High-Precision Tungsten Isotopic Analysis by Multicollection Negative Thermal Ionization Mass Spectrometry based on Simultaneous Measurement of W and ^{18}O/^{16}O Isotope Ratios for Accurate Fractionation Correction.

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ABSTRACT: Determination of the ^{182}W/^{184}W ratio to a precision of ± 5 ppm (2σ) is desirable for constraining the timing of core-formation and other early planetary differentiation processes. However, WO$_3^-$ analysis by negative thermal ionization mass spectrometry (N-TIMS) normally results in a residual correlation between instrumental mass fractionation corrected ^{182}W/^{184}W and ^{183}W/^{184}W ratios that is attributed to mass-dependent variability of O isotopes over the course of an analysis and between different analyses. A second order correction using the ratio ^{183}W/^{184}W relies on the assumption that this ratio is constant in nature. This may prove invalid, as has already been realized for other isotope systems. The present study utilizes simultaneous monitoring of ^{18}O/^{16}O ratios and W isotope ratios, in order to correct oxide interferences on a per integration basis, and thus avoid the need for a double normalization of W isotopes. After normalizing W isotope ratios to a pair of W isotopes, following the exponential law, no residual W-O isotope correlation is observed. However, there is a non-ideal mass bias residual correlation between ^{182}W/^{i}W and ^{183}W/^{i}W with time. Without double normalization of W isotopes, and based on 3-4 duplicate analyses, the external reproducibility per session of ^{182}W/^{184}W and ^{183}W/^{184}W normalized to ^{186}W/^{183}W is 5-6 ppm (2σ, 1-3 μg loads). The combined uncertainty per session is less than 4 ppm on ^{183}W/^{184}W and less than 6 ppm on ^{182}W/^{184}W (2σ$_m$) for loads of between 3000 and 50 ng.

The lithophile-siderophile ^{182}Hf-^{182}W decay pair is well-suited for constraining the timing of planetary core-formation events by coupling the isotopic ingrowth of ^{182}W from the decay of ^{182}Hf (T$_{1/2}$ = 8.9 Myr) and elemental Hf/W ratios[1-13]. In addition, it has been proposed that the presence of late-accreted extraterrestrial and/or core-derived materials in mantle materials can be detected through high-precision analysis of W isotopes[6]. Towards this end, high-precision W isotope analysis of ^{182}W/^{184}W, with long-term reproducibility of < 5 ppm (relative standard deviation, 2σ), has been achieved by N-TIMS analysis[1-3,6,13]. However, a residual correlation has been observed between mass fractionation corrected ^{182}W/^{184}W and ^{183}W/^{184}W ratios that has been attributed to mass dependent variability of O isotopes between runs[6]. In order to obtain 5 ppm reproducibility (2σ) on ^{182}W/^{184}W, a double normalization scheme to ^{183}W/^{14}W has previously been applied. However, the residual correlation precludes high precision measurement of ^{183}W/^{184}W and, as such, the method does not permit verification of whether or not this ratio is invariant in nature. This is potentially problematic when analyzing cosmochemical materials for which ^{183}W/^{184}W has been documented to vary[8]. Natural variability in this ratio would introduce an analytical bias, as previously observed when using double normalization protocols in the analysis of other isotopic systems[14].

The present study on a Thermo Scientific™ TRITON Plus™ is aimed at monitoring the isotopic variability of ^{18}O/^{16}O during W isotope analysis to apply oxide interference correction on a per integration basis, in order to determine ^{182}W/^{184}W and ^{183}W/^{184}W isotope ratios to high-precision

without double normalization of W isotopes. This is combined with propagation of the uncertainty on the ^{183}W/^{184}W ratio into the ^{182}W/^{184}W uncertainty when normalizing to ^{183}W for instrumental mass bias correction.

