JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

JAAS Technical Note

Precise determination of Os isotope ratios in 15–4000 pg range using a sparging method using enhanced-sensitivity multiple Faraday collector–inductively coupled plasma–mass spectrometry†

Jun-Ichi Kimura[1], Tatsuo Nozaki[1,2], Ryoko Senda[1], and Katsuhiko Suzuki[1,2]

We have developed a protocol for Os isotope analysis employing a sparging method coupled with an enhanced-sensitivity multiple Faraday collector–inductively coupled plasma–mass spectrometry (MFC-ICP-MS) technique. The enhanced-sensitivity ICP interface with 10^{12} Ω high-gain amplifiers allowed for the stable and precise isotopic ratio analysis of Os by sparging in a very wide concentration range of 15–4000 pg. The analytical reproducibility of Johnson Matthey chemical (JMC) Os standards at 50, 100, 200, 400, and 2000 pg Os were 0.8, 0.5, 0.2, 0.1, and 0.02% within two standard deviations (2SD), respectively. The low Os (50–200 pg) results compared with those obtained by sparging multiple-ion counter (MIC)-ICP-MS and high Os (400–2000 pg) results rivalled those of desolvating nebulisation MFC-ICP-MS and negative thermal ionisation mass spectrometry (N-TIMS). The analysed geological standards consisting of JCh-1 (chert; ~15 pg, *n* = 3), JMS-2 (marine sediment; ~150 pg, *n* = 5), UB-N (lherzoritic peridotite; ~4 ng, *n* = 4), and JP-1 (harzburgitic peridotite; ~3 ng, *n* = 5) showed ^{187}Os/^{188}Os = 0.657 ± 0.065, 0.842 ± 0.053, 0.12752 ± 0.00016, and 0.12071 ± 0.00069 (errors are in 2SD), respectively; these results are comparable with those obtained by MIC-ICP-MS and N-TIMS. The results showed that the sparging method coupled with enhanced-sensitivity MFC-ICP-MS is a strong tool for determining Os isotope ratios in natural samples over a wide range of Os concentrations. Simple sample digestion and low procedural blanks using Carius tube digestion alone without any further element separation provides an additional advantage for Os isotope analysis by the method. (256 words; 4340 words in total)

[1.] Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-Cho, Yokosuka 237-0061, Japan.

[2.] Submarine Resources Research Project (SRRP), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-Cho, Yokosuka 237-0061, Japan.

E-mail: jkimura@jamstec.go.jp; Fax: +81-46-867-9625; Tel.: +81-46-867-9765

† Electronic supplementary information (ESI) available. See DOI:10.1039/c2jaxxxxx

1. Introduction

The sparging method employed for Os isotopic ratio analysis by inductively coupled plasma–mass spectrometry (ICP-MS) is a highly versatile technique owing to its ease of sample preparation.[1-5] Many sample types, including solutions and rock powders, can be digested in an inverse aqua regia solution heated at ~220–240 °C in a Carius pressure vessel tube, allowing for Os oxidation to OsO_4. Oxidised Os is then vaporised by Ar-gas bubbling (sparging)[1, 2, 4] and transferred into the ICP apparatus for mass spectrometric analysis. No chemical separation or purification is needed because of the selective vaporisation of Os from concomitant impurities including Re and W.[1, 2, 4] A low total analytical blank is achievable owing to the need for less acid reagent and fewer chemical steps for sample preparation.[1-4] Instrumental memory effects in ICP-MS are almost nil at a few counts per second (cps),[3] in contrast to very strong Os memories at 0.01–0.03% Os sample signals[6] in normal nebulisation[7] or desolvating nebulisation ICP-MS,[6] in which glassware surfaces and desolvating membrane filters are memory sources.

Sparging ICP-MS analyses of Os isotope ratios using a single-ion counter (IC)[1] or multiple ICs (MICs)[3] have been successfully applied to natural samples with low Os contents (15–200 pg) at a precision of 2–0.5% within two-standard deviations (2SD). For a higher precision analysis, early sparging analyses used multiple Faraday collector (MFC)-ICP-MS;[2, 4] the necessary sample amount for a high precision analysis using this method was 10–50 ng for a precision of 0.38[2]–0.02%[4] (2SD). A large amount of sample (10–50 ng) was necessary for a precision comparable to negative thermal ionisation mass spectrometry (N-TIMS)[2, 4] or enhanced-sensitivity solution MFC-ICP-MS using desolvating nebulisation,[6] both of which required ng quantities of Os for a precision of

0.02% (2SD).

Recent developments in MFC-ICP-MS have improved instrumental sensitivities five-fold by using high-transmission sampler–skimmer cones with a high vacuum at the ICP interface.[8, 9] Use of high-gain amplifiers[10] has also improved both analytical precision and reproducibility in low-signal samples.[9-12] We have applied the enhanced-sensitivity interface and high-gain amplifiers with 10^{12} Ω resistors toward sparging MFC-ICP-MS, and examined the applicability of this method using Johnson Matthey chemical (JMC) Os standard solutions containing 50–2000 pg Os. The results indicated a comparable precision with that of sparging MIC-MC-ICP-MS for 50–200 pg samples and N-TIMS for 400–2000 pg samples. We also report the results obtained from analysis of a chert (JCh-1 (Geological Survey of Japan (GSJ)), containing ~15 pg Os[3, 13]), marine sediment (JMS-2 (GSJ), ~145 pg[3, 14]), and two peridotite geological standard samples (UB-N (Association Nationale de la Recherche Technique (ANRT)), ~4 ng;[15-18] JP-1 (GSJ), ~3 ng[19-22]), demonstrating that the sparging MFC-ICP-MS method described herein is applicable to almost all natural rock samples containing 15–4000 pg Os.

2. Experimental

2.1. Reagents

Ultrapure water (electrical resistivity > 18.2 MΩ cm) produced with a Milli-Q system from Millipore (Massachusetts, USA) was used for sample preparation. HNO_3 (68% m/m) and HCl (20 m/m), used to prepare the inverse aqua regia reagent, were TAMAPURE AA-10 grade from Tama Chemicals Co., Ltd. (Kanagawa, Japan).

2.2. Samples

Diluted Os standard solutions obtained from Johnson Matthey (London, United Kingdom) as chemical standards (JMC; Alfa Aesar 1000 ICP Os standard solution) were used for the experiments. Rock reference materials consisting of two sedimentary and one peridotite sample provided by the Geological Survey of Japan (GSJ) (JCh-1, chert; JMS-2, deep-sea pelagic sediments; JP-1, harzburgite) and a peridotite rock reference material (UB-N) provided by the United State Geological Survey (USGS) were analysed for Os concentration and isotope ratios.

2.3. Sample preparation

The sample preparation method is the same described by Nozaki et al. (2012),[3] which is briefly described below. Powders of the rock reference materials (1–3 g) were weighed, spiked with ^{190}Os, and digested in 4 mL of inverse aqua regia solution in a sealed Carius tube at 220 °C for 24 h (sediments) or at 240 °C for 72 h (peridotites), dependent on material and sample size[3, 20]. After cooling, the Carius tube was frozen in a dry ice–ethanol slush and carefully opened; the solution was then transferred into a 20 mL Teflon perfluoroalkoxy polymer resin (PFA) vessel. After centrifugation to remove residues, the solution was transferred to a 30 mL Teflon PFA vessel and diluted with 15 mL of ultrapure water; this solution was used for sparging MFC-ICP-MS analysis. Os concentration was also determined by the isotope dilution (ID) method combined with Carius tube digestion[23] and sparging.[1, 3, 4]

JMC standard solutions containing 6 ng of total Os were also oxidised in 4 mL of inverse aqua regia solution in a sealed Carius tube under the same conditions as those employed for the rock reference materials, and were split into several solutions containing 50–2000 pg of total Os in of inverse aqua regia solution. After dilution by 7 mL of inverse aqua regia solution in a 20 or 30 mL Teflon PFA vessel, the samples were used for sparging MFC-ICP-MS analysis.[3]

2.4. Sparging MFC-ICP-MS analysis

Os isotope ratios were measured by MFC-ICP-MS (NEPTUNE; Thermo Fisher, Bremen, Germany) combined with preliminary sparging. The 20 or 30 mL Teflon PFA vessel was inserted into the sample Ar gas line of the MFC-ICP-MS instrument.[3] Ar gas was bubbled into and then extracted from the sample solution through a Teflon PFA transfer cap with two transfer ports attached to 1/8 inch Teflon PFA tubing.[1] An empty 20 or 30 mL Teflon PFA vial with a transfer cap was placed between the sample vial and ICP quartz glass torch to trap any liquid droplets that may have escaped from the sample vial during sparging.[2]

The MFC-ICP-MS interface was modified by the addition of a high-efficiency rotary pump,[9, 24] and high-transmission JET sampler and X-skimmer cones[8] were used along with the guard electrode (GE) turned on (electrically connected) to achieve the best instrument sensitivity (~3000 V ppm^{-1} Pb in solution mode using an Aridus desolvating nebuliser).[8, 9] Oxide molecular yield under this condition was monitored by the ^{192}Os/^{192}Os^{16}O ratio, which was < 5%; no mass-independent isotopic fractionation[25, 26] was identified as indicated by the reproducible ^{187}Os/^{188}Os isotope ratios of the JMC standard (^{187}Os/^{188}Os = 0.10688 ± 0.00006 (2SD) for 0.10684–0.10695;[4, 6] see **Section 3.1** below).

