Electronic Supplementary Information

Precise and accurate analytical method for determination of osmium isotope ratios at the 1–15 pg level by MC-ICP-MS equipped with sparging introduction and high-sensitivity discrete dynode-type ion-counting detectors

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Sample preparation procedure

First, ~0.05 g of JMS-2 (~15 pg Os) and ~1.0 g of JCh-1 (~ 5 pg Os) were weighed for isotopic measurements using CDD detectors, and ~1.0 g of JMS-2 (~300 pg Os) and ~2.0 g of JCh-1 (~10 pg Os) were weighed for isotopic measurements using FC detectors. The weighed samples were spiked with solutions with enriched isotopes of ^{190}Os and ^{185}Re, and then 1 mL of the concentrated HCl and 3 mL of the concentrated HNO_3 that had been prepared by boiling at 190 °C for the sample digestion were added to the Carius tubes while the bottoms of the tubes were cooled with dry ice to prevent oxidization of Os and leakage of volatile OsO_4. The Carius tubes containing the samples and acid were sealed by melting their necks. The samples were then digested at 220 °C for 24 hours. After cooling, the solutions in the Carius tubes were frozen in dry ice to prevent OsO_4 leakage while the tubes were opened. After opening the tubes, the liquid solutions were transferred into 15-mL centrifuge tubes and centrifuged at 3000 rpm for 5 minutes. The supernatant liquids were then transferred into 30-mL PFA vials and diluted with deionized water to bring the total volume of the sample solution to 15 mL. The vials were then used for Os isotope measurements via MC-ICP-MS with sparging introduction. The Os concentrations were calculated by the isotope dilution (ID) method. The Os standards were prepared from the Os standard solution. We oxidized 100 μL of the 10 ng g^{-1} Os standard solution (1 ng Os) by heating the solution with 4 mL of inverse *aqua regia* (HNO_3:HCl = 3:1) in Carius tubes at 220 °C for 24 hours. After opening the tubes, aliquots of the solution necessary to prepare standard samples containing 1, 2, 5, 10, 20, 30, 50, and 100 pg of Os were transferred into 22-mL PFA vials and diluted with diluted inverse *aqua regia* (HNO_3:HCl:deionized water = 3:1:21) to bring the total solution volume to 7 mL. For the Os standard sample containing 1000 pg Os, the oxidized Os standard (1 ng Os) was transferred into 30-mL PFA vials and diluted with deionized water to bring the total solution volume to 15 mL.

After the Os isotope measurements, the sample solutions were heated at 120 °C until the liquid volumes were reduced to ~200 μL. Then 1 mL of 6M HCl was added, and the vials were heated at 80 °C for 30 minutes with their caps closed. The caps were then removed, and the solutions were heated at 120 °C until dryness. The residue was then dissolved with 10 mL of 1M HCl. The Re was purified in a two-step column separation using an anion exchange resin (Muromac AG1-X8 100-200 mesh) as previously described[1,2]. It should be noted that we added a resin-washing step to minimize Re contamination from the resin. The washing involved addition of 6M HNO_3 twice before conditioning the anion exchange resin. After the second column separation, sample solutions were heated at 120 °C until the liquid volume was reduced to ~50 μL and then diluted with deionized water to bring the total volume to 1 mL. Finally, 15 μL of a 100 ng g^{-1} iridium (Ir) standard solution traceable to a chemical standard solution (AccuStandard 1000 μg g^{-1} Ir ICP standard solution) was added into each sample solution to adjust the Ir concentration to ~1.5 ng g^{-1}. The measured ratio of $^{193}Ir/^{191}Ir$ was used to make an external correction for mass bias effects during the measurement. The Re concentrations were calculated by the ID method. In addition to the sample solutions, Re-Ir mixed standard solutions were prepared from the Re and Ir standard solutions. These standard solutions were mixed and diluted with 2 % m m^{-1} HNO_3 prepared from the concentrated HNO_3 and deionized water. In this study, we used a Re-Ir mixed-standard solution containing 1.5 ng g^{-1} of Re and Ir to tune the operating conditions of the MC-ICP-MS and to monitor mass bias effects during the measurement.

