# Precise and accurate $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ measurements by Multi-Collector Plasma Ionisation Mass Spectrometry (MC-ICP-MS) part I: solution analyses.

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## Abstract

We present new high precision Os isotope data obtained by solution-mode MC-ICP-MS for 4 different Os isotope reference materials and compare the data to that obtained by the N-TIMS method. Mass fractionation effects for MC-ICP-MS are evaluated and we demonstrate excellent adherence to the exponential law. An improved and robust method for the derivation of interfering element isotope ratios is presented and evaluated via analysis of solutions with widely varying interfering element/analyte ratios. We show experiments that illustrate the extent of memory with a conventional solution introduction system and establish a protocol that reduces washout time and memory effects to the same level as those common for other elements typically analysed at high precision by MC-ICP-MS.

Data for standard solutions show excellent agreement between MC-ICP-MS and N-TIMS for all Os isotope ratios except $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os which are consistently lower by ~100 ppm and 3-5‰ respectively for MC-ICP-MS. These differences are highly unlikely to arise from problems relating to Faraday cup or amplifier efficiency variations, residual mass fractionation effects or inaccuracies in the applied W interference corrections on $^{186}$Os and $^{184}$Os for MC-ICP-MS analyses. These issues require further investigation if the Pt-Os system is to find routine application as a geochemical tracer.

**Keywords:** Osmium, Isotopes, MC-ICP-MS, Re-Os, Highly Siderophile

## 1. Introduction

Over the past 15 years negative thermal ionisation mass spectrometry (N-TIMS) has become the method of choice for the analysis of Os isotope ratios for geochemical studies. Much of the reason for this centres around the impressive ionisation efficiencies reported using this method (Creaser et al., 1991; Völkening et al., 1991a), that allow the routine analysis of very small samples and because until recently, most measurements have focussed on the Re-Os system, where resulting variations in the $^{187}$Os/$^{188}$Os ratio are often very large. Advances in instrumentation combined with a desire to exploit the Pt-Os decay system have resulted in a new drive to measure $^{186}$Os/$^{188}$Os ratios. The smaller fractionation of Pt from Os in most geological systems coupled to the low natural abundance of the parent isotope ($^{190}$Pt ~ 0.0129%) and long half-life (~450 billion years; Smoliar et al., 1996; Begeman et al., 2001) means that $^{186}$Os/$^{188}$Os ratios have to be measured to levels of precision and accuracy that are at least 2-orders of magnitude better than those required for typical $^{187}$Os/$^{188}$Os measurements.

Despite the attractions of N-TIMS measurements for $^{186}$Os/$^{188}$Os analysis (Walker et al., 1997; Brandon et al., 2006) complications arise due to the ionisation of Os as a negative trioxide ion, which require oxygen isotope corrections, and due to the more complex mass spectrum generated during negative-ion analyses because of the ready formation of molecular ions (see Luguet et al., this volume for further elaboration). In an attempt to constrain the accuracy of N-TIMS measurements and develop alternative methods for the precise and accurate analysis of Os isotopes we have investigated in detail the potential offered by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Our main rationale is that the positive ions produced by the plasma source at such high masses generally have relatively simple mass spectra that are less likely to be significantly influenced by molecular ions. In addition, although interfering isobaric elemental ions are efficiently generated by the plasma, it has been shown that such interferences can be accurately corrected for (e.g., Nowell and Parrish, 2002; Pearson & Nowell, 2003). Although previous publications have outlined the use of MC-ICP-MS for the analysis of Os isotope measurements, these studies have primarily addressed the measurement of $^{187}$Os/$^{188}$Os ratios (e.g., Schoenberg et al., 2000; N.J. Pearson et al., 2002). Here we present the first section of a two part study that evaluates the potential for high precision measurement of Os isotope ratios with a focus on both $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios using first solution (Part 1) and then laser-ablation (Part 2) introduction systems. In this part of the study we quantify the potential effects of mixing due to memory in the introduction system on accuracy. We demonstrate the effectiveness of our interfering element corrections, assess the mass bias behaviour of Os in solution MC-ICP-MS and compare data generated using these methodologies to that produced by N-TIMS. We conclude that MC-ICP-MS holds great promise as a complimentary technique to N-TIMS, in particular in the certification of isotope reference materials for use in the geochemistry community.

## 2. Aims

In contrast to earlier Os isotope studies by MC-ICP-MS the aim of this study was not to experiment with novel sample introduction methods to try and improve overall transmission efficiency, and thereby push the detection limits to sub-ng sized samples, or to reduce/eliminate Os memory effects. Our aim was simply to obtain high precision measurements on all the isotope ratios of Os, but specifically the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios in order to compare MC-ICP-MS data with the high precision Triton N-TIMS data obtained in our laboratory (Luguet et al., this volume) and with other published N-TIMS data (Brandon et al., 1999, 2006; Meibom et al., 2004; Walker et al., 1997, 2005).

In order to accomplish this aim it was necessary to analyse high concentration Os standards (from 200ng ml$^{-1}$ to 2.5µg ml$^{-1}$) in order to obtain large beam intensities on all the Os isotopes, which meant consuming large amounts of Os per analysis, in some cases as much as 600ng.

## 3. Methodology:

During this study Os isotope ratios four different isotope reference materials (RMs), referred to as UMd, DTM, LOsST and DROsS, were measured using two different MC-ICP-MS instruments (UMd: University of Maryland; DTM: Dept. Terrestrial Magmatism; LOsST: and DROsS; Durham Romil Osmium Standard). The UMd, DTM (see Luguet et al., this volume) LOsST and DROsS Os RMs were all measured on a Neptune MC-ICP-MS at the Arthur Holmes Isotope Geology Laboratory, Durham. For comparative purpose, the DTM and LOsST Os RMs were also analysed using a Nu Plasma MC-ICP-MS at the NERC Isotope Geosciences Laboratory (NIGL). The instrument setups employed for the Neptune and Nu Plasma measurements were different and are described separately below.

The reporting of isotope data follows the guidelines outlined by the Chemical Geology editorial board (2003). The uncertainties for the short-term reproducibility of standards analysed in a single analytical session and/or long-term reproducibility over multiple sessions are quoted as 2standard deviations (2SD). Within run errors for individual analyses are quoted as 2 standard errors of the mean (2SE = 2SD/n$^{0.5}$; where n=45 for the Neptune analyses and n=50 for the Nu Plasma analyses).

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## 3.1Neptune measurements

The Durham Neptune has a 9 Faraday collector array equipped with $10^{11}$ Ω resistor amplifiers which allow a maximum beam of 50V per channel. An Elemental Scientific Incorporated (ESI) PFA-50 micro-flow nebuliser and Glass Expansion 'Cinnabar' micro-cyclonic borosilicate glass spraychamber were used as the sample introduction system for all Os isotope measurements on the Neptune during this study. The sensitivity for Os with this set-up was approximately 50V for a 1μg ml$^{-1}$ Os solution at a free-aspiration rate of around 80μL min$^{-1}$. Although greater sensitivity could be attained using a desolvating nebuliser such systems have been shown to suffer severe memory problems for Os (Pearson et al 1999), presumably due to the very large surface area of the desolvating membrane.

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At the start of each analytical session the Neptune was tuned for maximum sensitivity and optimal peak shape using an Os solution, either the UMd or DTM standard, and the mass calibration was updated by peak-centering on the centre-cup mass $^{187}$Os (Table 2a). Instrument electronic baselines and amplifier gains were then measured, on peak with the line of sight valve closed, while the Neptune was allowed to warm up for half an hour. The Durham Neptune does not have an RPQ energy filter and abundance sensitivity was determined by scanning the low mass tail of a 30V $^{192}$Os beam using the SEM and fitting a curve to the tail in order to calculate the contribution of $^{192}$Os at mass 191. In general the abundance sensitivity was less than 1ppm in the Os mass range, consistent with the low analyser pressure of between <7 and 9x10$^{-9}$mbar.

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The Neptune collector array allowed for the simultaneous collection of all Os isotopes together with the $^{182}$W and $^{185}$Re isotopes necessary for interfering element corrections (Table 2a; see section 3.6). Os isotopes were measured using a static multi-collection routine consisting of 9 blocks of 5 cycles per block with an integration time of 4 seconds per cycle. Although amplifier gains were measured at the start of each session the Virtual Amplifier was used in rotation mode to cancel out amplifier gains. Peak centering and baseline measurements were not carried out at the start of each analysis to reduce measurement time and conserve sample but were repeated several times during an analytical session. Total analysis time was approximately 3.75 minutes and consumed around 300µL of solution depending upon the exact aspiration rate during any session.

Following analysis all intensity data was exported and re-processed offline using Excel. Corrections were applied to the raw data for abundance sensitivity, W and Re atomic interferences (see section 4 for full details) and instrumental mass bias.

During analytical sessions involving only one Os standard it was not necessary to aspirate a wash acid between analyses. In those sessions where 2 or more RMs of different Os isotopic composition were measured Teflon-distilled (TD) 3 or 5mol/L HCl acid was aspirated between analyses until the $^{192}$Os beam decreased to acceptable background levels (see section 3.4 for a more detailed discussion).

### 3.2Nu Plasma measurements

The NIGL Nu Plasma at the time of the Os measurements was fitted with a 7 Faraday 'U-Pb' collector block and $10^{11}$ Ω resistor amplifiers which permitted maximum beam sizes of 10V per channel. The sample introduction system for Os isotope measurements on the Nu Plasma comprised a Glass Expansion MicroMist nebuliser and Cinnabar spray-chamber. The sensitivity for Os with this set-up was approximately 20V for a 1µg ml$^{-1}$ Os solution at a free-aspiration rate of around 400µL min$^{-1}$.

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The 7 Faraday 'U-Pb' collector block did not permit simultaneous measurement of all masses from $^{182}$W to $^{192}$Os in a single configuration. Instead a two sequence collector configuration, shown in Table 2b, was used with masses $^{183}$W to $^{189}$Os collected in the first sequence and $^{188}$Os to $^{192}$Os collected in the second sequence with a 4 second magnet settle time between sequences. $^{188}$Os was used for peak-centering in both sequences and the zoom quad was adjusted to give optimal peak alignment. Abundance sensitivity was not measured but is likely to be slightly greater than 1ppm since the analyser pressure was higher at ~ 2x10$^{-8}$mbar.

Os isotopes were measured using a two-sequence static multi-collection routine consisting of 1 block of 50 cycles with an integration time of 8 seconds for sequence 1 and 4 seconds for sequence 2 (Table 2b). The total analysis time was approximately 16 minutes and consumed around 6400μL of solution depending upon the exact aspiration rate. Samples were processed on-line for W and Re interferences and instrumental mass bias.

No washout was necessary between measurements during the one Nu Plasma analytical session undertaken as part of the present study since only one Os isotope standard was used.

