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RESEARCH ARTICLE

A comparison using Faraday cups with 10^{13} Ω amplifiers and a secondary electron multiplier to measure Os isotopes by negative thermal ionization mass spectrometry

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Rationale: According to the Johnson-Nyquist noise equation, the value of electron noise is proportional to the square root of the resistor value. This relationship gives a theoretical improvement of $\sqrt{100}$ in the signal/noise ratio by going from 10^{11} Ω to 10^{13} Ω amplifiers for Faraday detection in thermal ionization mass spectrometry (TIMS).

Methods: We measured Os isotopes using static Faraday cups with 10^{13} Ω amplifiers in negative thermal ionization mass spectrometry (NTIMS) and compared the results with those obtained with 10^{11} Ω amplifiers and by peak-hopping on a single secondary electron multiplier (SEM). We analysed large loads of Os (1 μg) at a range of intensities of $^{187}OsO_3$ (0.02–10 mV) in addition to small loads of Os (5–500 pg) to compare the results of the three methods.

Results: Using 10^{13} Ω amplifiers, the long-term reproducibility determined from Merck Os was $^{187}Os/^{188}Os$ = 0.1211 ± 0.0086 and 0.120229 ± 0.000034 at 0.02 mV and 10 mV of $^{187}OsO_3$ intensities. Meanwhile, the analysed JMC Os loadings of 5 and 500 pg showed $^{187}Os/^{188}Os$ = 0.10669 ± 0.00036 and 0.106807 ± 0.000023. In comparison, the values measured by the SEM were $^{187}Os/^{188}Os$ = 0.10704 ± 0.00056 and 0.10690 ± 0.00013. All errors are in 2 standard deviation (SD).

Conclusions: Both the accuracy and the precision determined using the 10^{13} Ω amplifiers and the SEM are identical when the Os amounts are within 10–50 pg. However, the former analysis time can be shortened by approximately two-thirds. The SEM measurement is still the most precise method for Os amounts <10 pg, but the analyses using 10^{13} Ω amplifiers suggest they are significantly better than the SEM for Os amounts >50 pg.

1 | INTRODUCTION

The Re-Os isotope system has been widely used in the fields of cosmochemistry and high-temperature geochemistry,[1-6] as well as in low-temperature geochemistry, to study features and processes including weathering,[7-9] marine sediments,[10-12] and the chemical evolution of seawater.[12-14] Most terrestrial materials have very low abundances of Re and Os; for example, the Os content is typically 10–100 pg g^{-1} in crustal rocks and 1–5 ng g^{-1} in mantle peridotites. For this reason, the research development of the Re-Os isotope system has always depended on the advantages of analytical techniques. Until now, negative thermal ionization mass spectrometry (NTIMS) has been the best method due to its high precision and lower required sample loading. In previous research, Brandon et al[15] obtained a precision for $^{187}Os/^{188}Os$ that was better than 50 ppm (2 RSE) for more than 5 ng of Os and better than 40 ppm (2 RSE) for intensities from 80 to 120 mV at mass 234 (i.e., $^{186}OsO_3$). With the adoption of amplifiers equipped with 10^{12} ohm feedback resistors (referred to here as 10^{12} Ω amplifiers for brevity, with corresponding 10^{13} Ω amplifiers below), the method using static multi-collector Faraday cups can produce higher precision and accuracy for $^{187}Os/^{188}Os$, reaching better than 0.2% (2 RSE) for 25 pg of Os.[16] Although 10^{13} Ω amplifiers have been used in several studies of Sr,[17,18] Nd,[17,18] Pb[19,20] and U[21] isotopes using static Faraday detection with 10^{13} Ω amplifiers in positive ionization mode TIMS (PTIMS), the use of 10^{13} Ω amplifiers for Os isotopic measurement in negative ionization mode TIMS (NTIMS) has not yet been reported.