Table S1 MC-ICP-MS setup parameters and detector configurations for Os and Re measurements

Component	**Experimental settings**					
	Os by CDD				Os by FC	Re by FC
Sparging chamber	22 or 30 mL PFA vial with 1/8 inch PFA tubing					
Sparging chamber temperature	~20 °C					
Sparging Ar gas flow	~1.1 L/min					
Sample Ar gas flow						~1.1 L/min
Sample solution flow						~100 µL/min
MC-ICP-MS	Neptune Plus (Thermo Fisher Scientific)					
RF-power	1200 W					
Guard electrode	On					
Sampling cone	Ni					
Skimmer cone	Ni H				Ni X	Ni X
Cooling Ar gas	16 L/min					
Auxiliary Ar gas	0.8 L/min					
Detector configurations						
Sub-configuration	1	2	3	4		
IC4 (CDD)	^{190}Os^{a,b}			^{185}Re^{d}		
IC5 (CDD)	^{192}Os^{c}	^{190}Os^{b}		^{187}Os		
IC6 (CDD)			^{190}Os^{b}	^{188}Os^{c}		
L4 (FC)					^{183}W^{e}	^{185}Re^{f}
L3 (FC)					^{185}Re^{d}	^{187}Re
L2 (FC)					^{186}Os	^{189}Os
L1 (FC)					^{187}Os	^{190}Os
Axial (FC)					^{188}Os^{c}	^{191}Ir^{g}
H1 (FC)					^{189}Os	^{192}Os
H2 (FC)					^{190}Os^{a}	^{193}Ir^{g}
H3 (FC)					^{192}Os^{c}	
Acquisition time	4 s	1 s	1 s	4 s	8 s	8 s

[a] Os spike (ID calculation), [b] counting efficiency calibration, [c] Os mass bias correction, [d] Re monitor, [e] W monitor, [f] Re spike (ID calculation), [g] Re mass bias correction.

Table S2 Analytical results of JMC Os standard samples containing 1, 2, 5, 10, 20, 30, 50, 100, and 1000 pg of Os measured with CDD and FC detectors

	Measured by CDD			Measured by FC		
Os amount (pg)	$^{187}Os/^{188}Os$	2 S.D.	2 R.S.D. (%)	$^{187}Os/^{188}Os$	2 S.D.	2 R.S.D. (%)
1	0.10461	0.01825	17.44623			
1	0.10722	0.00994	9.26872			
1	0.10303	0.01349	13.09413			
2	0.10596	0.00751	7.08788			
2	0.10545	0.00935	8.86744			
2	0.10488	0.01023	9.75216			
5	0.10524	0.00608	5.77658			
5	0.10561	0.00483	4.57585			
5	0.10657	0.00525	4.92365			
10	0.10693	0.00323	3.02354			
10	0.10717	0.00302	2.82026			
10	0.10557	0.00384	3.63872			
20	0.10661	0.00301	2.82598			
20	0.10676	0.00266	2.49478			
20	0.10609	0.00228	2.14922			
30	0.10680	0.00239	2.24043	0.10784	0.01240	11.49991
30	0.10672	0.00223	2.09300	0.10746	0.01568	14.58877
30	0.10612	0.00194	1.83146	0.10981	0.01569	14.28953
50				0.10818	0.00765	7.07593
50				0.10546	0.00901	8.53882
50				0.10671	0.00722	6.76481
100				0.10735	0.00409	3.81340
100				0.10702	0.00415	3.87526
100				0.10737	0.00430	4.00225
1,000				0.10680	0.00041	0.37983
1,000				0.10671	0.00050	0.46773
1,000				0.10680	0.00042	0.39048