### 3.3 Os transmission efficiency

An Os isotope measurement on the Neptune, using the method described above, consumed 300μl (3.75min analysis at an aspiration rate of 80μl $min^{-1}$) of solution per analysis which equates to 60ng of Os consumed when analysing a 200ng $ml^{-1}$ Os standard. This, in turn, represents 1.9 x $10^{14}$ atoms of Os consumed during an analysis. The total number of ions actually detected per analysis for a 200ng $ml^{-1}$ Os standard was 1.34 x $10^{11}$, based on an average total beam intensity of 9.56V over 3.75mins using a $10^{11}\Omega$ resistor. This represents an overall sample transport, ionisation and ion extraction efficiency of approximately 0.071%. Similar calculations based on the average beam sizes for 1, 1.5 and 2μg $ml^{-1}$ Os standard solutions yield very similar total overall efficiencies of between 0.075% and 0.079%, with the small variation almost certainly being due to slight differences in aspiration rate, tuning of the Neptune and the absolute accuracy of standard concentrations. The overall transport and ionisation efficiency for Os on the Nu Plasma was less than the Neptune at 0.013% but this was mainly due to the use of a high uptake rate nebuliser (400μL $min^{-1}$), which generated significantly more waste within the spray-chamber than the low uptake PFA-50 nebuliser used during the Neptune measurements.

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The transmission efficiencies determined for solution mode introduction of Os in this study are very similar to the 0.082% and 0.02-0.12% efficiencies quoted for Os introduction methods involving either direct micro-distillation or sparging (Schoenberg et al., 2000, Norman et al., 2002).

### 3.4 Os washout and sample to sample memory

One factor that limits the precision and accuracy of isotope ratio measurements of any element by MC-ICP-MS is cross contamination associated with washout of the analyte element from the sample introduction system, often referred to as memory. Previous studies (D.G.Pearson et al, 1999; Schoenberg et al., 2000; Hirata, 2000; Norman et al., 2002) identified the 'conventional' solution introduction system in plasma mass spectrometry, the nebuliser and spray-chamber, as being the major source of Os memory due to the formation of $OsO_4$ which is particularly 'sticky' and easily adsorbed onto surfaces of the introduction system. To keep Os in a reduced state, and hence aid in the washout of Os, Meisel et al (2001) added small amounts of a 15% w/w hydroxylamine HCl solution to Os samples/standards. Although few details are presented this approach is reported to have reduced washout times to 5 min or less (Meisel et al., 2001). Malinovsky et al (2002) used a 5% v/v ammonia solution to improve the Os washout which for dilute Os solutions (1ng $ml^{-1}$ Os) led to a 99.9% decrease in Os signal in about 40 seconds. Alternative methods for improving the washout of Os and reducing the problem of memory during conventional solution introduction measurements have involved modifying the sample introduction system. D.G.Pearson et al (1999) used a low dead volume direct injection nebuliser while Hirata (2000) developed a spray-chamber with an additional port which allowed the introduction of water to continuously flush the spray-chamber. Direct injection resulted in a 90% decrease in Os signal within 10 seconds and >99% decrease in 3mins for a 7.4ng $ml^{-1}$ solution. The flushing spray-chamber approach was partially successful in that it reduced the washout times for dilute Os solutions of 1ng $ml^{-1}$ to ~150 seconds. For solutions with an Os concentration of 1µg $ml^{-1}$ there was no improvement in the washout time and it was not possible to reduce the background Os signal to <0.1% of the peak signal. This difference was probably due to the flush water being re-circulated and becoming progressively contaminated. Novel introduction methods such as sparging (Hassler et al., 2000; Norman et al., 2002) or direct micro-distillation (Schoenberg et al., 2000) have also been developed, in part, to try and minimise the Os memory by eliminating the nebuliser and spray-chamber. These approaches have also been partially successful and have reduced the background Os to approximately 0.05% of the peak intensity. However, repeated washout times of 300-600 seconds (Schoenberg et al., 2000) are still lengthy. In addition, introduction of Os via sparging and micro-distillation suffers the major disadvantage that the Os is slowly released from a fixed sample volume at a finite rate. Hence the measured Os beam intensity decreases throughout an analysis, resulting in a progressive decrease in the ratio of the analyte to background and/or interferences.

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For this study we used conventional solution introduction because it meant that fresh Os solution was introduced continuously and the measured Os signal therefore remained constant throughout each analysis. The ESI PFA-50 low uptake nebuliser, which generates little waste, and Cinnabar micro-cyclonic spraychamber (section 3.1) were used in the hope these would reduce the long Os washout times and poor memory usually associated with solution introduction of Os

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Figure 1a shows a typical Os washout profile for the UMd and DTM Os RMs analysed in this study, obtained at the end of an analytical session. For clarity the x-axis time scale has been re-normalised so that it starts from zero. In this example the Os concentration of both RMs was 200ng $ml^{-1}$. The host acid solution was 3mol/L HCl, the lowest concentration used in this study, and was also used as the wash acid between RM analyses. Each RM was aspirated for approximately 40seconds before the sample probe was placed in the wash acid. The maximum $^{192}$Os signal for both RMs was 3.6V and the stable background $^{192}$Os signal after washout was <0.5mV in both cases; a 99.99% or >7200 fold decrease in $^{192}$Os signal. In the case of the DTM standard this background value was reached after 220s whereas the UMd standard washed out four times more rapidly, reaching a similar background in just 50 seconds. The reason for the difference in rapidity of Os washout for the DTM and UMd RMs is not clear but is possibly related to the speciation of Os in each standard. Regardless of the reason for the different washout profiles the important point illustrated in Figure 1a is that the post-washout $^{192}$Os background was, at most, only 0.014% the peak signal. Figure 1b shows the washout profile for a 2.5ng $ml^{-1}$ DROsS Os standard in 5mol/L HCl, which was the most concentrated Os solution analysed in this study. Rinse out of the introduction set up was with a 5 mol/L HCl wash acid following more than 3hrs of constant aspiration of the DROsS solution. This is an extreme test of the Os washout since approximately 40µg of Os would have passed through the sample introduction system prior to washout. Despite this the $^{192}$Os signal decreased from 34V to a background signal of <1mV within 200 seconds of the probe being placed in the wash acid (T2, Fig 1b); a 99.997% or 34000 fold decrease. The absolute background $^{192}$Os intensity following washout of the DROsS standard was only twice the size of that following washout of the 200ppb UMd and DTM RMs despite being 12.5 times more concentrated. The background $^{192}$Os following washout of the DROsS standard was <0.003% the peak Os intensity.

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The washout of Os in these two examples is actually no worse than that commonly observed when analysing elements such as Sr, Pb and Hf (the latter when analysed with a desolvating nebuliser). The post-washout background or Os memory, as a percentage of peak Os signal, of 0.003 – 0.014% observed in our experiments is actually less than the 0.1% reported by Malinovsky et al (2002) when using ammonia to washout 1ng ml$^{-1}$ Os solutions and the 0.05% quoted for direct micro-distillation of Os (Schoenberg et al., 2000).

An additional observation that was made during the period of this study was the occasional presence of a high Os background ($^{192}$Os >300mV) at the start of some analytical sessions on the Neptune. These high backgrounds always followed a previous Os analytical session during which high concentration Os RMs were run. Although the $^{192}$Os background was <1mV at the end of the preceding session it nevertheless increased by the start of the following session and we attribute this to drying out of the spray-chamber and injector and the partial oxidation of residual Os. To avoid this, the spray-chamber and injector were either replaced, along with the cones, at the start of each session or removed at the end of a session and filled with 3 mol/L HCl overnight to avoid oxidation of the Os. On those occasions where the Os background was initially high, an extended 3 mol/L HCl washout during the warm-up and gain-calibration period was sufficient to reduce the $^{192}$Os to <10mV and with an additional 30 minutes washout to ~1mV.

A more rigorous assessment of the extent of Os memory in the sample introduction system can be made from the repeated back-to-back analysis of two Os solutions of distinct Os isotopic composition. The UMd and DTM Os RMs are perfectly suited to such an experiment since they have very distinct Os isotope compositions as shown in Figure 2. The difference in the accepted $^{187}$Os/$^{188}$Os ratio for the two RMs is approximately 53% while for the $^{186}$Os/$^{188}$Os it is 0.106% (Fig. 2). If there is any Os memory from one analysis to the next then it is expected that the Os isotope composition of each standard should be displaced toward that of the other standard. In the case of Fig 2 this means that each standard would show a displacement along a mixing line between the two RMs. The washout profiles in Figure 1 suggest Os memory should be minimal (<<1%) and this initial observation is supported by the lack of any sign of mixing at the scale of Fig 2. Figure 3a&b, however, shows close ups of all the UMd and DTM RMs analysed as part of this study and at this reduced scale there is some evidence for minor Os memory.

The UMd and DTM RMs in Fig 3a&b were analysed during 9 analytical sessions over a an 11 month period, some of which comprised analysis of just one of the RMs and others in which both RMs were run either in blocks or back-to-back. The UMd RM data in Fig3a can be broadly divided into two groups, one that is tightly clustered about $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios of 0.11379 and 0.11983 respectively, representing analyses of the 1-2.5µg ml$^{-1}$ UMd RM solution, and a more diffuse group with a greater variation in $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios that represent analyses of the 200ng ml$^{-1}$ UMd RM solution. Analyses of the latter group were interspersed with the DTM standard and it is these 200ppb analyses that result in the slight skew in the UMd data towards higher $^{187}$Os/$^{188}$Os ratios (Figure 3c). This skew is almost certainly due to memory of DTM Os but since many of the UMd and DTM RMs were also doped with Re and W (see section 3.6) it is also worth considering the possibility that it reflects a very slight under-correction for the interference of $^{187}$Re on $^{187}$Os during analysis of the 200ng ml$^{-1}$ UMd RM solution. We actually consider it highly unlikely that the skew in the UMd data toward high $^{187}$Os/$^{188}$Os ratios is related to an under-correction for $^{187}$Re since our interfering element correction method is extremely accurate (see section 3.6.2) and more importantly because a similar skew is not observed in the DTM standard data (Fig 3c), despite being doped with even greater amounts of Re. Although the skew to high $^{187}$Os/$^{188}$Os values in the UMd RM data is most likely due to Os memory the displacement is, nevertheless, very small and amounts to less than a 0.05% contribution of DTM Os.

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Except for 3 analyses, the DTM RM data shown in Fig3b is all tightly clustered and show a normal Gaussian distribution in $^{187}$Os/$^{188}$Os values (Fig. 3c). This suggests that in general the memory of UMd Os in the introduction system is either absent or is so minor (<0.05%) that it is beyond the resolution of our analytical method even during mixed DTM-UMd analytical sessions. Although the displacement of 3 DTM RM analyses to low $^{187}$Os/$^{188}$Os could result from an over-correction for $^{187}$Re this is extremely unlikely for the same reasoning outlined above. The amount of UMd Os necessary to explain the low $^{187}$Os/$^{188}$Os ratios for the 3 DTM analyses is still limited and only amounts to between 0.05 and 0.15%. This probably results either from inadequate washout or contamination of the wash acid.

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At the scale of Fig3a&b, and therefore at the level of uncertainty of our method, mixing between the UMd and DTM RMs as a result of memory in the sample introduction system would not cause a shift in the $^{186}$Os/$^{188}$Os ratio of either RM. This is despite the fact that the difference in $^{186}$Os/$^{188}$Os ratio between the UMd and DTM RMs, at approximately 0.106%, is more than an order of magnitude greater than the total variation expected in silicate rocks. The absence of mixing is confirmed by the fact that both the UMd and DTM RMs show Gaussian distributions in $^{186}$Os/$^{188}$Os (Fig. 3d).