It is generally known that the noise of the Faraday detectors is an important factor limiting the precision of analysing samples as small as a few picograms. Although the SEM resolves the noise problem, it is limited by the instability and dynamic range (1–600,000 counts per second (cps), convert into voltage 0–12 mV) of the ion counters. There certainly remains a gap in the dynamic range between ion counters

of SEM and Faraday cups detectors, i.e., a gap ranging from 12 mV (maximum of SEM) to 50 mV (minimum of 10^{11} Ω amplifier). However, newly developed 10^{13} Ω amplifiers have increased the signal/noise ratios. According to the Johnson noise formula, using 10^{13} Ω amplifiers instead of 10^{11} amplifiers could improve the signal/noise ratio 10-fold. In this paper, we present data collected on Os isotopic compositions using static Faraday cup collections with five newly designed 10^{13} Ω amplifiers and two 10^{12} Ω amplifiers. We measured the Os isotopes in various sample sizes (including some small samples containing 5–500pg of Os and several large samples containing 1 μg of Os) with different ion beam intensities to assess the potential of the new 10^{13} Ω amplifiers by NTIMS. We compared the data from static Faraday cups with that from the new 10^{13} Ω amplifiers and the default 10^{11} Ω amplifiers with the dynamic peak-hopping of the SEM. The main aim of this work is to demonstrate whether the Os isotopic ratios in 5–500 pg Os amounts or the intensities of $^{187}OsO_3$ between 20 μV and 10 mV can be precisely and accurately investigated by the prototype 10^{13} Ω amplifiers. The results show that the gap in dynamic range between ion-counters and Faraday cup detectors is eliminated for the above range of Os amount and intensity.

2 | EXPERIMENTAL

In this study, Os isotopes were measured at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG, CAS; Guangzhou, China).

2.1 | Standard materials

Two solution standards were used in this study, namely, Merck Os (purchased from Merck Corp., Darmstadt, Germany) and JMC Os (Johnson Matthey Co., Royston and Brimsdown, UK, provided by Dr Suzuki, JAMSTEC, Yokosuka, Japan). Ten Pt-filaments were loaded with 1 μg of Merck Os each and these samples were measured at different intensities by adjusting the evaporation filament current. Different amounts of JMC Os were loaded on the Pt-filament, i.e., 10 pg, 20 pg, 50 pg, 100 pg and 500 pg. Each amount was individually loaded on three different Pt-filaments, and a 5 pg amount was loaded on two different Pt-filaments. The description of the filament loading techniques and details on the operation of the TIMS method are given in Wang et al.[22] All measurements were performed at GIG, CAS.

2.2 | Mass spectrometry

In this study, two TIMS instruments (a TRITON Plus and a TRITON; Thermo Fisher Scientific Inc., Waltham, MA, USA) were used. One instrument (the TRITON Plus) was equipped with 10 Faraday cups and 10 amplifiers: one 10^{11} Ω, four 10^{12} Ω, and five 10^{13} Ω. Another instrument (the TRITON) was equipped with nine Faraday cups and nine 10^{11} Ω amplifiers, and this was used to compare 10^{11} Ω and 10^{13} Ω amplifiers. Each Faraday cup can be flexibly connected to any amplifier.

A ^{190}Os spike is normally added to samples to obtain an intensity level similar to that of ^{192}Os for determining the Os content of the measured sample. Therefore, the signals of $^{190}OsO_3$ and $^{192}OsO_3$ will be approximately three times higher than those of $^{188}OsO_3$ and $^{189}OsO_3$ and approximately 20 times higher than those of $^{186}OsO_3$ and $^{187}OsO_3$ in a measured sample. In this study, the Os isotopic compositions were measured using static multiple Faraday collectors measured by mixed 10^{13} Ω and 10^{12} Ω current amplifiers. The four lower-abundance isotopes, $^{186}OsO_3$, $^{187}OsO_3$, $^{188}OsO_3$, and $^{189}OsO_3$, and the interference monitor, $^{185}ReO_3$, were collected by the Faraday cups with the 10^{13} Ω current amplifiers, and the higher-abundance isotopes, $^{190}OsO_3$ and $^{192}OsO_3$, were collected by the Faraday cups with the 10^{12} Ω current amplifiers (see Table 1).

