Osmium concentrations and ^{187}Os/^{188}Os ratios of three sediment reference materials

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^{187}Os/^{188}Os ratios and osmium concentrations were analyzed in sedimentary reference materials JSd-3, JMS-1, and JMS-2, issued by the Geological Survey of Japan, using the isotope dilution method with negative thermal ionization mass spectrometry (ID-N-TIMS). The chemical procedures used in this study are based on Carius tube digestion combined with carbon tetrachloride extraction to separate Os. The obtained ^{187}Os/^{188}Os ratios of JSd-3, JMS-1, and JMS-2 were 0.941–1.149, 0.3894–0.465, and 0.747–0.848, respectively, and their Os abundances were 27.07–39.32 ppt, 80.8–106.6 ppt, and 281–317.2 ppt, respectively. Variations among the samples presumably reflect differences in sources and depositional environments. The Os isotopic ratios and abundances were variable within individual samples. The relative 95% confidence intervals of Os concentrations and isotopic ratios were respectively 13% and 6.2% for JSd-3, 15% and 9.8% for JMS-1, and 4.3% and 4.2% for JMS-2. These variations probably reflect the heterogeneity of the original rock of each reference material. Low concentration and high isotope ratio of JSd-3 probably results from the derivation of the original rocks from continental components with low Os abundance and elevated ^{187}Os/^{188}Os. Inputs of anthropogenic Os were inferred in JMS-1, a nearshore sediment from an urbanized locality, which had high Os contents and relatively low Os isotopic ratios. Greatly elevated Os concentrations and high ^{187}Os/^{188}Os in JMS-2, a pelagic clay, may reflect the scavenging of Os in seawater into Mn–Fe oxyhydroxides deposited on the seafloor.

Keywords: Os concentration, Os isotope, sediment reference material, Geochemical Survey of Japan, heterogeneous Os

INTRODUCTION

The Re–Os isotopic system has recently found increasing applications in various fields in Earth science. The Re–Os system is useful for obtaining information on sources of samples because Os isotopic ratios differ between crustal and mantle rocks due to strong Re–Os fractionation during melting and crystallization. This arises from the fact that Os is a highly compatible element whereas Re is slightly incompatible. In addition, Os can possess oxidation states from –2 to +8 depending on environmental redox conditions. Osmium data thus may help constrain values of oxygen fugacity in the depositional environment of sediments (Peucker-Ehrenbrink and Ravizza, 2000). Therefore, the Re–Os system can be applied widely to derive constraints on many geological processes and environmental issues related to sedimentary rocks (e.g., Peucker-Ehrenbrink and Ravizza, 2000).

Siliceous sediments and sedimentary rocks are commonly used for investigations of surface processes and material transportation, specifically in relation to environmental problems. However, the abundances of Os in those materials are usually no more than a few tens of parts per trillion (Shirey and Walker, 1998; Peucker-Ehrenbrink and Ravizza, 2000; Peucker-Ehrenbrink and Jahn, 2001; Kato et al., 2005; Kuroda et al., 2010), requiring great care in chemical treatments of the samples and measurement of isotopes. Although Os data exist for reference igneous rocks, peridotite, and serpentinite (Suzuki and Tatsumi, 2001; Meisel et al., 2001, 2003; Peucker-Ehrenbrink et al., 2003; Meisel and Moser,

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2004a, b), there are very few Re–Os data available for sedimentary reference materials (RMs) (Hattori *et al.*, 2003; Meisel and Moser, 2004b), probably because of the difficulty in measuring Os for sediments and sedimentary rocks with low Os abundance. The recent improvements in analyses of Re and Os isotopes in sediments have made it desirable to obtain Os data for reference materials of modern sediments to aid in interlaboratory comparisons and consistency. In this contribution, we report Os abundance and isotopic compositions of three selected geochemical sedimentary RMs, JSd-3, JMS-1, and JMS-2, which were issued by the Geological Survey of Japan (GSJ). The potential implications are also discussed.