The washout experiments (Fig1a&b) and analyses shown in Fig3a-d suggest that Os washout can be very effective even with conventional solution nebulisation and that as a consequence, memory is actually very limited and no worse than that for elements such as Sr and Pb. Os memory is certainly not an issue when measuring $^{186}$Os/$^{188}$Os ratios given the current analytical uncertainties for such measurements (see Section 5) and the limited natural variation of $^{186}$Os/$^{188}$Os in silicate rocks. Even for $^{187}$Os/$^{188}$Os measurements, the extent of memory observed in this study is not prohibitively high. However, since the variation of $^{187}$Os/$^{188}$Os ratios in the crust-mantle system can reach 100,000% even the limited memory observed here could constitute a problem unless the following basic precautions are taken:

- Use a low volume micro spray-chamber to minimise surface area (preferably PFA).
- Use microflow PFA nebulisers (20-50µl min$^{-1}$), which generate low waste.
- Try to keep Os in a reduced or complexed state to aid in rapid washout.
- Keep all standards and samples in the same chemical form and do not introduce any oxidising acids during an analytical session.
- Ensure samples and standards all have similar Os concentrations.
- Avoid analysing mixed sample batches with large variations in $^{187}$Os/$^{188}$Os composition (>1-5%).
- Do not allow the spray-chamber to dry out between analytical sessions.

### 3.5 Mass bias correction and behaviour.

The correction of mass bias during MC-ICP-MS Os isotope measurements should be straightforward since it has several stable isotope ratios and is hence amenable to an internal correction. However, the situation is complicated by the fact that there is little consensus in the literature over which Os isotope pair to use, and also what reference values should be used for the various ratios that have been employed for mass bias corrections (N.J. Pearson et al., 2002; Schoenberg et al., 2000). Since the primary aim of this study was to compare high precision MC-ICP-MS and N-TIMS Os measurements we chose to correct for mass bias using both the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios, which are the two that were used in the published high-precision N-TIMS studies (Brandon et al., 1999, 2006; Luguet et al., this volume). The reference values used for the two ratios, $^{192}$Os/$^{188}$Os = 3.083 and $^{189}$Os/$^{188}$Os = 1.21978, were also selected on the basis that they were used in the published high-precision N-TIMS isotope studies (Brandon et al., 1999, 2006).

Both exponential and power fractionation laws have been applied in MC-ICP-MS isotope studies, some favouring the former (Marechal et al., 1999), while others the latter (Rehkämper and Halliday, 1998). N.J.Pearson et al, (2002) argued that the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os values we used in this study were more consistent with Os mass bias on the Nu plasma following the power law while D.G. Pearson and Nowell (2005) found that for the Neptune the opposite was true and the values suggested a closer fit to the exponential law.

Whether Os mass bias in MC-ICP-MS more closely approximates the power or exponential law for a particular instrument can be assessed by plotting the natural logarithms of the measured values obtained on any Os solution for two different Os isotope pairs. The advantage of this approach is that it does not require knowledge of any values for specific Os isotope ratios. In such a plot measured Os data should define a line whose slope is related to the difference in mass between the two isotopes on each axis and the nature of the mass bias. The measured slope of the data can then be compared with the theoretical slopes predicted for exponential and power laws. The disadvantage of this method, certainly for the Neptune, which has very stable mass bias, is that ideally it requires a relatively large variation in absolute mass bias in order to precisely constrain the slope from measured data.

Figure 4a&b shows the variation in the natural logarithms of the measured, but W interference corrected, ratios of $^{186}$Os/$^{188}$Os against those of $^{192}$Os/$^{188}$Os for all the RMs analysed in this study. Some individual analytical sessions (highlighted in Figure 4a) show almost no spread in ln($^{186}$Os/$^{188}$Os) and ln($^{192}$Os/$^{188}$Os) values, which reflects the extremely stable instrumental mass bias commonly observed for the Neptune, while other sessions show slightly more variation, albeit small compared to older generations of MC-ICP-MS. On an individual basis the majority of analytical sessions in Figure 4a provide little information on the mass bias behaviour of Os because the range in ln($^{186}$Os/$^{188}$Os) and ln($^{192}$Os/$^{188}$Os) values is too limited to determine an accurate and precise slope. To investigate the Os mass bias behaviour on the Neptune it is necessary to consider all the Os analytical sessions together and only the UMd and DTM RMs were analysed over a sufficient number of sessions to be useful in this regard.

The UMd (n=94) and DTM (n=121) RM analyses define two very distinct parallel arrays in Figure 4a, the displacement of the arrays in the y-axis being due to the different absolute $^{186}$Os/$^{188}$Os ratios of each standard. The slopes for these arrays, determined using the York regression tool in Isoplot3.0 (Ludwig, 2003), are similar and very precise at -0.50677±0.0025 and -0.50864±0.0055, the slightly better precision for the slope of the DTM standards resulting from the greater spread of values. The measured slopes for both the UMd and DTM RMs are extremely close to the theoretical slope for exponential mass fractionation behavior, within 1.6‰ and 2‰ respectively. Given the uncertainties on the former this is well within uncertainty of the value for the exponential law. In contrast, the theoretical slope for power law mass fractionation is well below, and outside the uncertainty, of the measured slopes for both the UMd and DTM standards by some 17.5‰ and 13.9‰ respectively.

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Figure 4b shows the measured N-TIMS values of Luguet et al (this volume) for the UMd and DTM RMs relative to our MC-ICP-MS values together with the mass bias corrected ‘reference’ N-TIMS values obtained by Luguet et al (this volume). Also shown are the modelled exponential and power law curves for mass bias of Os with the UMd and DTM N-TIMS ‘reference’ values. At the absolute degree of mass fractionation associated with N-TIMS, between 0.008% and 0.1% per atomic mass unit (a.m.u.), the exponential and power laws are essentially identical given the precision and reproducibility of the best N-TIMS analytical methods and either law could be used to correct measured Os data. However, at the absolute degree of mass bias typical of our Neptune measurements, between 0.7% and 0.94% per amu, the difference between the exponential and power laws would amount to an approximate 200-300ppm disparity between the measured values for $^{186}$Os/$^{188}$Os at a given $^{192}$Os/$^{188}$Os ratio and would, as shown in the close up in Figure 4c, be clearly resolvable. Using the N-TIMS reference values (Luguet et al., this volume) the exponential model provides a better fit and is almost indistinguishable from the measured ln($^{186}$Os/$^{188}$Os) and ln($^{192}$Os/$^{188}$Os) values for both the UMd and DTM RM Neptune analyses.

On the basis of this evaluation, the exponential fractionation law was used to correct for mass bias during all Os isotope measurements on the Neptune and was also used for the Nu Plasma measurements. No residual correlations between mass bias corrected Os isotope ratios were found for either the UMd or DTM standards. All subsequent discussions of Os data collected as part this study will be based on the $^{192}$Os/$^{188}$Os corrected values, unless specifically stated otherwise.

### 3.6 Interference corrections for non molecular singularly charged elemental species (Re and W).

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Since a MC-ICP-MS plasma source operates at a steady state instrumental mass bias is essentially constant with time, or at least is extremely limited. There is no time dependant fractionation of one element relative to another so that, unlike with TIMS, very accurate corrections can be applied for singularly charged elemental interferences. The usual approach to making interfering element corrections (IECs) is to measure a 'monitor' isotope of the interfering element, which is itself free of interferences. Knowing the ratio of the monitor isotope to that which interferes on the analyte isotope, the Interfering Element Ratio (IER), a simple subtraction can be made. In practice a 'true' IER cannot be used directly for making IECs since the interfering element, like the analyte element, is subject to instrumental mass bias effects. The true IER must therefore be corrected for these mass bias effects and a 'measured' IER calculated before making the appropriate IEC on the analyte. Although, in theory, it is possible to make very large IECs in MC-ICP-MS analyses, the accuracy of such corrections is almost always limited by a lack of knowledge of the natural isotopic composition of the interfering element in question.

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In the case of Os isotopes the main elemental interferences are from W and Re since they overlap on 3 isotopes of Os including the two important radiogenic isotopes $^{186}$Os and $^{187}$Os. For accurate IECs it is essential to know 'true' $^{187}$Re/$^{185}$Re, $^{186}$W/$^{182}$W and $^{184}$W/$^{182}$W IERs although the denominator/monitor isotope for W could also be $^{183}$W. There is also an interference from Pt on both the $^{190}$Os and $^{192}$Os although in this study it was not possible to use

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the monitor isotope approach for making a Pt IEC without increasing the analysis time by adding a second sequence with a cup configuration for including a Pt isotope. Although Pt was not directly monitored during each Os analysis there is nevertheless an internal check for Pt in the form of the $^{192}$Os/$^{188}$Os normalised Os isotope ratios. The presence of any Pt would compromise the mass bias correction which would then be manifest on all the corrected Os isotope ratios. The good agreement between MC-ICP-MS and N-TIMS values for the stable Os isotope ratios and $^{187}$Os/$^{188}$Os (see sections 4 and 5) is taken to indicate that the levels of Pt during this study were negligible and that $^{192}$Pt and $^{190}$Pt were below the limits of detection for the Faradays.

### 3.6.1 Determining the $^{185}$Re/$^{187}$Re, $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W ratios for making IECs

The first step in making accurate atomic IECs is to determine the necessary isotope ratios for the interfering element and two methods have been commonly used in the literature. One approach for determining ‘true’ IERs that has been applied to a range of elements analysed by MC-ICP-MS is to make repeated analyses of the analyte element doped with the interfering element and iteratively adjusting the IER ratio until the ‘correct’ analyte isotope ratio is obtained. For example, N.J.Pearson et al (2002) used this iteration approach to determine the $^{187}$Re/$^{185}$Re ratio necessary for correcting the Re interference during $^{187}$Os/$^{188}$Os ratio measurements while Griffin et al (1999) used it to determine the $^{175}$Lu/$^{176}$Lu and $^{173}$Yb/$^{176}$Yb ratios for correcting the Lu and Yb interferences on $^{176}$Hf.

This is an inherently un-satisfactory method because it relies upon knowing accurate values for at least two isotope ratios of the analyte element to determine each IER; a stable isotope ratio used for mass bias correction and the value for each analyte isotope ratio on which there is an atomic interference. Furthermore, if the mass bias of the interfering element is being corrected internally, this method would then also require knowing an independent isotope ratio of the interfering element. In this scenario, values for 3 isotope ratios would be necessary to determine each IER. For determining the Re and W IERs on Os by iteration, while using the measured Os mass bias, an accurate stable isotope value for Os would be required together with precise and accurate $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios, which means using well characterised Os isotope RMs. This is a problem since there are few isotopically well constrained RMs and indeed even for a single Os RM there is often considerable variation in values obtained in different labs (Meisel, pers comm). The accuracy and precision to which IERs can be determined with this method is strongly controlled by the accuracy and precision to which the Os isotope ratios for the RM are known but also by the amount of the interfering element added to the analyte element used to determine the IER. In the case of Os, the more Re and W in a sample the more accurate and precise the Re and W IERs would need to be in order to make accurate IECs on $^{187}$Os, $^{186}$Os and $^{184}$Os. Very high levels of Re and W during an Os analysis are not usually a problem for solution analyses on processed samples but laser ablation analyses could pose a serious test for IEC accuracy.

