



Low level Os isotopic measurements using multiple ion counting

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Introduction

The Re-Os chronometer is an important chronometer in earth sciences. The most striking feature is that both elements preferentially partition into the metallic core of planets rather than into the crust and mantle. In silicate partitioning, Os prefers the earth's mantle rather than the crust, although this is a little less true for Re, resulting in crustal rocks with very high Re/Os ratios, leading to variations of the $^{187}\text{Os}/^{188}\text{Os}$ ($x=186$ or 188 or 189) from radioactive decay of ^{187}Re into ^{187}Os . Relative to the other common radioactive chronometers, the $^{187}\text{Os}/^{188}\text{Os}$ variations are large and extend over at least 3 orders of magnitude, e.g. ranging from around 0.12 for mantle rock to ~ 1 for average terrestrial crustal rock to up to several 100 in molybdenites or Archean basalts. Nevertheless, there are caveats to these attractive properties: the very low level of Re and Os concentration in most terrestrial surface rocks on one hand and the high ionization potential of Os on the other. Hence, until the development of high efficiency n-TIMS, the Re-Os chronometer has been only marginally used for the study of earth's surface rocks. Although n-TIMS ionization yields range up to 20% for Re-Os, silicate rocks in general have such low concentrations of Os, that the use of an electron multiplier is required. Until recently, the later was used in a single detector mode using magnetic field peak hopping to measure the required number of isotopes.

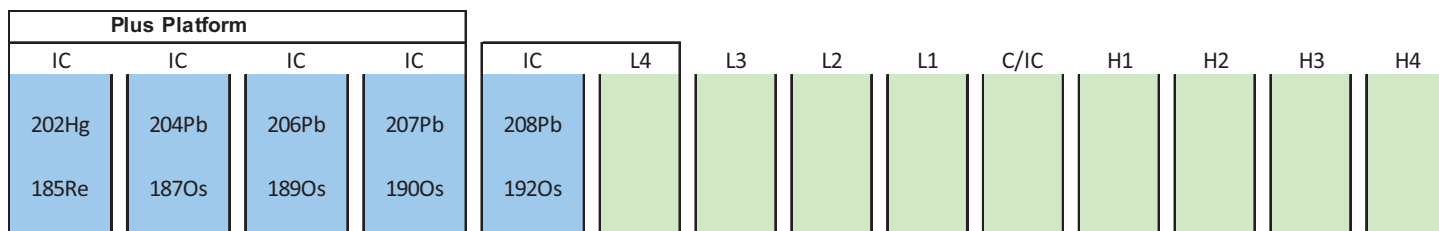


Figure 1. Multiple Ion Counting configuration for Pb and Os isotope ratio analysis on Neptune Plus MC-ICP-MS.

The purpose of this note is to extend the low level Os isotopic measurements to multicollector ICP-MS instrumentation. Peak hopping on a single electron multiplier is excluded for two major reasons: 1) ICP-MS is at least 5 times less sensitive than n-TIMS and 2) beam stability in plasma sources is usually poorer than for TIMS. The possibility to use static multiple collection on secondary electron multiplier ion counters can compensate for these two drawbacks. Here we describe a procedure for calibrating the multiple ion counting system using Os standards using at least ten times larger intensities than the samples. This strategy allows for the precise correction of detector yield drift.

Detector configuration

A Thermo Scientific™ Neptune Plus™ MC-ICP-MS was configured with a multi-ion-counting array that is designed for the collection of Pb isotopes (Figure 1), with the collector spacings fixed for Pb isotopes. The dynamic zoom lens system of the Neptune Plus MC-ICP-MS was used to adjust the dispersion of the Re-Os ion beam into these collectors (dispersion lens +90 V, focus lens -15 V). Figures 2 and 3 show the peak shape and overlap for the Re-Os isotopes in low resolution and medium resolution modes. The peak shape proves to be adequate at least for low level Re-Os measurements, where the precision is limited by counting statistics only.

The peak shapes drastically improve when using the Medium Resolution mode (Figure 3), implying that both the off-axis location of the multiple ion counter and the extreme values of the zoom lens voltages do not produce visible optical aberrations in the Os mass spectrum.