ANALYTICAL PROCEDURES AND REFERENCE MATERIALS

The analytical procedures used for this study are based on Carius tube digestion (Shirey and Walker, 1995) combined with carbon tetrachloride extraction (Cohen and Waters, 1996; Pearson and Woodland, 2000) with a few modifications (Suzuki and Tatsumi, 2001; Kato *et al.*, 2005). Based on results of preliminary tests, many samples were taken of RMs JSd-3, JMS-1, and JMS-2, weighing about 1.0–2.6, 0.5–2.7, and 0.3–2.5 g, respectively. Variable amounts were used in an effort to investigate the effect of inhomogeneities in the RMs. A spike solution containing ^{190}Os (~10–35 μL of 0.95344 ppb Os in 6N HCl) was added, and the mixture was heated in inverse aqua regia in a sealed Carius tube at 225°C for 24 h.

Carbon tetrachloride extraction was used to separate Os from the digested solution, followed by back-extraction in HBr. The Os-bearing HBr was filtrated with an organic solvent filter and then evaporated into a small volume. Os was further purified by microdistillation (Roy-Barman, 1993). The separated Os sample was loaded on a Pt filament (H. Cross Co., Ltd.; US; 99.999%; 0.025 × 1.0 mm), which was ready for mass spectrometry.

Osmium concentrations were determined using the isotope dilution method by negative thermal ionization mass spectrometry (NTI-MS) (Völkening *et al.*, 1991; Creaser *et al.*, 1991). The instrumental measurements were performed using the Finnigan MAT 262 at the Institute of Geothermal Sciences, Kyoto University, and the ThermoFinnigan TRITON at JAMSTEC. Instrumental mass fractionation of Os was corrected by normalizing the ^{192}Os/^{188}Os ratio to 3.08271 (Nier, 1937). The subtraction of oxygen contributions for Os was conducted using the ratios of ^{17}O/^{16}O = 0.0003708 and ^{18}O/^{16}O = 0.002045 (Nier, 1950). Total blank level was 2.0 ± 0.4 pg for Os (2σ, $n = 13$), and the blank ^{187}Os/^{188}Os ratio was 0.298 ± 0.028 (2σ, $n = 13$). An Os standard diluted from a 1000 μg/mL Johnson & Matthey Os ICP standard solu-

Table 1. Basic data for the GSJ RMs of this study

Sample ID	JSd-3	JMS-1	JMS-2
Location	Central Ibaraki	Tokyo Bay	South Pacific
Lithology	Stream sediment	Marine sediment	Marine sediment
Date issued	1989	1999	2000
Chemical composition of major elements (w/w %)			
SiO_2	76.0	53.74	41.78
TiO_2	0.403	0.700	1.40
Al_2O_3	9.908	15.82	14.18
Fe_2O_3	3.057	4.54	10.96
FeO	1.16	2.12	0.04
MnO	0.148	0.102	0.226
MgO	0.117	2.87	3.24
CaO	0.56	2.13	4.68
Na_2O	0.411	4.07	5.79
K_2O	1.97	2.24	2.70
P_2O_5	0.0817	0.180	1.26
tot-C	0.62	1.69	0.39
tot-S	0.399	1.32	0.29
tot-Fe_2O_3	4.368	6.90	10.96

Data from the published references for GSJ reference materials at http://riodb02.ibase.aist.go.jp/geostand/

tion was repeatedly run during the course of the analysis that yielded ^{187}Os/^{188}Os = 0.1071 ± 0.0011 (2σ, $n = 25$).

Basic information about the RMs is shown in Table 1, including sample type, sampling location, and bulk compositions of selected elements. The sampling locations, distribution of particle size, and microscopic images of thin sections of these reference materials are given on the GSJ website (http://riodb02.ibase.aist.go.jp/geostand/gsj1maine.html). In JMS-1 and JMS-2, more than 95% of the grains were smaller than 74 μm, similar to other RMs (Terashima *et al.*, 2002).

Reference material JSd-3 is a stream deposit from central Ibaraki Prefecture of Japan, which was issued as an RM for terrestrial (riverine) sediments in 1989 (Terashima *et al.*, 1990). JMS-1 is a typical terrigenous bay sediment obtained 5 km offshore in northeastern Tokyo Bay near the Tokyo Haneda International Airport. Tokyo Bay has an area of 1000 km^2 and is surrounded by densely populated and highly industrialized areas. About 500 kg of bottom sediment (from 0 to 2 m) comprising muddy, clay-rich, and mostly anoxic facies was dredged in March 1997 (Terashima *et al.*, 2002). The sediment contains a few shell fragments, which were not removed. The RM JMS-2 is composed of a mixture of different polygenetic deep-sea pelagic sediments collected from the Penrhyn Basin, South Pacific Ocean, and issued in 1999 (Terashima *et al.*, 2002). The sediment is mainly dark brown to very dark reddish-brown pelagic clay containing many single crystals and aggregations of zeolite minerals. Both calcareous biogenic and siliceous biogenic components are rather rare because the ocean floor lies below the cal-