Configurations of the Faraday collectors (FCs) and Faraday amplifiers used are given in **Table 1** along with other instrumental settings. The high-gain amplifiers using a 10^{12} Ω resistor were assigned to all Os isotopes apart from the spiked ^{190}Os sample, which used a 10^{11} Ω resistor amplifier. ^{184}W and ^{185}Re were also monitored by FCs with 10^{11} Ω amplifiers (**Table 1**). The isotope ratios of ^{186}Os/^{188}Os, ^{187}Os/^{188}Os, ^{189}Os/^{188}Os,

^{190}Os/^{188}Os, and ^{192}Os/^{188}Os, and Os concentrations were measured by the isotope dilution method (see **†E.S.I. Data Table 1**). The instrumental mass fractionation of Os was corrected for by normalising ^{192}Os/^{188}Os = 3.08271[27] with an exponential law. Slow responses of the Faraday amplifiers[28, 29] were reported for transient signals, but we did not see any problems with the gradual signal decay in Os sparging analyses.

The Os signals were observed to decay to about 30% of their initial intensities after ~15 min of sparging (**Fig. 1f**). Accordingly, adjustment of acquisition time is necessary to obtain the best statistics in isotope ratios, as the signal intensities cannot be adjusted during sparging unlike TIMS, which allows for measurement of ion yield by increasing the temperature of the ionisation filament. We also tested for changes in signal intensities, averages, and two-standard error of the mean (2SE = $2\sigma/\sqrt{n}$: two-standard deviation divided by square route of *n*, where *n* is scan number) values over 100 scans of ~8 s data-acquisition increments (**Fig. 1**). The 2SE values improved by 60 scans and almost stabilised after 60 scans for all concentration levels (see **Fig. 1a–e**). The average values also stabilised after 60 scans, but gradually approached the reference value even after 60 scans. We therefore chose 100 scans for all analytical runs throughout this study, based on these observations.

3. Results and discussion

3.1. JMC Os standard solutions at 50–2000 pg

3.1.1. Precision of ^{187}Os/^{188}Os isotope ratio analysis

The sparging method coupled with enhanced-sensitivity MFC-ICP-MS was first tested by analysing the JMC standard solutions at 50, 100, 200, 400, and 2000 pg. The summary of analysis is given in **Table 2** and all analytical results are given in **†E.S.I.**

Data Table 1.

The typical two-standard error of the mean of JMC solutions containing 50, 100, 200, 400, and 2000 pg Os were 0.8, 0.5, 0.2, 0.1, and 0.02% (2SE%), respectively (**Fig. 2**). Based on the data, 2SE% of this sparging method can be estimated by

$$2\text{SE}\% = 39.4994 \times C_{Os}{}^{-0.97365},$$

where C_{Os} is amount of Os in sample in pg. By using this equation, a 20 pg sample can be measured at 2.1% (2SE%) and 5 ng sample at 0.01% (2SE%). These numbers are comparable with those obtained by desolvating nebulisation MFC-ICP-MS analyses of 1.7% (2SE%) at 20 pg and 0.01% (2SE%) at 5 ng.[6]

It is noteworthy that a 2SE% of < 0.8% was achievable for the ^{187}Os/^{188}Os ratio at an ^{187}Os 0.00016 V signal intensity (**†E.S.I. Data Table 1**). This improvement is obviously attributed to the combination of the enhanced-sensitivity ICP interface and high-gain amplifiers.

3.1.2. Intermediate precision of ^{187}Os/^{188}Os isotope ratio analysis

We analysed JMC standard 3 days over six months. The instrumental sensitivity on day one was inferior, about two times lower than the others due likely to a worn-out skimmer cone. Analyses on the other two days showed reasonable sensitivities. Even so, isotope ratios were indistinguishable between the first day and the others (**Fig. 3** and **Table 2**). The grand average of JMC was ^{187}Os/^{188}Os = 0.10688 ± 0.00006 (2SD) for the 2 ng sample, which is in accordance with the obtained N-TIMS values of ^{187}Os/^{188}Os = 0.10684 ± 0.00002 (IFREE/JAMSTEC; **Table 2**) and 0.10695 ± 0.00002,[4] desolvating nebulisation MFC-ICP-MS values of ^{187}Os/^{188}Os = 0.10686 ± 0.00001 (5 ng),[6] and sparging MFC-ICP-MS values of ^{187}Os/^{188}Os = 0.10694 ± 0.00002 (50 ng)[4] (**Table 2**). Considering the low sample consumption of 2 ng by our method, the precision and reproducibility are comparable with those of desolvating nebulisation MFC-ICP-MS using 5 ng sample amounts (see **Section 3.1.1.** above).

The above-described improvement is reasonable since the enhanced-sensitivity ICP interface improved sensitivity ~3–5 times that of normal (N)-sample–X-skimmer cones. This sensitivity enhancement is comparable with or slightly inferior to that of the Aridus desolvating nebuliser, which exhibits a 5–7-fold improvement in sensitivity.[6] Additional use of high-gain amplifiers helped to improve counting statistics for low signals at ^{187}Os = 6.2 mV (average of 100 scans) from 2 ng Os samples (**Table 2**). This improvement was also obvious by comparison to the initial sparging MFC-ICP-MS results, which required 50 ng JMC samples for the precision/reproducibility found in this study (see **Table 2**).[4]

The sparging method presented here is free from Os memory,[1-3] in contrast to nebulisation MFC-ICP-MS methods in which severe memory effects must be corrected for.[6] N-TIMS is also free from memory; however, a comparable reproducibility with N-TIMS[4] (see **Table 2**) was achieved without chemical isolation of Os after Carius tube digestion, which is requisite of N-TIMS.[2, 3] The sparging method with enhanced-sensitivity MFC-ICP-MS used here is truly advantageous for a simple, rapid, precise, and reproducible Os isotopic analysis technique. Long-term stability of this method is assured by the low oxide yield of Os at the enhanced-sensitivity ICP interface, unlike Nd,[25, 26, 30] and the stable MFC–high-gain amplifier system, both of which were shown to guarantee stable isotope ratio analyses and internal mass-bias corrections over six months (**†E.S.I. Data Table 1**).

3.2. Sedimentary rock reference materials

To demonstrate the application of sparging MFC-ICP-MS, we analysed Os concentrations and ^{187}Os/^{188}Os isotope ratios of standard reference sediment samples. JCh-1 chert and JMS-2 marine sediment were analysed for ~15 pg and ~150 pg levels, respectively.

The Os concentration of JCh-1 was 5.03 ± 0.40 ppt (n = 3, 2SD error), a 7.9% (2SD) error with 0.4–0.8% (2SE) precision in each run. Those of JMS-2 were 289 ± 20 ppt (n = 5, 2SD), a 6.9% (2SD) error with ~0.07% (2SE) precision in each run (**Table 3**). The Os concentrations were in good agreement with 5.71 ± 0.97 ppt by N-TIMS[13] and 5.45 ± 0.51 ppt by MIC-ICP-MS[3] for JCh-1, and 292 ± 13 ppt by N-TIMS[14] and 264 ± 46 ppt by MIC-ICP-MS[3] for JMS-2.

The ^{187}O/^{188}Os ratios of JCh-1 samples were ^{187}O/^{188}Os = 0.657 ± 0.065 (n = 3), a 9.8% (2SD) error with 1.7–2.2% (2SE) in-run precision, and those for JMS-2 samples were ^{187}O/^{188}Os = 0.842 ± 0.053 (n = 5), a 6.3% (2SD) error with 0.12–0.14% (2SE) in-run precision (**Fig. 4**, **Table 3**). These values were also in good agreement with JCh-1 values of ^{187}O/^{188}Os = 0.606 ± 0.044 by N-TIMS[14] and 0.599 ± 0.051 by MIC-ICP-MS,[3] and JMS-2 values of ^{187}O/^{188}Os = 0.823 ± 0.035 by N-TIMS[14] and 0.787 ± 0.036 by MIC-ICP-MS.[3]

Although analysed signals for ^{187}Os were ~0.14 mV for JCh-1 and ~2.76 mV for JMS-2 (overall average of 100 scans, not shown), both analytical precisions and analysed values compared quite well with those by MIC-ICP-MS and N-TIMS using ion counter(s). Such precisions and reproducibilities are sufficient for the measurement of sediments toward applications in earth science. The use of MFC is advantageous to both single IC, which requires frequent gain and dead-time calibrations, and MIC, which requires a standard bracketing measurement protocol.[3]

3.3. Peridotite rock reference materials

We also analysed Os concentrations using isotope dilution method[3, 20] and $^{187}Os/^{188}Os$ isotope ratios of UB-N and JP-1 peridotites at ~3 ng and ~4 ng levels. The Os concentrations of UB-N were 3.62 ± 0.26 ppb ($n = 4$), a 7.2% (2SD%) with 0.3–0.8% (2SE) in-run precision. Those of JP-1 were 3.37 ± 0.22 ppb ($n = 5$), a 6.5% (2SD%) with ~0.03% (2SE%) in-run precision (**Table 3**). The Os concentrations were in good agreement, with 3.51 ± 0.26 ppb,[15] 3.85 ± 0.62 ppb,[17] and 3.53 ± 0.50 ppb[18] by N-TIMS for UB-N and 2.58 ± 0.40 ppb by N-TIMS[20] for JP-1.

