

Simplified technique for the measurements of Re–Os isotope by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS)

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A method for the rapid determination of Re–Os isotopes by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) was developed. For Os measurements, samples were introduced into the plasma through conventional solution mode. The main Os memory occurs in the nebulizer; therefore, the use of a glass nebulizer rather than a Teflon nebulizer leads to a significant reduction in the Os memory effect. The Os memory is quickly and easily eliminated by washing the inlet system with 5% HCl–EtOH. The external reproducibility of the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the Johnson–Matthey Chemical ICP (JMC) Os standard solution, as measured using the multi-ion counter system, is 0.07% (2σ , $n = 12$) for analyte amounts ranging from 0.1 to 1 ng total Os. Using MC-ICP-MS, the mean values of $^{187}\text{Os}/^{188}\text{Os}$ obtained for standards were found to be within analytical uncertainty of values obtained by negative thermal ionization mass spectrometry (N-TIMS). An improved mass-fractionation correction technique using Ir was applied to the isotopic analysis of Re. The present methods demonstrate the feasibility of MC-ICP-MS for precision measurements of the ^{187}Re – ^{187}Os isotope system.

Keywords: Re–Os, MC-ICP-MS, isotope measurements

INTRODUCTION

The Re–Os isotopic system, based on the negative β decay of ^{187}Re to ^{187}Os , has been widely used in geochemistry and cosmochemistry over the past decade (Smoliar *et al.*, 1996; Shen *et al.*, 1996; Shirey and Walker, 1998; Meibom and Frei, 2002). However, this approach has been limited by difficulties encountered with Re and Os isotope analysis, mainly due to their low abundance in geological materials, high ionization potential, and the high volatility of OsO_4 (Reisberg and Meisel, 2002). The relatively recent development of negative thermal ionization mass spectrometry (N-TIMS) techniques has significantly enhanced the sensitivity and precision of Re and Os isotope analyses (Creaser *et al.*, 1991; Volkening *et al.*, 1991). N-TIMS is the most widely used method for Re–Os determination due to the 20% and 10% ionization efficiencies for Os and Re (as OsO_3^- and ReO_4^-), respectively.

Inductively coupled plasma mass spectrometry (ICP-MS) had been applied to measurements of Os isotopes because of its high plasma ionization efficiency (as Re^+ and Os^+) (Russ *et al.*, 1987; Gregoire, 1990; Sun *et al.*, 2001). In particular, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has great potential in determining Re–Os isotopes (Hirata *et al.*, 1998; Schoenberg *et al.*, 2000; Yin *et al.*, 2001; Makishima and Nakamura, 2006; Nowell *et al.*, 2007). The limitations of this method are the low overall efficiency ($\sim 1\%$) in the ICP-MS transmission process and a pronounced Os memory effect in the sample-introduction system. To overcome these problems, previous studies have sought to introduce Os into ICP-MS as the volatile species OsO_4 (Hassler *et al.*, 2000; Malinovsky *et al.*, 2002). This approach was found to offer enhanced sensitivity over traditional solution introduction, via a nebulizer and spray chamber, thereby allowing the in-run precision of $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio to be improved to 1.2% (2σ) for 25 pg Os standard samples and 0.016% (2σ) for 50 ng Os standard samples, using a multiple ion-counter and Faraday cup (Schoenberg *et al.*, 2000), respectively. However, a problem associated with the analysis of Os as OsO_4 (i.e., by sparging directly from the digestion vessel into the

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plasma) is that it is released over a long period (30–40 min), meaning that small Os signals are obtained and that a significant memory effect may result. This memory effect can be reduced by replacement with an evaporation vessel for each sample and connecting tube but it requires the plasma to be extinguished, thereby increasing the analysis time (Sun *et al.*, 2001; Malinovsky *et al.*, 2002).

Makishima and Nakamura (2006) measured Os and Re isotope ratios at sub-picogram levels using MC-ICP-MS with an Aridus[®] desolvating sample-introduction system (CETAC Technologies) and multiple ion-counters. This method yields a marked increase in detector sensitivity, generating a reproducibility (1σ) of 2.7–0.14% for $^{187}\text{Os}/^{188}\text{Os}$ measurements in samples with Os concentrations of 1–100 pg mL^{-1} . However, the method is somewhat time-consuming (40 min and 20 min per sample for analyses of Os and Re, respectively) because the standard bracketing method is inappropriate and the wash solution (0.5 mol L^{-1} HF) is relatively ineffective. These problems have reduced the traditional ICP-MS advantage of short measurement time.

In the present study, we improved the analytical protocols for Re–Os analysis using MC-ICP-MS with solution nebulization. Os samples were prepared in 2% HCl–EtOH solution and samples were introduced into plasma via a highly sensitive glass MicroMist nebulizer. The washout time was 8 min using 5% HCl–EtOH solution. Mass fractionation in Re measurements was externally corrected using the isotope ratio of the added Ir and Os ratios and by normalizing measured $^{192}\text{Os}/^{188}\text{Os}$ values to 3.08271 (Nier, 1937). Using this method, the total time required for Os and Re measurements is shorter than that required using the standard bracketing method. The employed method enables a higher sample throughput, using more convenient sample preparation than that reported in previous works (Creaser *et al.*, 1991; Volkening *et al.*, 1991; Schoenberg *et al.*, 2000; Yin *et al.*, 2001; Suzuki *et al.*, 2004; Makishima and Nakamura, 2006).