High-purity Pt ribbon (99.995%, 0.025 mm × 1 mm) was bought from the H. Cross Company (Moonachie, NJ, USA). The filament degassing, emitter $Ba(OH)_2$ and loading procedure were the same for all samples.[22] The measurement parameters were somewhat different among the 10^{11} Ω amplifiers, the 10^{13} Ω amplifiers and the SEM, as shown in Table 2. The oxygen subtraction procedure and the mass fractionation correction method were the same as described by Xu et al.[23] When using the 10^{13} Ω amplifiers, the magnet delay time was set to 8 s to account for the slower response time of the higher ohm amplifiers, and the baseline measurement time was extended compared with previous analysis by 10^{11} Ω amplifiers. To ensure a consistent frame of reference, we always report the intensities (V) relative to the 10^{11} Ω amplifiers. This means that we will report a beam current of 3×10^{-14} A as an intensity of 3 mV independently of the amplifier type because we apply a gain factor of 1 for the 10^{11} Ω amplifiers, a factor of 0.1 for the 10^{12} Ω amplifiers, and a factor of 0.01 for the 10^{13} Ω amplifiers. The gain calibration of 10^{13} Ω amplifiers was carried out every day following the method recommended by Thermo Fisher.[24]

A duplicate test was conducted in order to compare the analytical results of the solution standards by peak-hopping on the SEM in the TRITON Plus TIMS instrument and by static Faraday cups with 10^{11} Ω amplifiers in the TRITON TIMS instrument. For the SEM measurements in this study, all data were collected via the centre SEM with 1 block and 50 cycles. The integration time for $^{190}OsO_3$ and $^{192}OsO_3$ was 2 s, and it was 4 s for $^{189}OsO_3$, $^{188}OsO_3$, $^{187}OsO_3$, and $^{188}OsO_3$. The idle time was 2 s for each mass number (see Table 2). The cup configuration for static Faraday cups with 10^{11} Ω amplifiers was the same as that for Faraday cups with 10^{13} Ω amplifiers for Os isotope measurement. The ion beam was kept stable during the measurement.

TABLE 1 Cup configuration used for the static analysis of Os isotopes using the Triton Plus NTIMS instrument with mixed 10^{13} Ω and 10^{12} Ω amplifiers

Faraday cups	L2	L1	C	H1	H2	H3	H4
Collected mass	$^{185}ReO_3$	$^{186}OsO_3$	$^{187}OsO_3$	$^{188}OsO_3$	$^{189}OsO_3$	$^{190}OsO_3$	$^{192}OsO_3$
Amplifiers (Ω)	10^{13}	10^{13}	10^{13}	10^{13}	10^{13}	10^{12}	10^{12}

TABLE 2 Measurement parameters of 10^{11} Ω amplifiers, 10^{13} Ω and 10^{12} Ω amplifiers, and the SEM for the analysis of Os isotopes

Instrument configuration	Triton TIMS 10^{11} Ω amplifiers	Triton Plus TIMS 10^{12} + 10^{13} Ω amplifiers	Secondary electron multiplier
Method	Static Faraday cups	Static Faraday cups	Peak-hopping
Baseline	Each nth block	At start	At start
	Pre-wait 10 s and 30 cycles	Pre-wait 35 s and 120 cycles	Pre-wait 10 s and 30 cycles
Rotate	Yes	No	No
Block	8	10	1
Cycle	15	15	50
Integration	4 s	4 s	2 s for $^{190}OsO_3$ and $^{192}OsO_3$; 4 s for all other species
Number of integration	1	1	1
Idle time (s)	3	8	2
Filament temperature (°C)	800–900	800–850	750–850

3 | RESULTS AND DISCUSSION

3.1 | Detector noise and baseline reproducibility

For a small amount of sample, the precision and accuracy are limited by the signal/noise ratio, calibration of the detection system and analytical blanks. The electrical noise follows the Johnson-Nyquist equation: $\frac{U}{\Delta U} = \sqrt{t/4KRT} \times U$. Here, U is the measured voltage, ΔU is the Johnson noise voltage, t is the integration time, K is Boltzmann's constant, T is the resistor's absolute temperature, and R is the resistor value in ohms. From the Johnson-Nyquist noise equation, the value of ΔU is proportional to the square root of the resistor value. This value gives a theoretical improvement of $\sqrt{10}$ in the signal/noise ratio by going from 10^{11} Ω to 10^{12} Ω amplifiers or by going from 10^{12} Ω to 10^{13} Ω amplifiers.