The $^{187}O/^{188}Os$ ratios were $^{187}O/^{188}Os = 0.12752 \pm 0.00016$ ($n = 4$), a 0.1% (2SD%) with 0.03–0.07% (2SE%) in-run precision for UB-N, and $^{187}O/^{188}Os = 0.12071 \pm 0.00069$ ($n = 5$), a 0.6% (2SD%) with 0.03–0.05% (2SE%) in-run precision for JP-1 (**Fig. 4**, **Table 3**). These were also in good agreement with $^{187}O/^{188}Os = 0.12722 \pm 0.00076$,[15] 0.12737 ± 0.00064,[17] and 0.12722 ± 0.00054[18] by N-TIMS for UB-N, and $^{187}O/^{188}Os = 0.12055 \pm 0.0007$ by N-TIMS[20] for JP-1.

Analysed signals for ^{187}Os were ~4.40 mV for UB-N and ~4.17 mV for JP-1 (both overall averages of 100 scans, not shown); analytical precisions and analysed values reproduced quite well with those obtained by N-TIMS using Faraday collectors.[15, 18, 20] Such the results are more than sufficient for peridotite analyses in earth science applications. The sparging method described here is advantageous over N-TIMS, which requires the isolation of Os after Carius tube digestion.[15, 18, 20] The additional chemical steps required for N-TIMS results in an increase in Os blanks and preparation time. Total procedural blanks in the sparging method were 0.60–0.78 pg over 6 months with average of 0.69 pg (**Table 3**). The sparging MFC-ICP-MS method with enhanced-sensitivity instrumentation used in this study is anticipated to become a new standard technique in geosciences for Os isotope and concentration analyses.

4. Conclusions

We investigated a sparging MFC-ICP-MS technique for Os concentration and isotope ratio analyses of JMC standards and natural rock reference materials. The combination of enhanced sensitivity achieved by a high-transmission ICP interface and improved counting statistics by use of high-gain amplifiers allowed for the precise and stable analysis of Os using Faraday collectors. Less than 2% (2SE%) precision and reproducibility were achieved for ~15 pg Os samples, and < 0.03% (2SE%) precision and reproducibility were obtained for ~3 ng Os. These results are comparable with those using MIC-ICP-MS and N-TIMS. The improved instrumentation will allow the application of sparging MFC-ICP-MS to almost all of the rock samples analysed in the geosciences field. The simple and low-blank sample preparation (Carius tube digestion only) constitutes a significant improvement in Os isotope analysis throughput, which is the true benefit of this sparging MFC-ICP-MS technique.

Acknowledgments

We thank Dr. C. Bouman of Thermo Fisher Scientific for helpful discussions concerning the properties of MFC-ICP-MS. Discussions with Dr. A. Ishikawa at the University of Tokyo proved useful for the recovery of platinum-group elements during Carius tube digestion. The authors also thank to an anonymous referee and Dr. Bert Muller for their constructive comments, which improved the manuscript.

References

1. D. R. Hassler, B. Peucker-Ehrenbrink and G. E. Ravizza, *Chemical Geology*,

2000, **166**, 1-14. DOI: 10.1016/s0009-2541(99)00180-1.

2. M. Norman, V. Bennett, M. McCulloch and L. Kinsley, *Journal of Analytical Atomic Spectrometry*, 2002, **17**, 1394-1397. DOI: 10.1039/b204518d.

3. T. Nozaki, K. Suzuki, G. E. Ravizza, J.-I. Kimura and Q. Chang, *Geostandards and Geoanalytical Research*, 2012, **36**, 131-148. DOI: 10.1111/j.1751-908X.2011.00125.x.

4. R. Schoenberg, T. F. Nägler and J. D. Kramers, *International Journal of Mass Spectrometry*, 2000, **197**, 85-94. DOI: 10.1016/s1387-3806(99)00215-8.

5. T. Meisel, J. Moser, N. Fellner, W. Wegscheider and R. Schoenberg, *Analyst*, 2001, **126**, 322-328. DOI: 10.1039/b007575m.

6. A. Makishima and E. Nakamura, *Analytical Chemistry*, 2006, **78**, 3794-3799. DOI: 10.1021/ac060183t.

7. T. Hirata, *Journal of Analytical Atomic Spectrometry*, 2000, **15**, 1447-1450. DOI: 10.1039/b006626p.

8. C. Bouman, M. Deerberg and J. B. Schwieters, *Thermo Scientific Application Note*, 2009, **30187**, 1-4.

9. J.-I. Kimura, H. Kawabata, Q. Chang, T. Miyazaki and T. Hanyu, *Geochemical Journal*, 2013, **47**, 369-384.

10. M. E. Wieser and J. B. Schwieters, *International Journal of Mass Spectrometry*, 2005, **242**, 97-115. DOI: 10.1016/j.ijms.2004.11.029.

11. A. Makishima and E. Nakamura, *Journal of Analytical Atomic Spectrometry*, 2010, **25**, 1712-1716. DOI: 10.1039/c0ja00015a.

12. J. M. Koornneef, C. Bouman, J. B. Schwieters and G. R. Davies, *Journal of Analytical Atomic Spectrometry*, 2013, **28**, 749-754. DOI: 10.1039/c3ja30326h.

13. J. Kuroda, R. S. Hori, K. Suzuki, R. G. Darren and N. Ohkouchi, *Geology*, 2010, **38**, 1095-1098. DOI: 10.1130/G31223.1.

14. G. Zheng, K. Suzuki, Y. Miyata and H. Shimizu, *Geochemical Journal*, 2012, **143**, 143-149.

15. H. Becker, M. F. Horan, R. J. Walker, S. Gao, J. P. Lorand and R. L. Rudnick, *Geochimica et Cosmochimica Acta*, 2006, **70**, 4528-4550. DOI: 10.1016/j.gca.2006.06.004.

16. A. Luguet, S. B. Shirey, J.-P. Lorand, M. F. Horan and R. W. Carlson, *Geochimica et Cosmochimica Acta*, 2007, **71**, 3082-3097. DOI: 10.1016/j.gca.2007.04.011.

17. I. S. Puchtel, R. J. Walker, O. B. James and D. A. Kring, *Geochimica et Cosmochimica Acta*, 2008, **72**, 3022-3042. DOI: 10.1016/j.gca.2008.04.006.

18. M. Fischer-Göedde, H. Becker and F. Wombacher, *Chemical Geology*, 2011, **280**, 365-383. DOI: 10.1016/j.chemgeo.2010.11.024.

19. K. Shinotsuka and K. Suzuki, *Analytica Chimica Acta*, 2007, **603**, 129-139. DOI: 10.1016/j.aca.2007.09.042.

20. K. Suzuki and Y. Tatsumi, *Geochemical Journal*, 2001, **35**, 207-210.

21. T. Meisel and J. Moser, *Chemical Geology*, 2004, **208**, 319-338. DOI: 10.1016/j.chemgeo.2004.04.019.

22. N. Shirai, T. Nishio, X. Li, H. Amakawa and M. Ebihara, *Geochemical Journal*, 2003, **37**, 531-536.

23. S. B. Shirey and R. J. Walker, *Analytical Chemistry*, 1995, **67**, 2136-2141. DOI: 10.1021/ac00109a036.

24. J.-I. Kimura, T. Takahashi and Q. Chang, *Journal of Analytical Atomic Spectrometry*, 2013, **28**, 945-957. DOI: 10.1039/c3ja30329b.

25. K. Newman, *Journal of Analytical Atomic Spectrometry*, 2011, **27**, 63-70. DOI: 10.1039/c1ja10222b.

26. K. Newman, P. A. Freedman, J. Williams, N. S. Belshaw and A. N. Halliday, *Journal of Analytical Atomic Spectrometry*, 2009, **24**, 742-751. DOI: 10.1039/b819065h.

27. A. O. Nier, *Physical Review*, 1937, **52**, 885.

28. T. Iizuka, S. M. Eggins, M. T. McCulloch, L. P. J. Kinsley and G. E. Mortimer, *Chemical Geology*, 2011, **282**, 45-57. DOI: 10.1016/j.chemgeo.2011.01.008.

