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Origin of the analytical [183]W effect and its implications for tungsten isotope analyses†

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Mass-independent tungsten isotope variations provide critical insights into the timing and nature of processes that occurred in the early Solar System and during planetary differentiation. However, W isotope analyses are often compromised by an analytical artifact manifesting itself as an apparent deficit in [183]W, whose origin and nature have remained enigmatic. Here, by evaluating previously published high-precision W isotope data for a large and diverse set of terrestrial samples, we demonstrate that this artifact occurs independent of the type of mass spectrometer and confirm that it can be attributed to mass-independent fractionation of [183]W. Contrary to previous proposals, we find that this '*analytical [183]W effect*' cannot be explained by a nuclear field shift, but may instead reflect a magnetic isotope effect. Regardless of its exact origin, our investigation reveals that this artifact is induced during the chemical separation of W, and that the specific combination of chromatographic purification and dry-down procedure determines its overall magnitude. Within a given analytical protocol, however, its size is strongly controlled by the amount of W that is processed, where the [183]W effect increases with decreasing amount of W. Therefore, this work resolves apparent inconsistencies between previous studies regarding the occurrence and magnitude of the [183]W effect, and provides directions for its mitigation and reliable correction. This in turn is crucial for the accurate interpretation of W isotope data with respect to radiogenic and nucleosynthetic anomalies for both terrestrial and meteoritic materials.

1. Introduction

Mass-independent tungsten (W) isotope variations are a versatile tool in cosmochemical and geochemical research, as they provide critical insights into the timing and nature of processes that range from the formation of the Solar System to the inner workings of the ancient and modern silicate Earth (see review by Kleine and Walker[1]). For instance, radiogenic variations, resulting from decay of short-lived [182]Hf to [182]W ($t_{\frac{1}{2}} \approx 8.9$ Ma),[2] have proven uniquely useful for constraining the timescales of planetary accretion and differentiation.[3] Moreover, there is growing evidence for the presence of widespread nucleosynthetic W isotope anomalies among Solar System materials, including meteoritic components as well as bulk meteorites.[4–9] These anomalies arise from the heterogeneous

distribution of presolar matter and, as such, carry important information on the origin and genetic relationships of meteoritic and planetary materials.

Using state-of-the-art multicollector inductively-coupled plasma mass spectrometers (MC-ICP-MS) as well as refined techniques for negative thermal ionization mass spectrometry (N-TIMS), it has become possible to determine W isotope ratios with a precision of a few parts per million (ppm).[10–13] However, most high-precision MC-ICP-MS studies report a significant (*i.e.*, up to a few tens of ppm), albeit variable, analytical artifact that compromises the isotopic data and occurs independent of sample matrix, measurement protocol, and MC-ICP-MS model. This artifact manifests itself as spurious W isotope anomalies that reflect an apparent deficit in [183]W (relative to the even-numbered W isotopes), and is hereafter referred to as the '*analytical [183]W effect*'. As demonstrated in Fig. 1, this results in a complex interplay of natural and analytical effects that severely complicates the interpretation of W isotope data and, consequently, a precise quantification of the [183]W effect is crucial for identifying and disentangling genuine W isotope anomalies.

It is currently unclear, however, when and how the [183]W effect is created, and why its magnitude varies between different studies and even among different samples within the same study. Previously, this artifact was attributed to mass-