The iteration approach works best for elements for which there are very well characterised isotopic RMs and when the IERs are determined on RM solutions doped with levels of interfering element in excess of geologically reasonable values.

An alternative, but more convoluted, method that has been used to determine 'true' IERs and which only requires knowledge of one analyte isotope ratio is to use a third element that is close in mass but non-overlapping with either the analyte or interfering element. N.J.Pearson et al., (2002) used this method to determine the Re IER by doping pure Os and Re solutions with Ir. In this approach, the 'true' $^{193}$Ir/$^{191}$Ir ratio was first derived by analysing the mixed Os-Ir solution over several analytical sessions and correcting the measured $^{193}$Ir/$^{191}$Ir for mass bias using a stable Os isotope pair (e.g. $^{189}$Os/$^{192}$Os; N.J.Pearson et al., (2002)). Having established the isotopic composition of Ir, a mixed Re-Ir solution was measured to derive the 'true' $^{187}$Re/$^{185}$Re ratio, this time correcting the measured $^{187}$Re/$^{185}$Re ratio for mass bias using the $^{193}$Ir/$^{191}$Ir ratio determined from the mixed Ir-Os solutions. Ultimately the 'true' $^{187}$Re/$^{185}$Re ratio derived in this manner is essentially referenced back to the stable Os isotope ratio via a two stage measurement process with Ir as the intermediary element. However, the mass bias coefficients for Os and Ir are not quite equal and do not exactly fit the exponential mass bias law and this can result in a small inaccuracy being introduced on the $^{193}$Ir/$^{191}$Ir ratio through the mass bias correction. A similar argument applies to the introduction of an inaccuracy on the $^{187}$Re/$^{185}$Re ratio through the mass bias correction to the 'true' $^{193}$Ir/$^{191}$Ir ratio although in this case there is also a potential inaccuracy on the Ir carried over from the Ir-Os measurement. Any combined inaccuracy on the 'true' $^{187}$Re/$^{185}$Re will lead to inaccurate $^{187}$Re corrections on $^{187}$Os.

The approach taken here for determining the 'true' $^{185}$Re/$^{187}$Re, $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W IERs is based on the procedure of Nowell and Parrish (2002), Nowell et al (2003) and D.G.Pearson and Nowell (2003). Rather than deriving the IERs iteratively or through the use of an additional element, they are determined from the analysis of a series of Os solutions doped with various amounts of Re and W. It is similar to the 'standard addition' method often used in ICP-MS for highly accurate trace element concentration determinations. In the present study we used the DTM Os RM for the Re and W doping experiments although any natural Os solution would suffice since one significant advantage of this method over the iteration approach is that it does not require any prior knowledge of the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os or $^{184}$Os/$^{188}$Os ratios. Deriving the Re and W IER ratios via this method relies upon knowing only a *single* stable isotope ratio for making mass bias corrections. In the case of Re IER measurements, mass bias corrections have to be based on the measured Os mass bias since the former has only two isotopes, one of which overlaps with $^{187}$Os. For the W IER measurements mass bias could be corrected by using a stable W isotope ratio but since the Neptune cup configuration only allowed for the measurement of one interference-free W isotope (Table 2a) we also used the measured Os mass bias.

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In order to derive the IERs the total signal of the analyte isotope and its interfering isotope ($^{187}$Os+$^{187}$Re, $^{186}$Os+$^{186}$W or $^{184}$Os+$^{184}$W) was normalised to that of a stable isotope of the analyte element, in this case we used $^{188}$Os, and corrected for mass bias. This ratio was then plotted against the mass bias corrected ratio of the non-overlapping isotope of the interfering element, the selected monitor isotope $^{185}$Re or $^{182}$W, normalised to the same stable isotope of the analyte element, $^{188}$Os. Measurements were repeated for a series of Os solutions doped with increasing levels of Re and W such that on an 'IER plot' a series of data points is obtained that define a straight line. The slope of the line defined by the data provides the 'true' $^{187}$Re/$^{185}$Re, $^{186}$W/$^{182}$W and $^{184}$W/$^{182}$W ratios. In practice Re and W IERs could be derived from one set of Os solutions doped with both Re and W but in our case we used two sets of four Os solution each with different levels of Re and W doping. The $^{185}$Re/$^{188}$Os ratio of the Re-doped DTM solutions varied between 0 and 0.34, equivalent to Re/Os elemental ratios of 0-0.1. The $^{182}$W/$^{188}$Os ratio for the W-doped DTM solutions varied between 0 and 0.5; equivalent to W/Os elemental ratios of 0-0.25.

Figure 5a-c shows ‘IER plots’ obtained for the Re and W doping experiments conducted on the DTM Os RM. All measurements were conducted on the Neptune during one analytical session on the 10-03-06. Each plot comprises 16 pure DTM RM analyses and 4 to 5 analyses of each of the Re and W doped DTM RM solutions. The slope of the line in each plot yields the ‘true’ IER and is calculated along with the uncertainty using the regression analysis package in Isoplot3. Two values are quoted for each of the $^{187}$Re/$^{185}$Re, $^{186}$W/$^{182}$W and $^{184}$W/$^{182}$W ratios since the measured data are corrected for mass bias using both the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios. The difference between the two IER values is constant for each isotope ratio at 60ppm amu$^{-1}$ which is due to the values for the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios used in the mass bias correction not being directly equivalent. The reason for deriving IERs relative to both the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios is that for solution work the former ratio is used for mass bias correction whereas for laser ablation Os analyses (Nowell et al., this volume) mass bias is corrected using the latter ratio since the type of samples that are analysed by laser ablation often contain sufficient levels of Pt to have a noticeable interference on $^{192}$Os and $^{190}$Os.

The Re and W IERs derived from the DTM doping experiments in this study (March 2006; Fig5a-c) are listed in Table 3, together with the $^{186}$W/$^{184}$W ratio derived from the two W IERs. The Re and W IERs in Table 3 are corrected for instrumental mass bias using Os since for Re there is no other option and for W our cup configuration (Table 2a) did not permit measurement of a stable W isotope ratio without loss of the $^{192}$Os isotope. The only potential concern arising from this approach to deriving IERs, but one which is common to the iteration approach and indeed most methods, is the fact that mass bias factors ($\beta$) for different elements are not necessarily equal in a plasma source (Maréchal et al., 1999; Albarède et al., 2004) and the relative difference in $\beta$ values may differ from one analytical session to the next. In this case it might be necessary to derive the Re and W IERs on a daily basis such that any slight difference in $\beta$ factors between Os and Re or W would be accounted for through the mass bias correction to one of the Os isotope ratios. In practice the variation in $\beta$ factors from one session to the next is likely to be sufficiently limited that deriving IERs on a daily basis would not be necessary unless the magnitude of the Re and/or W IECs were expected to be large, on the order of >10’s %. In fact the IERs in Table 3 were used throughout this study, and that of Nowell et al (this volume), and there is no apparent evidence for significant variations in $\beta$Os/$\beta$Re or βOs/βW, which would be manifest as over- or under-corrections on the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios. Furthermore, also listed in Table 3 are the same Re and W IERs derived from UMd-doping experiments conducted on the Neptune in September 2002 using the same experimental method and corrected for mass bias using the same $^{189}$Os/$^{188}$Os ratio (D.G.Pearson and Nowell., 2003). The 2002 and 2006 Re IERs are within 65ppm of one another while the W IERs are different by only 1 to 17ppm. Such consistency in the IERs is remarkable considering the two sets of values were derived on two different Os RMs of different concentrations fours years apart. Indeed, at least in the case of the W IERs the reproducibility (<20ppm, 2SD), albeit based on only two measurements, is well within the typical long-term reproducibility obtained on the Neptune for Nd and Hf isotopic RMs (<40ppm 2SD; D.G.Pearson and Nowell, 2005). The excellent reproducibility of both the Re and W IERs suggest that our method for determining IERs is robust and stable over long periods and although it is possible to derive them on a daily basis this is apparently not necessary.

While our Re and W IERs (Table 3) are very precise and have clearly not changed noticeably over a four year period the absolute values nevertheless differ noticeably from published values. Table 4 is a compilation of published $^{185}$Re/$^{187}$Re values. Although there is a 1500ppm variation within the literature it is clear that our value, while being the most precise, is between 700 and 1300ppm higher than most values, including the preferred IUPAC value. The one exception to this is the value of Walczyk et al. (1991) which is actually 117ppm higher than our value. The only Re isotope values in Table 4 that were determined relative to Os, as in this study, are those of N.J. Pearson et al (2002) and the reason for the discrepancy in these values is the use of different Os isotope pairs for the mass bias correction and the choice of 'accepted' values ($^{189}$Os/$^{192}$Os = 0.39593 versus $^{192}$Os/$^{188}$Os = 3.083).

Table 5 is a compilation of published $^{182}$W/$^{184}$W values and shows that the range in published W isotope ratios, as with Re, varies considerably and amounts to approximately 1200ppm for those values corrected for mass bias using an internal W isotope ratio. This variation is mainly due to the adoption of different W ratios for mass bias corrections, including the use of various 'true' values for a particular ratio (Schoenberg et al., 2002).

The $^{182}$W/$^{184}$W ratio derived in this study is consistently lower than all the published values that use an internal W mass bias correction (Table 5) by between 1307ppm and

2514ppm. Since our values for the W ratios in Table 3 are corrected for mass bias using the $^{192}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios and not to an internal W ratio it might be expected for there to be a difference. Irisawa and Hirata (2006) observed a similar systematic deviation of their W isotope ratios from published values when corrected for mass bias using a $^{185}$Re/$^{187}$Re ratio of 0.59738 and, as they referred to it, a ‘conventional’ exponential law. They attributed this deviation to the ratio of the mass bias factors ($\beta$) for Re and W deviating from unity due to different mass bias behaviour in the plasma and introduced a term $\gamma$, which is the $\beta_{Re}/\beta_W$ ratio, into the exponential law to account for this. With the modified exponential law their W ratios are in much better agreement with published values with the ‘modified’ $^{182}$W/$^{184}$W being within 87ppm of the high precision value of Scherstén et al (2006). Although the relative mass bias behaviour of Re-W, or Os-W, in the plasma may vary slightly it is unlikely that it varies to the extent implied by Irisawa and Hirata (2006). In some way this is illustrated by the small variation in $\gamma$ they observed between sessions (<0.017, 2SD) versus the absolute value of $\gamma$ (~1.151). Since the absolute values of $\beta_{Re}$, $\beta_W$ or $\beta_{Os}$ depend on the reference values of the relevant Re, W and Os ratios as well as their mass bias behaviour in the plasma it is likely that the main cause for the difference in $\beta$ factors, or $\gamma$, is simply the choice of reference values.