29. T. Hirata, Y. Hayano and T. Ohno, *Journal of Analytical Atomic Spectrometry*, 2003, **18**, 1283-1288.

30. J.-I. Kimura, Q. Chang and H. Kawabata, *Journal of Analytical Atomic Spectrometry*, 2013, **28**, 1522-1529. DOI: 10.1039/c3ja50109d.

Fig. 1 Temporal changes of average and two-standard error of the mean (2SE) values with decaying Os signals over 100 scans in Os isotope measurement at various Os concentrations from 50–2000 pg. Data from †E.S.I. Data Table 1.

Fig. 2 Achievable analytical precision at different concentration levels by sparging MFC-ICP-MS. In-run precision is given by 2SE. Data from †E.S.I. Data Table 1.

Fig. 3 Analytical results of JMC standard solutions. †E.S.I. Data Table 1.

Fig. 4 Analytical results of JCh-1, JMS-2, UB-N, and JP-1 geological reference materials. Data from Table 3.

Table 1 Mass spectrometer setup parameters for sparging MC-ICP-MS.

Table 2 Analytical results of JMC Os standard solution.

Table 3 Analytical results of JCh-1, JMS-2, UB-N, and JP-1.

†E.S.I. Data Table 1 All analytical results of JMC Os standard solutions at various concentrations.

Graphical Abstract Precise determination of Os isotope ratios in 15–4000pg Os by sparging-Multiple Faraday Cup-ICP-MS (14 wards)

Table 1 Mass spectrometer setup parameters for sparging-MC-ICP-MS.

Apparatus	Experimental setting		
Sparging chamber	20 or 30 mL PFA Teflon jar with 1/8 inch Teflon tubing		
Sparging chamber temperature	~22 °C (room temperature)		
Sparging gas flow	~1.2 L/min (Ar)		
MC-ICPMS	Neptune (Thermo Fisher) modified		
RF-power	1200 W		
Guard electrode	on (electronically connected)		
Sampling cone	JET-sample cone (Ni)		
Skimmer cone	X-skimmer cone (Ni)		
Cooling gas (Ar)	13 L/min		
Auxiliary gas (Ar)	1.2 L/min		
Interface vacuum with E2M80	1.2 mbar		
Mass resolution	Low resolution		
Acquisition time	~8 s × 100 scans in one block		
Baseline	On peak (300 s) before block		
Cup configuration			
^{184}W (10^{11} Ω amplifier)	FC	L3	W monitor
^{185}Re (10^{11} Ω amplifier)	FC	L2	Re monitor
^{186}Os (10^{12} Ω amplifier)	FC	L1	
^{187}Os (10^{12} Ω amplifier)	FC	Axial	
^{188}Os (10^{12} Ω amplifier)	FC	H1	Os mass-bias correction
^{189}Os (10^{12} Ω amplifier)	FC	H2	
^{190}Os (10^{11} Ω amplifier)	FC	H3	Os spike
^{192}Os (10^{12} Ω amplifier)	FC	H4	Os mass-bias correction

FC: Faraday cup; amplifiers used are shown in parentheses. Mass bias is corrected for using ^{192}Os/^{188}Os = 3.08271

Table 2 Analytical results of JMC Os standard solution

Day	Wt.(pg)	^{187}Os (V)	^{186}Os/^{188}Os	2SD	^{187}Os/^{188}Os	2SD	^{189}Os/^{188}Os	2SD
Day 1 (*n* = 5)	50	0.00009	0.11888	0.01120	0.10530	0.00785	1.22118	0.00399
Day 3 (*n* = 5)	50	0.00016	0.11946	0.00464	0.10657	0.00161	1.21914	0.00504
Day 4 (*n* = 5)	50	0.00019	0.12031	0.00154	0.10715	0.00141	1.21975	0.00148
G.AVG/ 2SD			0.11955	0.00144	0.10634	0.00189	1.22002	0.00209
Day 1 (*n* = 5)	100	0.00020	0.11971	0.00128	0.10667	0.00192	1.22055	0.00307
Day 3 (*n* = 5)	100	0.00027	0.12037	0.00267	0.10712	0.00062	1.22081	0.00231
Day 4 (*n* = 5)	100	0.00036	0.12038	0.00164	0.10690	0.00091	1.21997	0.00195
G.AVG/ 2SD			0.12015	0.00077	0.10689	0.00045	1.22044	0.00086
Day 1 (*n* = 5)	200	0.00043	0.11962	0.00067	0.10722	0.00129	1.21958	0.00118
Day 3 (*n* = 5)	200	0.00053	0.12013	0.00124	0.10696	0.00066	1.21970	0.00078
Day 4 (*n* = 5)	200	0.00076	0.12034	0.00094	0.10699	0.00064	1.21968	0.00079
G.AVG/ 2SD			0.12003	0.00074	0.10706	0.00028	1.21965	0.00012
Day 1 (*n* = 5)	400	0.00072	0.11992	0.00119	0.10683	0.00073	1.21939	0.00307
Day 2 (*n* = 5)	400	0.00092	0.11969	0.00085	0.10686	0.00073	1.21930	0.00312
Day 3 (*n* = 5)	400	0.00122	0.11988	0.00030	0.10694	0.00012	1.22000	0.00046
Day 4 (*n* = 5)	400	0.00156	0.11978	0.00022	0.10688	0.00017	1.21969	0.00042
G.AVG/ 2SD			0.11982	0.00020	0.10688	0.00010	1.21959	0.00063
Day 1 (*n* = 5)	2000	0.00447	0.11982	0.00009	0.10692	0.00005	1.21985	0.00023
Day 3 (*n* = 5)	2000	0.00620	0.11982	0.00012	0.10687	0.00003	1.21983	0.00012
Day 4 (*n* = 5)	2000	0.00836	0.11983	0.00006	0.10687	0.00001	1.21968	0.00008
G.AVG/ 2SD			0.11982	0.00001	0.10689	0.00006	1.21979	0.00018
IFREE/JAMSTEC								
N-TIMS	100000				0.10684	0.00002		
Makishima and Nakamura (2006); Desolvating nebulisation MFC-ICP-MS; errors in 2SE								
MFC-ICPMS	20		0.12033		0.10715	0.00185	1.22086	
MFC-ICPMS	200		0.11988		0.10662	0.00034	1.21967	
MFC-ICPMS	1000		0.11986		0.10682	0.00017	1.21976	
MFC-ICPMS	5000		0.11982		0.10686	0.00001	1.21977	
MFC-ICPMS	20000		0.11982		0.10686	0.00000	1.21978	
Schoenberg et al. (2000); Sparging MFC-ICP-MS; errors in 2SE								
MFC-ICPMS	50000		0.11983	0.00002	0.10694	0.00002		
N-TIMS	na		0.11983	0.00001	0.10695	0.00002		

AVG: average; G. AVG.: grand average; 2SD: two-standard deviation; 2SE: two-standard error of the mean (2SE = $2\sigma/\sqrt{n}$: two-standard deviation divided by square route of *n*, where *n* is scan number). Note: previous works gave errors in various criteria, all of which have been re-calculated to 2SD.