In this study, the reproducibility for five 10^{13} Ω amplifiers was assessed by 10 repeat baseline measurements, each 18 min in duration. These baseline measurements were carried out immediately following the gain calibration performed by reference to Trinquier.[24] According to the measurement, the 2 SD (standard deviation) reproducibility values for the 10^{11}, 10^{12}, and 10^{13} Ω amplifiers were 6 μV, 1.5 μV, and 0.6 μV (normalized to the 10^{11} Ω amplifier), respectively (see Figure 1). These values are consistent with those of the 11 min baseline measured over a 3 h period by PTIMS[18] and the 14 min baseline measured over a 4.5 h period, as recommended by the instrument suppliers[24,25] The stability appears to be sufficient for 10^{13} Ω of resistance, and the drift is almost undetectable. According to these data, the baseline (ΔU) of the 10^{12} Ω amplifiers was improved approximately 3 times compared with that of the 10^{11} Ω amplifiers, and the baseline of the 10^{13} Ω amplifiers was increased almost 10 times compared with that of the 10^{11} Ω amplifiers. Both the 10^{12} Ω and the 10^{13} Ω amplifiers have signal/noise ratios consistent with those of Johnson noise.

3.2 | Precision and accuracy of Os isotopic ratio analyses using 10^{13} Ω amplifiers

The reproducibility of the $^{187}Os/^{188}Os$ ratios was measured on large loads of standard solutions of Merck Os using 10^{13} Ω amplifiers over a period of 6 months (see Figure 2). Compared with the long-term reproducibility of $^{187}Os/^{188}Os$ measured by Faraday cups with 10^{11} Ω amplifiers for 6 months, the accuracy was excellent when the intensities of the $^{187}OsO_3$ varied from 20 μV to 10 mV. The ratio of $^{187}Os/^{188}Os$ was 0.1211 ± 0.0086 (2 SD, n = 9) when the $^{187}OsO_3$ intensity was 0.02 mV (equivalent to 1000 cps), and 0.120229 ± 0.000034 (2 SD, n = 21) when the $^{187}OsO_3$ intensity was approximately 10 mV. Both values were consistent with the ratio of 0.120228 ± 0.000036 (2 SD, n = 11) for the 0.4 V $^{187}OsO_3$ intensity measured using the 10^{11} Ω amplifiers by our other Triton TIMS instrument (see Table 3). Although the values of $^{187}Os/^{188}Os$ were somewhat low at the $^{187}OsO_3$ intensities of 1 mV, 2 mV, and 4 mV on 10^{11} Ω amplifiers, they were in

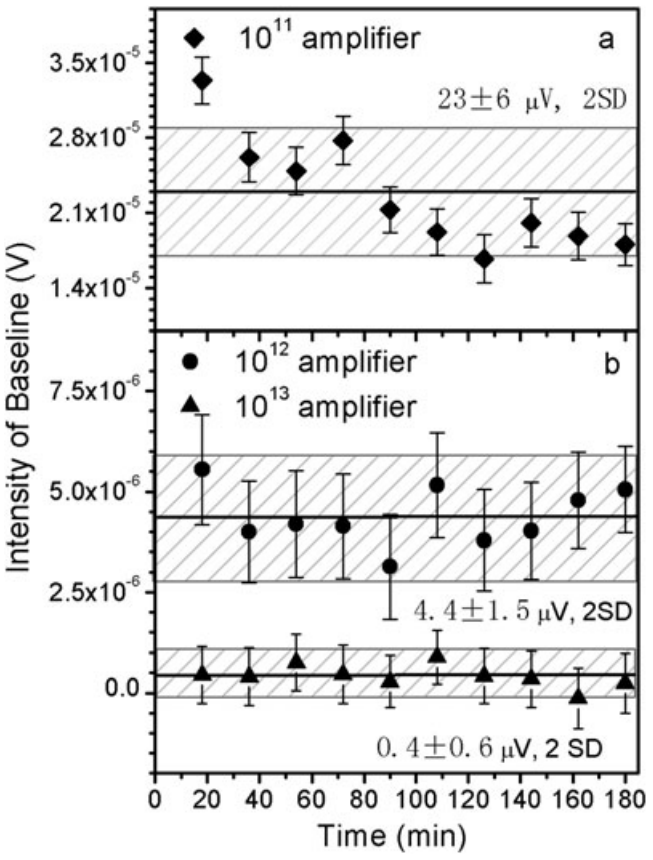

FIGURE 1 The baseline stability of the 10^{13} Ω amplifier, the 10^{12} Ω amplifier, and the 10^{11} Ω amplifier. Note: For each data point, the baseline was averaged over an integration time of 18 min