EXPERIMENTAL

Materials and reagents

The Re standard was a natural Re standard solution prepared by dissolving Re ribbon (Niloco Co., Japan) with concentrated nitric acid. The Re (^{185}Re -enriched) and Os spikes (^{190}Os -enriched) were purchased from Oak Ridge National Laboratory (USA) and dissolved with aqua regia in a closed glass tube. The Ir standard solution (GSB G62066-90) was purchased from the National Analysis Center for Iron and Steel (China). Two different Os standard solutions (Johnson-Matthey Chemicals ICP standard solution and Merck Chemical AA standard solution) were used for measurements of Os isotopic ratios. Dilute solutions of acids or elements for mass spectrometry were

prepared with water obtained from a 18.2 M Ω grade Millipore system. All solutions and samples were mixed and prepared in a clean lab prior to analysis.

Apparatus

The bulk of the study was carried out using a Micromass (Manchester, UK) IsoProbe[®] MC-ICP-MS housed at the Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China. The instrument is described in detail in previous publications (Rehkämper and Mezger, 2000; Thirlwall, 2002; Liang *et al.*, 2003). The IsoProbe produces flat-top, symmetrical peaks and is equipped with nine independently adjustable Faraday cups and four adjustable ion-counters. The operating conditions were finely tuned daily to achieve maximum ion intensity of ^{192}Os and ^{187}Re . The gain of each ion-counter was obtained by measuring two different standard solutions of Os. The sample solution of Re was introduced into the plasma using an Aridus[®] desolvating sample-introduction system (CETAC Technologies). This system removes water from the sample solutions by passing them through a desolvating membrane at 140°C, thus providing a “dry” aerosol to the plasma. This increases introduction efficiency by a factor of 15–20 over conventional sample introduction systems. Os sample solutions were introduced into the ICP via a self-aspirating MicroMist nebulizer (Glass Expansion, Australia). This glass concentric nebulizer provides high performance and sensitivity for samples of limited-volume.

N-TIMS analyses were performed using a Thermo-Finnigan Triton[®] instrument housed at the Japan Agency for Marine–Earth Science and Technology (JAMSTEC), in negative ion detection mode, equipped with an oxygen gas-leak valve and an ion counting multiplier (Kato *et al.*, 2005). The Os was loaded on high-purity Pt filament (99.999%; H. Cross Co., USA), previously baked in till the temperature was high enough for the filament to appear bright red in colour and it was maintained at this temperature for more than 3 minutes. The sample was covered with 10 μg $\text{Ba}(\text{NO}_3)_2$ (Claritas, Spex Inc.). Os and Re isotopic compositions were respectively measured in pulse-ion-counting electron multiplier mode and in static multiple Faraday collector mode. Instrumental mass fractionation of Os was corrected for by normalizing the measured $^{192}\text{Os}/^{188}\text{Os}$ values to 3.08271 (Nier, 1937), using an exponential law. Oxygen subtraction for Os was performed using values of $^{17}\text{O}/^{16}\text{O} = 0.00037$ and $^{18}\text{O}/^{16}\text{O} = 0.002047$ (Nier, 1950). Rhenium isotope compositions were measured using a total evaporation technique (Suzuki *et al.*, 2004).

Os measurement procedures

All Os standards and samples were freshly prepared

in 2% HCl–EtOH solution made from 2 mL of concentrated HCl and 2 mL of absolute alcohol diluted in 96 mL of water. The addition of small amounts of alcohol resulted in an increase in the sensitivity of Os measurements by ICP-MS. Compared to 5% HCl and 5% HBr, it was found that the sensitivity of Os was increased about 5–10% by using 2% HCl–EtOH. It is possible that the enhancement of the Os signal by addition of alcohol is caused by an improved degree of ionization of Os and nebulization efficiency (Cao *et al.*, 2000). Sample solutions with Os concentrations less than 2 ng g⁻¹ were measured by channeltron. In our previous study, ¹⁸⁵Re, ¹⁸⁶Os, ¹⁸⁷Os, ¹⁸⁸Os, ¹⁸⁹Os, and ¹⁹⁰Os were measured in sequences of two cycles by ion-counter: the first was a ¹⁸⁵Re, ¹⁸⁷Os, ¹⁸⁸Os, and ¹⁸⁹Os set, and the second involved ¹⁸⁶Os, ¹⁸⁸Os, ¹⁸⁹Os, and ¹⁹⁰Os. In the first cycle, ¹⁸⁵Re was monitored for the interference of ¹⁸⁷Re on ¹⁸⁷Os. Data from the first cycle were used to determine ¹⁸⁷Os/¹⁸⁸Os and ¹⁸⁹Os/¹⁸⁸Os ratios, the latter of which was used to correct for mass fractionation by normalizing ¹⁸⁹Os/¹⁸⁸Os to 1.21966 (Yin *et al.*, 2001). ¹⁹⁰Os/¹⁸⁹Os and ¹⁸⁹Os/¹⁸⁸Os ratios from the second cycle were used to calculate Os concentrations using the isotope dilution method and to determine mass fractionation using an exponential law.