Table 2. Os concentrations and isotopic ratios of the GSJ reference materials

Sample ID and run	Sample size (g)	Os concentration (ppt)			$^{187}Os/^{188}Os$		
JSd-3a	2.65106	29.83	±	0.21	1.096	±	0.006
JSd-3b	2.15995	33.0	±	0.5	1.056	±	0.011
JSd-3c	1.95720	30.04	±	0.07	1.149	±	0.002
JSd-3d	2.61954	38.2	±	0.4	0.989	±	0.008
JSd-3e	1.03234	39.32	±	0.28	0.941	±	0.006
JSd-3f	1.03202	30.57	±	0.27	1.023	±	0.010
JSd-3g	1.06455	27.07	±	0.12	1.108	±	0.008
Average		31.6			1.08		
95% CI		4.22			0.0672		
Relative CI			13%			6.2%	
JMS-1a	2.73666	87.7	±	0.5	0.4072	±	0.0005
JMS-1b	0.54661	106.4	±	2.1	0.465	±	0.017
JMS-1c	0.54242	106.6	±	2.4	0.450	±	0.007
JMS-1d	0.53597	95.8	±	0.4	0.3894	±	0.0021
JMS-1e	0.54870	80.8	±	0.3	0.4214	±	0.0024
Average		95.5			0.426		
95% CI		14.1			0.0411		
Relative CI			15%			9.6%	
JMS-2a	2.53142	281	±	5	0.8481	±	0.0013
JMS-2b	2.58584	305	±	3	0.7986	±	0.0021
JMS-2c	2.55101	293.4	±	2.1	0.8324	±	0.0013
JMS-2d	2.56294	298	±	3	0.8173	±	0.0023
JMS-2e	0.33285	317.2	±	0.3	0.762	±	0.010
JMS-2f	0.32818	311.0	±	0.7	0.7470	±	0.0020
JMS-2g	0.34711	284.2	±	0.9	0.824	±	0.003
Average		292			0.823		
95% CI		12.6			0.0345		
Relative CI			4.3%			4.2%	

Errors of Os data are based on 2σ of the mean.
The 95% CIs take the two-sided student t-distribution into account.

cium carbonate compensation depth, and it is also well out of the equatorial high productivity zone. The geological, sedimentary, and bathymetric features of the sediments were reported by Nishimura and Saito (1994).

The procedure for the RM preparation was described in Terashima *et al*., (2002). Information on certified and recommended values of the RMs issued by the GSJ is given on the GSJ website (http://riodb02.ibase.aist.go.jp/geostand/welcome.html). No Os data are shown for JSd-3, JMS-1, and JMS-2. The certification process for JSd-3 and the analytical data used for certification are shown in Imai *et al*. (1996).

RESULTS AND DISCUSSION

The Os concentrations and $^{187}Os/^{188}Os$ ratios measured in the three RMs are listed in Table 2. Repeated analyses showed some variations among different runs of the same RM, even though the sample size for the experiments was varied over a considerable range (Table 2). The Os isotopic ratios ranged from 0.941 to 1.149 (av. 1.08) for JSd-3, from 0.3894 to 0.465 (av. 0.426) for JMS-1, and from 0.7470 to 0.8481 (av. 0.824) for JMS-2. The Os concentrations were 27.07–39.32 (av. 31.6) ppt for JSd-3, 80.8–106.6 (av. 95.5) ppt for JMS-1, and 281–317.2 (av. 292) ppt for JMS-2.