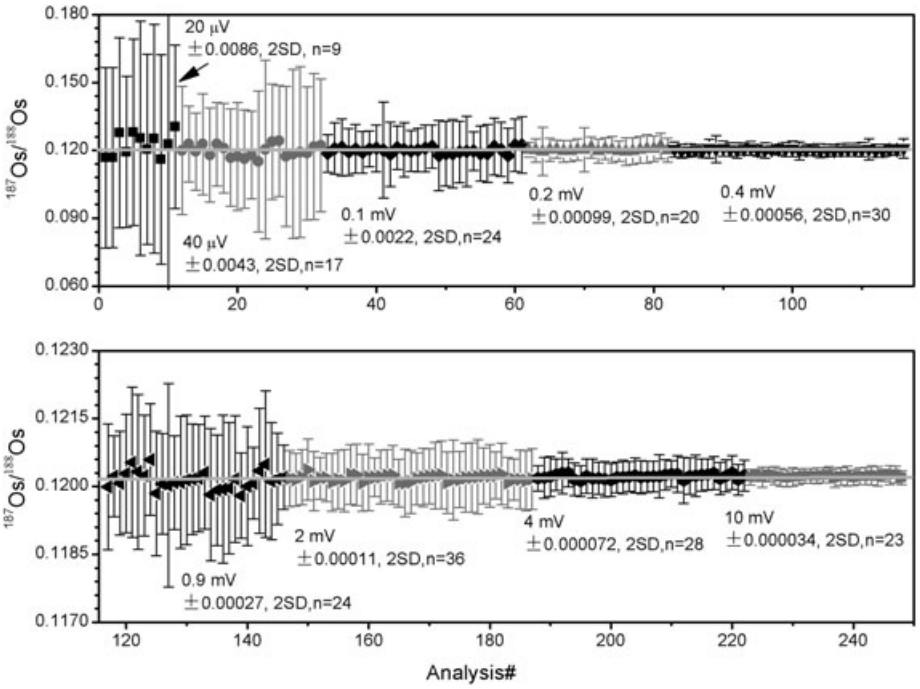

FIGURE 2 Accuracy and precision of the $^{187}Os/^{188}Os$ ratios measured using the 10^{13} Ω amplifiers. Note: The error bar is 2 SE for each point. The dark horizontal lines represent the long-term average of the high intensities (0.1–0.4 V on 10^{11} Ω) of Merck $^{187}OsO_3$ ($^{187}Os/^{188}Os$ = 0.120228 ± 36, 2 SD, n = 23, t = 6 months) at the GIG, CAS

TABLE 3 Accuracy and precision of the $^{187}Os/^{188}Os$ ratios with various $^{187}OsO_3$ intensities by the 10^{13} Ω amplifier, the 10^{11} Ω amplifier, and the SEM

Static Faraday cups with amplifiers of 10^{11} Ω				Static Faraday cups with amplifiers of 10^{13} Ω				Peak-hopping with the SEM			
$^{187}OsO_3$ (mV)	$^{187}Os/^{188}Os$	2 SD	n	$^{187}OsO_3$ (mV)	$^{187}Os/^{188}Os$	2 SD	n	$^{187}OsO_3$ (mV)	$^{187}Os/^{188}Os$	2 SD	n
				0.02	0.1211	0.0086	9	0.0005	0.1160	0.0052	3
				0.04	0.1202	0.0043	17	0.001	0.1205	0.0042	3
1	0.1083	0.0024	5	0.1	0.1202	0.0022	24	0.002	0.1213	0.0025	3
2	0.10797	0.00043	5	0.2	0.12011	0.00099	20	0.01	0.1210	0.0013	3
4	0.10807	0.00025	9	0.4	0.12020	0.00056	30	0.02	0.12062	0.00084	3
10	0.12022	0.00021	15	1	0.12013	0.00027	24	0.05	0.12086	0.00048	3
25	0.12023	0.00011	8	2	0.12020	0.00011	36	0.1	0.12007	0.00034	3
100	0.120222	0.000068	12	4	0.120218	0.000072	28	0.2	0.12035	0.00031	3
400	0.120228	0.000036	11	10	0.120229	0.000034	21	0.4	0.12044	0.00024	3