EXPERIMENTAL SECTION

Analyses were conducted over a period of 9 months. SPEX CertiPrep™ tungsten standard loads of 3 to 0.05 μg were loaded onto double filament assemblies made from previously outgassed zone refined Re filaments[1]. Lanthanum and Gadolinium were subsequently added as electron emitters[6]. The analytical protocol and results are summarized in Table S-1. Tungsten loads were analyzed for 60 to 240 min, depending on the amounts of W loaded. The analyses typically consisted of alternations of twenty 33 s integrations and one 120 s baseline. Oxygen was bled in the source (P$_{O2}$ ∼ 1-2 x 10^{-7} mbar) to enhance oxide production. Modifying the weight proportion of La-Gd additives with respect to the W amount in the smaller loads (50-200ng) did not noticeably influence the length of analyses nor did it affect the Re/W ratio, nor the ^{18}O/^{16}O composition.

^{182,183,184,186}W^{16}O$_3$, ^{186}W^{18}O^{16}O$_2$ and ^{185,187}Re^{16}O$_3$ species were measured in static multiple collection mode. ^{18}O/^{16}O ratios were inferred from the ^{186}W^{18}O^{16}O$_2$/^{186}W^{16}O$_3$ ratios measured on a per integration basis and were averaged by intervals of 5 min (typically 10 integrations). A 10^{13} ohm resistor amplifier with 10 times higher signal-to-noise (Johnson) ratio compared to 10^{11} ohm resistor amplifiers was used for amplifying

the low ion beam intensities on $^{186}W^{18}O^{16}O_2$, typically < 100 fA. The gain calibration of the 10^{13} ohm resistor current amplifier was performed using the JNdi-1 neodymium reference standard in positive mode[15]. Typical external reproducibility of the gains on 10^{13} ohm resistor current amplifiers over a year was ≤ 100 ppm (2σ, 95% confidence level), and the amplifier gains were measured to < 50 ppm precision (relative standard error, $2\sigma_m$). The relative uncertainty on $^{18}O/^{16}O$ using integrations of 5 min intervals was typically 200 ppm, which is significantly larger than the gain calibration uncertainty of 50 ppm, and reflects $^{18}O/^{16}O$ variability over a timescale of a few min. Consequently, the uncertainty associated with the gain calibration was found to be negligible and has not been propagated in the uncertainty assessment.

Rhenium ion beams were monitored with high ohmic current amplifiers (10^{12} or 10^{13} ohm) for ion beams less than 500 fA, and 10^{11} ohm current amplifiers, otherwise.

The cups collecting W oxide species were sequentially connected to the same set of 10^{11} ohm amplifiers, in order to average out the stochastic calibration biases of the amplifiers and limit the propagation of the uncertainty of the gain calibration procedure to less than 1 ppm.

DATA REDUCTION, RESULTS AND DISCUSSION

W and Re species, monitored simultaneously with the $^{18}O/^{16}O$ ratio were corrected for oxide interference on a per integration basis. Then, 3 exponential normalization schemes have been evaluated, including normalization to $^{186}W/^{184}W$ (N64) or $^{186}W/^{183}W$ (N63) with ^{184}W or ^{183}W as denominators. Results are summarized in Table S-1. It is shown that, in normal running conditions, there is no residual W-O isotope correlation after oxide interference and instrumental mass bias correction. However, non-ideal mass fractionation is evidenced by residual linear correlations between corrected W isotope ratios over time (Figs 1-5). Two strategies are evaluated to improve reproducibility: (1) a double normalization scheme of W isotopes (2) averaging 3-4 duplicates. Finally, recognizing the body of evidence supporting that the ^{183}W relative abundance is not invariant in nature and propagating the ^{183}W abundance uncertainty into the uncertainty on the ^{182}W relative abundance, it is found that averaging 3-4 duplicates is the most robust approach to optimize reproducibility and accuracy on both $^{182}W/^{184}W$ and $^{183}W/^{184}W$ ratios.