Our W-doping experiments yield 3 W isotope ratios (Table 3) which makes it possible to use one ratio to re-normalise the remaining two to an accepted W ratio and check their accuracy relative to published values. This is essentially similar to applying the $\gamma$ term of Irisawa and Hirata (2006). If the $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W IER values in Table 3 are normalised corrected to an ‘accepted’ $^{186}$W/$^{184}$W ratio of 0.927672 (Völkening et al., 1991b), using the $^{186}$W/$^{184}$W value in Table 3 and an exponential law, our W values then agree extremely well with those in the literature. Our average internally corrected $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W IER values are 0.932269±18 (2SD) and 0.864838±16 (2SD), which is within 19ppm and 10pppm respectively of the high precision values published by Scherstén et al. (2006). Our $^{182}$W/$^{186}$W, $^{182}$W/$^{184}$W and $^{186}$W/$^{184}$W isotope ratios are therefore internally consistent (ie. the absolute difference between each ratio is the same as for published W isotope values) and they are accurate but they are simply accurate relative to the Os ratios used for mass bias correction during a typical analysis.

The differences between published Re and W values and those derived in this study (Tables 5&6) are primarily down to the selection of the isotope ratio used for the mass bias correction and the preferred value used for that ratio. In our case we use two Os isotope ratios such that our data are not strictly comparable to published values that normalize relative to different element ratios. This illustrates an extremely important point, which is that for accurate interfering element corrections the IERs should *always* be determined relative to the isotope ratio that is used to apply the mass bias correction to the IER before subtracting the interference from the analyte. Ideally they should also be determined for each individual instrument using exactly the same method and cup configuration that is used for measuring the analyte element so as to account for Faraday cup/amplifier efficiency biases. Although using ‘accepted’ or ‘recommended’ values for any IER from the literature may provide reasonably accurate IECs at very low interference/analyte ratios they break down at higher interference/analyte ratios if they are not appropriate for the analysis method being employed.

The IER values determined in this study (Table 3) are in no way recommended as new ‘true’ values and are not necessarily even applicable for IECs on other MC-ICP-MS instruments. They are simply the most appropriate values for applying the most accurate and precise Re and W interference corrections during Os isotope measurements on the Durham Neptune using the method outlined in Section 4.1. Once derived, the Re and W isotope ratios can be applied to all subsequent sample analyses and appear to be robust over long time periods such that they probably only need to be re-determined should cup efficiencies change or a new method with a different cup configuration is used.

### 3.6.2 Accuracy of the Re and W interference corrections

The Re and W IERs in Table 3 were used for the Re and W corrections during all Neptune Os isotope analyses in this study, many of which were doped with various amounts of Re and W (see Section 4). Figure 6a-c provides a clear illustration of the accuracy of the Re and W IECs applied to the UMd and DTM RMs as a function of the size of the correction. Each data point in Figure 6a-c represents a single analysis of the UMd and DTM RMs following W and Re interference corrections.

The Re corrected $^{187}Os/^{188}Os$ ratios (Fig 6a) for the DTM RM are all within 136ppm of the reference value, irrespective of the size of the interference correction and indeed the majority are actually within 50ppm, even where the IEC reaches levels as high as ~325%. There is only one session, with an IEC around ~60%, where 3 analyses are in excess of 100ppm from the reference value. The UMd RM shows more scatter but all analyses are, nevertheless, within 380ppm of the reference value. The UMd RM analyses with the greatest offset from the reference value (values up to 380 ppm high) actually have an IEC of ~0%, which means this offset cannot be related to an under-correction for $^{187}Re$ and, in this case, it can be attributed to slight memory of DTM Os RM in the sample introduction system (see section 3.4). Indeed, memory of DTM Os, which did not wash out as rapidly as UMd Os, probably accounts for the slightly increased scatter of all the low concentration UMd analyses (200ng $ml^{-1}$ Os).

The W corrected $^{186}Os/^{188}Os$ (Fig 6b) ratios for both the UMd and DTM RMs show even less variation from their respective reference values than for the $^{187}Os/^{188}Os$ ratio and are all essentially within 150ppm. Indeed, the DTM RM analyses with the highest W IECs of 190 and 460% are within just 100ppm and 50ppm of the reference values respectively. This illustrates the accuracy of the W corrections even at extremely high W/Os ratios. The reduced scatter of the $^{186}Os/^{188}Os$ ratio about the reference values, compared to the $^{187}Os/^{188}Os$ ratio, as well as illustrating the accuracy of the $^{186}W$ corrections also, reflects the fact that the $^{186}Os/^{188}Os$ ratio is far less susceptible to Os memory because of the small difference in absolute values between the UMd and DTM RMs (0.106%).

The accuracy of the $^{184}W$ corrected $^{184}Os/^{188}Os$ ratios (Fig. 6c) for the UMd and DTM analyses is excellent considering it is the most sensitive of the Os isotope ratios to W interferences and the fact that the size of the $^{184}Os$ beam for the UMd and DTM analyses was only between 1and 17mV. All the W corrected UMd and DTM RM analyses are within 9‰ of the reference values. More remarkable is the fact that the DTM analyses with a W IEC of ~18500% are within 4‰ and those with an extreme IEC of ~45500% are within just 2‰ of the reference values (Fig. 6c)..

For the three Os isotope ratios shown in Figure 6 the greatest divergence of the UMd and DTM RM analyses from their respective ‘reference’ values always occurs where the IEC was ~0%, which rules out the W or Re IEC being the cause of the slightly increased inaccuracy. The high UMd $^{187}$Os/$^{188}$Os values can be explained in terms of Os memory but this can not explain the increased spread in $^{186}$Os/$^{188}$Os or $^{184}$Os/$^{188}$Os ratios at an IEC of 0% since UMd and DTM are too close in terms of $^{186}$Os/$^{188}$Os composition and the $^{184}$Os/$^{188}$Os ratio is essentially invariant in nature. Figure 6d shows the accuracy of the W corrected $^{184}$Os/$^{188}$Os ratio relative to the reference value as a function of the $^{184}$Os beam size. From this is it clear that the greatest divergence of the UMd and DTM RMs from their respective ‘reference’ values is restricted to those analyses that ran with the lowest $^{184}$Os beam intensity (<2mV for the 200ppb solutions), The same relationship also holds for the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios (not shown). The greater divergence from reference values at an apparent IEC of 0% is hence probably related to poor counting statistics and because at such low Os intensities a very minor amount of Re or W, within the actual noise of the faraday detectors can, nevertheless, represent a fairly significant interference on $^{187}$Os, $^{186}$Os and $^{184}$Os.

What is clear from Figure 6a-c is that there is no systematic over- or under-correction on the $^{187}$Os/$^{188}$Os or $^{186}$Os/$^{188}$Os ratios with increasing IEC and this shows that the IERs determined by our method allow very accurate interference corrections over a wide range in Re/Os and W/Os ratios.

### 3.6.3 Determining analyte (Os isotope) ratios from W- and Re-doped analyses

In addition to providing precise and accurate interfering element ratios the doping method presented here has the added and significant advantage over other methods for deriving IERs in that it also yields precise and accurate values for the analyte isotope ratio affected by the interference through the y-axis intercepts of Figure 5a-c. With the iterative method, knowledge of the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios is absolutely essential to determine the Re and W IERs while our doping method, which is akin to the standard addition method often used in trace element analysis, actually provides these ratios, and hence it can be used with any Os solution. To take full advantage of this approach it is necessary to analyse the analyte element at several interferent/analyte element ratios and this was only carried out in this study on the DTM RM.

$^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values for the DTM RM, derived by regression analysis of the various Re and W doped DTM anlyses are presented in Table 6. Several values are given for each ratio based on regression of different doping levels, where group 1 represents the pure DTM Os RM and group 4 the DTM solution with the highest level of Re and W doping. The y-axis intercept values and associated uncertainty errors in Table 7 were derived using the Yorkfit tool in Isoplot 3.0 for regression of the doped anlyses presented in Figure 5a-c. The 2SD error of each intercept value increases as the number of groups included in the regression decreases, if the spread in Re/Os and W/Os ratios is too narrow, or if the standards closest the intercept are excluded from the regression. Nevertheless, even if non optimal regressions are used the absolute intercept values change by only 80ppm and 40ppm for the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os respectively. The variation in the intercept values for $^{184}$Os/$^{188}$Os is greater (3400ppm) but this is less than the reproducibility obtained on all DTM analyses measured in this study (see Section 4.1). The average values for the Os isotope ratios derived from the regression intercepts (Table 6) agree extremely well with the long-term average measured values for the DTM RM determined in this study (see Section 4.1) and by N-TIMS (Luguet et al., this volume).

## 4. Results

The two isotopically well characterised UMd and DTM Os RMs formed the main focus of the present study since there are published high precision Faraday-based N-TIMS measurements (Brandon et al., 1999, 2006), which provide a basis for the comparison of N-TIMS and MC-ICP-MS Os measurements. Preliminary high precision MC-ICP-MS measurements were also obtained on two new/proposed RMs; LOsST (Meisel, pers comm) and DROsS.

### 4.1 UMd and DTM Os reference materials

At total of 94 and 121 analyses of the UMd and DTM RMs were carried out during 9 analytical sessions over an 11 month period. Individual analytical sessions comprised either the analysis of one RM throughout or both RMs run alternately in blocks or individual measurements. The concentration of the UMd and DTM RMs varied from 200ng ml$^{-1}$ to 2.5µg ml$^{-1}$, analysed either as pure solutions or doped with varying amounts of Re and W.

The average within-run precision on the $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios for RM solutions with an Os concentration of 200ng ml$^{-1}$ varied from 0.005% to 0.025% (2SE) while for RM solutions with >1µg ml$^{-1}$ Os the internal precision was <0.004%, comparable with N-TIMS. For the $^{184}$Os/$^{188}$Os ratio, the within-run precision varied between 4‰ and 1.2% for 200ng ml$^{-1}$ Os RM solutions and 1.5 to <2‰ for RM solutions with >1µg ml$^{-1}$ Os.

Figure 7a-c shows the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os Osmium isotope ratios for all 215 UMd and DTM RM analyses carried out on the Neptune in this study following Re and W IECs. The extreme level of Re and W interference in some of the analyses is clearly illustrated in Figure 5a-c with non-corrected $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios as high as 0.74 and 0.67 respectively in the DTM RM; approximately 425% and 558% higher than the ratios obtained on the pure DTM RM by MC-ICP-MS and by N-TIMS (Luguet et al, this volume). The stable $^{184}$Os/$^{188}$Os ratio ratio is the most sensitive to any W interference since $^{184}$Os is the least abundant (0.0197%) isotope of Os whilst $^{184}$W is the most abundant (30.64%) isotope of W. The non W-corrected $^{184}$Os/$^{188}$Os ratio reaches values as high as 0.594 in the most extreme W-doped DTM RM solutions (Figure 5b), which is in excess of 45000% higher than the values for pure DTM by MC-ICP-MS and N-TIMS (Luguet et al, this volume). Following corrections for Re and W interferences the Re and W doped UMd and DTM RMs are indistinguishable from analyses of pure UMd and DTM RM analyses (Figure 7 a-c), irrespective of the level of Re and W doping. The average values for all Re and W interference-corrected Os isotope ratios obtained on the UMd and DTM RMs during each analytical session are presented in Table 7a&b corrected for mass bias using both the $^{192}$Os/$^{188}$Os (a) and $^{189}$Os/$^{188}$Os (b) ratios. Also shown for comparison are N-TIMS values for the UMd and DTM RMs measured on the Triton (Luguet et al., this volume). The N-TIMS values are corrected for oxygen isotope composition, mass bias corrected using an exponential law and a $^{192}$Os/$^{188}$Os ratio of 3.083 and corrected for PtO$_2^-$ interferences. The data are not, however, double-normalised on the basis of the residual correlation between $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios (see Luguet et al., this volume).