Occasionally, very weak signals of ¹⁸⁵Re were detected during measurements of natural rock samples. Although it is possible to perform a mathematical correction for the isobaric overlap of ¹⁸⁷Re on ¹⁸⁷Os, this leads to an increase in the uncertainty budget. Therefore, further purification by micro-distillation was undertaken to separate Os completely from the interfering Re (Roy-Barman and Allègre, 1995). Following this purification, ¹⁸⁵Re interference on ¹⁸⁷Os was negligible. In this study, ¹⁸⁷Os, ¹⁸⁸Os, ¹⁹⁰Os, and ¹⁹²Os were detected simultaneously by four ion-counters, yielding ¹⁸⁷Os/¹⁸⁸Os, ¹⁹⁰Os/¹⁸⁸Os, ¹⁹²Os/¹⁹⁰Os and ¹⁹²Os/¹⁸⁸Os ratios. A gain calibration of the ion counters was required. This was done by adjusting the cup efficiency of the channeltrons to obtain the ¹⁸⁷Os/¹⁸⁸Os, ¹⁹⁰Os/¹⁸⁸Os and ¹⁹²Os/¹⁹⁰Os corrected ratios equal to the reference values. Another Os standard solution was then used to check if the corrected ratios were still equal to the reference values.

Mass fractionation was internally corrected by normalizing the observed ¹⁹²Os/¹⁸⁸Os to 3.08271 (Nier, 1937). The acquisition of a run comprised 5 blocks of 10 ratios, with 5 s of integration time per mass and required 0.5 mL of sample solution. In total, each measurement required 8 min, including the on-peak zero (OPZ) procedure. Using a routine tuning method, sensitivities of ~2 × 10⁴ cps for ¹⁹²Os (0.2 ng g⁻¹) were obtained. Between analyses, the inlet system was cleaned with 5% HCl–EtOH mixture solution followed by 5% HCl for 8 min. The total measurement time was therefore 16 min per sample.

For Faraday cup measurements of Os, the nine Fara-

day collectors of the IsoProbe ICP-MS enabled the simultaneous monitoring of the isotopes of other elements that might have interfered with Os isotope masses. We measured, but failed to detect, the isotopes of ¹⁸³W (¹⁸⁶W → ¹⁸⁶Os), ¹⁸⁵Re (¹⁸⁷Re → ¹⁸⁷Os), and ¹⁹⁴Pt (¹⁹⁰Pt → ¹⁹⁰Os and ¹⁹²Pt → ¹⁹²Os). Their contribution can therefore be considered negligible. ¹⁸⁷Os/¹⁸⁸Os, ¹⁹⁰Os/¹⁸⁸Os, ¹⁹²Os/¹⁹⁰Os, and ¹⁹²Os/¹⁸⁸Os were measured in 50 ratios with an integration time of 2 s for each run. The ¹⁹²Os/¹⁸⁸Os ratio of 3.08271 (Nier, 1937) was used for internal normalization using an exponential law (Russell *et al.*, 1978). All other analytical conditions were the same as those adopted in ion counting mode.

Re measurement procedures

Rhenium has two isotopes (¹⁸⁵Re and ¹⁸⁷Re), thereby preventing correction for mass fractionation by internal normalization without the use of artificial radioactive isotopes. An advantage of MC-ICP-MS is the ability to monitor on-line and to correct for mass fractionation during measurement, by the addition of Ir to Re analyte solutions (Schoenberg *et al.*, 2000; Liang *et al.*, 2005; Maréchal *et al.*, 1999; Rehkämper and Mezger, 2000; Waight *et al.*, 2002; Kehm *et al.*, 2003). The Re standard and sample solutions were diluted using Milli-Q water. Ir solution was added to Re analyte samples till a Re–Ir mixture solution ratio of 0.2–5 was achieved. Five Faraday cups (Axial, High2, High4, High5, and High6) were used to collect the ion currents corresponding to ¹⁸⁵Re, ¹⁸⁷Re, ¹⁹⁰Os, ¹⁹¹Ir, and ¹⁹³Ir in static mode, respectively. ¹⁹⁰Os was monitored to assess possible mass interference of ¹⁸⁷Os on ¹⁸⁷Re. No Os was detected in measurements of Re standard solutions or spiked natural samples, thereby demonstrating the effectiveness of the procedures used to chemically separate Re and Os. Fifty values of ¹⁸⁷Re/¹⁸⁵Re and ¹⁹³Ir/¹⁹¹Ir were obtained with an integration time of 2 s for each run. Between samples, the inlet system was cleaned with 6% HCl followed by Milli-Q water with a washout time of 8 min.

RESULTS AND DISCUSSION

Os measurements by ion-counter and Faraday cup

Herein, we refer to the Os standard of the Johnson-Matthey Chemicals ICP standard solution and the Merck Chemical AA standard solution respectively as J-Os standard and M-Os standard. For static multi-ion counter measurements, 200 and 2000 pg g⁻¹ of J-Os and M-Os standards (corresponding to 100 and 1000 pg of Os, respectively) were freshly prepared in 2% HCl–EtOH and measured alternately. The value and precision (2σ) of ¹⁸⁷Os/¹⁸⁸Os for the two standards were then calculated (Table 1). For large (1 ng) and small (0.1 ng) amounts of J-Os standard, in-run precision (2σ_m uncertainty) for ¹⁸⁷Os/

Table 1. $^{187}\text{Os}/^{188}\text{Os}$ values measured for the J-Os and M-Os standards using MC-ICP-MS