Oxide interference correction. The oxygen isotopic composition was determined by an iterative process. In a first step, the O composition from Nier[16] was used as reference and $^{18}O/^{16}O$ ratios of all integrations were inferred from the $^{186}W^{18}O^{16}O_2/^{186}W^{16}O_3$ ratios. Corresponding $^{17}O/^{16}O$ ratios were inferred using $^{18}O/^{16}O$ ratios and the terrestrial fractionation line. In a second step, the obtained $^{18}O/^{16}O$ and $^{17}O/^{16}O$ mean compositions of each analysis were used as new references, until the numerical difference between reference and derived values was within the analytical uncertainty. After correction of the oxide interferences on a per integration basis (typically 33 s each), the W species were normalized to $^{186}W/^{184}W = 0.92767$ or $^{186}W/^{183}W = 1.98594$ (ref. 17).

Residual correlation with O isotopes? When considering mass bias corrected W isotope ratios determined in small W loads (50-200 ng) with Re/W > 0.3, higher than average W isotope ratios are associated with higher than average O isotope ratios. This is accompanied by a correlation between W isotope ratios and the Re/W variation (Fig. S-1) and with a covariation between O isotope ratios and Re/W ratios. This could result from differences in mass fractionation behavior for W and Re oxide species, perhaps resulting from differences in the Re and W to O complexing behavior at elevated Re/W ratios, leading to inaccurate estimates of both W and O isotope abundances, which are all inferred from W oxide species after Re oxide interference correction. On one 50 ng load, the mean Re/W ratio is 4, implying that the contribution of the interfering $^{187}Re^{17}O^{16}O_2$ ion beam is twice as large as the interfered $^{186}W^{18}O^{16}O_2$ species. Thus, for W loads < 200 ng, alternative loading strategies should be sought in order to minimize the uncertainty associated with large Re oxide correction, including using non Re filaments[2]. As a result, only the W ratios for analyses characterized by Re/W < 0.3 are considered in the following sections. The other values, in *italic* form in Table S-1, are not included in the statistics calculation.

Internal precision (Table S-1). For 1 to 3 µg loads, the mean internal precision ($2\sigma_m$, n=45) on the oxide interference and mass fractionation corrected ratios is 6 ppm for $^{182}W/^{184}W_{N6/4}$, 5 ppm for $^{182}W/^{183}W_{N6/3}$, 4 ppm for $^{182}W/^{184}W_{N6/3}$, 5 ppm for $^{183}W/^{184}W_{N6/4}$ and 3 ppm for $^{183}W/^{184}W_{N6/3}$.

For 200 ng loads, the mean internal precision ($2\sigma_m$, n=3) on the oxide interference and mass fractionation corrected ratios is 10 ppm for $^{182}W/^{184}W_{N6/4}$ and $^{182}W/^{183}W_{N6/3}$, 8 ppm for $^{182}W/^{184}W_{N6/3}$, 9 ppm for $^{183}W/^{184}W_{N6/4}$ and 6 ppm for $^{183}W/^{184}W_{N6/3}$.

For 50 ng loads, the mean internal precision ($2\sigma_m$, n=2) on the oxide interference and mass fractionation corrected ratios is 9 ppm for $^{182}W/^{184}W_{N6/4}$, 10 ppm for $^{182}W/^{183}W_{N6/3}$, 7 ppm for $^{182}W/^{184}W_{N6/3}$, 9 ppm for $^{183}W/^{184}W_{N6/4}$ and 6 ppm for $^{183}W/^{184}W_{N6/3}$.

Residual correlation between W isotopes corrected for instrumental mass bias. The external reproducibility on ^{182}W and ^{183}W relative abundances over 9 months on 1-3 µg loads ranges from 10-11 ppm (normalization to $^{186}W/^{183}W$) to 17-18 ppm (normalization to $^{186}W/^{184}W$) (2σ, n=45, no outlier), which is significantly less than the 30-40 and 60-70 ppm (n=39) previously observed[6].