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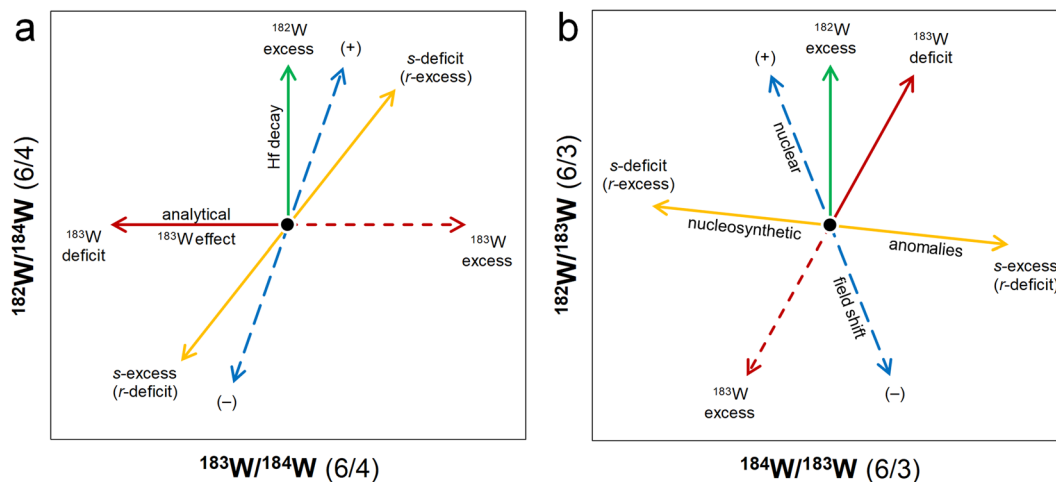
Fig. 1 Schematic diagrams illustrating different origins of mass–independent W isotope variations. Radiogenic variations (from ^{182}Hf decay) only affect ^{182}W, whereas nucleosynthetic anomalies and the nuclear field shift (see Fig. 6 for details) result in correlated ^{182}W and ^{183}W (or ^{184}W) variations. The analytical ^{183}W effect, which essentially represents a pure ^{183}W deficit (Section 4), directly affects all ratios except ^{182}W/^{184}W (6/4). Isotope ratios are internally normalized to ^{186}W/^{184}W (a) or ^{186}W/^{183}W (b). For clarity, cosmogenic variations (from interaction with galactic cosmic rays) that predominantly affect ^{182}W are not shown. Slopes for nucleosynthetic variations of 1.41 (a) and −0.12 (b) are from Burkhardt and Schönbächler;[33] other slopes are provided in Table S2.†

independent fractionation by the nuclear field shift (NFS) effect;[14] but, as we will demonstrate here, such NFS-driven W isotope fractionation is difficult to reconcile with revised nuclear parameters and other characteristics of this artifact. Moreover, the interpretation that the ^{183}W effect is induced during the chemical separation of W (*e.g.*, ref. 13 and 15) appears to be at odds with the fact that studies utilizing N-TIMS did not recognize such an artifact,[16,17] which would imply that it is specific to MC-ICP-MS measurements.

Consequently, major unknowns regarding the analytical ^{183}W effect have remained to date, which we address here by evaluating high-precision W isotope data for diverse terrestrial samples from numerous recent studies. Our investigation yields novel insights into the origin and nature of the ^{183}W effect with important implications for its mitigation and correction, which will aid in the reliable interpretation of W isotope data with respect to radiogenic and nucleosynthetic anomalies. Finally, we use data for different W solution standards and the observations from this study to better constrain the W isotope composition of bulk silicate Earth (BSE), which is an important prerequisite for the evaluation of isotopic variations in terrestrial and meteoritic materials.

2. Materials and methods

2.1. Samples and data sources

In this study, we primarily evaluate W isotope data obtained by MC-ICP-MS in the Institut für Planetologie (IfP) at the University of Münster (since 2012), as these studies generally followed the same analytical protocol (Section 2.2) and provided comprehensive sets of W isotope ratios and normalizations.[4,6,7,11,18–25] Because many of the investigated (mostly meteoritic) samples have radiogenic or nucleosynthetic anomalies, which complicates the assessment of any analytical artifacts (Fig. 1), we here

consider only terrestrial samples for which the presence of such natural W isotope anomalies can essentially be ruled out.

In particular, we focus on a recently obtained data set for a comprehensive suite of kimberlites (30 individual analyses) from 18 occurrences across sub-Saharan Africa.[26] These high-precision W concentration and isotope data reveal no radiogenic or nucleosynthetic variations (Section 4), but show that these samples are characterized by large variations in W concentrations and in the magnitude of the analytical ^{183}W effect. As such, the kimberlite sample set, combined with data for other geological reference materials measured at the IfP (BHVO-2, BCR-2, JB-2, JG-1, JA-2, DTS-2b, AGV-2, SRM 129c), provides a unique opportunity for investigating the origin and nature of the analytical ^{183}W effect. For further comparison, we also compiled MC-ICP-MS data from other laboratories as well as W isotope data obtained by N-TIMS (for references see Sections 3 and 5.1).