The intensities of the $^{187}OsO_3$ signal are expressed as $^{187}OsO_3$ (mV), and those for SEM are also expressed as voltage (mV) converted from counts per second. Raw data have been corrected off-line for O isotope interferences and mass fractionation (using $^{192}Os/^{188}Os$ = 3.08271). The $^{187}Os/^{188}Os$ ratios were measured by static Faraday cups with 10^{11} Ω amplifiers in the TRITON TIMS instrument.

agreement with those at 0.4 V intensities within the error range. The deviation of these values could be caused by the higher signal/noise ratio of 10^{11} Ω amplifiers.

As mentioned in Table 1, ^{190}Os and ^{192}Os were measured by 10^{12} Ω amplifiers, while the other Os isotopes (e.g., ^{187}Os and ^{188}Os) were measured by 10^{13} Ω amplifiers in this work. A possible problem is that differences in delay time between 10^{12} Ω and 10^{13} Ω amplifiers could result in deviation of the $^{192}Os/^{188}Os$ ratio, which was used to correct mass-dependent fractionation. However, our results show that the accuracy levels of both standard solutions analysed in this study are reasonably good even when the intensity of $^{187}OsO_3$ was as low as 0.02 mV, and therefore the difference in response time between 10^{12} and 10^{13} Ω amplifiers can be ignored.

In addition to static Faraday cups with 10^{13} Ω amplifiers and 10^{12} Ω amplifiers, the $^{187}Os/^{188}Os$ ratios were also measured by peak-hopping for comparison. The SEM was set for the detection of very low signals with an ion counter (trace analysis) for higher sensitivity. The permitted intensity range of the SEM is 1 to 1 × 10^6 cps, but the lifetime of the SEM can be quickly shortened if the ion current exceeds 6 × 10^5 cps (corresponding to 12 mV of Faraday cups voltage). Table 3 shows that the precision of $^{187}Os/^{188}Os$ determined by the SEM is 0.1160 ± 0.0052 (2 SD, n = 3) for the intensity of $^{187}OsO_3$ at 0.5 μV (equivalent to 25 cps), and 0.12044 ± 0.00024 (2 SD, n = 3) for the intensity of $^{187}OsO_3$ at 0.4 mV (equivalent to 20000 cps), which is similar to the precisions of $^{187}Os/^{188}Os$ for intensities of $^{187}OsO_3$ of 1–10 mV by 10^{11} Ω amplifiers and 0.04–1 mV by 10^{13} Ω amplifiers

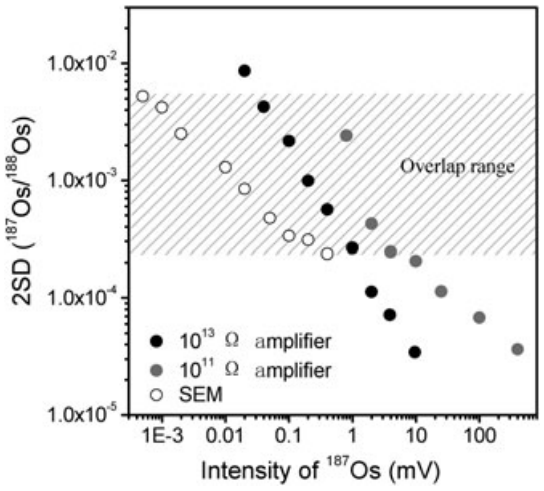

FIGURE 3 Precision (2 SD) of $^{187}Os/^{188}Os$ vs $^{187}OsO_3$ intensities for the 10^{13} Ω amplifiers, the 10^{11} Ω amplifiers, and the SEM. Note: Solid black circles are 2 SD of $^{187}Os/^{188}Os$ analysed using the static Faraday cups with the 10^{13} Ω amplifier; grey circles are analysed using the static Faraday cups with the 10^{11} Ω amplifier; hollow circles are those analysed via peak-hopping on the SEM; and the hatched area is the overlap range of precision (2 SD) on the SEM, 10^{13} Ω, and 10^{11} Ω

(see Figure 3). Therefore, when the intensity of $^{187}OsO_3$ is lower than 0.4 mV, measurement with the SEM can obtain precision better than that of the 10^{13} Ω resistors. For ion beam intensities greater than 0.4 mV (20 kcps), the 10^{13} Ω amplifiers yield more precise data than the SEM, and this suggests a potential benefit of using the 10^{13} Ω amplifiers.