The external reproducibility on W ratios measured in 200 ng loads is 23 ppm on $^{183}W/^{184}W_{N6/4}$, 26 ppm on $^{182}W/^{184}W_{N6/4}$, 15 ppm on $^{183}W/^{184}W_{N6/3}$, 18 ppm on $^{182}W/^{183}W_{N6/3}$ and 10 ppm on $^{182}W/^{184}W_{N6/3}$ (2σ, n=3, Table S-1).

The external reproducibility on W ratios measured in 50 ng loads is 10 ppm on $^{183}W/^{184}W_{N6/4}$, 13 ppm on $^{182}W/^{184}W_{N6/4}$, 6 ppm on $^{183}W/^{184}W_{N6/3}$, 4 ppm on $^{182}W/^{183}W_{N6/3}$ and 7 ppm on $^{182}W/^{184}W_{N6/3}$ (2σ, n=2, Table S-1).

Residual correlations are resolvable between $^{182}W/^{183}W_{N6/i}$ and $^{184}W/^{183}W_{N6/i}$ ratios for 1 µg analyses that span over 9 months (Figs. 1-3). The most marked residual correlation is observed with the normalization to $^{186}W/^{184}W$, which is the normalization ratio most far removed from the masses of interest.

Notably, the residual correlations between $^{182}W/^{183}W_{N6/i}$ and $^{184}W/^{183}W_{N6/i}$ ratios are not accompanied by W-O isotope correlations, nor correlations between W isotope and Re/W ratios, nor correlations between W isotope ratios and instrumental mass bias. Instead, there seems to be a monotonous drift over time of the W corrected isotope ratios (Fig.4) that could point towards non-ideal mass fractionation behavior. It cannot be

excluded that the electron deflection magnet in the source induces small changes in the ion optics, as such non-ideal mass bias effects, at the ppm level of reproducibility, have previously been reported in positive mode analysis[18]. However, based on the present set of data only, it is not clear why there would be a monotonous drift with time. On the other hand, it cannot be ruled out that slight cup aging induces non linearity of W and O isotope acquisition and subsequent mass-dependent fractionation of W isotopes as previously observed on other isotope systems[14]. Besides, it is assumed but not verified that oxidation of W by the La -Gd additives at the surface of the filament and oxidation by addition of oxygen through the bleed valve follow the same mass fractionation laws. Recognizing that the variability of O isotope composition with time plays a pivotal role in the instrumental mass bias correction, the assumption of a linear mass fractionation between O isotopes needs further validation through direct analysis of $^{17}O/^{16}O$ ratios.

The regression slopes and associated uncertainties have been determined for 1-3 µg loads using ISOPLOT 4 (developed by Dr Ken Ludwig of the Berkeley Geochronology Center). One 1σ outlier in all three data reduction schemes has been rejected from the data reduction (*italic* in Table S-1).
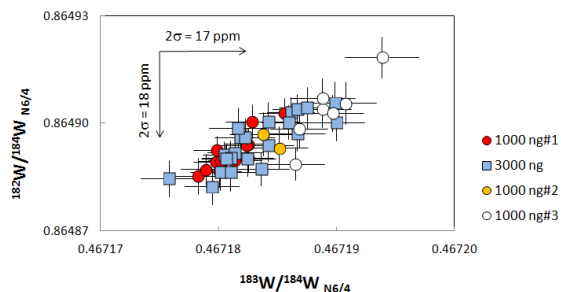

Figure 1. $^{183}W/^{184}W$ N6/4 -$^{182}W/^{184}W$ N6/4 diagram after normalization to $^{186}W/^{184}W$. 1-3 µg analyses are reported. Slope = 1.96 ± 0.27. MSWD=1.2