Table 3 Analytical results of JCh-1, JMS-2, UB-N, and JP-1

Day	Sample	Os (ppt)	2SE	^{187}Os/^{188}Os	2SE	2SE%
Sediment reference material						
[Day 2]	Blank	4.3	0.1	0.078	0.034	-
[Day 2]	JCh-1-1	5.10	0.03	0.645	0.011	1.7
[Day 2]	JCh-1-2	5.19	0.04	0.633	0.014	2.2
[Day 2]	JCh-1-3	4.81	0.02	0.694	0.014	2.0
AVG/ 2SD		5.03	0.40	0.657	0.065	9.8
Nozaki et al. (2012)		5.45	0.51	0.599	0.051	8.5
[Day 2]	JMS-2-1	287.6	0.2	0.8469	0.0012	0.14
[Day 2]	JMS-2-2	277.2	0.2	0.8753	0.0012	0.13
[Day 2]	JMS-2-3	288.7	0.2	0.8429	0.0012	0.14
[Day 2]	JMS-2-4	305.4	0.2	0.8009	0.0010	0.12
[Day 2]	JMS-2-5	289.2	0.2	0.8423	0.0011	0.13
AVG/ 2SD		289	20	0.842	0.053	6.3
Nozaki et al. (2012)		264	46	0.787	0.036	4.6
Day	Sample	Os (ppt)	2SE	^{187}Os/^{188}Os	2SE	2SE%
Peridotite reference material						
[Day 5]	Blank1-2	0.69	0.08	0.155	0.017	-
[Day 5]	UB-N-1	3976.3	0.8	0.12775	0.00004	0.031
[Day 5]	UB-N -2	3675.3	0.8	0.12739	0.00004	0.033
[Day 5]	UB-N -3	3423.8	0.8	0.12743	0.00009	0.073
[Day 5]	UB-N -5	3418.2	0.3	0.12749	0.00004	0.030
AVG/ 2SD		3623	264	0.12752	0.00016	0.13
Meisel et al. (2003) (*n* = 15, 2SD)		3740	520	0.1278	0.0004	0.31
Becker et al. (2006) (*n* = 4, 2SD)		3510	260	0.12737	0.00064	0.50
Luguet et al. (2007) (*n* = 6, 2SD)		3660	300	0.1279	0.0010	0.78
Puchtel et al. (2008) (*n* = 4, 2SD)		3850	620	0.12722	0.00076	0.60
Fisher-Gödde et al. (2011) (*n* = 19, 2SD)		3530	500	0.12722	0.00054	0.42
[Day 5]	Blank1-2	0.69	0.08	0.155	0.017	-
[Day 5]	JP-1-1	3640.4	0.3	0.12024	0.00004	0.030
[Day 5]	JP-1-2	3557.1	0.3	0.12030	0.00004	0.031
[Day 5]	JP-1-3	3213.5	0.3	0.12192	0.00004	0.031
[Day 5]	JP-1-4	3143.6	0.3	0.12046	0.00004	0.030
[Day 5]	JP-1-5	3272.0	0.4	0.12064	0.00006	0.051
AVG/ 2SD		3365	220	0.12071	0.00069	0.57
Suzuki & Tatsumi (2001) (*n* = 2, 2SD)		2580	400	0.12055	0.00070	0.58
Shinotsuka & Suzuki (2007) (*n* = 7, 2SD)		3430	1060	0.120	-	

AVG: average; G. AVG.: grand average; 2SD: two-standard deviation; 2SE: two-standard error of the mean (2SE = 2σ/√n: two-standard deviation divided by square route of *n*, where *n* is scan number); 2SE% is given based on 2SE; Note: all errors are reported in 2SD (2SD%) for reference values and averaged values in this study, otherwise are given by 2SE (2SE%) in single analytical runs.

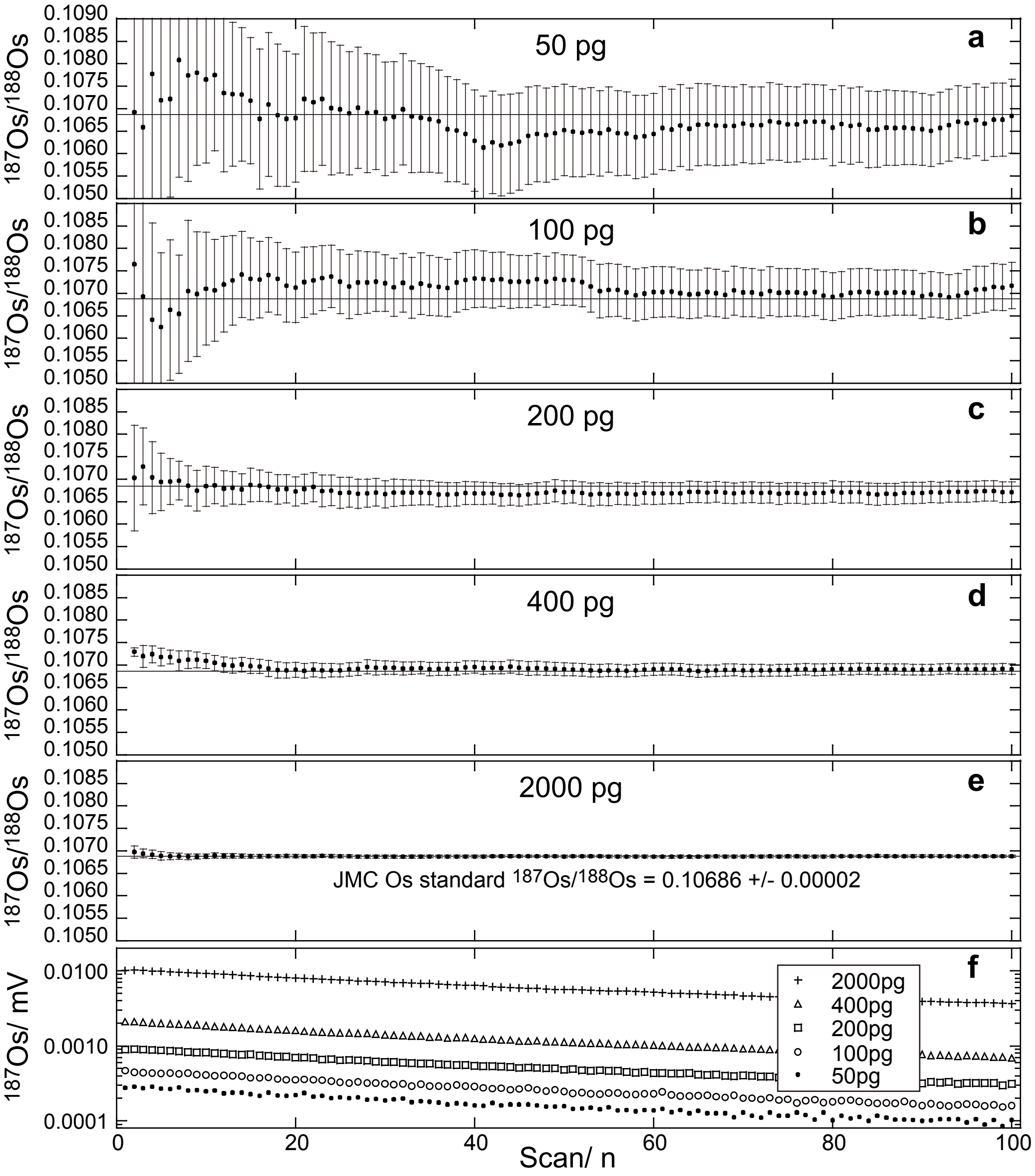

a
50 pg
b
100 pg
c
200 pg
d
400 pg
e
2000 pg
JMC Os standard $^{187}Os/^{188}Os$ = 0.10686 +/- 0.00002
f
2000pg
400pg
200pg
100pg
50pg
$^{187}Os/^{188}Os$
^{187}Os/ mV
0.1090
0.1085
0.1080
0.1075
0.1070
0.1065
0.1060
0.1055
0.1050
0.0100
0.0010
0.0001
0
20
40
60
80
100
Scan/ n

Fig. 1

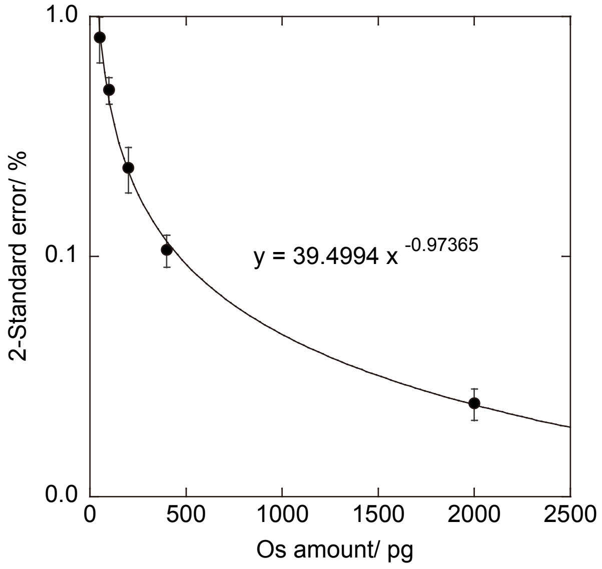

1.0
0.1
0.0
2-Standard error/ %
y = 39.4994 x -0.97365
0
500
1000
1500
2000
2500
Os amount/ pg