Table S3 Measurement results of geological reference materials JMS-2 and JCh-1

Sample No.	Sample mass (g)	Re (pg g^{-1})	2 S.D.	2 S.E.	Os (pg g^{-1})	2 S.D.	2 S.E.	^{187}Re/^{188}Os	2 S.D.	2 S.E.	^{187}Os/^{188}Os	2 S.D.	2 S.E.
Measured by CDD													
JMS-2-1	0.052	135.71	5.75	1.07	323.71	2.59	0.49	2.195	0.349	0.066	0.794	0.009	0.002
JMS-2-2	0.056	136.14	4.61	0.86	305.79	2.44	0.46	2.344	0.346	0.065	0.840	0.009	0.002
JMS-2-3	0.060	136.90	3.76	0.70	305.77	2.94	0.55	2.358	0.382	0.071	0.844	0.011	0.002
JMS-2-4	0.054	133.89	4.34	0.82	293.62	3.32	0.62	2.405	0.510	0.095	0.856	0.014	0.003
JMS-2-5	0.052	135.06	5.60	1.03	293.85	3.41	0.64	2.432	0.551	0.104	0.883	0.014	0.003
Average		135.54	2.28	1.02	304.55	24.58	10.99	2.347	0.184	0.082	0.843	0.064	0.029
JCh-1-1	1.0	19.37	0.37	0.07	5.06	0.09	0.02	19.612	0.500	0.094	0.613	0.015	0.003
JCh-1-2	1.0	19.08	0.35	0.06	4.93	0.05	0.01	19.899	0.416	0.077	0.644	0.009	0.002
JCh-1-3	1.0	20.09	0.31	0.06	5.40	0.07	0.01	19.036	0.388	0.072	0.601	0.011	0.002
JCh-1-4	1.0	20.87	0.34	0.06	7.03	0.07	0.01	14.984	0.287	0.053	0.491	0.007	0.001
JCh-1-5	1.0	20.24	0.32	0.06	5.78	0.09	0.02	17.909	0.394	0.073	0.598	0.013	0.002
Average		19.93	1.43	0.64	5.64	1.69	0.75	18.288	3.996	1.787	0.589	0.115	0.052
Measured by FC													
JMS-2-1	1.0	136.74	0.35	0.06	324.58	0.26	0.05	2.211	0.006	0.001	0.813	0.001	0.000
JMS-2-2	1.1	137.14	0.31	0.06	302.77	0.32	0.06	2.393	0.006	0.001	0.868	0.001	0.000
JMS-2-3	1.0	136.89	0.38	0.07	307.59	0.24	0.05	2.346	0.007	0.001	0.851	0.001	0.000
JMS-2-4	1.0	142.49	0.34	0.06	390.73	0.43	0.08	1.885	0.005	0.001	0.686	0.001	0.000
JMS-2-5	1.0	141.40	0.45	0.08	362.09	0.34	0.06	2.030	0.007	0.001	0.734	0.001	0.000
Average		138.93	5.56	2.49	337.55	75.54	33.78	2.173	0.428	0.192	0.790	0.156	0.070
JCh-1-1	2.0	21.04	0.15	0.03	5.34	0.08	0.02	20.185	0.218	0.041	0.612	0.014	0.003
JCh-1-2	1.9	19.67	0.17	0.03	5.63	0.09	0.02	17.832	0.216	0.041	0.581	0.013	0.003
JCh-1-3	1.9	20.09	0.20	0.04	5.56	0.10	0.02	18.445	0.253	0.048	0.581	0.015	0.003
JCh-1-4	1.9	20.71	0.15	0.03	5.88	0.13	0.02	17.932	0.242	0.045	0.563	0.017	0.003
JCh-1-5	1.9	20.58	0.20	0.04	5.64	0.08	0.02	18.630	0.234	0.043	0.588	0.012	0.002
Average		20.42	1.08	0.48	5.61	0.39	0.17	18.605	1.890	0.845	0.585	0.035	0.016
Blank (measured by CDD)													
Blank-1		0.48	0.22	0.04	0.012	0.015	0.003	196	265	51	0.215	0.017	0.075
Blank-2		0.45	0.19	0.04	0.005	0.017	0.003	445	1,506	295	0.285	0.029	0.266
Blank-3		0.51	0.21	0.04	0.003	0.017	0.003	817	4,665	866	0.297	0.030	0.443
Blank-4		0.51	0.16	0.03	0.003	0.014	0.003	765	3,177	623	0.511	0.055	0.587
Blank-5		0.50	0.13	0.02	0.002	0.018	0.003	977	6,975	1,295	0.172	0.016	0.322
Average		0.49	0.05	0.02	0.005	0.008	0.004	640	629	281	0.296	0.261	0.117

The average rows indicate average values, 2 S.D., and 2 S.E. of data from five samples.