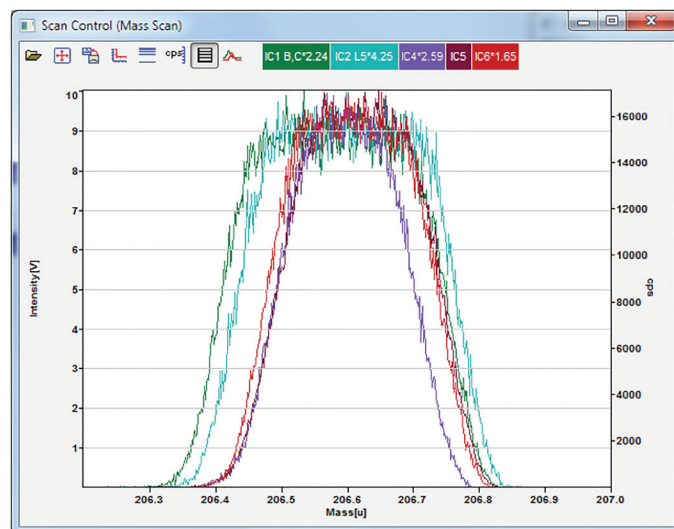


Figure 2. Mass overlap in the Os mass range in the low resolution mode. 1 ppt Os standard solutions are used for these displays. For measurements in the low resolution mode, the mass is set at 206.60 on the axis of the instrument.

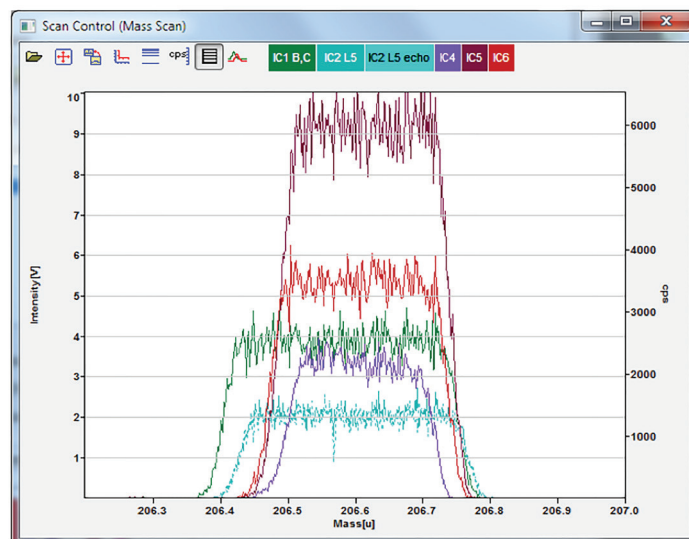


Figure 3. Mass overlap in the Os mass range in the medium resolution mode. A 1 ppt Os standard solution is used to produce these spectra. When measuring a sample, mass is set at 206.66 on the axis of the instrument.

Background spectra and ion source settings

Usually Os is stored in solution in more than 4N HBr media provided it is stabilized as an $\text{Os}(\text{Br})_6^{2-}$ complex. In our opinion, it is not wise to use such high halogenate solutions in an ICP-MS as it would lead to undesired interferences in the mass spectrum and possible corrosion problems on the metal parts of the source region. Solutions of Os were prepared in nitric acid. Nitric acid is not oxidizing below 2N, but because of the absence of the stabilizing HBr, we added a reducing agent which prevents the escape of Os from solution as OsO_4 and retention in a reduced form in the plastic bottles or vials. All final solutions are in 0.3% HNO_3 + 0.03% hydroxylamine. Our experience has shown that such solutions are stable in concentration over a few years.

The introduction system is an Apex™ desolvation nebulizer (ESI, Omaha, USA) with a self-aspirating nebulizer and an uptake rate of 0.1 ml per minute. The cones are a Jet sample cone and a standard H skimmer cone (for enhanced heavy mass sensitivity with low oxides). Typical beam sizes for a 100 ppq Os solution are about 1600 cps of ^{192}Os translating into an ion per atom yields around 0.6%. The minimum amount of Os required to carry out a measurement within the precision frame of this technical note is close to 33 fg.

Unlike TIMS, which usually displays less than 0.5 cps in the OsO_3^- mass range, ICP-MS always displays residual signals in the 180–190 mass range. The spectrum depends on the history of the instruments in the days before the Os measurement and is a combination of memory effects on Re-Os and interferences resulting from molecular ions which include combinations of iron group elements with Ar. The later are mass shifted downwards relative to elemental Os in medium resolution mode (Figure 4). In this figure these polyatomic interference ions were deliberately enhanced for visibility.