Method	Sample	Os amount (ng)	$^{187}\text{Os}/^{188}\text{Os}$	Reproducibility (2σ , $n = 4$)
Ion-counter	J-Os std	0.1	0.1067	0.22
		0.5	0.10701	0.024
		1	0.106980	0.0078
	M-Os std	0.1	0.1207	0.30
		0.5	0.11991	0.034
		1	0.12031	0.016
		Average (J-Os std) ($n = 12$, 2σ)		0.10688
Average (M-Os std) ($n = 12$, 2σ)		0.12032	0.090	
Reproducibility (2σ , $n = 5$)				
Faraday cup	J-Os std	20	0.106945	0.020
	M-Os std	20	0.120318	0.013
N-TIMS (J-Os std) ($n = 14$, 2σ)			0.106937	0.0056
N-TIMS (M-Os std) ($n = 14$, 2σ)			0.12022	0.020

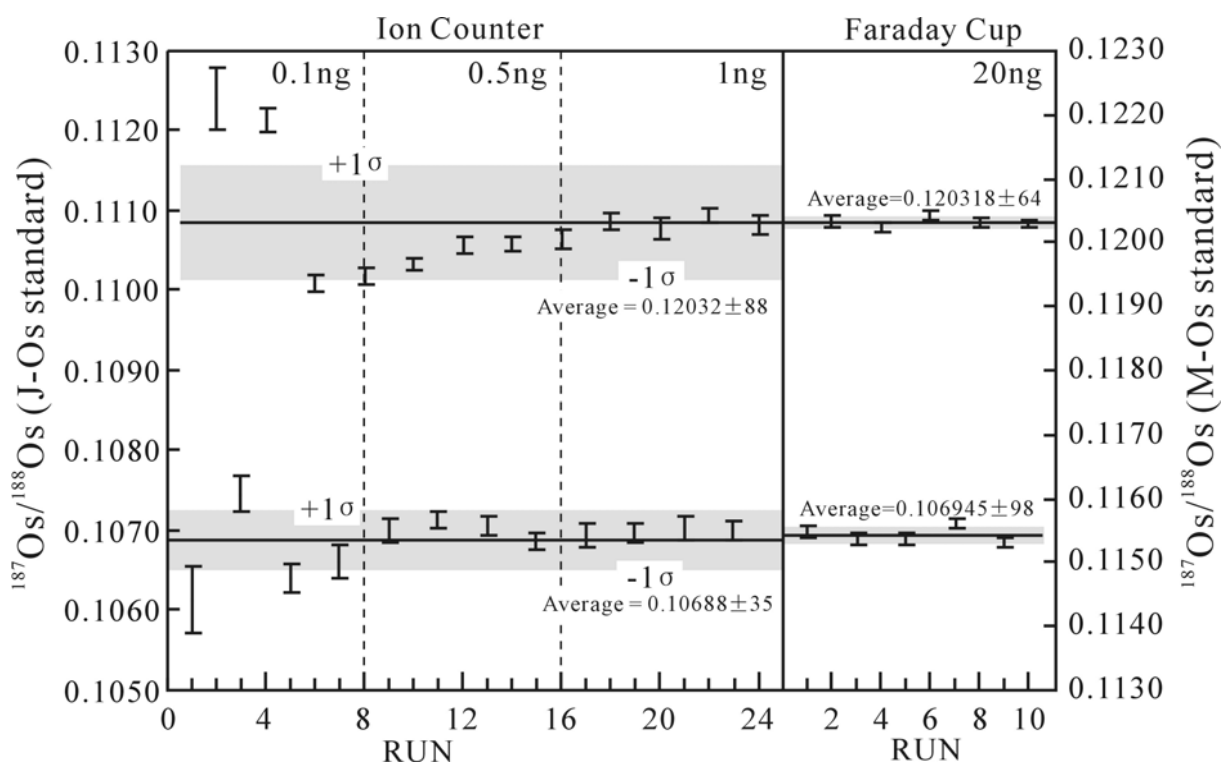


Fig. 1. External reproducibility of $^{187}\text{Os}/^{188}\text{Os}$ values determined by MC-ICP-MS for the J-Os and M-Os standards measured alternately (shown with $\pm 1\sigma$ uncertainties). The dashed lines in the shaded region represent the average $^{187}\text{Os}/^{188}\text{Os}$ values for the J-Os and M-Os standards. The shaded regions indicate the areas bounded by $\pm 1\sigma$. The average $^{187}\text{Os}/^{188}\text{Os}$ values for the J-Os and M-Os standards, as measured by N-TIMS, are 0.106937 ± 56 and 0.12022 ± 20 , respectively.