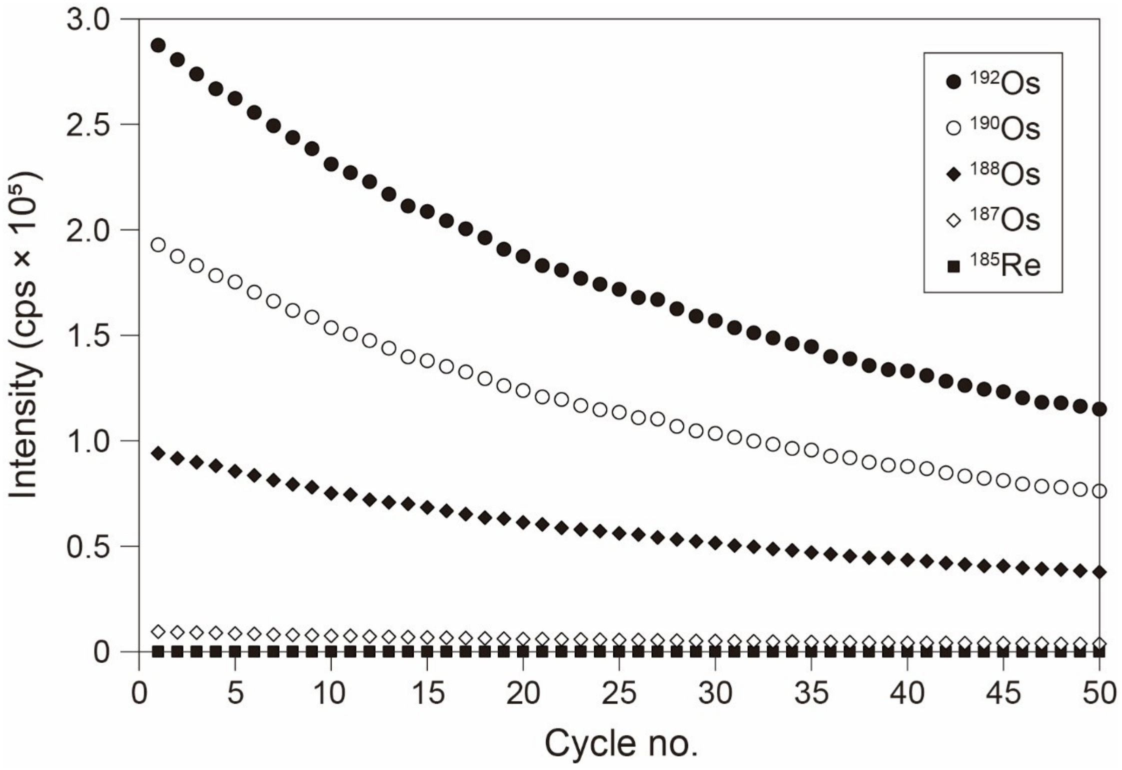

Fig. S1 Exponential decrease of ion intensities of Os isotopes measured with CDD detectors for a single run of 50 cycles for a JMC Os standard sample containing 30 pg of Os.

