francise, 1994), even the estuary area for such waste treatment in a proper grade. Organic matter in the core sediments is rich with high concentration of sulfur, iron and selenium, high rate of biological activity such as sulfur reducing bacteria, penetration of pore water from the surface water into estuary sediments. Clay minerals may be another component to absorb Os and other heavy metals into the estuarine sediments.

5. Conclusions

The estuarine sediments from the Tama and Yasaka rivers were analyzed for their rhenium–osmium systematics using refined chemical procedures and NTI-MS measurement in this study. The results showed the supply of anthropogenic Os to the environment in the estuaries of Japan by the concentrations of Os and the isotope ratios $^{187}Os/^{188}Os$, particularly the estuary located in the industrialized urban area such as Tama River, which flows through Tokyo metropolitan area. Even in the far less polluted rivers, some portion of Os by transportation tools may also give impact to the Os in river sediments such as the Yasaka River estuary, which is indicated by the topmost and lower part of the cored profile.

Fixation of Os with other metals sulfides may take an important role in the enrichment of Os to the sediments under reducing condition. Sulfur reducing bacteria in the estuarine sediments may be helpful to enrich these elements under anaerobic conditions. If this were the case, some treatment using bacteria under reducing conditions would be significant to many heavy metals including osmium. In addition, the estuarine sediments should be treated when the sediments are necessary to remove from the estuary areas, especially the industrialized estuaries, to reduce adverse environmental impact.

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