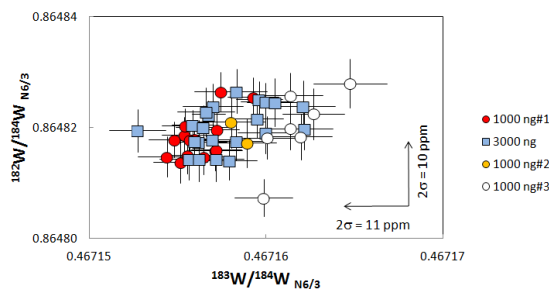Figure 2. $^{184}W/^{183}W$ N6/3 -$^{182}W/^{183}W$ N6/3 diagram after normalization to $^{186}W/^{183}W$. 1-3 µg analyses are reported. Slope = 0.55 ± 0.20. MSWD=2.0

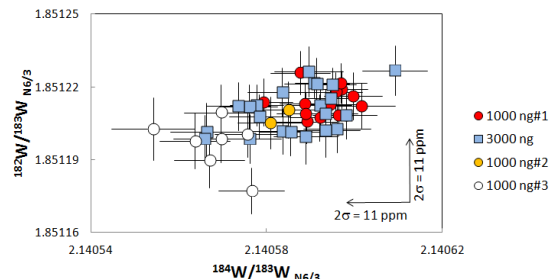Figure 3. $^{182}W/^{184}W$ N6/3 -$^{183}W/^{184}W$ N6/3 diagram after normalization to $^{186}W/^{183}W$. 1-3 µg analyses are reported. Slope = 1.09 ± 0.45. MSWD=2.9
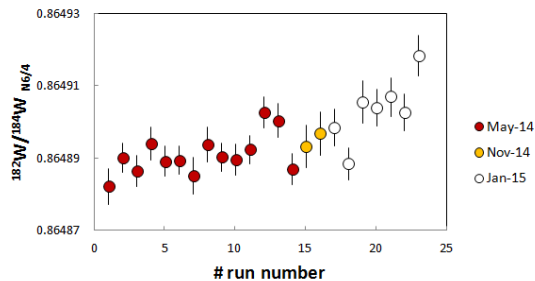

Figure 4. $^{182}W/^{184}W$ N6/4 versus time for 1 µg analyses.

When reduced on a per session basis (May 2014/November 2014/January 2015), the external reproducibility (2σ) on W ratios measured on 1-3 µg loads ranges from 4 to 15 ppm (normalization to $^{186}W/^{184}W$) and 3 to 9 ppm (normalization to $^{186}W/^{183}W$).

Implications of normalizing to $^{183}W/^{184}W$ or $^{186}W/^{183}W$. A few ppm to ε level (part per 10,000) isotopic heterogeneity on the $^{183}W/^{184}W$ ratio could result from nucleosynthetic variability in cosmochemical materials[8]. The contribution of an isotopic variability on the $^{183}W/^{184}W$ ratio into the $^{182}W/^{184}W$ through normalization schemes has to be evaluated.

In the following, the effects of a potential isotopic variability of the ^{183}W relative abundance is evaluated on 1-3 µg load analyses, with the subsequent uncertainty propagation to $^{182}W/^{183}W$ and $^{182}W/^{184}W$, when using normalization schemes to $^{184}W/^{183}W$ and $^{186}W/^{183}W$.

The reproducibility on $^{183}W/^{184}W_{N6/4}$ by session ranges from 4 to 14 ppm (2σ, Table S-1). When applying a linear normalization to $^{183}W/^{184}W$ (similarly to ref.6), using the slope defined in the $^{183}W/^{184}W_{N6/4}$ -$^{182}W/^{184}W_{N6/4}$ diagram (Fig.2), one would obtain a reproducibility of 7 to 10 ppm per session on $^{182}W/^{184}W_{N6/4}$ (2σ, Table S-1). The uncertainty on the $^{183}W/^{184}W_{N6/4}$ ratio per session of 5-6 ppm (defined as the larger between the mean $2\sigma_m$ of the runs and the 2σ of the replicate values divided by square root of the number of replicates), has been propagated into the $2\sigma_m$ uncertainty per session of the $^{182}W/^{184}W_{N6/4}$ ratios ($2\sigma_m$ = 9 to 11 ppm).