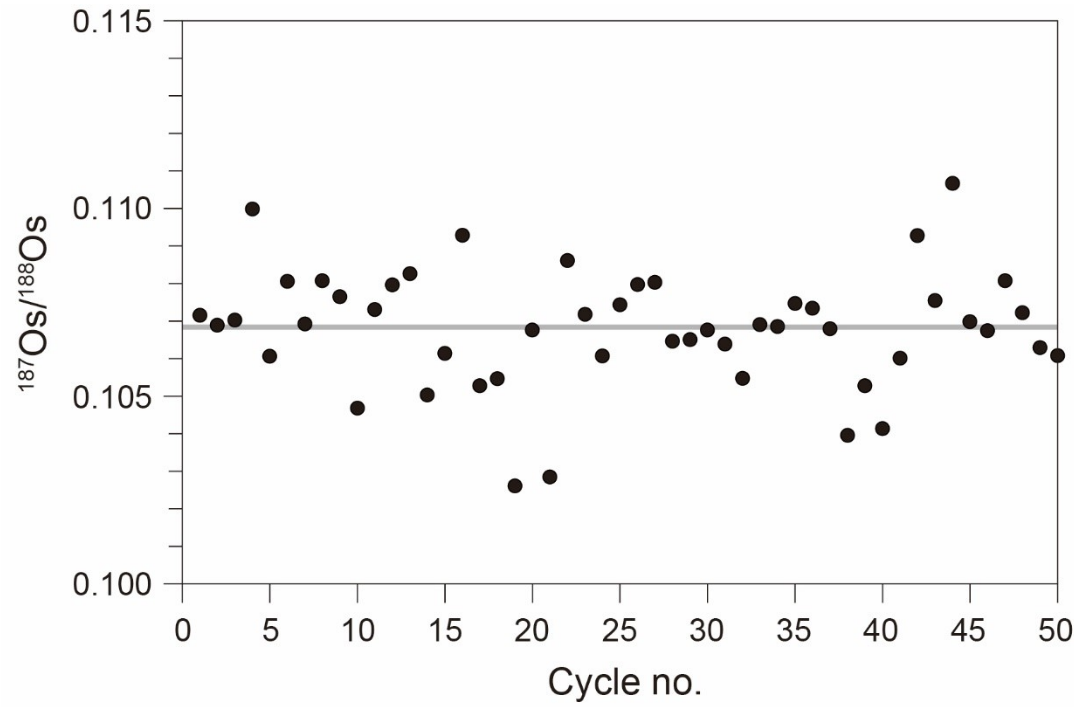

Fig. S2 $^{187}Os/^{188}Os$ ratios in a single run of 50 cycles for an Os standard sample containing 30 pg of Os. The differences of counting efficiencies between CDD detectors and mass bias effects were corrected in each cycle. The isotope ratio varied in value from cycle to cycle, but there was no obvious drift from the beginning to the end of a single run. The gray line indicates the JMC $^{187}Os/^{188}Os$ reference values of 0.106838 determined by N-TIMS[3].