Fig. 2

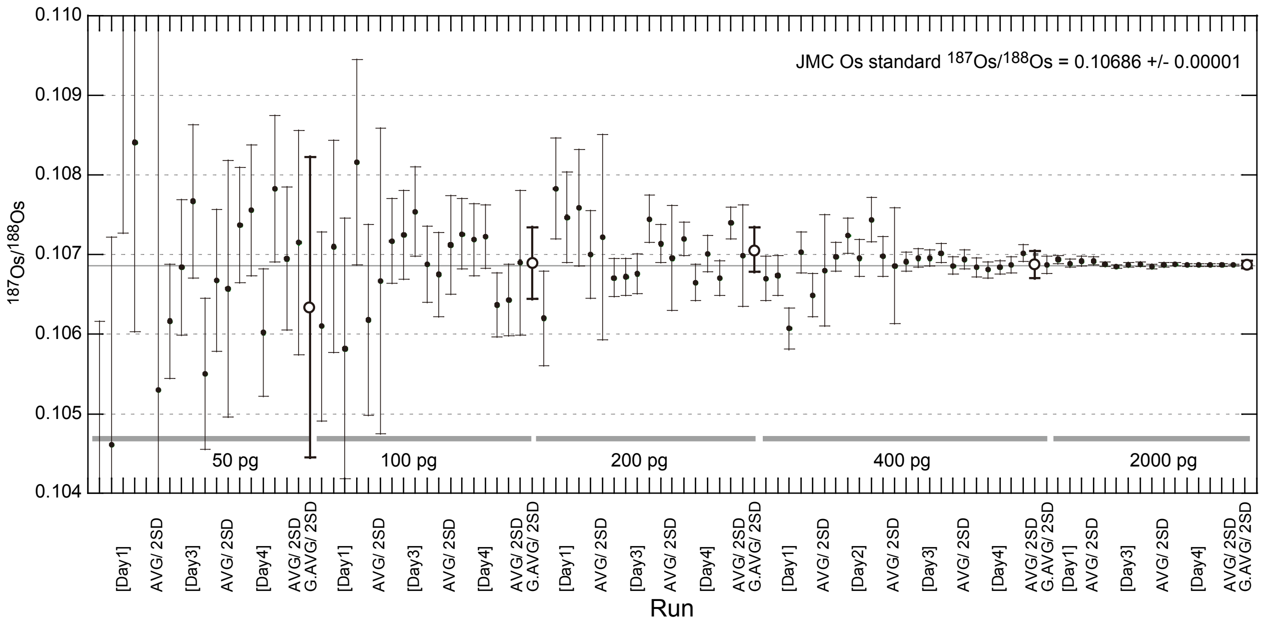

JMC Os standard 187Os/188Os = 0.10686 +/- 0.00001
0.110
0.109
0.108
0.107
0.106
0.105
0.104
187Os/188Os
50 pg
100 pg
200 pg
400 pg
2000 pg
[Day1]
AVG/ 2SD
[Day3]
AVG/ 2SD
[Day4]
AVG/ 2SD
G.AVG/ 2SD
[Day1]
AVG/ 2SD
[Day3]
AVG/ 2SD
[Day4]
AVG/ 2SD
G.AVG/ 2SD
[Day1]
AVG/ 2SD
[Day3]
AVG/ 2SD
[Day4]
AVG/ 2SD
G.AVG/ 2SD
[Day1]
AVG/ 2SD
[Day2]
AVG/ 2SD
[Day3]
AVG/ 2SD
[Day4]
AVG/ 2SD
G.AVG/ 2SD
[Day1]
AVG/ 2SD
[Day3]
AVG/ 2SD
[Day4]
AVG/ 2SD
G.AVG/ 2SD
Run

Fig. 3

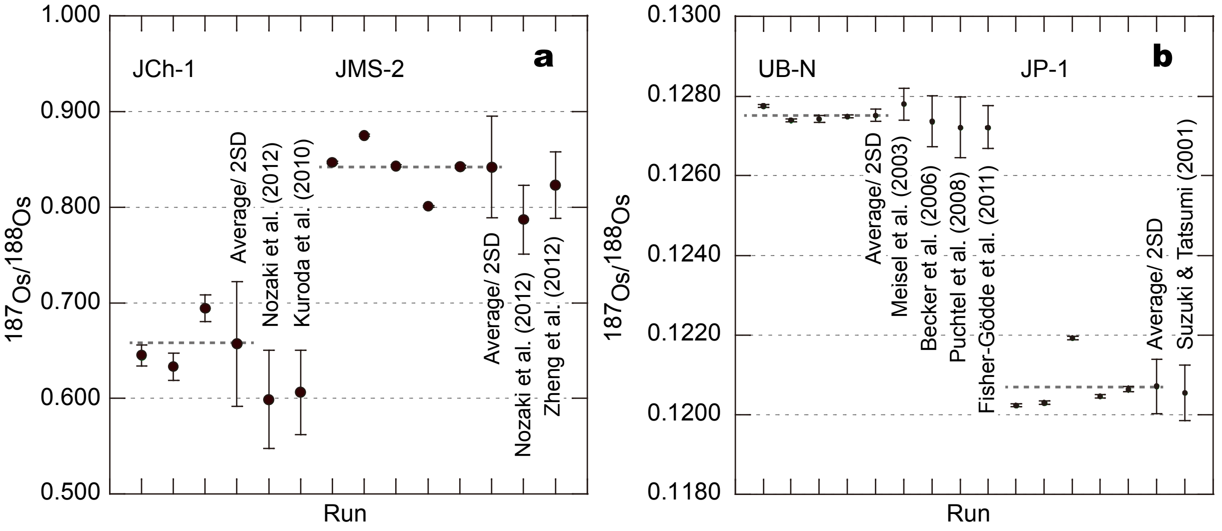
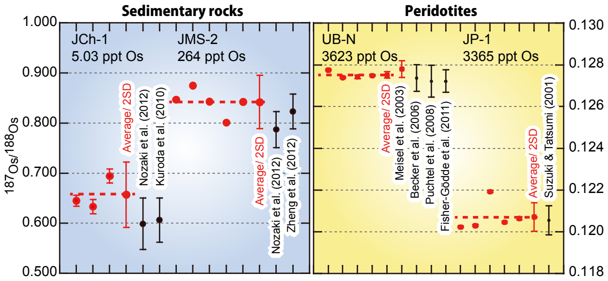

a
JCh-1
JMS-2
$^{187}Os/^{188}Os$
1.000
0.900
0.800
0.700
0.600
0.500
Average/ 2SD
Nozaki et al. (2012)
Kuroda et al. (2010)
Average/ 2SD
Nozaki et al. (2012)
Zheng et al. (2012)
Run
b
UB-N
JP-1
$^{187}Os/^{188}Os$
0.1300
0.1280
0.1260
0.1240
0.1220
0.1200
0.1180
Average/ 2SD
Meisel et al. (2003)
Becker et al. (2006)
Puchtel et al. (2008)
Fisher-Gödde et al. (2011)
Average/ 2SD
Suzuki & Tatsumi (2001)
Run

Fig. 4



Graphical abstract
Precise determination of Os isotope ratios in 15–4000pg Os by sparging-Multiple Faraday Cup-ICP-MS

†E.S.I. Data Table 1 All analytical results of JMC Os standard solution at various concentrations