^{188}Os , in ion counting mode, was 0.011% and 0.22%, respectively. The external reproducibility of $^{187}\text{Os}/^{188}\text{Os}$ measurements, based on 24 analyses of 0.1–1 ng total Os for the J-Os and M-Os standards, was 0.07% and 0.17% (2σ) with an average $^{187}\text{Os}/^{188}\text{Os}$ value of 0.10688 and

0.12032, respectively. Accuracy was evaluated by comparison of ratios measured using MC-ICP-MS with those determined by N-TIMS. The average N-TIMS $^{187}\text{Os}/^{188}\text{Os}$ values for the J-Os and M-Os standards were 0.106937 ± 56 (2σ , $n = 14$) and 0.12022 ± 20 (2σ , $n = 14$), respec-

Table 2. Mean values of non-radiogenic Os isotopic ratios determined by MC-ICP-MS, compared with published data

Reference	Method	$^{190}\text{Os}/^{188}\text{Os}$	$^{192}\text{Os}/^{190}\text{Os}$
Birck and Allègre (1998)	N-TIMS	1.98375	1.55393
Shirley and Walker (1998)	N-TIMS	1.98448	1.55336
Volkening <i>et al.</i> (1991)	N-TIMS	1.98380	1.55389
Creaser <i>et al.</i> (1991)	N-TIMS	1.98422	1.55349
Boulyga <i>et al.</i> (2002)	MC-ICPMS	1.98378	1.55395
Hirata <i>et al.</i> (1998)	MC-ICPMS	1.98375	1.55393
Yin <i>et al.</i> (2001)	MC-ICPMS	1.98406	1.55369
Average ($2\sigma, n = 7$)		1.98398 ± 58	1.55375 ± 48
This study	MC-ICPMS* ($2\sigma, n = 24$)	1.98370 ± 150	1.55280 ± 120
	MC-ICPMS** ($2\sigma, n = 10$)	1.98387 ± 58	1.55388 ± 46

*Using multi-ion counter measurements.

**Using Faraday cup measurements.

tively, and were within the uncertainty of the values obtained by MC-ICP-MS. The mean $^{187}\text{Os}/^{188}\text{Os}$ values of the J-Os and M-Os standards, as measured from 40 ng g^{-1} (corresponding to 20 ng) Os by MC-ICP-MS with Faraday cups, were 0.10694 ± 19 ($2\sigma, n = 5$) and 0.12032 ± 13 ($2\sigma, n = 5$), respectively. These values are within analytical uncertainty of those determined by N-TIMS using the same Os standard solutions (Fig. 1).

The non-radiogenic Os isotopic ratios (e.g., $^{190}\text{Os}/^{188}\text{Os}$ and $^{192}\text{Os}/^{190}\text{Os}$) are important in assessing the accuracy of MC-ICP-MS measurements. Table 2 lists the average values of $^{190}\text{Os}/^{188}\text{Os}$ and $^{192}\text{Os}/^{190}\text{Os}$ obtained for the J-Os and M-Os standards by MC-ICP-MS, as well as Os isotopic data reported previously (Creaser *et al.*, 1991; Volkening *et al.*, 1991; Shirley and Walker, 1998; Hirata *et al.*, 1998; Birck and Allègre, 1998; Yin *et al.*, 2001; Boulyga *et al.*, 2002). The present $^{190}\text{Os}/^{188}\text{Os}$ values are within analytical precision of those reported previously. The $^{192}\text{Os}/^{190}\text{Os}$ values measured by Faraday cups are also consistent with previous data. However, the values determined by multi-ion counters are slightly lower, probably due to inaccurate gain calibration of the ion-counters.

In summary, the precision and accuracy of Os isotopic measurements performed using the present MC-ICP-MS are similar to those obtained by N-TIMS.

Re measurements using iridium to correct for mass fractionation

Makishima and Nakamura (2006) demonstrated that mass fractionation can be corrected using a standard bracketing method during MC-ICP-MS measurements of Re isotope ratios. This is achieved by interpolating the mass fractionation of an unknown sample from the fractionations of two standard runs performed before and

after the unknown sample. However, mass fractionation by simple interpolation between standards (i.e., without internal or external isotopic normalization) is only valid if the nature of mass fractionation does not change between standards and samples, thereby requiring extremely strict sample purification because a heavy sample matrix can also result in a marked change in fractionation factors (Woodhead, 2002).

In the present study, the element Ir was used as an internal isotopic standard, added to Re–Ir solutions to enable on-line correction for mass fractionation (Schoenberg *et al.*, 2000). Initially, $^{187}\text{Re}/^{185}\text{Re}$ values were corrected for mass fractionation using an exponential law and assuming the same mass fractionation factor for Re and Ir. However, the corrected $^{187}\text{Re}/^{185}\text{Re}$ ratios showed a systematic deviation from reported values (Gramlich *et al.*, 1973; Suzuki *et al.*, 2004), in that the $^{187}\text{Re}/^{185}\text{Re}$ value obtained by MC-ICP-MS ($^{187}\text{Re}/^{185}\text{Re} = 1.66969 \pm 22$) (Liang *et al.*, 2005) was systematically lower (by approximately 0.35%) than the fractionation-corrected value determined by N-TIMS ($^{187}\text{Re}/^{185}\text{Re} = 1.6755 \pm 14$) (Suzuki *et al.*, 2004). It should also be noted that our values were significantly lower than the certified isotope ratio adopted by International Union of Pure and Applied Chemistry (IUPAC) ($^{187}\text{Re}/^{185}\text{Re} = 1.6740 \pm 11$) (Rosman and Taylor, 1998). To obtain more reliable and consistent Re isotopic data, a methodology similar to that applied to measurements of W isotopes was employed, using $^{187}\text{Re}/^{185}\text{Re}$ for mass fractionation (Irisawa and Hirata, 2006). Following the modified exponential law of Irisawa and Hirata (2006), the correction law for Re can be written as

$$\left(\frac{^{187}\text{Re}}{^{185}\text{Re}}\right)_c = \left(\frac{^{187}\text{Re}}{^{185}\text{Re}}\right)_m \left[\frac{(^{193}\text{Ir}/^{191}\text{Ir})_m}{(^{193}\text{Ir}/^{191}\text{Ir})_s} \right]^{f \times \ln(M187/M185) / \ln(M193/M191)}$$