These variations indicate heterogeneous distribution of Os-bearing phases derived from different sources in each sediment sample. The 95% confidence intervals (CIs taking the two-sided students *t*-distribution into account) of the Os concentration data, expressed as relative CIs (RCIs), were 13%, 15%, and 4.3% for JSd-3, JMS-1, and JMS-2, respectively. By comparison, RCIs of RMs with high Os concentrations (more than 1 ppb Os), such as platinum-group element ores and peridotites, are less than 10% (e.g., Meisel *et al*., 2003). However, most RMs with

(a)

Fig. 2. Osmium abundance versus isotopic compositions of the GSJ sediment reference materials. UCC denotes upper continental crust, and Volcanic Source indicates the Os characteristics of volcanic rocks in arc settings.
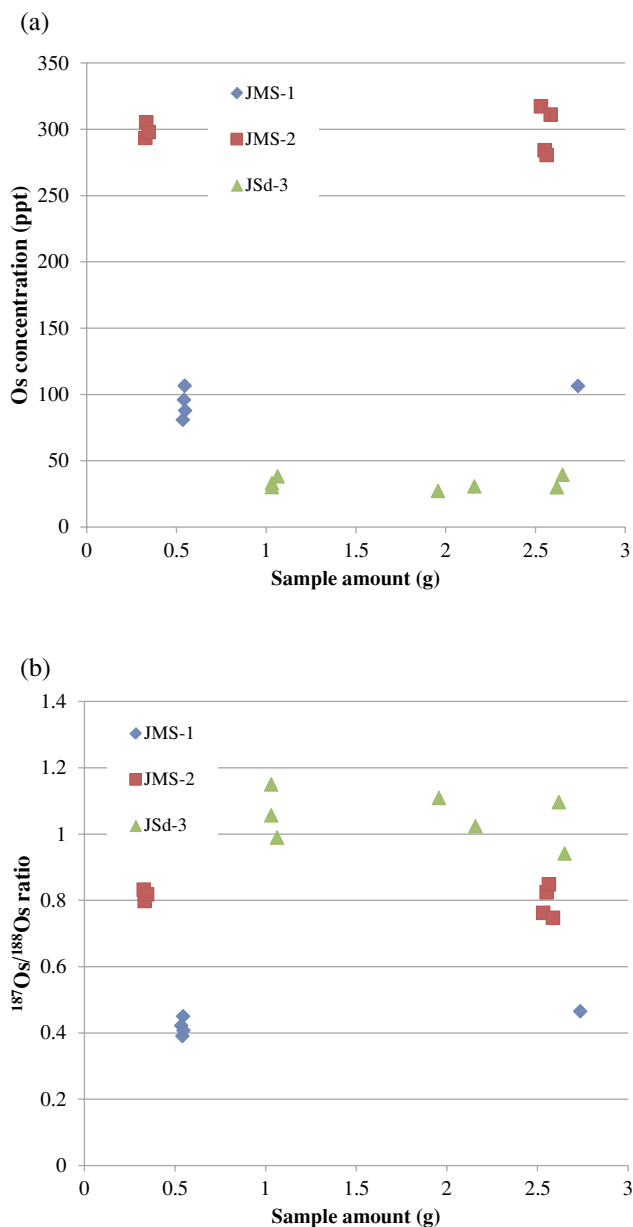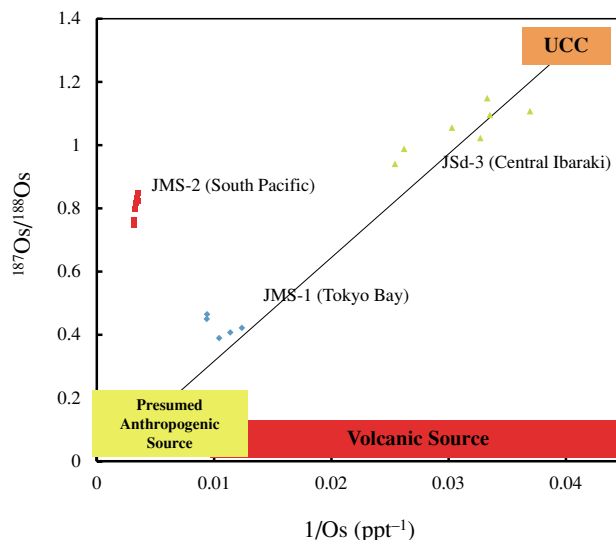
(b)

Fig. 1. Variations in (a) osmium abundance and (b) isotopic composition with sample weights of the GSJ sediment reference materials.