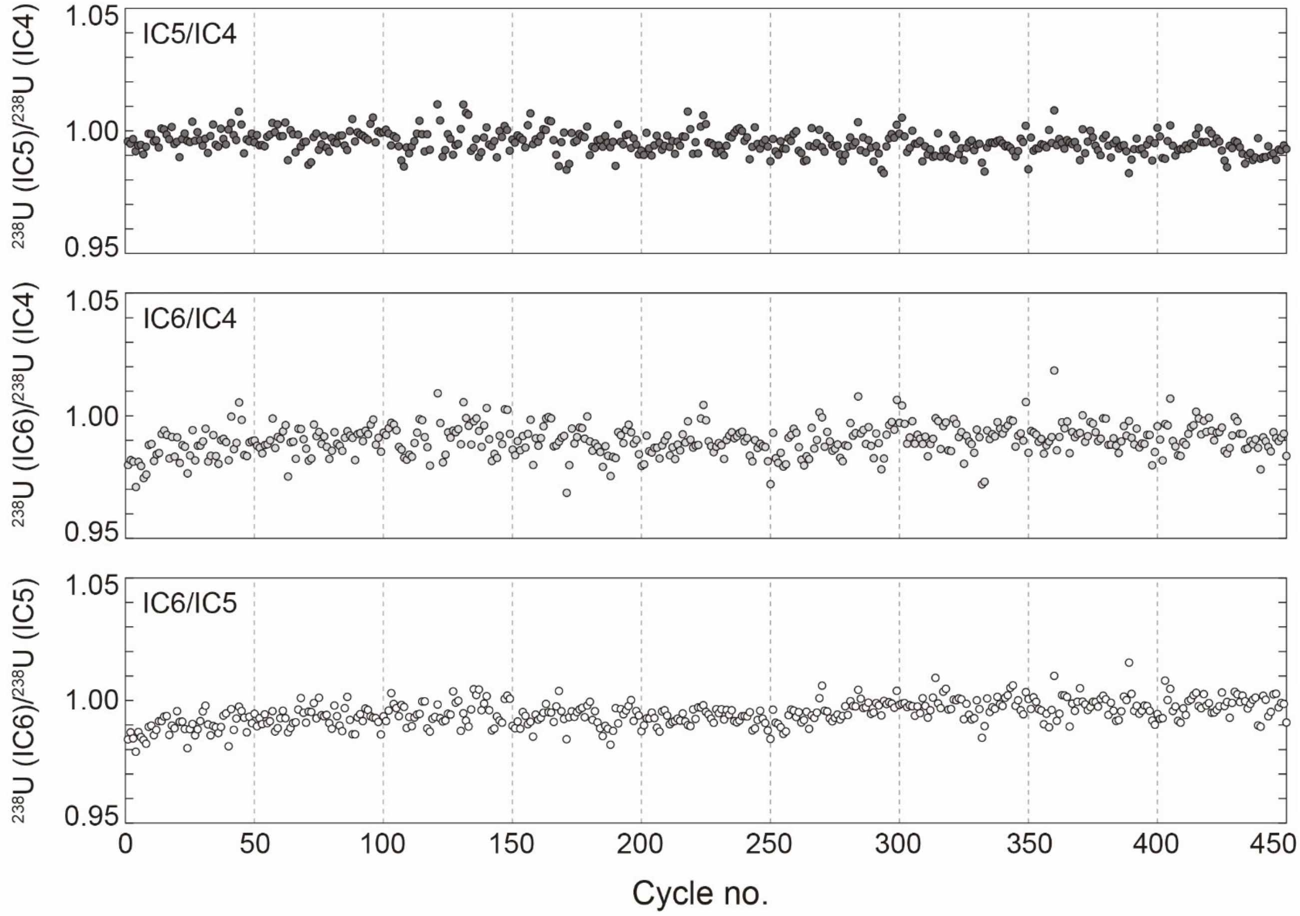

Fig. S3 IC5/IC4, IC6/IC4, and IC6/IC5 values of 450 cycles (nine runs of 50 cycles each) determined by introducing a ^{238}U ion beam to each CDD detector. The amount of U in solution was adjusted to be equivalent to ~300,000 cps of ^{238}U.