Satisfactory background levels (typically less than 50 cps $^{192}\text{Os}^+$), equivalent to about 1 ppq Os can be obtained by using clean cones and alternating: the above running solution, 5% HNO_3 and dilute hydroxylamine in water.

Measurement procedure

The instrument is tuned on Faraday cups using a tungsten standard. The zoom voltages are adjusted using a 1 ppt Re-Os standard solution to fit the Os isotopes in the detectors according to the schematics in Figure 1.

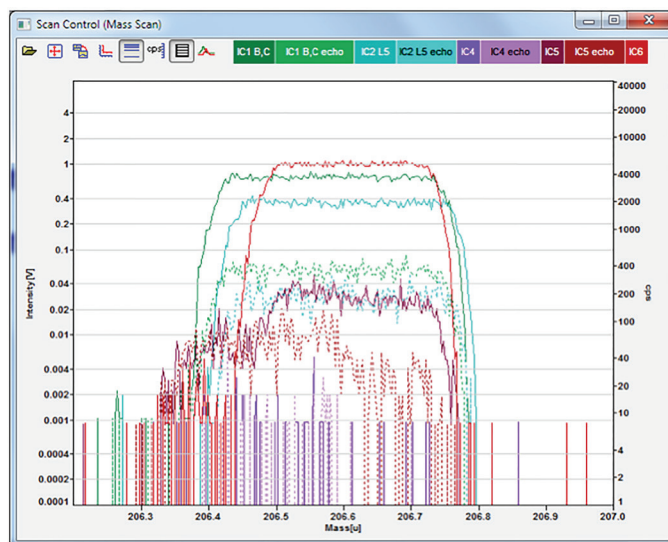


Figure 4a. Interference on mass 187 (IC5, light brown or CDD 3 in Figure 1) from a low mass cluster on mass 187 shown in the medium mass resolution mode. For a Re-Os measurement, the axis mass is set on 206.66 to discard the cluster from mass ^{187}Os or ^{187}Re .

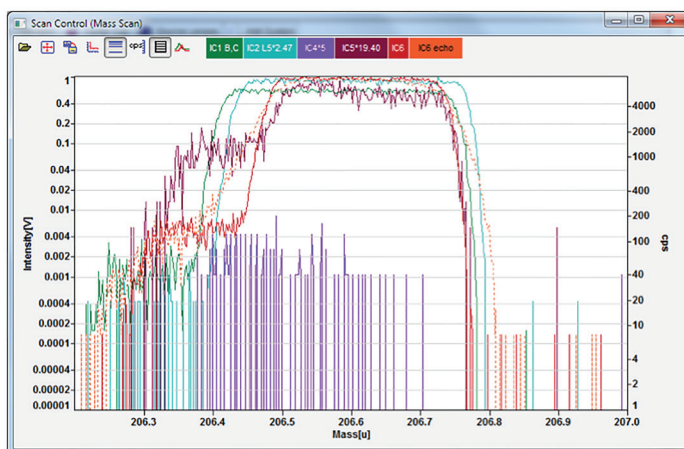


Figure 4b. For demonstration in medium mass resolution mode, the interfering clusters on mass 187 have been enhanced by adding V to the running solution.

Every three samples, and after a few minutes of rinsing, a blank (on-peak zero) is measured for 3–4 minutes. The average of the background levels on the different masses taken before and after each set of three sample measurements is subtracted from the sample signals. Generally this background is stable over the day or tends to decrease very slowly as far as < 10 ppt Os solutions are introduced into the instrument and bromides are only at trace levels in the solution. A single sample measurement consists of 210 seconds data (50 cycles of 4.2 seconds integrations). Standards solutions from 0.1 to 50 ppt were used in this study.

Ratios are all referred to ^{189}Os , because the collector setup of our instrument does not permit the measurement of ^{188}Os together with ^{187}Os , ^{189}Os , ^{190}Os (spike), ^{192}Os and ^{185}Re . Instead, we use ^{189}Os as reference isotope. An additional advantage of using ^{189}Os is that ^{189}Os is not affected by interferences from clustering ions of iron group elements with argon (resulting from impure solutions or insufficient instrument cleaning).

The following data evaluation procedure is used: For each ratio after background correction, the measurements of all solution equal or above 10 ppt are averaged and a bias factor is calculated relative to the reference value obtained on a Faraday cup. This bias factor is then applied to all individual ratios to obtain the corrected values. It combines the mass bias and ion counter yield corrections. No further normalization is applied. This procedure assumes that once the instrument is tuned, the instrumental fractionation drift over the session duration is insignificant to the uncertainty from counting statistics. The data show that this assumption is valid. A rhenium correction is applied for mass 187 using the measured mass 185 with a reference value measured for $^{187}\text{Re}/^{185}\text{Re}$ from a 0.2 ppt Re standard solution measured within the same session.