low Os concentrations (<1 ppb) have RCIs above 10%. For example, WGB-1 (Triassic Wellgreen Complex) has published RCIs of 51% (Peucker-Ehrenbrink et al., 2003), 22% (Meisel et al., 2001), and 14% (Meisel and Moser, 2004a); for TDB-1 (diabase from Tremblay Lake, Saskatchewan) the RCI is 10% (Meisel and Moser, 2004a, b), for NIM-D (dunite from the Bushveld Complex) it is 85% (Meisel and Moser, 2004a), for BVHO-1 (Hawaiian basalt) it is 26%, for BCR-2 (Columbia River basalt) it is 14%, for SCo-1 (Cody Shale from Wyoming) it is 13%,

and for BHVO-2 (Hawaiian basalt) it is 25% (Meisel and Moser, 2004b). The RCIs for the RMs in this study are comparable to those in previous studies. Therefore, the relatively high RCIs are unlikely to be caused by analytical problems and likely to derive from heterogeneity of the RMs, as generally found for other RMs.

The RCIs of the Os isotopic compositions (6.2%, 9.6%, and 4.2% for JSd-3, JMS-1, and JMS-2, respectively) are smaller than those of Os concentrations but similar to those shown in other studies (Peucker-Ehrenbrink et al., 2003; Meisel et al., 2003). This variation also points to sample heterogeneity.

Terashima and co-workers have evaluated the homogeneity of RMs JSd-3 (Terashima et al., 1995) and JMS-1 and JMS-2 (Terashima et al., 2002). They found that the relative standard deviations (RSD) of six major elements were less than 1.5% for 100 mg samples of the three RMs. RSDs of six trace elements in JSd-3 were less than 3% for 500 mg samples (Terashima et al., 1990), and those of 20 trace elements in JMS-1 and JMS-2 were less than 3% for 100 mg samples (Terashima et al., 2002). Therefore, the GSJ sedimentary RMs can be considered homogeneous for major and incompatible trace elements. Because RSDs for trace elements were <3% for 500 and 100 mg samples, we think that our sample sizes, ranging from approximately 0.3 to 2.7 g (Table 2), were appropriate for Os analyses.

The Os isotope ratios and concentrations of the three RMs, plotted against the sample weights in Fig. 1, show no significant difference with size of the sample. There-

fore, the RMs are heterogeneous in terms of Os at our largest sample size, even though they are homogeneous for major and incompatible trace elements. It appears that repeated analyses of samples are necessary when sediments or sedimentary rocks are the subject of geochemical studies. In addition, the homogenization of the sample powder prior to analysis is important.

The wide range of the Os concentrations and isotopic ratios among the three RMs may result not only from the types of sediments but also from the geographical and geological environments of the sampling sites, reflecting the sources of each sample.

In our measurements, the stream sediment RM JSd-3 had a lower Os concentration and higher $^{187}Os/^{188}Os$ ratio than the marine sediments of the other two RMs. The seven runs of this material yielded Os concentrations of 27.07–39.32 ppt and isotopic ratios of 0.941–1.149. The concentration range is very close to the average Os abundance of the upper continental crust, 30 ppt (Peucker-Ehrenbrink and Jahn, 2001; Hattori *et al.*, 2003). The $^{187}Os/^{188}Os$ ratios are slightly lower than the upper continental crust average, determined as about 1.2–1.3 in loess from the Loess Plateau and other areas (Peucker-Ehrenbrink and Jahn, 2001) and in Taklimakan Desert sands and glacial moraines from the Kunlun Mountains in western China (Hattori *et al.*, 2003). This slightly lower $^{187}Os/^{188}Os$ ratio may indicate that the Os in the sediments is derived from relatively young crustal rocks. Geologically, the main island of Japan is dominated by Mesozoic and Cenozoic sequences. The radiogenic accumulation of ^{187}Os should be less in Japan than in western China, where rocks range in age from Precambrian to Cenozoic (Li *et al.*, 2004). The mixing line of Os shows that the data from RM JSd-3 lie near the upper continental crust field (Fig. 2). This may suggest a smaller proportion of volcanic Os input in this sample of stream sediment that was collected from central Ibaraki Prefecture.