2.2. Chemical separation and isotope ratio measurements of W

As will be discussed below (Sections 4.2 and 5.2), the magnitude of the analytical ^{183}W effect depends on details of the analytical protocol and, therefore, the methods for the chemical separation of W and isotope composition measurements commonly used at the IfP are briefly summarized here (details of the established procedures are described in numerous previous studies[7,11,19]). In general, sample powders are digested in Savillex® PFA vials on a hotplate using concentrated HF–HNO$_3$(–HClO$_4$), followed by treatments with HNO$_3$ or aqua regia (HCl–HNO$_3$) to re-dissolve fluoride precipitates. At this point, complete dissolution is achieved in dilute HCl (+trace HF), from which a small aliquot is typically taken to determine W (and Hf) concentrations by isotope dilution using a mixed ^{180}Hf–^{183}W tracer.[27]

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The purification of W from the remaining solution is accomplished by a two-stage anion exchange chromatography utilizing AG1-X8 resin, where W is first separated from most of the sample matrix and, subsequently, from high-field-strength elements (HFSEs) using different HCl–HF(–H_2O_2) mixtures. To destroy (*i.e.*, oxidize and volatilize) resin-derived organic material, the W cuts from both chromatography stages are generally evaporated with ~50 μl of conc. $HClO_4$ and then dried down at 180–200 °C, during which a few drops of conc. HF are added several times to wash down condensed $HClO_4$ from the beaker wall. Once all $HClO_4$ is removed, the samples are fluxed in conc. HF (+trace HNO_3) over night at 130 °C before further processing. This dry-down procedure has proven effective at preventing organic interferences during the mass spectrometric analyses.[4,7] The total procedural yield is typically 60–80%, which refers to the amount of W left after the chemical separation procedure, as inferred from the signal intensity of the sample solution (relative to that of the bracketing solution standard), compared to the initial amount derived from the isotope dilution analyses.

Tungsten isotope compositions are determined using a Thermo Scientific® Neptune *Plus* MC-ICP-MS, which is equipped with a Cetac® Aridus II desolvator and a combination of (Ni) Jet sampler and X skimmer cones. The measurements are performed in low-resolution mode using analyte concentrations of usually ~30–50 ng ml^{-1} W and consume, for example, ~200 ng W for high-precision quintuple measurements. Instrumental mass bias is corrected by internal normalization to $^{186}W/^{184}W =$ 0.92767 (denoted '6/4') or $^{186}W/^{183}W = 1.98590$ (denoted '6/3') using the exponential law.[28] The W isotope data are reported as ε-unit (*i.e.*, parts per 10 000) or μ-unit (*i.e.*, parts per million) deviations relative to the bracketing Alfa Aesar® solution standard (prepared from a pure W metal, batch no. 22312; ref. 27), where $\mu^{i/k}W = [(^iW/^kW)_{sample}/(^iW/^kW)_{standard} - 1] \times 10^6$ ($i,k =$ 182, 183, 184, 186; unless stated otherwise, k is the denominator of the normalization ratio). Typically, an external reproducibility (uncertainty for a single measurement consuming ~40 ng W, as defined by the 2SD for repeated analyses of rock standards) of ~10 ppm is obtained for all W isotope ratios, and a precision of ≤5 ppm (95% CI) is routinely achieved by repeated ($n \geq 5$) measurements (Kruijer and Kleine;[11] Table S1†). Note that no ^{180}W data were obtained in most of the aforementioned studies because of its very low abundance (~0.1%) and anomalous fractionation effects for ^{180}W measurements using X skimmer cones (see Cook and Schönbächler[14] for further discussion).