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The long-term average values for the $^{190}$Os/$^{188}$Os, $^{189}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios for all the UMd and DTM RM analyses are within 25ppm, 5ppm and 79ppm respectively of the N-

TIMS values of Luguet et al (this volume). The agreement between MC-ICP-MS and N-TIMS values for the isotope ratios above is even better for Os solutions with a concentration of 1µg ml$^{-1}$ Os or greater, at 17ppm, 5ppm and 26ppm respectively. This excellent agreement between MC-ICP-MS and N-TIMS illustrates that during the analysis of pure Os reference materials hydrides (OsH$^{+}$) or other isobaric molecular interferences are extremely low (see Table 1) and cause no resolvable inaccuracies in the Os isotope data. In contrast, to the above ratios the long-term average Neptune $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values for the UMd and DTM RMs are consistently lower than the N-TIMS values (Luguet et al., this volume) by 108ppm to 125ppm and 3.1‰ to 5.3‰ respectively.

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## 4.2 Preliminary data for the LOsST and DROsS Os reference materials

As an addition to the main aim of the present study preliminary Os isotope data were also obtained on the LOsST (Meisel, pers comm) and the new DROsS Os RMs during three analytical sessions. It is the intention of the CRC to establish these Os solutions as certified reference materials for Os isotope geochemistry.

The average values for all interference-corrected Os isotope ratios obtained on the LOsST (n=11) and DROsS (n=20) RMs are presented in Table 8a&b corrected for mass bias using both the $^{192}$Os/$^{188}$Os (a) and $^{189}$Os/$^{188}$Os (b) ratios. Also shown for comparison are the $^{192}$Os/$^{188}$Os corrected N-TIMS values for the LOsST and DROsS RMs measured on the Triton (Luguet et al., this volume).

The LOsST 1µg ml$^{-1}$ RM was analysed on the Durham Neptune (17-03-06) and the NIGL Nu Plasma (23-05-06). During the Neptune analytical session the UMd RM was also analysed in parallel as a cross reference to an established RM of known composition. UMd was selected to run in parallel because the $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios are closer to those of LOsST than the DTM RM. Any Os memory should be minimal and can be seen to be well within the analytical uncertainty as confirmed by the Gaussian distribution of $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os values (Figure 8a). Although the Os concentration of the UMd RM was only 200ng ml$^{-1}$, the average values for the $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios were within 55, 7.8 and 414ppm of the average values for UMd RM solutions of >1µg ml$^{-1}$ and well within the long-term reproducibility of UMd analysed in this study (Table 7). The average $^{190}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios for the 200ng ml$^{-1}$ UMd RM analyses were also within just 4ppm and 3ppm of the long-term average for UMd Os RM solutions of >1.5µg ml$^{-1}$ Os, respectively (Table 7). The accuracy of the analytical session of 17-03-06 was therefore typical of that normally achieved with the Neptune. The $^{190}$Os/$^{188}$Os, $^{189}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios for the LOsST RM were within 0.5ppm, 5ppm and 1.54‰ of the values for the UMd RM run in parallel; also well inside the observed long-term reproducibility for all reference materials analysed in this study.

During the NIGL Nu Plasma analytical session the LOsST RM had to be run in parallel with the DTM rather than UMd RM due to a short supply of the latter. The LOsST and DTM RMs were analysed in blocks rather than alternately in an attempt to limit any effects of Os memory. $^{190}$Os/$^{188}$Os and $^{189}$Os/$^{188}$Os ratios were not reported for the Nu Plasma measurements although the average $^{187}$Os/$^{188}$Os, $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios obtained on the DTM RM (Table 7) were within 33ppm, 86ppm and 2.1‰ of the average values obtained on the Neptune for >1.5µg ml$^{-1}$ DTM RM solutions. The Nu Plasma LOsST $^{186}$Os/$^{188}$Os analyses in Figure 8b show a skew toward higher values although this is not thought to be due to Os memory from the DTM RM since a similar skew to high, DTM-like values is absent in the $^{187}$Os/$^{188}$Os data. In fact, the $^{187}$Os/$^{188}$Os data actually show a skew to lower values, i.e. in the opposite sense to that expected if memory were the problem.

Although the LOsST RM was run on two different MC-ICP-MS instruments in parallel with two isotopically distinct Os RMs the difference in the average $^{186}$Os/$^{188}$Os values obtained on each instrument (Table 8) is only ~8ppm, well within analytical uncertainties for both instruments. The absolute $^{186}$Os/$^{188}$Os values are at the low end of the range obtained by various laboratories (Meisel, pers. comm..). The difference in values for the $^{187}$Os/$^{188}$Os ratio between the Neptune and Nu Plasma is much greater at ~580ppm (Table 8) and is well outside our typical analytical uncertainty for RM solutions with >lµg ml$^{-1}$ Os. This discrepancy is not due to analytical artifacts or Os memory and appears to be related to an actual isotopic variability of different batches of the LOsST RM. The Neptune and Nu Plasma measurements were made on two different aliquots of the LOsST RM and N-TIMS $^{187}$Os/$^{188}$Os values for these two aliquots showed almost exactly the same difference of ~500ppm (Table 8; Luguet, pers. comm..). The LOsST MC-ICP-MS values for the $^{190}$Os/$^{188}$Os, $^{189}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios all agree with the N-TIMS values to within 37ppm whereas the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values are consistently lower by 100ppm and 6.1‰ respectively (Table 8). This difference in $^{187}$Os/$^{188}$Os ratio between batches is one of the reasons why the LOsST RM will be superseded by the DROsS RM.

The DROsS Os RM was analysed on the Neptune in parallel with the DTM Os RM, which has a similar $^{186}$Os/$^{188}$Os ratio (<240ppm difference) but a 62% higher $^{187}$Os/$^{188}$Os ratio. To avoid any problems of potential Os memory the DTM and DROsS Os RMs were analysed in blocks rather than alternately. Figure 8c shows the probability density plots for the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios for the DROsS RM and the Gaussian distribution for both ratios confirms the lack of any carryover of DTM Os during measurements of the DROsS RM. The average values obtained on the various Os isotope ratios for the DTM RM for the session of the 17-01-07 were all within error of the long-term reproducibility for high concentration DTM Os RM solutions on the Neptune and with the N-TIMS values reported by Luguet et al (this volume). The $^{190}$Os/$^{188}$Os, $^{189}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os values for the DROsS RM obtained on the Neptune all agree with the N-TIMS values to within 14ppm or less, indeed the $^{187}$Os/$^{188}$Os ratios are identical (Table 8). As with the UMd, DTM and LOsST RM, the average Neptune $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values for the DROsS RM are lower than the TIMS values by 100ppm and 6.1‰ respectively.

Figure 9 summarises the average Os isotopic composition of the four Os isotope reference materials analysed during this study (Tables 7 and 8) relative to the N-TIMS values of Luguet et al (this volume). A common theme for all four Os RMs is the extremely good agreement between the MC-ICP-MS and N-TIMS values for the $^{190}$Os/$^{188}$Os, $^{189}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios and the consistently lower values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios obtained by MC-ICP-MS. The magnitude in the offset between MC-ICP-MS and TIMS values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios are also remarkably consistent for the various RMs and this suggests perhaps a common cause for the relative difference between the two analytical methods.

## 5. Discussion

The potential sources of error with MC-ICP-MS isotope measurements are generally more numerous than for TIMS measurements. This translates into an increased potential for inaccuracies on measured isotope ratios during MC-ICP-MS analyses and may explain the difference between MC-ICP-MS and N-TIMS values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios. Since the magnitude of mass bias corrections is greater for MC-ICP-MS compared to TIMS measurements (~1% vs. <0.1% per amu respectively) any slight deviation of the mass bias behaviour of the analyte in the plasma source from the chosen mass fractionation law will lead to the propagation of inaccuracies, relative to TIMS values, on the corrected isotope ratios. Moreover, these relative inaccuracies will generally increase as the average mass of the corrected isotope ratio deviates further from the average mass of the isotope pair used for the mass bias correction (Vance and Thirlwall, 2002). This has been observed for Nd isotope measurements on the Durham Neptune (Pearson and Nowell, 2005) where Nd isotope ratios with a deviation in average mass from the mass bias pair ($^{146}$Nd/$^{145}$Nd) of ~1.5% differed from the TIMS Nd values of Thirlwall and Anczkiewicz (2004) by between 100 and 300ppm. However, there are slight variations in published TIMS values for Nd and if the Neptune Nd data are compared to the values of Wasserburg et al (1981) then they differ by significantly less than 100ppm, even when the average mass of the two isotopes forming the ratio pair deviates from the mass bias pair by 1.5%. It is tempting to attribute the difference between N-TIMS and MC-ICP-MS values for Os isotope ratios shown in Figure 9 to the mass bias correction since the difference in average mass of the ratio from the mass bias pair increases toward the right. However, some caution must be exercised with this interpretation since there is considerable uncertainty with the actual N-TIMS values (Luguet et al., this volume) and there are no 'accepted' values. Furthermore, while mass bias effects could explain the consistent 100ppm offset in $^{186}$Os/$^{188}$Os it is unlikely to be able to account for the 3-6‰ offset in the $^{184}$Os/$^{188}$Os ratio.

The potential inaccuracies and increased uncertainty that might be introduced through the mass bias correction are compounded by the fact that the mass spectrum during plasma source mass spectrometry is usually far more complex than with TIMS. For example, molecular and doubly charged interferences generated in the plasma source are very difficult to accurately correct for unlike isobaric interferences such as Re or W. It has therefore become common practice to assess the accuracy of MC-ICP-MS values by comparison with high precision TIMS 'reference' values. Whereas this may be a suitable practice for certain elements, such as Nd, where high precision multi-dynamic TIMS values are available, it is not as appropriate for elements such as Os. Osmium is ionised as a negative trioxide during N-TIMS analysis ($OsO_3^-$)

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and, as illustrated by Luguet et al (this volume), there is a cascade of other Pt, W and Re negative oxide and chloride polyatomic species in the same mass range. Indeed the analysis of Os is one of the few examples where, given a pure Os solution, the N-TIMS mass spectrum is considerably more complex than the MC-ICP-MS mass spectrum.

To take the approach of comparing the Neptune data from this study with N-TIMS 'reference' values would lead to the immediate conclusion that the Neptune $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values are inaccurate by 100-125ppm and ~5‰ for some unidentified reason (see Figure 9). The problem with this conclusion is that it is extremely difficult to explain in terms of an inaccuracy with the Neptune data resulting from interferences, Faraday-amplifier efficiencies or mass bias corrections.

The Neptune values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios are lower than those for N-TIMS. The only way that this could be explained by the presence of an interference on the $^{186}$Os and $^{184}$Os isotopes is to appeal to an *over*-correction for such interferences, otherwise the values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios would be higher. The only atomic interference on $^{186}$Os and $^{184}$Os for which a correction is applied is W. Section 3.6.2 illustrated the accuracy of the W corrections even at very high W/Os ratios. Hence, we do not consider it likely that problems with the W corrections can explain the observed difference between MC-ICP-MS and N-TIMS values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios. Furthermore, this couldn't explain the fact that even the pure Os RMs analysed in this study, which required no W correction, still show the same characteristic low $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios.