The sample from RM JMS-1 had a higher concentration and much lower isotopic ratio of Os than JSd-3. This material was collected from Tokyo Bay where both river water and seawater mix with tidal circulation. Some proportion of Os in this reference material may be derived from an anthropogenic source, as described in the United States by Esser and Turekian (1993) in New Haven harbor and by Helz *et al.* (2000) in Chesapeake Bay. Anthropogenic Os has a low isotopic ratio of about 0.14 (Esser and Turekian, 1993; Ravizza and Bothner, 1996), because Os-bearing materials used for industry and vehicles originate from ore deposits with low $^{187}Os/^{188}Os$. Our data thus may indicate that Os in Tokyo Bay sediments comes from a more radiogenic natural source released from weathered rocks and a less radiogenic anthropogenic source. As shown in Fig. 2, data from JMS-1 lie on a smooth mixing line between crustal and anthropogenic sources

of Os, suggesting a predominance of anthropogenic Os. Matsumoto and Yokota (1977) reported high concentrations of heavy metals such as Cd, Cu, Cr, Hg, Mo, Ni, Pb, and Zn in the uppermost sediments of Tokyo Bay due to anthropogenic pollution, which is consistent with our results.

The data for JSd-3 varies and lie along the mixing line between crustal and anthropogenic sources of Os (Fig. 2). Though we proposed above that the slightly low Os isotopic compositions of JSd-3 than that of upper continental crust is possibly resulted from involvement of the volcanic component, anthropogenic Os is another possible source of Os with the low isotopic composition. Even in such case, the proportion of a volcanic or anthropogenic component is small.

JMS-2, the pelagic clay, contained much higher Os concentrations and isotopic ratios than JMS-1, 281–317.2 ppt and 0.7470–0.8481, respectively. The high concentrations of Mn and Fe in JMS-2 (Table 1) likely result from the deposition of a Mn-bearing crust on the surface of the sediments. The Mn–Fe oxyhydroxides that form this crust scavenge Os from seawater (Ravizza *et al.*, 1996). The Os isotopic ratio obtained for JMS-2 is slightly lower than that of the present seawater, which is approximately 1.0 (Sharma *et al.*, 1997; Levasseur *et al.*, 1998; Woodhouse *et al.*, 1999; Burton *et al.*, 1999). The Os isotopic composition of seawater has gradually increased from 0.5 to 1.0 in the last 50 million years, including a pronounced minimum (0.22–0.27) in the late Eocene between 34 and 34.5 Ma and a subsequent rapid increase to approximately 0.6 by 32 Ma (Ravizza and Peucker-Ehrenbrink, 2003). It has been proposed that the increase in seawater $^{187}Os/^{188}Os$ is due to increased continental weathering (Peucker-Ehrenbrink and Ravizza, 2000). The original material of JMS-2 was collected from the seven box cores collected from the Penrhyn Basin, South Pacific Ocean (Terashima *et al.*, 2002). Compared with the description of the piston cores collected in the same area in the cruise, the age of the box core samples ranges in age from Oligocene to recent (Nishimura and Saito, 1994). Therefore, the obtained Os isotopic composition (0.7470–0.8481) is possibly the averaged data of the samples including both recent and the older sediments with the Os isotopic composition lower than that of the present.

CONCLUSIONS

Three sedimentary RMs issued by the Geological Survey of Japan were analyzed for their Os concentration and isotopic ratios. The data obtained are more variable than those from volcanic rock RMs. The multiple sources of sediment deposits may result in heterogeneous distribution of Os-bearing phases, but the data obtained in this study should reliably reflect the different sedimentary

environments. Of the three RMs, JSd-3 had the lowest Os concentration and highest ^{187}Os/^{188}Os ratio, consistent with Os features of continental stream deposits. JMS-1, with its high Os concentration and the lowest ^{187}Os/^{188}Os ratio, likely incorporates Os from anthropogenic sources. JMS-2 had the highest Os concentration and a high ^{187}Os/^{188}Os ratio, consistent with enrichment of Os by Mn–Fe seafloor crust and a rise in Os isotopic ratio in seawater during Cenozoic time.

Our Os data have large variations, and it is not yet possible to propose certified or recommended values. Therefore, we propose that the Os concentrations and isotopic compositions obtained in this study be regarded as "reference values with uncertainties." The relative confidence intervals of the Os data may be used as the uncertainties; for Os concentrations of JSd-3, JMS-1, and JMS-2 these are 13%, 15%, and 4.3% respectively, and for Os isotopic compositions they are 6.2%, 9.6%, and 4.2% respectively.