3. Results

The W isotope data, literature sources, and further details for the investigated kimberlite samples and several geological reference materials are summarized in Table S1,† which also reports some additional isotope ratios and normalizations that were not provided in the original publications. The data set evaluated in this study is characterized by very different sample matrices (silicates and metals) as well as highly variable W concentrations, ranging from about 0.01–0.16 μg g^{-1} (DTS-2b, kimberlite 'K2') up to 21.8 μg g^{-1} (kimberlite 'K18').

Depending on the amount of sample material digested (mostly ~0.5 g), the total amount of W that was processed through the entire analytical protocol varies by almost three orders of magnitude, ranging between ~0.04 and ~12 μg W. We note, however, that the large W amounts processed for many kimberlites are not representative of samples typically processed at the IfP (usually <0.5 μg W).

None of these samples show resolved variations in $\mu^{182}W$ (6/4) relative to the bracketing solution standard. By contrast, isotope ratios involving ^{183}W show variable and resolved anomalies of up to ~15–30 ppm, which are well correlated and consistently largest for $\mu^{182}W$ (6/3). The $\mu^{183/184}W$ values (6/4- and 6/3-normalized) are characterized by negative anomalies, whereas other ratios [*e.g.*, $\mu^{182}W$ (6/3), $\mu^{184}W$ (6/3)] display excesses relative to the solution standard. As demonstrated in Fig. 2, these variations are best described as pure deficit in ^{183}W, where the largest measured anomalies correspond to a deficit of ~2.3 per 10^5 atoms of ^{183}W. These observations were not only made throughout the analyses at the IfP (Kruijer and Kleine,[11] and references in Section 2.1), but similar systematics were also reported for processed terrestrial standards in high-precision MC-ICP-MS studies conducted in numerous other laboratories (*e.g.*, Cook and Schönbächler,[14] ETH Zürich; Holst *et al.*,[29] University of Copenhagen; Shirai and Humayun,[30] Florida State University; Takamasa *et al.*,[31] JAMSTEC; Tusch *et al.*,[15] University of Cologne; Willbold *et al.*,[13] University of Bristol).

Given the internal normalization of the isotopic data (Section 2.2), any natural and analytical mass-dependent W isotope fractionation following the exponential law is cancelled out. As such, the residual μ^iW variations observed for isotope ratios involving ^{183}W either reflect non-exponential mass fractionation effects or, more likely, are mass-independent in nature. In addition to the internally normalized isotope ratios, we also determined $\delta^{186/184}W$ values using the standard-sample bracketing technique (from the same measurements), which represent the permil deviations of the raw $^{186}W/^{184}W$ relative to the IfP (Alfa Aesar) solution standard. Given that natural mass-dependent variations are generally small for W,[32] these $\delta^{186/184}W$ values, which range between about −0.4 and +0.1‰ (Table S1†), can be used as a first-order measure of mass-dependent W isotope fractionation induced during the chemical separation procedure.