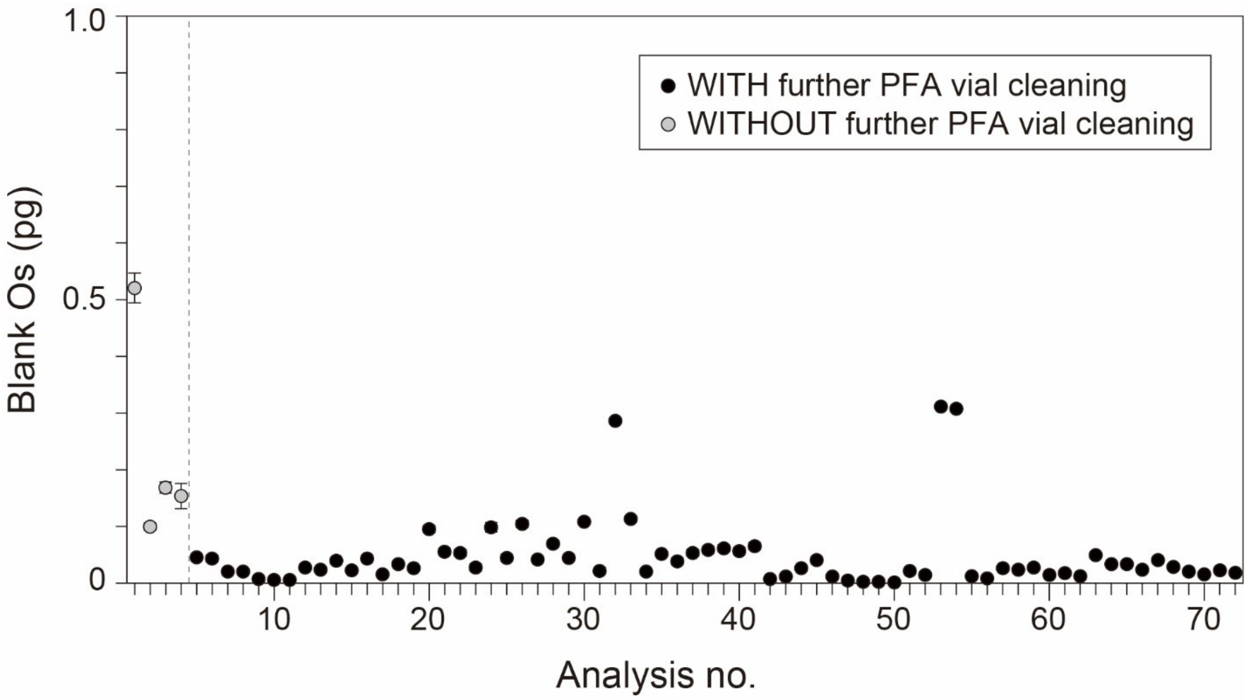

Fig. S4 Record of amounts of Os in procedural blank samples obtained by our method. The first four samples were analyzed in PFA vials without the further cleaning step by heating with HNO_3 solution at 190 °C. The further cleaning step was applied to the rest of the samples. The error bars indicate 2 S.E. Most of the error bars are smaller than the plot symbols.

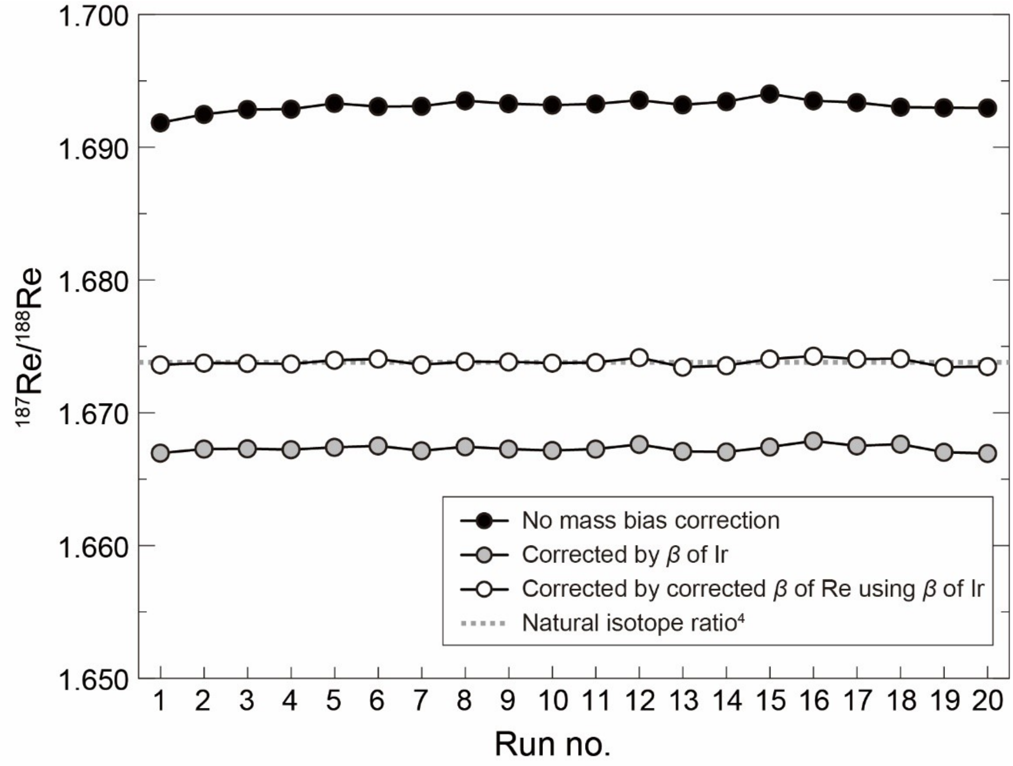

Fig. S5 Results of 20 runs of measurement for a Re-Ir mixed standard solution containing 1.5 ng g^{-1} Re and Ir.