REFERENCES

Burton, K. W., Bourdon, B., Birck, J.-L., Allegre, C. J. and Hein, J. R. (1999) Osmium isotope variations in the oceans recorded by Fe–Mn crusts. *Earth Planet. Sci. Lett.* **171**, 185–197.

Cohen, A. S. and Waters, G. G. (1996) Separation of osmium from geological materials by solvent extraction for analysis by thermal ionization mass spectrometry. *Anal. Chim. Acta* **332**, 269–275.

Creaser, R. A., Papanastassiou, D. A. and Wasserburg, G. J. (1991) Negative thermal ion mass spectrometry of osmium, rhenium, and iridium. *Geochim. Cosmochim. Acta* **55**, 397–401.

Esser, B. K. and Turekian, K. K. (1993) The osmium isotopic composition of the continental crust. *Geochim. Cosmochim. Acta* **57**, 3093–3104.

Hattori, Y., Suzuki, K., Honda, M. and Shimizu, H. (2003) Re–Os isotope systematics of the Taklimakan Desert sands, moraines and river sediments around the Taklimakan Desert, and of Tibetan soils. *Geochim. Cosmochim. Acta* **67**, 1195–1205.

Helz, G. R., Adelson, J. M., Cornwell, J. C., Hill, J. M., Horan, M. and Walker, R. J. (2000) Osmium isotopes demonstrate distal transport of contaminated sediments in Chesapeake Bay. *Environ. Sci. Technol.* **334**, 2528–2534.

Imai, N., Terashima, S., Itoh, S. and Ando, A. (1996) 1996 compilation of analytical data on nine GSJ geochemical reference samples, "Sedimentary rock series". *Geostand. Newsl.* **20**, 165–216.

Kato, Y., Fujinaga, K. and Suzuki, K. (2005) Major, trace, and rare earth element geochemistry and Os isotopic composition of metalliferous umbers from the late Cretaceous Japanese accretionary complex. *Geochem. Geophys. Geosys.* **6**, Q07004, doi:10.1029/2005GC000920.

Kuroda, J., Hori, R. S., Suzuki, K., Gröcke, D. R. and Ohkouchi, N. (2010) A marine osmium isotopic record across the Triassic–Jurassic boundary from a Pacific pelagic site. *Geology* **38**, 1095–1098, doi:10.1130/G31223.1.

Levasseur, S., Birck, J.-L. and Allegre, C. J. (1998) Direct measurement of femtomoles of osmium and the ^{187}Os/^{188}Os ratio in seawater. *Science* **282**, 272–274.

Li, Z., Song, W., Peng, S., Wang, D. and Zhang, Z. (2004) Mesozoic–Cenozoic tectonic relationships between the Kuqa subbasin and Tian Shan, northwest China: constraints from depositional records. *Sediment. Geol.* **172**, 223–249.

Matsumoto, E. and Yokota, S. (1977) Records of pollution in Tokyo Bay sediments. *Chikyu Kagaku* **11**, 51–57 (in Japanese).

Meisel, T. and Moser, J. (2004a) Reference materials for geochemical PGE analysis: new analytical data for Ru, Rh, Pd, Os, Ir, Pt and Re by isotope dilution ICP-MS in 11 geological reference materials. *Chem. Geol.* **208**, 319–338.

Meisel, T. and Moser, J. (2004b) Platinum-group element and rhenium concentrations in low abundance reference materials. *Geostand. Geoanal. Res.* **28**, 233–250.

Meisel, T., Moser, J., Fellner, N., Wegscheider, W. and Schoenberg, R. (2001) Simplified method for the determination of Ru, Pd, Re, Os, Ir and Pt in chromitites and other geological materials by isotope dilution ICP-MS and acid digestion. *Analyst* **126**, 322–328.

Meisel, T., Reisberg, L., Moser, J., Carignan, J., Melcher, F. and Brugmann, G. (2003) Re–Os systematics of UB-N, a serpentinized peridotite reference material. *Chem. Geol.* **201**, 161–179.

Nier, A. O. (1937) The isotopic constitution of osmium. *Phys. Rev.* **B52**, 885.