4. Origin of the analytical ^{183}W effect

The samples investigated here yield well-defined correlation lines in diagrams of μ^iW *versus* μ^jW (Fig. 2), indicating that the isotopic variations are dominated by a single process. As illustrated in Fig. 1, however, the measured isotope systematics cannot be of nucleosynthetic or radiogenic origin, which is evident from the lack of $\mu^{182}W$ (6/4) anomalies. For instance, nucleosynthetic variations (affecting all isotope ratios) would be most pronounced in $\mu^{182}W$ (6/4), about 1.4 times the anomaly in $\mu^{183}W$ (6/4),[33] meaning that resolvable $\mu^{182}W$ (6/4) excesses of up to ~30 ppm would be expected. Moreover, a radiogenic origin (from ^{182}Hf decay) can be ruled out as it would only affect ratios involving ^{182}W and thus result in (1 : 1) correlated $\mu^{182}W$
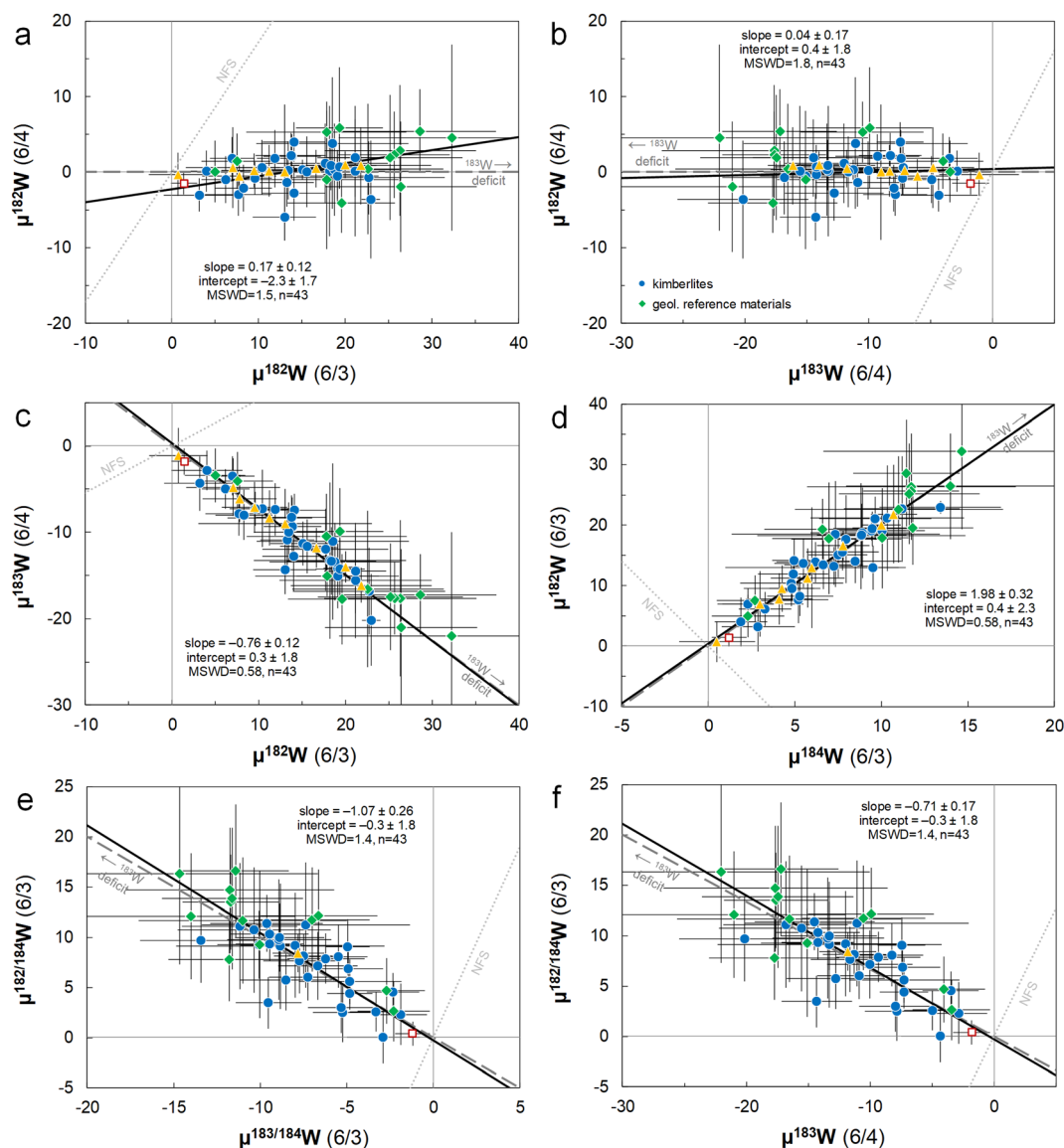
Fig. 2 W isotope diagrams for kimberlite samples (blue) and geological reference materials (green) obtained by MC-ICP-MS. While the μ^{182}W (6/4) values are indistinguishable from the (IfP) solution standard, there are well-resolved anomalies in isotope ratios involving ^{183}W. These variations are inconsistent with the predicted effects of a nuclear field shift (NFS), but in excellent agreement with a pure deficit in ^{183}W (Table S2†). Isotope ratios are internally normalized to ^{186}W/^{184}W ('6/4') or ^{186}W/^{183}W ('6/3'). Regressions (solid lines) were calculated using the 'Model 1 fit' of *Isoplot* (v3.76); uncertainties represent 95% CI. Selected data from other studies/laboratories are shown for comparison (orange triangles); red open squares represent the IGL solution standard (Section 5.1). All data and references are provided in Table S1.†