The normal running setup uses the Elemental Scientific Apex™ desolvating nebulizer system and the Low Resolution mode in order to have the highest possible signal level. A series of standards at various concentrations are measured in a row and also by alternating two solutions different by a factor of 30. The results are displayed in Figures 5 and 6. The results show that for $^{187}\text{Os}/^{189}\text{Os}$ the reproducibility increases from the percent level for 0.1 ppt solutions to the permil level for solutions above 4 ppt. For $^{190}\text{Os}/^{189}\text{Os}$ and ^{192}Os the 2 permil level of reproducibility is already reached for 0.3 ppt Os solution. The error bars from the different Os concentrations overlap both for the individual measurements and for the average ratios and show that there is no significant signal dependence within the explored range from 1,500 to 500,000 cps ^{192}Os signal. We mention here that the Os standard has a very low $^{187}\text{Os}/^{189}\text{Os}$ mantle-like isotopic composition.

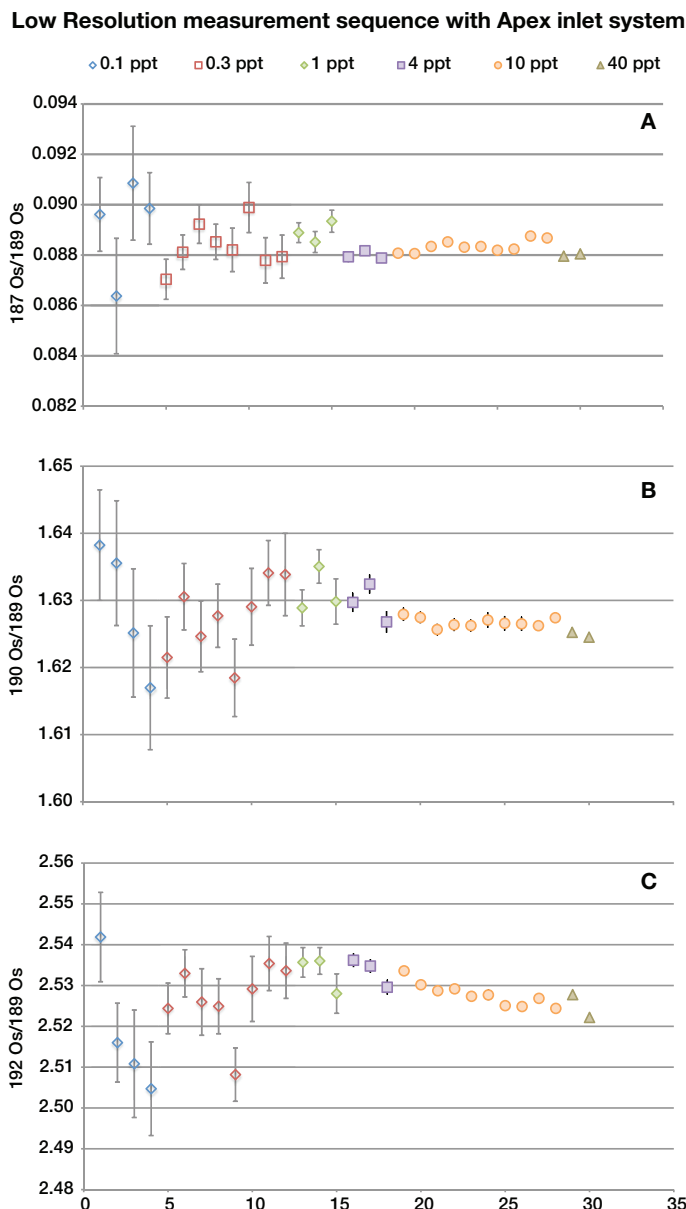


Figure 5. Individual measurements of 210 s over the whole concentration range of this study in Low Resolution mode. Error Bars from Standard Error of the Mean for each measurement (1σ).

With seawater-like compositions, which have about ten times more ^{187}Os relative to e.g. 189, a reproducibility of ca. 0.5% is anticipated with a 0.1 ppt solution.