Nier, A. O. (1950) A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. *Phys. Rev.* **B77**, 789–793.

Nishimura, A. and Saito, Y. (1994) Deep-sea sediments in the Penrhyn Basin, South Pacific (GH 83-3 area). *Geological Survey of Japan Cruise Report* **23**, 41–60.

Pearson, D. G. and Woodland, S. J. (2000) Solvent extraction/anion exchange separation and determination of PGEs (Os, Ir, Pt, Ru) and Re–Os isotopes in geological samples by isotope dilution ICP-MS. *Chem. Geol.* **165**, 57–107.

Peucker-Ehrenbrink, B. and Jahn, B. M. (2001) Rhenium–osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust. *Geochem. Geophys. Geosys.* **2**, Paper 2001GC000172.

Peucker-Ehrenbrink, B. and Ravizza, G. (2000) The marine osmium isotope record. *Terra Nova* **12**, 205–219.

Peucker-Ehrenbrink, B., Bach, W., Hart, S. R., Blusztajn, J. and Abbruzzese, T. (2003) Rhenium–osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. *Geochem. Geophys. Geosys.*, doi:10.1029/2002GC000414.

Ravizza, G. and Bothner, M. H. (1996) Osmium isotopes and silver as tracers of anthropogenic metals in sediments from Massachusetts and Cape Cod bays. *Geochim. Cosmochim. Acta* **60**, 2753–2763.

Ravizza, G. and Peucker-Ehrenbrink, B. (2003) The marine $^{187}Os/^{188}Os$ record of the Eocene–Oligocene transition: the interplay of weathering and glaciation. *Earth Planet. Sci. Lett.* **210**, 151–165.

Ravizza, G., Martin, C. E., German, C. R. and Thompson, G. (1996) Os isotopes as tracers in seafloor hydrothermal systems: metalliferous deposits from the TAG hydrothermal area, 26′N Mid-Atlantic Ridge. *Earth Planet. Sci. Lett.* **138**, 105–119.

Roy-Barman, M. (1993) Mesure du rapport $^{187}Os/^{188}Os$ dans les basaltes et les peridotites: contribution a la systematique ^{187}Re–^{187}Os dans le manteau. Ph.D. Thesis, Universite de Paris, France.

Sharma, M., Papanastassiou, D. A. and Wasserburg, G. J. (1997) The concentration and isotopic composition of osmium in the ocean. *Geochim. Cosmochim. Acta* **61**, 3287–3299.

Shirey, S. B. and Walker, R. J. (1995) Carius tube digestion for low-blank rhenium–osmium analysis. *Anal. Chem.* **67**, 2136–2141.

Shirey, S. B. and Walker, R. J. (1998) The Re–Os isotope system in cosmochemistry and high-temperature geochemistry. *Annu. Rev. Earth Planet. Sci.*, **26**, 435–500.

Suzuki, K. and Tatsumi, Y. (2001) Osmium concentrations and $^{187}Os/^{188}Os$ ratios of GSJ reference samples, JB-1a, JA-2 and JP-1. *Geochem. J.* **35**, 207–210.

Terashima, S., Okai, T., Ando, A. and Itoh, S. (1990) Homogeneity tests of twenty-four GSJ rock reference samples. *Bull. Geol. Surv. Japan* **41**, 129–138.

Terashima, S., Imai, N. and Ujiie, M. (1995) Examination of analytical errors caused by an uneven element distribution in the analyses of a small amount of rock reference samples. *BUNSEKI KAGAKU* **44**, 965–969.

Terashima, S., Imai, N., Taniguchi, M., Okai, T. and Nishimura, A. (2002) The preparation and preliminary characterization of four new Geological Survey of Japan geochemical reference materials: Soils, JSO-1 and JSO-2; and marine sediments, JMS-1 and JMS-2. *Geostand. Newsl.* **26**, 85–94.

Völkening, J., Walczyk, T. and Heumann, K. G. (1991) Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *Intern. J. Mass Spectrom. Ion Phys.* **105**, 147–159.

Woodhouse, O. B., Ravizza, G. E., Falkner, K. K., Statham, P. J. and Peucker-Ehrenbrink, B. (1999) Osmium in sea water: concentration and isotopic composition vertical profiles in the eastern Pacific Ocean. *Earth Planet. Sci. Lett.* **173**, 223–233.