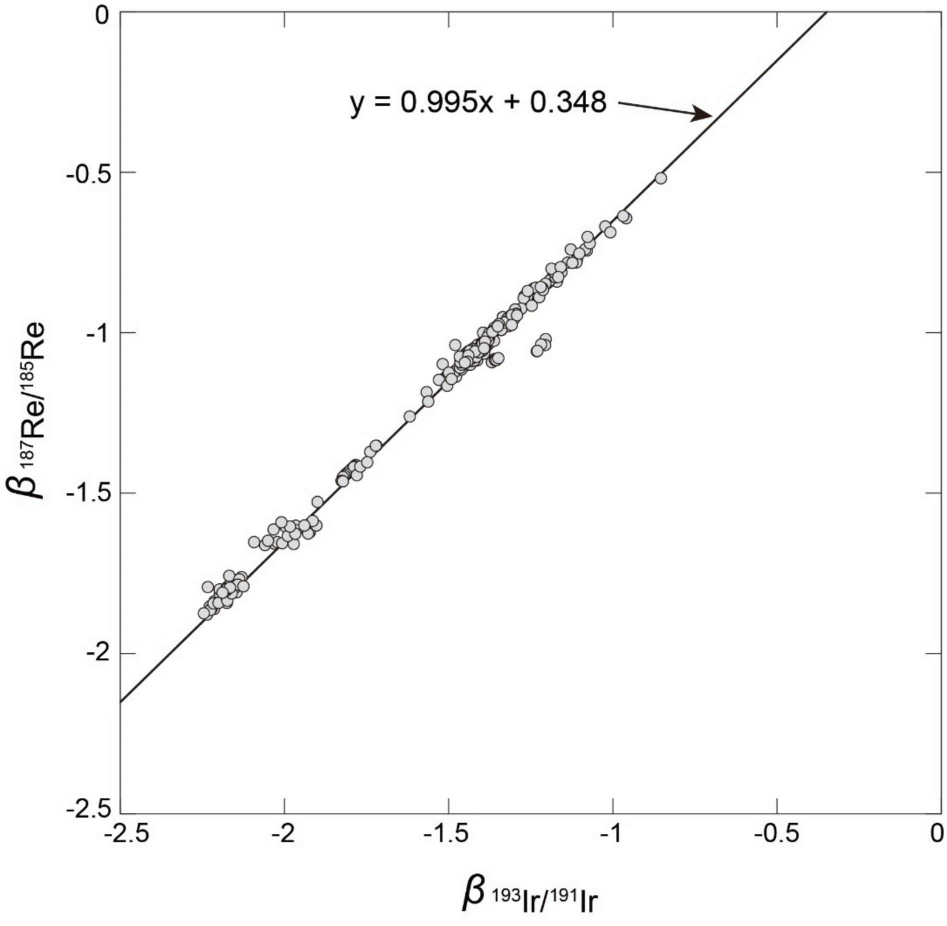

Fig. S6 Scatter diagram of β values for ^{187}Re/^{185}Re and ^{193}Ir/^{191}Ir recorded by 273 runs of the Re-Ir mixed standard solution containing various concentrations of Re and Ir with various instrument settings.

References for the Electronic Supplementary Information

1. T. Nozaki, K. Suzuki, G. E. Ravizza, J.-I. Kimura and Q. Chang, *Geostand. Geoanal. Res.*, 2012, **36**, 131–148, DOI: 10.1111/j.1751-908X.2011.00125.x.
2. J. W. Morgan, D. W. Golightly and A. F. Dorrzapf Jr., *Talanta*, 1991, **38**, 259–265, DOI: 10.1016/0039-9140(91)80045-2.
3. T. Nozaki, K. Suzuki, G. E. Ravizza, J.-I. Kimura and Q. Chang, *Geostand. Geoanal. Res.*, 2012, **36**, 131–148, DOI: 10.1111/j.1751-908X.2011.00125.x.
4. J. R. De Laeter, J. K., Böhlke P. De Bièvre, H. Hidaka, H. S. Peiser, K. J. R. Rosman and P. D. P. Taylor, *Pure Appl. Chem.*, 2003, **75**, 683–800, DOI: 10.1351/pac200375060683.