3.3 | Analysis of picogram amounts of Os isotopes using static Faraday cups with 10^{13} Ω amplifiers

When the loading amount is as low as a few picograms, the ion beam intensity will be very low, and the stable signal duration will be shortened. To confirm the accuracy and precision measured by 10^{13} Ω amplifiers for small samples, JMC Os standard solutions with different loading sizes were measured, i.e., for six sample amounts of 5 pg, 10 pg, 20 pg, 50 pg, 100 pg, and 500 pg of JMC Os were loaded on Pt-filaments, and each Os amount was loaded on three filaments to test the reproducibility, except for the 5 pg of Os sample, which was loaded on two filaments. All the samples were analysed using the static Faraday cups with 10^{13} Ω amplifiers and by peak-hopping on the SEM. Each sample on a filament was measured twice at different times except for the 5 pg, 10 pg, and 20 pg samples on Faraday cups and the 5 pg sample on the SEM because of too low an ion beam signal. The results indicated that the $^{187}Os/^{188}Os$ ratios on the SEM were consistent with those from the static Faraday with the 10^{13} Ω amplifier within the error range (see Table 4). In addition, for the $^{187}Os/^{188}Os$ ratios, the precision from both the static Faraday cups and the peak-hopping SEM was improved with increasing amounts of Os from 5 to 500 pg.

TABLE 4 Os-isotopic ratios of small samples measured by static Faraday cup with 10^{13} Ω amplifiers and peak-hopping on a SEM

Os (pg)	Faraday cups with amplifiers of 10^{13} Ω				Peak-hopping with the SEM			
	$^{187}Os/^{188}Os$	2 SD	n	2RSE	$^{187}Os/^{188}Os$	2 SD	n	2RSE
5	0.10669	0.00036	2	2.4 ‰	0.10704	0.00056	3	3.0 ‰
10	0.10681	0.00028	3	1.5 ‰	0.10681	0.00034	6	1.3 ‰
20	0.10676	0.00022	3	1.2 ‰	0.10682	0.00029	6	1.1 ‰
50	0.10688	0.00019	6	708 ppm	0.10690	0.00014	6	549 ppm
100	0.106822	0.000073	6	278 ppm	0.10686	0.00009	6	342 ppm
500	0.106807	0.000023	6	87 ppm	0.10690	0.00013	5	546 ppm

Raw data have been corrected off-line for O isotope interferences and mass fractionation (using $^{192}Os/^{188}Os$ = 3.08271).

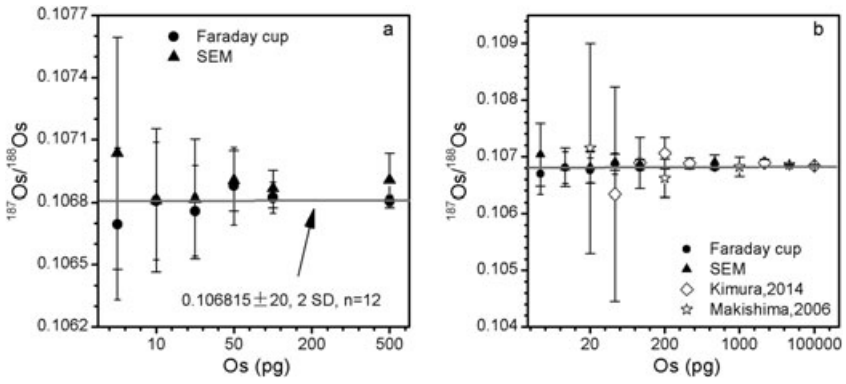

FIGURE 4 Comparison of the accuracy and precision of $^{187}Os/^{188}Os$ measured on 10^{13} Ω amplifiers and on the SEM for small Os samples. (a) Small samples (JMC Os) were measured in this study. The solid circles are the values of $^{187}Os/^{188}Os$ measured by static Faraday cups with 10^{13} Ω amplifiers, and the solid triangles are those measured by peak-hopping on a SEM; the error bar is 2 SD. The grey horizontal line represents the long-term average of large aliquots (100 - 500 pg) of JMC Os at GIG, CAS, and the precision value is for the last decimal place of the ratio. (b) Results from this study compared with published data. Solid circles and triangles are the same as in (a). The hollow diamonds are cited from Kimura et al[26] measured by MC-ICPMS with a combination of 10^{11} Ω and 10^{12} Ω amplifiers. The hollow stars are cited from Makishima et al[27] measured by MC-ICPMS with 10^{11} Ω amplifiers