Table 3. Measurement results for ^{185}Re -enriched spike using the Ir-based mass fractionation correction method and MC-ICP-MS

Run #	$^{187}\text{Re}/^{185}\text{Re}$ measured	$^{193}\text{Ir}/^{191}\text{Ir}$ measured	$^{187}\text{Re}/^{185}\text{Re}$ corrected
1	0.06065	1.71111	0.05978
2	0.06087	1.71075	0.06000
3	0.06078	1.71127	0.05990
4	0.06025	1.71125	0.05937
5	0.06082	1.71111	0.05994
6	0.06032	1.71104	0.05945
7	0.06068	1.71113	0.05980
8	0.06055	1.71117	0.05967
Average $\pm 2\sigma$ ($n = 8$)	0.06061 \pm 46	1.71110 \pm 32	0.05974 \pm 46

where $(^{187}\text{Re}/^{185}\text{Re})_m$ and $(^{193}\text{Ir}/^{191}\text{Ir})_m$ represent the measured $^{187}\text{Re}/^{185}\text{Re}$ and $^{193}\text{Ir}/^{191}\text{Ir}$ isotopic ratios, respectively; $(^{193}\text{Ir}/^{191}\text{Ir})_t$ represents the true value of $^{193}\text{Ir}/^{191}\text{Ir}$; M is the atomic mass of Re and Ir isotopes; and f denotes the ratio of the mass fractionation factor of β_{Re} and β_{Ir} ($\beta_{\text{Re}}/\beta_{\text{Ir}}$). In this study, $(^{193}\text{Ir}/^{191}\text{Ir})_t = 1.682979$ (Walczyk and Heumann, 1993) was used as the true ratio. To estimate the f value, we employed the Re isotopic data reported by Gramlich *et al.* (1973), which is also adopted by IUPAC. The f value was optimized to minimize the deviations of all measured $^{187}\text{Re}/^{185}\text{Re}$ values of the Re standard from the reference value of 1.6740 (Gramlich *et al.*, 1973; Rosman and Taylor, 1998). The overall average of the f value was 0.8512 ± 0.0016 ($n = 20$). This value was applied for correction of the mass fractionation effect.

To investigate the precision and accuracy of MC-ICP-MS analyses performed using this empirical technique, the $^{187}\text{Re}/^{185}\text{Re}$ ratio of the ^{185}Re -enriched spike was measured by both MC-ICP-MS and N-TIMS. The $^{187}\text{Re}/^{185}\text{Re}$ values of the ^{185}Re -enriched spike obtained by MC-ICP-MS are listed in Table 3, and are in agreement with those measured by N-TIMS (Suzuki *et al.*, 2004). The ^{185}Re -enriched spike concentration was also calibrated using this Ir normalization procedure. For measurements of the ^{185}Re -enriched spike concentration, the external reproducibility was 0.6% ($n = 6$, 2σ). This good reproducibility demonstrates that the employed method is effective in precisely measuring Re concentrations using isotope dilution.

Treatment of Os and Re memory effects

The memory effect of Os introduced as a solution into the ICP-MS is known to be severe (Hirata, 2000): high background levels and memories from previous samples can affect subsequent measurements. Low background levels are a prerequisite for achieving accurate measurements of Os isotope ratios at the picogram level. Previ-

ous studies have shown that OsO_4 can penetrate into plastic (Pearson *et al.*, 1999) or Teflon, or be absorbed into the wall of Teflon vessels (Suzuki *et al.*, 1992), making it difficult to eliminate. Therefore, it is preferable to introduce Os in a reduced form (e.g., OsBr_6^{2-} or OsCl_6^{2-}) (Nowell *et al.*, 2007). Hirata (2000) reported that the use of a FSC spray chamber can help in minimizing the Os memory effect. We found that the introduction of Os samples into the ICP through a glass nebulizer rather than a Teflon nebulizer lead to a significant reduction in the magnitude of the Os memory effect. This suggests that the source of the Os memory effect in the inlet system is not only in the spray chamber, but also in the nebulizer.

Makishima and Nakamura (2006), using 0.5 mol L⁻¹ of HF as a washing solution, reported only a slight Os memory in their Neptune[®] MC-ICP-MS using Aridus[®] after 15 min of cleaning. However, this approach was ineffective in our IsoProbe[®] MC-ICP-MS: the memory level in the IsoProbe[®] using Aridus[®] was at least several orders of magnitude higher than the level reported for the Neptune[®], especially after several hours of measurements. Therefore, we introduced Os samples into the ICP-MS by glass nebulizer rather than by Aridus[®]. We also found that the use of a reducing agent comprising 5% v/v HCl–EtOH mixture solution is more effective in eliminating the Os memory effect than the use of 5% v/v HCl, 5% v/v HBr, or 15% w/w $\text{NH}_2\text{OH}\cdot\text{HCl}$ (Meisel *et al.*, 2001). The resulting memory effects of Re and Ir were minor. When Re samples were introduced into the ICP by Aridus[®] and the inlet system was cleaned with 6% HCl, the residual signal after 10 min washout was less than 0.05% of the sample signal intensity. This memory effect is negligible in terms of isotope dilution measurements of Re. To avoid memory or contamination effects related to the sample inlet system, we used the glass nebulizer and Aridus[®] system for measurements of Os and Re, respectively.