A similar data set was obtained by replacing the Apex™ desolvation system by a cyclonic spray chamber (wet plasma) reducing signal levels by a factor of 4: range 330 to 170,000 cps for solutions from 0.1 ppt to 50 ppt with an injection rate of 0.1 mL/min. Due to poorer counting statistics, the $^{187}\text{Os}/^{189}\text{Os}$ reproducibility is better than 1% only above 1 ppt Os concentration.

The Medium Resolution mode ($R = 8,000$) was also investigated with the cyclonic spray chamber, reducing the signal level by another factor of 4, typically from 90 cps to about 45,000 cps of ^{192}Os beam for the standards from 0.1 to 50 ppt total Os. ^{187}Os signal are very low ranging from 3 to 1,500 cps. Measured ^{185}Re beams are below 0.5 cps.

Nevertheless the resulting data fit very well within increased error bars with higher signal data. This shows that there is no residual bias from the data correction process at very low signal. These results are displayed in Figure 6.

A similar data set was also obtained in the Medium Resolution mode using the Apex™ desolvating nebulizer and are not displayed here. The conclusion is the same: the data fit to the expected results within the error bars.

Conclusion

The dynamic zoom lens optics of the instrument allowed precise Os isotopic ratios in the ppt and sub-ppt concentration range. With 30 fg Os, a significant ^{187}Os measurement can be reached with the Pb MIC configuration on a Neptune Plus MC-ICP-MS. Depending on the $^{187}\text{Os}/^{188}\text{Os}$ ratio, such low amounts allow precisions from 1.5% for mantle type ratios to less than 0.5% for crustal radiogenic ratios. Within the range investigated here (0.05 to 20 pg), the final error is limited by counting statistics.

Medium Resolution measurement sequence with cyclonic spray chamber

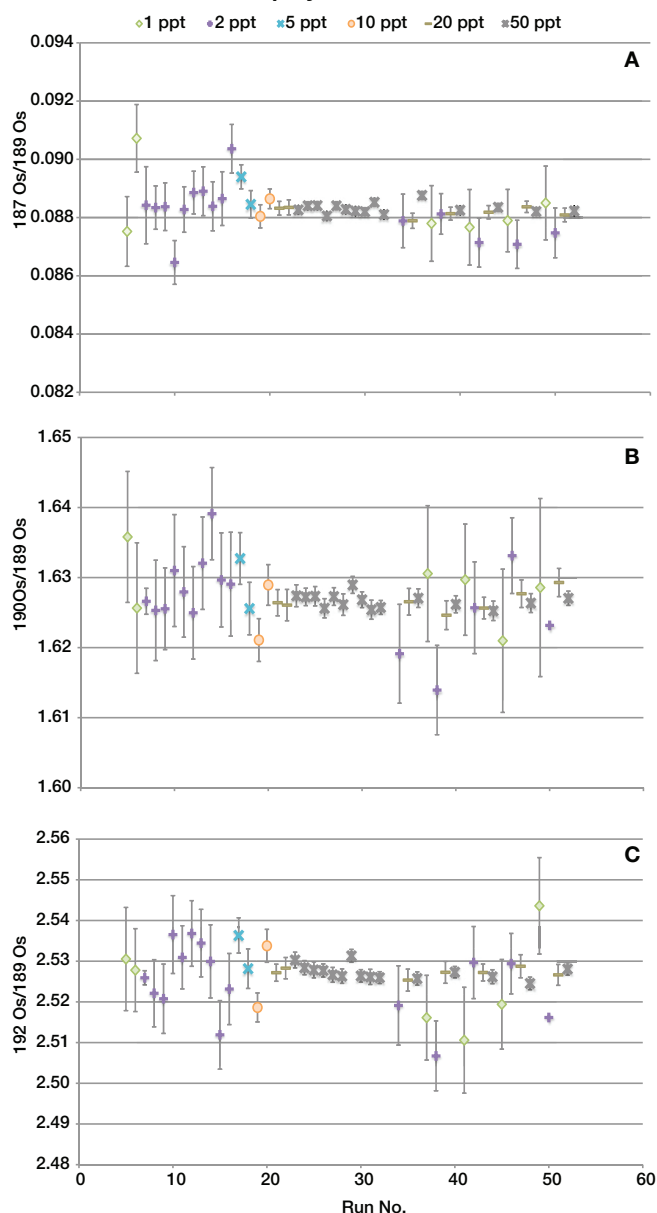


Figure 6. Average ratios for the different concentrations of solution: 1, 2, 5, 10, 20, and 50 ppt.

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