(6/4) and μ^{182}W (6/3) variations, which is not observed (Fig. 2a). As such, these isotopic anomalies are not genuine signatures of the samples, but result from an analytical artifact that manifests itself as an apparent ^{183}W deficit. In line with previous studies, we thus conclude that this analytical ^{183}W effect is created in the laboratory, either during the isotope composition measurements or during the chemical separation of W. As will be shown below, the data compiled in this study provide critical new insights into the origin and nature of the ^{183}W effect; in particular, as to why its magnitude varies between different studies and even among samples within the same study (*e.g.*, the kimberlite data set[26]).

4.1. Mass spectrometric artifacts

During mass spectrometric analyses, spurious isotope anomalies can potentially arise from unaccounted interferences or an inaccurate correction of instrumental mass bias. The observed W isotope variations, however, cannot reflect isobaric or molecular interferences, as has already been demonstrated in a previous MC-ICP-MS study that reports similar systematics.[13] This is, for example, because the measured anomalies reflect variable deficits in ^{183}W (Fig. 2), which is contrary to the effect of organic interferences on mass 183 that occasionally occurred in some studies.[5,29,34] Moreover, the generation of W hydrides, as suggested by Breton and Quitté,[35] cannot explain

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the observed isotope systematics, as this predicts, for example, a slope of about −0.8 for μ^{182}W *versus* μ^{183}W (6/4), which is inconsistent with the measured variations (Fig. 2b). The observed anomalies are also unlikely to reflect unaccounted mass-dependent fractionation effects that do not follow the exponential law. This is, for example, indicated by the inverse correlation of $\mu^{182/184}$W and $\mu^{183/184}$W (6/3) as well as the lack of a correlation for μ^{182}W and μ^{183}W (6/4), which would have slopes of about +3.0 and +2.7, respectively, in such a case (Fig. 2b and e). Moreover, consistent with the observations by Cook *et al.*,[21] the internally normalized ratios do not scale with the raw isotope ratios (quantified here as $\delta^{186/184}$W), meaning that there is no correlation between the magnitude of the analytical ^{183}W effect and the extent of (analytical) mass-dependent isotope fractionation that is not accounted for by the standard-sample bracketing technique (Fig. 3a).

Analytical artifacts during isotope ratio measurements can also arise from mass-independent fractionation processes at the interface region of the MC-ICP-MS (*e.g.*, ref. 30) particularly for the combination of Jet sampler and X skimmer cones that is typically used in recent W isotope studies.[4,7] For instance, the application of such high-sensitivity cones resulted in anomalous fractionation effects for Nd and for the low-abundance isotope ^{180}W.[21,36,37] However, W isotope studies that used combinations of standard sampler and either standard skimmer[14,21,25,38] or X skimmer[13,15] cones report essentially the

same systematics (for the major W isotopes) as observed for the Jet-X combination. As such, the use of a specific cone design cannot be responsible for the spurious W isotope anomalies.

Of note, almost all samples discussed in this study were measured under identical conditions (*e.g.*, analyte W concentration, cone setup, sample matrix) and often during the same analytical session. Thus, if the W isotope variations were induced during the mass spectrometric analyses, they would be expected to be approximately constant, but not highly variable as observed here. Moreover, aliquots of bracketing solution standards[13,25,31] as well as the DTS-2b rock standard doped (to ~80%) with W from the solution standard,[20] which were processed through the entire analytical protocol, showed the same systematic deviations from the unprocessed solution standard. Finally, Cook and Schönbächler[14] pointed out that the W isotope anomalies observed in many studies occur independent of the MC-ICP-MS instrument, measurement protocol, bracketing solution standard, and sample matrix. These observations combined strongly suggest that the spurious W isotope variations do not have a mass spectrometric origin, which is consistent with the conclusions reached in most of the aforementioned studies.