An interference affecting the isotope pair used for correcting mass bias is a possible way of explaining the difference between MC-ICP-MS and N-TIMS values for $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os (Table 7 and 8). An interference on just the $^{192}$Os isotope, either an atomic or molecular species, and hence an inaccuracy on the measured $^{192}$Os/$^{188}$Os ratio used for correcting mass bias could not explain the low $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values since the presence of such an interference would actually lead to an *over* estimate of degree of mass bias. This would translate to an *over*-correction of the measured $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios and hence lead to *higher* values. If an uncorrected isobaric interference were present on $^{192}$Os during all the RM analyses then the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values in Tables 7 and 8 would actually represent *maximum* values and the discrepancy between MC-ICP-MS and N-TIMS would be even greater.

The presence of an interference on the $^{188}$Os isotope, which would have to be a molecular species, would be a slightly more complex situation since not only would this lead to an inaccuracy on the $^{192}$Os/$^{188}$Os ratio used for correcting mass bias it would also effect every other Os isotope ratio as it is the denominator isotope. However, the end result of an isobaric interference on $^{188}$Os would be low values for $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios. The problem in trying to explain the low MC-ICP-MS $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values via an interference on the $^{192}$Os and/or $^{188}$Os is that it would be also manifest as systematic errors on *all* the Os isotope ratios to varying extents; this is clearly not the case (Tables 7 and 8). Such an explanation would also fail to account for the relative size in the offset of the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios, 100ppm versus ~3-6‰ respectively. Lastly, the mass bias behaviour exhibited by our Neptune during this study is consistent with theoretically predicted behaviour (see section 3.5) and is not indicative of the presence of an interference on the $^{192}$Os/$^{188}$Os or $^{189}$Os/$^{188}$Os ratios.

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Small inaccuracies on isotope ratios have often been attributed to variations in the efficiency of individual Faraday detectors and or amplifier circuits, especially when analyses are carried out with a static multi-collection measurement routine. Since the MC-ICP-MS measurements in this study were carried out with a static routine this is certainly a factor that must be considered. This also applies to many of the published N-TIMS measurements, however, since they too were carried out with static routines.

Variations in Faraday or amplifier efficiencies could certainly account for the degree of offset of the MC-ICP-MS value for the $^{186}$Os/$^{188}$Os ratio, around the 100ppm level, but would be highly unlikely to be able to account for the ~5‰ offset in the value of the $^{184}$Os/$^{188}$Os ratio. During the analytical session of the 07-03-06 10 measurements of the UMd RM were made with $^{188}$Os in the axial Faraday detector and $^{187}$Os and $^{186}$Os in the L1 and L2 Faradays detectors respectively. Unfortunately the $^{192}$Os and $^{184}$Os isotopes were not measured but the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os values, normalised to a $^{189}$Os/$^{188}$Os ratio of 1.21978, were within 22ppm and 1ppm respectively of the long-term average values reported in Table 7b for our normal cup configuration measurements. The value for the $^{187}$Os/$^{188}$Os ratio of the UMd RM was identical in both cup configurations and during normal Os measurements, when the $^{187}$Os/$^{188}$Os ratio was mass bias corrected to the $^{192}$Os/$^{188}$Os ratio (Table 7a), the value was within 12ppm of the N-TIMS value of Luguet et al (this volume). The DTM and LOsST RMs were also both measured on the NIGL Nu Plasma and the values for the $^{186}$Os/$^{188}$Os ratio were within 33ppm and 8ppm of the Neptune values (Table 7a and 8a) respectively. The values for the $^{184}$Os/$^{188}$Os ratios obtained on the NIGL Nu Plasma for the DTM and LOsST RMs were within 2.3‰ and 768ppm of the Neptune values, which is well within the analytical uncertainty of each instrument for the $^{184}$Os/$^{188}$Os ratio (Table 7a and 8a). Furthermore, the L3 Faraday detector in which the $^{184}$Os is normally collected during the Neptune measurements is also used to collect $^{143}$Nd during Nd isotope measurements and this allows an independent assessment of the L3 efficiency to be made since there are well established reference values for the Nd RM used at Durham. The long-term average Neptune value for the $^{143}$Nd/$^{144}$Nd ratio on our in house J&M Nd reference material differs from the TIMS value by only 13ppm, which again is well within the long-term reproducibility of <35ppm (D.G.Pearson and Nowell, 2005). All these observations are inconsistent with the low Neptune values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios being the result of low efficiencies for the L1 or L3 Faraday detectors or associated amplifiers. Efficiency variations on the H1 H2 and H4 Faraday detectors and amplifiers causing increased uncertainty on $^{188}$Os $^{189}$Os and $^{192}$Os measurements are also unable to explain the low $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios for same reasons as discussed above for interferences.

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Given the complexity of the mass spectrum for N-TIMS Os analyses, and the difficulties in making accurate PtO$_2^-$ and WO$_3^-$ corrections (see Luguet et al., this volume for full details), the difference between N-TIMS and MC-ICP-MS $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values could just as easily result from the under-correction for interferences on $^{186}$Os and $^{184}$Os during the N-TIMS measurements. Figure 10a&b shows the $^{186}$Os/$^{188}$Os ratio versus $^{184}$Os/$^{188}$Os ratio for the UMd and DTM RMS measured at Durham on the Neptune and Triton. The Neptune data is based only on those solutions with Os concentrations of >1µg ml$^{-1}$ and is corrected for mass bias and W interferences while the Triton data is corrected for oxygen composition, mass bias and PtO$_2^-$ interferences. There is clearly no residual correlation between the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios for UMd and DTM RMs analysed on the Neptune whereas residual correlations are very clear in the N-TIMS Triton data for both Os RMs (see Luguet et al., this volume for further details).

The residual correlation for the Triton Os data is not thought to be due to incomplete mass fractionation correction (Luguet et al., this volume). Although the exact cause is not yet clear and both Luguet et al (this volume) and Brandon et al (2006) apparently see no evidence for the presence of $WO_3^-$ during N-TIMS Os analyses, the vectors illustrated on Figure10a&b nonetheless define the expected slope for a W or $WO_3^-$ interference. This is not to imply that the residual correlation of the Triton data is due to $WO_3^-$ but there is an obvious similarity in the slope of the Durham Triton data and the W vector. Also, apart from two UMd analyses, the low end of the range in Triton $^{184}$Os/$^{188}$Os values for both the UMd and DTM standards happens to coincide with the average Neptune value of ~0.00130. Whatever the actual cause of the N-TIMS residual correlations defined by the UMd and DTM standards, they were used by Luguet et al (this volume) to re-normalise the Triton $^{186}$Os/$^{188}$Os data to the long-term Neptune $^{184}$Os/$^{188}$Os value of 0.001300. Despite this re-normalisation procedure the difference between the Neptune and Triton $^{186}$Os/$^{188}$Os values for the UMd and DTM standards is not eliminated. The post re-normalisation Triton $^{186}$Os/$^{188}$Os values for the UMd and DTM standards still remain between 106ppm and 65ppm higher than the Neptune values respectively, although the DTM values are just within uncertainty of one another. Whatever generates the residual correlation between the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios in Figures 10a&b does not account for the ~100ppm difference between the Neptune and Triton values for the $^{186}$Os/$^{188}$Os ratio. If the correlation results from an interference during N-TIMS measurements it would have to affect the $^{186}$Os isotope only and would have to be of a different magnitude during the UMd and DTM analyses to account for the difference in offset with MC-ICP-MS analyses. An appropriate candidate interference has not been identified by Luguet et al. (this volume).

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The average composition for the UMd standard measured by Brandon et al (2006) plots firmly within the range of the Triton data of Luguet et al (this volume) but is displaced to slightly higher $^{184}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os values (3; Figure 10a). The displacement from the normalised and re-normalised averages of Luguet et al (this volume) also happens to be very similar to that defined by the individual measurements of the UMd standard on the Durham Triton. If the average value for the $^{186}$Os/$^{188}$Os ratio of Brandon et al (2006) were re-normalised, in a similar manner to the Durham Triton data, then the average UMd $^{186}$Os/$^{188}$Os value would be within 20ppm of that of obtained by Luguet et al (this volume) and hence still approximately 100ppm higher than our Neptune value. The similarity of the Brandon et al (2006) and Luguet et al (this volume) $^{186}$Os/$^{188}$Os values for the UMd standard, with or without re-normalisation, would also seem to imply that it is unlikely that the difference between MC-ICP-MS and N-TIMS values is simply a matter of a cup efficiency problem during either our MC-ICP-MS or the N-TIMS studies.

The average N-TIMS composition for the DTM standard measured by Brandon et al (1999) using a dynamic multi-collection routine that would cancel out Faraday efficiency variations, plots outside the range of the Triton data of Luguet et al (this volume), again to higher $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os values (4; Figure 10b). In this case, however, the average dynamic value actually straddles a W vector that bisects the Neptune MC-ICP-MS data of this study (Figure 10b). Again, this does not imply that the DTM data of Brandon et al (1999) are compromised by a W interference but neither is it inconsistent with this conclusion. If the average DTM composition of Brandon et al (1999) were to be re-normalised to a $^{184}$Os/$^{188}$Os ratio of 0.0013, using the same residual correlation as used by Luguet et al (this volume) for correcting their DTM standards, the Brandon et al (1999) N-TIMS value would also be within the uncertainty of the Neptune MC-ICP-MS value.

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The ultimate cause for the difference between MC-ICP-MS and N-TIMS values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios remains very unclear. It can be quite reasonably argued that it is unlikely to be related to either an incomplete mass bias correction, an isobaric interference problem or a Faraday cup efficiency issue with the Neptune and Nu Plasma MC-ICP-MS measurements of this study. These explanations are equally unlikely as a source of problems for the N-TIMS measurements. The complexity of the mass spectrum during N-TIMS measurements is such that the presence of an isobaric molecular interference on the $^{186}$Os and $^{184}$Os isotopes is, nevertheless, a strong candidate for explaining the high N-TIMS values. This complexity is clearly illustrated by the residual correlations between $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os observed in N-TIMS data by Luguet and others (see Luguet et al., this volume). These residual correlations can be used to correct the $^{186}$Os/$^{188}$Os N-TIMS values to the average MC-ICP-MS $^{184}$Os/$^{188}$Os value of 0.0013 but the difference between MC-ICP-MS and N-TIMS $^{186}$Os/$^{188}$Os is not completely accounted for even with this approach. This suggests an additional interference may be present on just the $^{186}$Os isotope during N-TIMS measurements.