The reproducibility on $^{183}W/^{184}W_{N6/3}$ by session ranges from 3 to 9 ppm (2σ, Table S-1). The uncertainty on $^{183}W/^{184}W_{N6/3}$ (≤ 4 ppm), defined as the larger between the mean $2\sigma_m$ of all analyses and the 2σ of all replicates divided by square root of the number of replicates, has to be propagated. An anomaly of 4 ppm on $^{183}W/^{184}W_{N6/3}$ (i.e an anomaly of 6 ppm on the abundance of ^{183}W), by virtue of normalizing to $^{186}W/^{183}W$ using the exponential law, propagates into an anomaly of -8 ppm on $^{182}W/^{183}W_{N6/3}$, and -4 ppm on $^{182}W/^{184}W_{N6/3}$. The combined uncertainty on $^{182}W/^{184}W_{N6/3}$ and $^{182}W/^{183}W_{N6/3}$ thus becomes ≤ 6 and ≤ 10 ppm ($2\sigma_m$) respectively. If, in addition, one linear correction to $^{183}W/^{184}W$ (or $^{184}W/^{183}W$) is applied, using the regression lines defined in Figs. 1-3, the combined uncertainty reduces to ≤ 8 ppm on $^{182}W/^{183}W_{N6/3}$ or $^{182}W/^{184}W_{N6/3}$ after propagation of the $^{183}W/^{184}W_{N6/3}$ uncertainty through these double normalization schemes.

Averaging into means of 3-4 duplicate analyses. Here we evaluate an approach based on averaging three to four dupli-

cate analyses to improve reproducibility on both ^{183}W and ^{182}W relative abundances.

For 1-3 µg loads, this yields a 2σ external reproducibility per session of 6-8 ppm on ^{183}W/^{184}W$_{N6/4}$ and 9-11 ppm on ^{182}W/^{184}W$_{N6/4}$, ≤ 5 ppm on ^{183}W/^{184}W$_{N6/3}$ and ≤ 6 ppm on ^{182}W/^{183}W$_{N6/3}$ and ^{182}W/^{184}W$_{N6/3}$ (the session of November, with solely 2 runs, is not included).

In the following, the uncertainty represents the larger between the mean 2σ$_m$ of all analyses and the 2σ of all replicates divided by square root of the number of replicates. For ^{182}W/^{i}W$_{N6/3}$ (where i=183 or 184), the 2σ$_m$ uncertainty also includes the propagation of the 2σ$_m$ uncertainty on ^{184}W/^{183}W$_{N6/3}$.

For 1-3 µg loads, the mean of 3-4 duplicate analyses yields a 2σ$_m$ uncertainty per session of 3-6 ppm on ^{183}W/^{184}W$_{N6/4}$ and 4-8 ppm on ^{182}W/^{184}W$_{N6/4}$ (Table S-1). Alternatively, the mean of 3-4 duplicate analyses yields a 2σ$_m$ uncertainty per session of 2-4 ppm on ^{183}W/^{184}W$_{N6/3}$ and 8-9 ppm on ^{182}W/^{183}W$_{N6/3}$, and 5-6 ppm on ^{182}W/^{184}W$_{N6/3}$ (Table S-1).

For 200 ng loads, the 2σ$_m$ uncertainty is 13-15 ppm on ^{182}W/^{184}W$_{N6/4}$ and ^{183}W/^{184}W$_{N6/4}$, 9 ppm on ^{184}W/^{183}W$_{N6/3}$, 10 ppm on ^{182}W/^{183}W$_{N6/3}$ and 6 ppm on ^{182}W/^{184}W$_{N6/3}$ (Table S-1).