The precision from the SEM was approximately identical to that of 10^{13} Ω amplifiers for amounts of Os from 5 to 50 pg (see Figure 4a). However, the precision of the 10^{13} Ω resistors was significantly better than that of the SEM when the Os amounts were 100 and 500 pg. When the Os amount reached 500 pg, the precision of the $^{187}Os/^{188}Os$ ratio measured by the static 10^{13} Ω amplifier Faraday cup method was as good as 87 ppm, much better than that of the peak-hopping SEM (only 546 ppm, see Table 4). Meanwhile, the analysis time using the 10^{13} Ω amplifier is almost one-third of the measurement time using the SEM.

Furthermore, the accuracy and precision were also evaluated in comparison with data published by other labs. The average value of JMC Os was $^{187}Os/^{188}Os$ = 0.10681 ± 0.00002 (2 SD, n = 6) for the 500 pg sample in this work, which is in accordance with the NTIMS value of $^{187}Os/^{188}Os$ = 0.10684 ± 0.00002 (2 SD) obtained for 100 ng and the value of 0.10689 ± 0.00006 (2 SD) for 2 ng obtained by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) with a 10^{12} Ω amplifier value by Kimura et al.[26] It is also similar to the value of $^{187}Os/^{188}Os$ = 0.10686 ± 0.00001 (2 SD) for 5 ng obtained by MC-ICPMS on a 10^{11} Ω amplifier by Makishima et al.[27] Our data and published results are shown in Figure 4b for comparison and indicate that the precision of $^{187}Os/^{188}Os$ obtained by NTIMS with 10^{13} Ω amplifiers for small amounts of Os (5 pg) is equivalent to the precision obtained by MC-ICPMS with 10^{11} Ω amplifiers for 100 pg (to within approximately 2.4 ‰).

Compared with the precision of Os isotopes on NTIMS instruments in other labs, analysis of a 500 pg sample by 10^{13} Ω amplifiers in this study can obtain a precision of 87 ppm for $^{187}Os/^{188}Os$, which is similar to 40–74 ppm for a 5–70 ng sample analysed using 10^{11} Ω amplifiers[15] and 71 ppm for 1000 pg samples analysed using 10^{12} Ω amplifiers,[16] although we did load smaller amounts of Os than in the above studies.

4 | CONCLUSIONS

This study reports a detailed procedure to measure Os isotopic ratios with high precision using static Faraday cups with 10^{13} Ω amplifiers. The Os isotopic ratios were measured at different $^{187}OsO_3$ intensities from 0.02 to 10 mV for the standard solution of Merck Os and at Os amounts from 5 to 500 pg for JMC Os. The precision of the $^{187}Os/^{188}Os$ ratio was as good as 2.4 ‰ at 5 pg of Os or 0.1 mV for the intensity of $^{187}OsO_3$ and better than 87 ppm at 500 pg Os or 10 mV for the intensity of $^{187}OsO_3$. Using this new 10^{13} Ω amplifier configuration, the signal/noise ratios agreed with the Johnson-Nyquist value, and the precision of $^{187}Os/^{188}Os$ for 1–10 mV is enhanced approximately 10 times relative to that obtained with the static Faraday cups with 10^{11} Ω amplifiers. In addition, our results indicate that both the accuracy and the precision obtained using the 10^{13} Ω amplifiers and the SEM are identical when the Os amounts are within 10–50 pg, but the former measurement time can be shortened by approximately two-thirds. Our results indicated that a small amount of Os, i.e., 10–500 pg, can be quickly and accurately determined by static Faraday cups with 10^{13} Ω amplifiers.

In addition, the consistency of accuracy and precision obtained for 10^{11} Ω amplifiers, the SEM, and a combination of 10^{13} and 10^{12} Ω amplifiers indicates the potential availability and flexibility of mixed amplifier configurations.

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