To evaluate the magnitude of the memory effect, two Os standard solutions with different radiogenic ^{187}Os abundances were measured alternately by MC-ICP-MS (Fig. 1). The average $^{187}\text{Os}/^{188}\text{Os}$ values obtained for the J-Os and M-Os standards using MC-ICP-MS were 0.1069 ± 7 ($n = 12$, 2σ) and 0.1203 ± 9 ($n = 12$, 2σ), respectively. These values are within measurement uncertainty of the average $^{187}\text{Os}/^{188}\text{Os}$ values obtained by N-TIMS for J-Os (0.10694 ± 6) and M-Os (0.12022 ± 20). Therefore, the Os memory effect can be considered negligible, having no significant influence on the measured Os isotope ratios.

CONCLUSION

The pronounced memory effect and low sensitivity of Os represent problems in performing highly precise Os

isotope measurements by solution-mode MC-ICP-MS. With the aim of improving the sensitivity of Os, multi-ion counters and 2% HCl–EtOH as sample uptake solution were used and it was found that the use of glass nebulizer and a wash solution 5% v/v HCl–EtOH mixture solution are effective in eliminating the Os memory effect. For measurements of Re isotopes, improved Ir-based mass-fractionation correction methods were developed to eliminate errors arising from instrumental mass fractionation. The resulting data are in reasonable agreement with those obtained by N-TIMS. Compared with N-TIMS and existing MC-ICP-MS methods, the present method is more convenient and enables higher sample throughput.

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REFERENCES

- Birck, J. L. and Allègre, C. J. (1998) ^{187}Re – ^{187}Os in iron meteorites and the strange origin of the Kodaikanal meteorite. *Meteoritics Planet. Sci.* **33**, 647–653.
- Boulyga, S. F., Segal, I., Platzner, T. I., Halicz, L. and Sabine Becker, J. (2002) Precise isotope analysis of natural and enriched osmium samples using different ICP-MS instruments. *Int. J. Mass Spectrom.* **218**, 245–253.
- Cao, S. Q., Chen, H. T. and Zeng, X. J. (2000) Matrix effects in inductively coupled plasma mass Spectrometry by use of organic solvent. *Spectroscopy and Spectral Analysis* **20**, 498–500.
- 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.
- Gramlich, J. W., Murphy, T. J., Garner, E. L. and Shields, W. R. (1973) Absolute isotopic abundance ratio and atomic weight of a reference sample of rhenium. *J. Res. Nat. Bur. Stand., A Phys. Chem.* **77A**, 691.
- Gregoire, D. C. (1990) Sample introduction techniques for the determination of osmium isotope ratio by inductively coupled plasma source mass spectrometry. *Anal. Chem.* **62**, 141–146.
- Hassler, D. R., Peucker-Ehrenbrink, B. and Ravizza, G. E. (2000) Rapid determination of Os isotopic composition by sparging OsO_4 into a magnetic-sector ICP-MS. *Chem. Geol.* **166**, 1–14.
- Hirata, T. (2000) Development of a flushing spray chamber for inductively coupled plasma-mass spectrometry. *J. Anal. At. Spectrom.* **15**, 1447–1450.
- Hirata, T., Hattori, M. and Tanaka, T. (1998) *In-situ* osmium isotope ratio analyses of iridosmines by laser ablation-multiple collector-inductively coupled plasma mass spectrometry. *Chem. Geol.* **144**, 269–280.
- Irisawa, K. and Hirata, T. (2006) Tungsten isotopic analysis on six geochemical reference materials using multiple collector—ICP-mass spectrometry coupled with a rhenium-external correction technique. *J. Anal. At. Spectrom.* **21**, 1387–1395.
- Kato, Y., Fujinaga, K. and Suzuki, K. (2005) Major and trace element geochemistry and Os isotopic composition of metalliferous umbers from the Late Cretaceous Japanese accretionary complex, *Geochem. Geophys. Geosyst.* **6**, 1–20.
- Kehm, K., Hauri, E. H., Alexander, C. M. O. D. and Carlson, R. W. (2003) High precision iron isotope measurements of meteoritic material by cold plasma ICP-MS. *Geochim. Cosmochim. Acta* **67**, 2879–2891.
- Liang, X.-R., Wei, G.-J., Li, X.-H. and Liu, Y. (2003) Precise measurement of $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd ratios using multiple-collectors inductively coupled plasma-mass spectrometer (MC-ICPMS). *Geochimica* **32**, 1–6.
- Liang, X.-R., Li, J., Qi, L. and Ma, J.-L. (2005) Accurate measurement for the concentration and isotopic abundance of rhenium using multi-collector inductively coupled plasma mass spectrometer. *Rock and Mineral Analysis* **24**, 1–6.
- Makishima, A. and Nakamura, E. (2006) Determination of Os and Re isotope ratios at subpicogram levels using MC-ICPMS with solution nebulization and multiple ion counting. *Anal. Chem.* **78**, 3794–3799.
- Malinovsky, D., Rodushkin, I., Baxter, D. and Ohlander, B. (2002) Simplified method for the Re–Os dating of molybdenite using acid digestion and isotope dilution ICP-MS. *Anal. Chim. Acta* **463**, 111–124.
- Maréchal, C. N., Telouk, P. and Albarede, F. (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* **156**, 251–273.
- Meibom, A. and Frei, R. (2002) Evidence for an ancient osmium isotopic reservoir in Earth. *Science* **296**, 516–519.
- Meisel, T., Moser, J., Fellner, N. and Wegscheider, W. (2001) Simplified method for determination of Ru, Pd, Re, Os, Ir and Pt in chromitites and other materials by isotope dilution ICP-MS and acid digestion. *Analyst* **126**, 322–328.
- Nier, A. O. (1937) The isotopic composition of osmium. *Phys. Rev.* **52**, 885.
- Nier, A. O. (1950) A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. *Phys. Rev.* **77**, 789–793.
- Nowell, G. M., Luguét, A., Pearson, D. G. and Horstwood, M. A. (2007) Precise and accurate $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ measurements by multi-collector plasma ionisation mass spectrometry (MC-ICP-MS), part I: Solution analyses. *Chem. Geol.* **248**, 363–393.
- Pearson, D. G., Ottley, C. J. and Woodland, S. J. (1999) *Plasma Source Mass Spectrometry: New Developments and Applications*. The Royal Society of Chemistry, Cambridge, U.K., 277 pp.
- Rehkämper, M. and Mezger, K. (2000) Investigation of matrix effects for Pb isotope ratio measurements by multiple col-