For 50 ng loads, the 2σ$_m$ uncertainty is 9 ppm on ^{182}W/^{184}W$_{N6/4}$ and 7 ppm on ^{183}W/^{184}W$_{N6/4}$, 5 ppm on ^{184}W/^{183}W$_{N6/3}$, 3 ppm on ^{182}W/^{183}W$_{N6/3}$ and 5 ppm on ^{182}W/^{184}W$_{N6/3}$ (Table S-1).

Due to the limited amount of usable runs (n=3 for 200 ng and n=2 for 50 ng loads), however, more robust statistical information would require additional analyses.

The mean ^{182}W/^{183}W$_{N6/i}$ and ^{184}W/^{183}W$_{N6/i}$ of all analyses are indistinguishable within respective uncertainties, irrespective of the W amounts loaded.
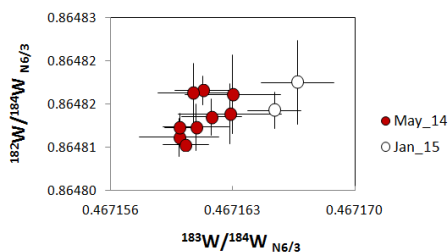

Figure 5. ^{183}W/^{184}W$_{N6/3}$ -^{182}W/^{184}W$_{N6/3}$ diagram after oxide correction and normalization to ^{186}W/^{183}W. Duplicates of 3-4 analyses of 1-3 µg analyses are reported. 2σ$_m$ per session < 5-6 ppm.

The 2σ reproducibility of 5-6 ppm on ^{182}W/^{184}W$_{N6/3}$ is similar to that obtained with double normalization to W isotopes[6]. Although derived by averaging 3-4 duplicate analyses, and thus requiring more data, the present analytical protocol offers the advantage of also measuring ^{184}W/^{183}W to high precision (2σ ≤ 5 ppm). This represents a 5 to 8-fold improvement in terms of reproducibility with respect to a protocol that does not doubly normalize. In addition, recognizing that ^{183}W relative abundance varies in nature, there is a requirement for propagating the uncertainty on the ^{183}W relative abundance in any normalizing scheme involving ^{183}W (exponential and linear), especially in previous studies that use double normalization schemes[6]. Thus, the approach consisting in averaging 3-4 duplicate analyses has been found to be the most reproducible

for determination of ^{182}W relative abundance, while allowing high precision determination of ^{183}W/^{184}W ratios.

CONCLUSION

By correcting oxide interference on a per integration basis, and provided Re/W < 0.3, the presented technique offers a W isotope analytical approach, in which there is no residual correlation between O isotopes and instrumental mass bias corrected ^{182}W/^{i}W and ^{183}W/^{i}W ratios. There are, however, correlations between instrumental mass bias corrected ^{182}W/^{i}W and ^{183}W/^{i}W ratios over 9 months, which can be mitigated by averaging data over shorter sessions. The external reproducibility on means of 3-4 duplicates of ^{182,183}W/^{184}W$_{N6/3}$ is 5-6 ppm per session of analysis (2σ). The 2σ$_m$ combined uncertainty on ^{182}W/^{184}W$_{N6/3}$ (including propagation of the 2σ$_m$ uncertainty on ^{183}W/^{184}W) is 5-6 ppm. This provides an analytical approach well-suited for meeting the requirements for high-precision W studies, such as investigations into the chronology of the late impact history on Earth. To characterize O isotope fractionation and oxide interferences correction further, the presented technique allows for including the in-run measurement of ^{17}O/^{16}O ratios, thus alleviating the need for providing better correction schemes for O-isotope fractionation correction.

ASSOCIATED CONTENT

Supporting Information

Table S-1 : W isotope analytical protocol and normalized data.
Fig. S-1 : ^{182}W/^{184}W$_{N6/4}$ – Re/W diagram.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

A.T. is employed at Thermo Fisher Scientific. M.T and R.J.W declare no competing financial interest.

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