Day	Conc. (pg)	^{187}Os/ V	^{188}Os/ V	^{190}Os/ V	^{192}Os/ V	^{186}Os/^{188}Os	2SE	^{187}Os/^{188}Os	2SE	^{189}Os/^{188}Os	2SE	^{190}Os/^{188}Os	2SE	^{192}Os/^{188}Os	2SE
[Day1]	50	0.00007	0.00068	0.00136	0.00213	0.12435	0.00233	0.10264	0.00352	1.22013	0.00223	1.97856	0.00281	3.12023	0.00724
[Day1]	50	0.00009	0.00088	0.00175	0.00273	0.12195	0.00180	0.10461	0.00261	1.22400	0.00205	1.98825	0.00279	3.11985	0.00548
[Day1]	50	0.00009	0.00079	0.00157	0.00246	0.12211	0.00164	0.11014	0.00287	1.22254	0.00229	1.98191	0.00288	3.10842	0.00599
[Day1]	50	0.00009	0.00087	0.00174	0.00270	0.11475	0.00167	0.10841	0.00238	1.21978	0.00226	1.98519	0.00304	3.09954	0.00802
[Day1]	50	0.00008	0.00082	0.00164	0.00256	0.11122	0.00265	0.10072	0.00317	1.21942	0.00238	1.98512	0.00289	3.10147	0.00630
AVG/ 2SD						0.11888	0.01120	0.10530	0.00785	1.22118	0.00399	1.98381	0.00738	3.10990	0.01965
[Day3]	50	0.00018	0.00168	0.00337	0.00528	0.12002	0.00102	0.10616	0.00072	1.22125	0.00094	1.98490	0.00178	3.14040	0.00306
[Day3]	50	0.00016	0.00155	0.00309	0.00484	0.12200	0.00094	0.10684	0.00085	1.21986	0.00114	1.98262	0.00184	3.12959	0.00308
[Day3]	50	0.00015	0.00139	0.00278	0.00437	0.12052	0.00121	0.10767	0.00096	1.21989	0.00123	1.97939	0.00190	3.13991	0.00344
[Day3]	50	0.00015	0.00140	0.00280	0.00439	0.11579	0.00163	0.10550	0.00095	1.21992	0.00125	1.98231	0.00214	3.13284	0.00389
[Day3]	50	0.00015	0.00139	0.00278	0.00435	0.11899	0.00122	0.10668	0.00089	1.21476	0.00144	1.97932	0.00198	3.11828	0.00428
AVG/ 2SD						0.11946	0.00464	0.10657	0.00161	1.21914	0.00504	1.98171	0.00474	3.13220	0.01810
[Day4]	50	0.00021	0.00194	0.00388	0.00609	0.11960	0.00093	0.10737	0.00072	1.21946	0.00093	1.98336	0.00132	3.13608	0.00236
[Day4]	50	0.00019	0.00181	0.00362	0.00567	0.12080	0.00111	0.10756	0.00082	1.22021	0.00115	1.98253	0.00143	3.13384	0.00289
[Day4]	50	0.00019	0.00181	0.00362	0.00566	0.12119	0.00089	0.10602	0.00080	1.21884	0.00132	1.98417	0.00166	3.13010	0.00261
[Day4]	50	0.00018	0.00171	0.00342	0.00537	0.12054	0.00110	0.10783	0.00092	1.22075	0.00120	1.98084	0.00153	3.14264	0.00301
[Day4]	50	0.00018	0.00170	0.00340	0.00533	0.11941	0.00127	0.10695	0.00090	1.21948	0.00115	1.98089	0.00163	3.13980	0.00291
AVG/ 2SD		0.00019	0.00179	0.00359	0.00563	0.12031	0.00154	0.10715	0.00141	1.21975	0.00148	1.98236	0.00296	3.13649	0.00984
G.AVG/ 2SD						0.11955	0.00144	0.10634	0.00189	1.22002	0.00209	1.98263	0.00215	3.12620	0.02855
[Day1]	100	0.00020	0.00192	0.00383	0.00596	0.11870	0.00064	0.10610	0.00119	1.22076	0.00108	1.98379	0.00115	3.09939	0.00277
[Day1]	100	0.00020	0.00189	0.00376	0.00586	0.11977	0.00072	0.10710	0.00133	1.22309	0.00107	1.98487	0.00157	3.10333	0.00291
[Day1]	100	0.00019	0.00182	0.00363	0.00565	0.11985	0.00096	0.10582	0.00164	1.21923	0.00108	1.98452	0.00152	3.09738	0.00332
[Day1]	100	0.00020	0.00185	0.00369	0.00575	0.12049	0.00094	0.10816	0.00129	1.22007	0.00119	1.98351	0.00154	3.09913	0.00315
[Day1]	100	0.00019	0.00183	0.00364	0.00566	0.11973	0.00079	0.10618	0.00120	1.21957	0.00096	1.98446	0.00132	3.09512	0.00376
AVG/ 2SD						0.11971	0.00128	0.10667	0.00192	1.22055	0.00307	1.98423	0.00112	3.09887	0.00604
[Day3]	100	0.00027	0.00251	0.00503	0.00789	0.12062	0.00072	0.10717	0.00053	1.22026	0.00077	1.98400	0.00100	3.14152	0.00193
[Day3]	100	0.00028	0.00261	0.00522	0.00818	0.12156	0.00061	0.10725	0.00056	1.22174	0.00080	1.98333	0.00107	3.13672	0.00193
[Day3]	100	0.00026	0.00243	0.00487	0.00764	0.12047	0.00079	0.10754	0.00056	1.22128	0.00077	1.98453	0.00120	3.14317	0.00195
[Day3]	100	0.00027	0.00257	0.00514	0.00805	0.12109	0.00062	0.10688	0.00048	1.21905	0.00058	1.98508	0.00097	3.13660	0.00152
[Day3]	100	0.00026	0.00248	0.00497	0.00779	0.11811	0.00057	0.10675	0.00053	1.22173	0.00070	1.98355	0.00109	3.14005	0.00208
AVG/ 2SD						0.12037	0.00267	0.10712	0.00062	1.22081	0.00231	1.98410	0.00143	3.13961	0.00583
[Day4]	100	0.00037	0.00346	0.00692	0.01084	0.12103	0.00047	0.10726	0.00044	1.21945	0.00062	1.98407	0.00074	3.13664	0.00144
[Day4]	100	0.00035	0.00331	0.00663	0.01040	0.11915	0.00061	0.10719	0.00045	1.22069	0.00062	1.98426	0.00085	3.13875	0.00128
[Day4]	100	0.00037	0.00344	0.00688	0.01078	0.12098	0.00064	0.10723	0.00040	1.21951	0.00051	1.98335	0.00093	3.13472	0.00118
[Day4]	100	0.00036	0.00342	0.00685	0.01074	0.12082	0.00064	0.10637	0.00040	1.21893	0.00051	1.98254	0.00093	3.13538	0.00118
[Day4]	100	0.00035	0.00331	0.00664	0.01040	0.11991	0.00053	0.10643	0.00045	1.22128	0.00070	1.98550	0.00088	3.14097	0.00174
AVG/ 2SD		0.00036	0.00339	0.00678	0.01063	0.12038	0.00164	0.10690	0.00091	1.21997	0.00195	1.98394	0.00220	3.13729	0.00514
G.AVG/ 2SD						0.12015	0.00077	0.10689	0.00045	1.22044	0.00086	1.98409	0.00029	3.12526	0.04577

Table 1. Continue

Day	Conc. (pg)	^{187}Os/ V	^{188}Os/ V	^{190}Os/ V	^{192}Os/ V	^{186}Os/^{188}Os	2SE	^{187}Os/^{188}Os	2SE	^{189}Os/^{188}Os	2SE	^{190}Os/^{188}Os	2SE	^{192}Os/^{188}Os	2SE
[Day1]	200	0.00043	0.00406	0.00807	0.01258	0.11925	0.00046	0.10620	0.00059	1.21938	0.00048	1.98258	0.00069	3.09429	0.00192
[Day1]	200	0.00044	0.00405	0.00806	0.01255	0.11996	0.00042	0.10783	0.00063	1.22009	0.00066	1.98601	0.00061	3.09561	0.00156
[Day1]	200	0.00042	0.00396	0.00788	0.01227	0.11995	0.00037	0.10747	0.00057	1.21949	0.00042	1.98478	0.00066	3.09345	0.00187
[Day1]	200	0.00042	0.00389	0.00772	0.01203	0.11933	0.00040	0.10759	0.00073	1.22020	0.00056	1.98354	0.00065	3.09478	0.00173
[Day1]	200	0.00043	0.00399	0.00793	0.01236	0.11961	0.00040	0.10700	0.00055	1.21875	0.00046	1.98286	0.00061	3.09183	0.00196
AVG/ 2SD						0.11962	0.00067	0.10722	0.00129	1.21958	0.00118	1.98395	0.00286	3.09399	0.00288
[Day3]	200	0.00053	0.00496	0.00992	0.01555	0.12008	0.00031	0.10671	0.00024	1.21976	0.00047	1.98216	0.00061	3.13491	0.00112
[Day3]	200	0.00053	0.00502	0.01004	0.01575	0.11978	0.00033	0.10672	0.00023	1.21980	0.00039	1.98300	0.00053	3.13554	0.00085
[Day3]	200	0.00053	0.00495	0.00991	0.01553	0.12104	0.00036	0.10676	0.00025	1.21909	0.00039	1.98272	0.00049	3.13572	0.00101
[Day3]	200	0.00051	0.00478	0.00956	0.01499	0.11940	0.00041	0.10745	0.00030	1.22018	0.00034	1.98408	0.00061	3.13819	0.00103
[Day3]	200	0.00055	0.00514	0.01029	0.01614	0.12038	0.00040	0.10714	0.00024	1.21965	0.00031	1.98383	0.00047	3.13748	0.00081
AVG/ 2SD						0.12013	0.00124	0.10696	0.00066	1.21970	0.00078	1.98316	0.00159	3.13636	0.00279
[Day4]	200	0.00080	0.00747	0.01494	0.02344	0.11988	0.00021	0.10720	0.00021	1.21950	0.00027	1.98273	0.00041	3.13652	0.00067
[Day4]	200	0.00075	0.00709	0.01418	0.02223	0.11996	0.00027	0.10665	0.00023	1.21921	0.00031	1.98300	0.00045	3.13552	0.00076
[Day4]	200	0.00072	0.00677	0.01356	0.02125	0.12100	0.00029	0.10701	0.00023	1.22023	0.00033	1.98400	0.00044	3.13921	0.00092
[Day4]	200	0.00073	0.00690	0.01381	0.02165	0.12064	0.00029	0.10671	0.00022	1.21954	0.00037	1.98374	0.00054	3.13746	0.00093
[Day4]	200	0.00079	0.00740	0.01481	0.02322	0.12025	0.00021	0.10740	0.00020	1.21990	0.00027	1.98270	0.00040	3.13685	0.00071
AVG/ 2SD		0.00076	0.00713	0.01426	0.02236	0.12034	0.00094	0.10699	0.00064	1.21968	0.00079	1.98323	0.00120	3.13711	0.00273
G.AVG/ 2SD						0.12003	0.00074	0.10706	0.00028	1.21965	0.00012	1.98345	0.00088	3.12249	0.04937
[Day1]	400	0.00093	0.00869	0.01728	0.02691	0.11966	0.00017	0.10670	0.00028	1.22028	0.00026	1.98339	0.00037	3.09516	0.00107
[Day1]	400	0.00091	0.00856	0.01700	0.02645	0.12011	0.00018	0.10674	0.00025	1.21959	0.00025	1.98380	0.00035	3.08904	0.00100
[Day1]	400	0.00090	0.00851	0.01683	0.02619	0.11868	0.00019	0.10607	0.00026	1.21493	0.00052	1.97889	0.00044	3.07148	0.00251
[Day1]	400	0.00090	0.00839	0.01671	0.02606	0.12016	0.00018	0.10703	0.00026	1.22068	0.00029	1.98410	0.00039	3.10777	0.00087
[Day1]	400	0.00091	0.00857	0.01707	0.02662	0.11979	0.00015	0.10649	0.00027	1.21976	0.00024	1.98363	0.00032	3.10474	0.00105
AVG/ 2SD		0.00072	0.00676	0.01346	0.02102	0.11992	0.00119	0.10683	0.00073	1.21939	0.00307	1.98309	0.00292	3.11579	0.04697
[Day2]	400	0.00109	0.01020	0.02036	0.03182	0.11951	0.00015	0.10697	0.00018	1.21960	0.00019	1.98388	0.00034	3.11914	0.00077
[Day2]	400	0.00101	0.00946	0.01887	0.02948	0.11958	0.00016	0.10724	0.00022	1.21878	0.00029	1.98353	0.00033	3.11378	0.00095
[Day2]	400	0.00094	0.00877	0.01749	0.02733	0.11971	0.00017	0.10696	0.00023	1.22049	0.00023	1.98354	0.00036	3.11410	0.00083
[Day2]	400	0.00090	0.00839	0.01671	0.02610	0.11938	0.00020	0.10744	0.00028	1.21897	0.00024	1.98247	0.00036	3.11113	0.00109
[Day2]	400	0.00088	0.00827	0.01647	0.02572	0.12012	0.00018	0.10698	0.00025	1.21982	0.00024	1.98302	0.00042	3.11067	0.00100
AVG/ 2SD		0.00092	0.00860	0.01711	0.02670	0.11969	0.00085	0.10686	0.00073	1.21930	0.00312	1.98303	0.00289	3.10480	0.02848
[Day3]	400	0.00121	0.01138	0.02275	0.03567	0.11994	0.00013	0.10691	0.00012	1.21981	0.00020	1.98290	0.00025	3.13632	0.00049
[Day3]	400	0.00123	0.01152	0.02304	0.03612	0.12003	0.00018	0.10696	0.00012	1.22028	0.00019	1.98320	0.00028	3.13691	0.00050
[Day3]	400	0.00123	0.01155	0.02310	0.03622	0.11998	0.00017	0.10696	0.00010	1.21978	0.00019	1.98315	0.00033	3.13611	0.00052
[Day3]	400	0.00120	0.01129	0.02259	0.03541	0.11968	0.00016	0.10702	0.00012	1.22019	0.00019	1.98335	0.00025	3.13728	0.00045
[Day3]	400	0.00125	0.01175	0.02350	0.03685	0.11975	0.00015	0.10686	0.00011	1.21994	0.00017	1.98336	0.00032	3.13691	0.00043
AVG/ 2SD		0.00122	0.01149	0.02300	0.03605	0.11988	0.00030	0.10694	0.00012	1.22000	0.00046	1.98319	0.00037	3.13671	0.00095
[Day4]	400	0.00153	0.01437	0.02873	0.04505	0.11979	0.00010	0.10684	0.00012	1.21933	0.00014	1.98312	0.00027	3.13565	0.00046
[Day4]	400	0.00161	0.01517	0.03034	0.04757	0.11972	0.00012	0.10681	0.00010	1.21970	0.00016	1.98321	0.00019	3.13630	0.00041