- lector ICP-MS: verification and application of optimized analytical protocols. *J. Anal. At. Spectrom.* **15**, 1451–1460.
- Reisberg, L. and Meisel, T. (2002) The Re–Os isotopic system: a review of analytical techniques. *Geostandard Newslett.* **26**, 249–267.
- Rosman, K. J. R. and Taylor, P. D. P. (1998) Isotopic compositions of the element 1997. *Pure Appl. Chem.* **70**, 217–238.
- Roy-Barman, M. and Allègre, C. J. (1995) $^{187}\text{Os}/^{186}\text{Os}$ in oceanic island basalts: tracing oceanic crust recycling in the mantle. *Earth Planet. Sci. Lett.* **129**, 145–161.
- Russ, G. P., Bazan, J. M. and Date, A. R. (1987) Osmium isotopic ratio measurements by inductively coupled plasma source mass spectrometry. *Anal. Chem.* **59**, 984–989.
- Russell, W. A., Papanastassiou, D. A. and Tombrello, T. A. (1978) Ca isotope fractionation on the earth and other solar system material. *Geochim. Cosmochim. Acta* **42**, 1075–1090.
- Schoenberg, R., Nagler, T. F. and Kramers, J. D. (2000) Precise Os isotope ratio and Re–Os isotope dilution measurements down to the picogram level using multicollector inductively coupled plasma mass spectrometry. *Int. J. Mass Spectrom.* **197**, 85–94.
- Shen, J. J., Papanastassiou, D. A. and Wasserburg, G. J. (1996) Precise Re–Os determinations and systematics of iron meteorites. *Geochim. Cosmochim. Acta* **60**, 2887–2900.
- Shirey, S. B. and Walker, R. J. (1998) The Re–Os isotope system in cosmochemistry and high-temperature geochemistry. *Ann. Rev. Earth Planet. Sci. Lett.* **26**, 423–500.
- Smoliar, M. I., Walker, R. J. and Morgan, J. W. (1996) Re–Os ages of Group IIA, IIIA, IVA, and IVB iron meteorites. *Science* **271**, 1099–1102.
- Sun, Y. L., Zhou, M.-F. and Sun, M. (2001) Routine Os analysis by isotope dilution-inductively coupled plasma source mass spectrometry: OsO_4 in water solution gives high sensitivity. *J. Anal. At. Spectrom.* **16**, 345–349.
- Suzuki, K., Qi, L., Shimizu, H. and Masuda, A. (1992) Determination of osmium abundance in molybdenite mineral by isotope dilution mass spectrometry with microwave digestion using potassium dichromate as oxidizing agent. *Analyst* **117**, 1151–1156.
- Suzuki, K., Miyata, Y. and Kanazawa, N. (2004) Precise Re isotope ratio measurements by negative thermal ion mass spectrometry (NTI-MS) using total evaporation technique. *Int. J. Mass Spectrom.* **235**, 97–101.
- Thirlwall, M. F. (2002) Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb – ^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in TI-normalization. *Chem. Geol.* **184**, 255–279.
- Volkering, J., Walczyk, T. and Heumann, K. G. (1991) Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion Proc.* **105**, 147–159.
- Waight, T., Baker, J. and Willigers, B. (2002) Rb isotope dilution analyses by MC-ICPMS using Zr to correct for mass fractionation: towards improved Rb–Sr geochronology? *Chem. Geol.* **186**, 99–116.
- Walczyk, T. and Heumann, K. G. (1993) Iridium isotope ratio measurements by negative thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion Proc.* **123**, 139–147.
- Woodhead, J. (2002) A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS. *J. Anal. At. Spectrom.* **17**, 1381–1385.
- Yin, Q., Jacobsen, S. B. and Lee, C.-T. (2001) A gravimetric K_2OsCl_6 standard: Application to precise and accurate Os spike calibration. *Geochim. Cosmochim. Acta* **65**, 2113–2127.