Figure 11 plots the difference between the average N-TIMS Luguet et al (this volume). and MC-ICP-MS values for the $^{186}$Os/$^{188}$Os ratio, following all corrections and re-normalisation to a $^{184}$Os/$^{188}$Os ratio of 0.001300, against the MC-ICP-MS $^{186}$Os/$^{188}$Os value for 3 different Os

RMs. The LOsST Os RM was only analysed by N-TIMS 7 times and showed insufficient spread in $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os to allow a re-normalisation of the $^{186}$Os/$^{188}$Os ratio and so although shown in Figure 11 it is not included in the regression. The average amount of Os loaded onto each filament for each RM was the same at ~50ng. Published data from Brandon et al (1999 and 2006) are not included in Figure 11 since there is little information on load size or control on what corrections were made to the data. Interestingly, despite the corrections and re-normalisation of the N-TIMS data, there remains an apparently excellent correlation between the difference in Triton and Neptune values and the actual $^{186}$Os/$^{188}$Os composition of each Os RM, including LOsST; the more radiogenic the $^{186}$Os/$^{188}$Os ratio of the RM the smaller the offset between the N-TIMS and MC-ICP-MS values. A simple explanation for this correlation is the presence of an interference on $^{186}$Os that remains constant relative to the $^{186}$Os intensity between the 3 RMs during N-TIMS analysis and is hence perhaps related to the filament or how the RMs are loaded. The more radiogenic the standard the less susceptible the $^{186}$Os/$^{188}$Os ratio is to the interference since the percentage abundance of the $^{186}$Os isotope increases and hence the $^{186}$Os/interference ratio decreases. This observation seems to support the argument that the high $^{186}$Os/$^{188}$Os ratios obtained on the Os standards run at Durham by N-TIMS could be related to the presence of an interference during N-TIMS analysis. More work is certainly required to understand more fully the cause(s) of the differences in MC-ICP-MS and N-TIMS values for the $^{186}$Os/$^{188}$Os and $^{184}$Os/$^{188}$Os ratios and more specifically to identity the interferences that are involved.

## 6. Conclusions

Previous studies have raised serious concerns over problems relating to memory during the analysis of Os by ICP mass spectrometry. We have performed experiments to document the extent of memory in a conventional solution introduction system (concentric nebuliser and cyclonic spray chamber). We find that when Os is kept in a reduced or complexed state and when precautions are taken to ensure that the sample introduction system is not allowed to dry in air, Os washout and memory are no worse than for elements such as Sr or Pb which are routinely analysed by MC-ICP-MS. Washout and memory therefore present no obstacle to high precision

Os isotope measurements by solution-mode MC-ICP-MS. We present a method for establishing appropriate interfering element isotope ratios that is not dependant on having isotopically characterised standards. The derived values appear to be constant over long time periods (years). We demonstrate the accuracy of interfering element corrections over a wide range of interference/analyte ratios.

Analysis of 4 Os standards of diverse Os isotope compositions over a 9 month period using 2 different MC-ICP-MS instruments, for standards of 1μg $ml^{-1}$ or higher concentration, show that it is possible to obtain highly reproducible values for some Os isotope ratios. Long-term reproducibility is best for $^{190}Os/^{188}Os$, $^{189}Os/^{188}Os$ and $^{187}Os/^{188}Os$ and these ratios also agree best with N-TIMS values. Significant discrepancies exist between $^{186}Os/^{188}Os$ (~ 100 ppm) and $^{184}Os/^{188}Os$ (~ 3-5 ‰) values obtained in this study by MC-ICP-MS and those obtained by N-TIMS. The reason for these differences is not immediately apparent but the difference in $^{186}Os/^{188}Os$ values encompasses the entire range of variation in oceanic basalts measured so far. The reason for these differences must be resolved if the Pt-Os system is to find routine application as a tracer in relatively low level silicate rocks.

## Acknowledgements

The authors would like to thank R.J. Walker, R.W. Carlson and T. Meisel for providing the UMd, DTM and LOsST Os reference material solutions together with J.L. Birk and an anonymous reviewer for constructive reviews. The instrumentation used in this study was supported by NERC/HEFCE grant JREI JRDUPEEQ to DGP.

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## Figure Captions

**Figure 1**. a) $^{192}$Os intensity as a function of time for a typical washout of the 200ppb DTM and 200ppb UMd Os reference materials. Heavy vertical line represents the point at which the sample probe was placed into the 3 mol/L HCl wash acid. b) $^{192}$Os intensity as a function of time for washout of a 2.5ppm DROsS Os reference material following 3hrs of continuous aspiration. Time scale is re-normalised to zero for clarity. T1 is the time when the sample probe was removed from the standard and wiped, and T2 is the time when the probe was placed in the 5 mol/L HCl wash acid.

**Figure 2**. $^{186}$Os/$^{188}$Os versus $^{187}$Os/$^{188}$Os plot illustrating the difference in isotopic composition between the UMd and DTM Os reference materials. Also shown is a modelled mixing line between the two RMs. At this scale there is no obvious displacement of the UMd or DTM analyses along the mixing line.

**Figure 3** a) and b) Mass bias and interference corrected $^{186}$Os/$^{188}$Os versus $^{187}$Os/$^{188}$Os ratios for the UMd and DTM Os RMs analysed during this study. Dashed line is the calculated mixing curve shown in Figure 2, with tick marks indicating percentage mixing. c) and d) Probability density plots for the mass bias and interference corrected $^{187}$Os/$^{188}$Os (c) and $^{186}$Os/$^{188}$Os (d) ratios for the UMd and DTM standards, calculated using Isoplot3 (Ludwig, 2003). Probability density curve for the DTM $^{187}$Os/$^{188}$Os ratio is re-scaled for comparison with the UMd curve and therefore excludes the 3 data points in (b) that are clearly displaced to lower $^{187}$Os/$^{188}$Os ratios.

**Figure 4**. a) ln($^{186}$Os/$^{188}$Os) versus ln($^{192}$Os/$^{188}$Os) for measured ratios of the UMd (filled squares), DTM (open squares), DROsS (closed circles) and LOsST (open diamonds) Os RMs measured on the Neptune and the DTM (open triangles) and LOsST (Grey triangles) Os RMs measured on the NIGL Nu Plasma. Neptune data were collected during 9 analytical sessions spread over a period of 11months while NIGL Nu Plasma data were collected during one analytical session. (b) Expanded view of Neptune UMd and DTM data together with N-TIMS data of Luguet et al (this volume), N-TIMS reference values (open circles) and curves illustrating power (long dashes) and exponential (short dashes) law fractionation. (c) Close up of UMd, DTM, LOsST and DROsS MC-ICP-MS data of this study with the power and exponential law fractionation curves from (b).

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**Figure 5.** Interfering element regression plots for (a) $^{187}$T/$^{188}$Os vs. $^{185}$Re/$^{188}$Os, (b) $^{186}$T/$^{188}$Os vs. $^{182}$W/$^{188}$Os and (c) $^{184}$T/$^{188}$Os vs. $^{182}$Re/$^{188}$Os, where T refers to the Total signal on that mass. Two values are presented for each of the $^{185}$Re/$^{187}$Re, $^{182}$W/$^{184}$W and $^{182}$W/$^{184}$W IERs and are based on data corrected for mass bias using $^{192}$Os/$^{188}$Os (1) or $^{189}$Os/$^{188}$Os (2). Regressions carried out using Isoplot3 (Ludwig, 2003).

**Figure 6.** $\Delta_{ref}$ $^{187}$Os/$^{188}$Os (a), $\Delta_{ref}$ $^{186}$Os/$^{188}$Os (b) and $\Delta_{ref}$ $^{184}$Os/$^{188}$Os (c) versus %IEC for the UMd (filled squares) and DTM (open squares) standards. $\Delta_{ref}$ is the difference between the average Re- and W-corrected ratio for the session and the reference value, where the reference value for each ratio is taken as the averages obtained on 1-2.5 μg ml$^{-1}$ pure UMd and DTM RM solutions. %IEC is the difference between the measured non Re- or W-corrected ratio for each analysis and the reference value for the appropriate Os isotope ratio. This provides a measure of the magnitude of the Re and W interference correction applied to each RM analysis. (d) $\Delta_{ref}$ $^{184}$Os/$^{188}$Os versus measured$^{184}$Os beam intensity after correction for W interference..

**Figure 7.** $^{187}$Os/$^{188}$Os (a) $^{186}$Os/$^{188}$Os (b) and $^{184}$Os/$^{188}$Os (c) values for all UMd and DTM Os RM analyses, mass bias corrected to the $^{192}$Os/$^{188}$Os ratio, and corrected for $^{187}$Re, $^{186}$W and $^{184}$W interferences. Values for the $^{185}$Re/$^{187}$Re, $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W ratios used in the IEC are the $^{192}$Os/$^{188}$Os mass bias corrected values in Table 4. Scales for UMd and DTM analyses in plots (a) and (b) are the primary (left hand side) y-axis and the secondary y-axis respectively. Within-run error bars for individual measurements are 2SE. Reproducibility on the reported long-term averages are 2SD.

**Figure 8.** (a) Probability density curve for the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os values obtained on the Neptune for the LOsST RM. (b) Probability density plot for the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os values obtained on the Nu Plasma at NIGL for the LOsST RM. (c) Probability density curve for the $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os values obtained on the Neptune for the DROsS RM. Lack of skew in the distribution is consistent with no Os memory of the DTM standard run in parallel. Dashed line, $^{186}$Os/$^{188}$Os; solid line, $^{187}$Os/$^{188}$Os.

**Figure 9.** Difference in Os isotope ratios between the MC-ICP-MS measurements of this study and the N-TIMS values of Luguet et al (this volume) expressed as parts per million. The N-TIMS reference value for $^{186}$Os/$^{188}$Os is double normalised to a $^{184}$Os/$^{188}$Os ratio of 0.0013, while the N-

TIMS reference value for $^{184}$Os/$^{188}$Os is corrected for mass bias, oxygen isotope composition and $PtO_2^-$ interferences; it is not double normalised.

**Figure 10.** $^{186}$Os/$^{188}$Os versus $^{184}$Os/$^{188}$Os for the UMd (a) and DTM (b) Os RMs measured by MC-ICP-MS (squares) and N-TIMS (diamonds; Luguet et al., this volume). Also shown as shaded circles are average value for the UMd and DTM RMs as defined below:

1: Average values for the UMd (a) and DTM (b) RMs (Luguet et al., this volume) corrected for mass bias, oxygen isotopes and $PtO_2^-$ interferences.

2: Average values for the UMd (a) and DTM (b) RMs (Luguet et al., this volume) corrected for mass bias, oxygen isotopes and $PtO_2^-$ interferences *and* re-normalised to a $^{184}$Os/$^{188}$Os value of 0.001300 using the slope defined by the individual standards.

3: Average value for UMd of Brandon et al (2006), corrected for mass bias and oxygen isotopes. Not corrected for $PtO_2^-$ interferences.

4: Average value for DTM of Brandon et al (1999) measured in dynamic mode.

**Figure 11.** Difference between N-TIMS and MC-ICP-MS values for the $^{186}$Os/$^{188}$Os ratio (expressed in parts per million) versus the MC-ICP-MS value for the UMd, DTM and DROsS Os RMs. N-TIMS values corrected for oxygen isotope composition, mass fractionation, $PtO_2^-$ interferences and re-normalised to a $^{184}$Os/$^{188}$Os ratio of 0.0013. MC-ICP-MS values based on the long-term average values for standards with an Os concentration >1ppm (Tables 9a and 10a), corrected for mass bias using the $^{192}$Os/$^{188}$Os ratio. Note there is a ~5.6 times vertical exaggeration which over emphasises the y-axis errors.