Table 1. Continue

Day	Conc. (pg)	^{187}Os/ V	^{188}Os/ V	^{190}Os/ V	^{192}Os/ V	^{186}Os/^{188}Os	2SE	^{187}Os/^{188}Os	2SE	^{189}Os/^{188}Os	2SE	^{190}Os/^{188}Os	2SE	^{192}Os/^{188}Os	2SE
[Day4]	400	0.00150	0.01409	0.02819	0.04420	0.11970	0.00014	0.10684	0.00009	1.21986	0.00017	1.98343	0.00025	3.13684	0.00040
[Day4]	400	0.00162	0.01524	0.03049	0.04779	0.11997	0.00012	0.10687	0.00010	1.21978	0.00016	1.98343	0.00025	3.13657	0.00041
[Day4]	400	0.00153	0.01436	0.02873	0.04505	0.11975	0.00015	0.10702	0.00010	1.21977	0.00019	1.98318	0.00021	3.13628	0.00047
AVG/ 2SD		0.00156	0.01464	0.02930	0.04593	0.11978	0.00022	0.10688	0.00017	1.21969	0.00042	1.98327	0.00029	3.13633	0.00088
G.AVG/ 2SD						0.11985	0.00030	0.10687	0.00011	1.21960	0.00063	1.98314	0.00022	3.12348	0.03147
[Day1]	2000	0.00468	0.04381	0.08717	0.13584	0.11986	0.00003	0.10694	0.00005	1.21974	0.00008	1.98392	0.00010	3.10034	0.00055
[Day1]	2000	0.00455	0.04264	0.08483	0.13218	0.11977	0.00003	0.10689	0.00005	1.21985	0.00008	1.98385	0.00010	3.09967	0.00050
[Day1]	2000	0.00417	0.03909	0.07776	0.12116	0.11983	0.00004	0.10692	0.00006	1.21997	0.00009	1.98398	0.00011	3.09907	0.00047
AVG/ 2SD						0.11982	0.00009	0.10692	0.00005	1.21985	0.00023	1.98392	0.00013	3.09970	0.00127
[Day3]	2000	0.00610	0.05734	0.11471	0.17985	0.11987	0.00003	0.10688	0.00003	1.21977	0.00006	1.98306	0.00008	3.13643	0.00017
[Day3]	2000	0.00620	0.05829	0.11661	0.18283	0.11974	0.00003	0.10685	0.00002	1.21979	0.00006	1.98318	0.00008	3.13628	0.00014
[Day3]	2000	0.00643	0.06041	0.12084	0.18945	0.11988	0.00003	0.10687	0.00003	1.21991	0.00005	1.98320	0.00008	3.13625	0.00016
[Day3]	2000	0.00613	0.05757	0.11516	0.18056	0.11984	0.00003	0.10688	0.00003	1.21988	0.00005	1.98315	0.00009	3.13664	0.00015
[Day3]	2000	0.00615	0.05784	0.11571	0.18140	0.11979	0.00003	0.10685	0.00003	1.21980	0.00006	1.98314	0.00008	3.13624	0.00016
AVG/ 2SD						0.11982	0.00012	0.10687	0.00003	1.21983	0.00012	1.98315	0.00011	3.13637	0.00034
[Day4]	2000	0.00834	0.07837	0.15675	0.24571	0.11979	0.00003	0.10688	0.00002	1.21971	0.00005	1.98317	0.00008	3.13497	0.00027
[Day4]	2000	0.00856	0.08042	0.16084	0.25210	0.11985	0.00003	0.10687	0.00002	1.21965	0.00005	1.98322	0.00007	3.13388	0.00036
[Day4]	2000	0.00824	0.07745	0.15493	0.24288	0.11986	0.00002	0.10687	0.00002	1.21964	0.00005	1.98324	0.00007	3.13554	0.00021
[Day4]	2000	0.00853	0.08014	0.16028	0.25125	0.11984	0.00002	0.10687	0.00002	1.21967	0.00005	1.98317	0.00008	3.13470	0.00024
[Day4]	2000	0.00813	0.07642	0.15288	0.23968	0.11981	0.00002	0.10687	0.00002	1.21974	0.00006	1.98329	0.00008	3.13632	0.00018
AVG/ 2SD		0.00836	0.07856	0.15714	0.24632	0.11983	0.00006	0.10687	0.00001	1.21968	0.00008	1.98322	0.00010	3.13508	0.00183
G.AVG/ 2SD						0.11982	0.00001	0.10689	0.00006	1.21979	0.00018	1.98343	0.00086	3.12372	0.04162
References															
N-TIMS (IFREE/ JAMSTEC); errors in 2SE								0.10684	0.00002						
Makishima and Nakamura (2006); MC-ICP-MS by Faraday Cup; errors in 2SE															
MC-ICPMS	20					0.12033		0.10715	0.00185	1.22086					
MC-ICPMS	200					0.11988		0.10662	0.00034	1.21967					
MC-ICPMS	1000					0.11986		0.10682	0.00017	1.21976					
MC-ICPMS	5000					0.11982		0.10686	0.00001	1.21977					
MC-ICPMS	20000					0.11982		0.10686	0.000003	1.21978					
Schoenberg et al. (2000); Sparging MC-ICP-MS by Faraday Cup; errors in 2SE															
MC-ICPMS	50000					0.11983	0.00002	0.10694	0.00002						
TIMS	n.a.					0.11983	0.00001	0.10695	0.00002						