4.2. Fractionation during chemical separation

Since it can essentially be ruled out that the observed W isotope anomalies are genuine signatures of the samples or reflect
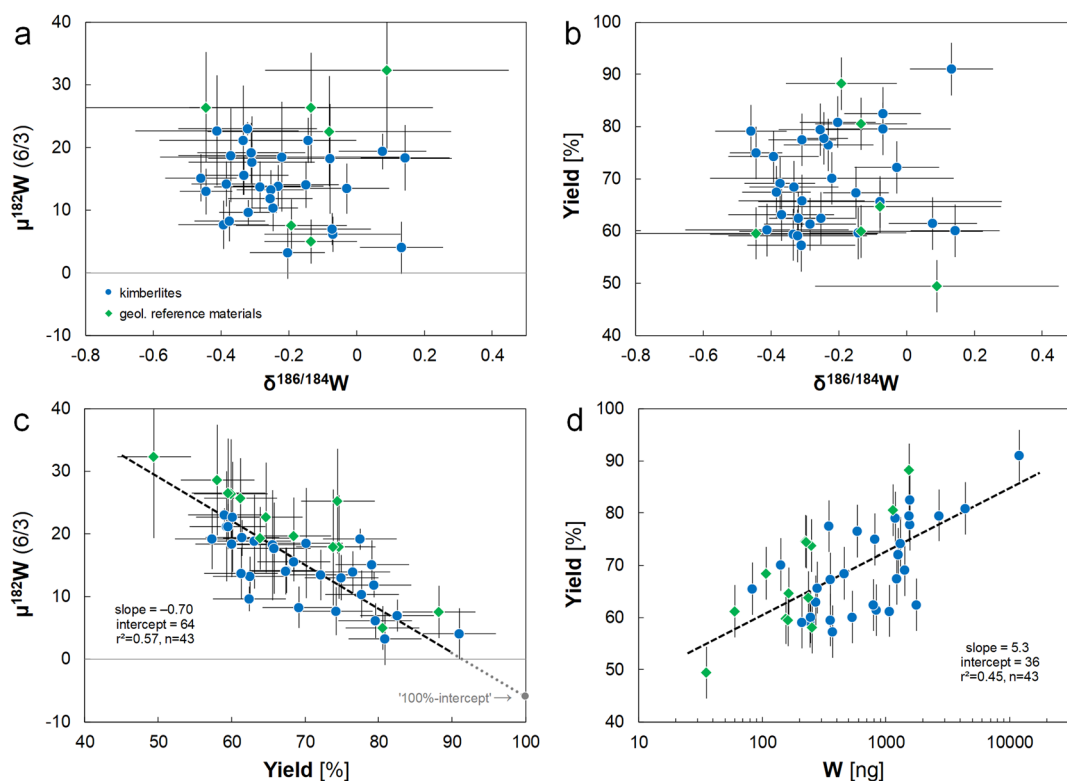

Fig. 3 The samples investigated here (same as in Fig. 2) display no correlation between the extent of (analytical) mass-dependent isotope fractionation ($\delta^{186/184}$W) and the magnitude of the analytical ^{183}W effect (a) or the total procedural W yield (b). By contrast, the correlations in (c) and (d) reveal an interrelationship between the ^{183}W effect, the relative loss of W, and the amount of W that was processed through the chemical separation procedure (see also Fig. 4). The ^{183}W effect is quantified here as μ^{182}W (normalized to ^{186}W/^{183}W), for which this artifact is most pronounced. For interpretation of the '100%-intercept' (c) see Section 6; uncertainty on the yield is estimated to be ±5 percentage points.

artifacts from the isotope composition measurements, they most likely result from the chemical separation procedure. In most analytical protocols (*e.g.*, IfP protocol, Section 2.2; Peters *et al.*;[39] Touboul and Walker[12]), bulk samples are loaded onto the first ion exchange column in a weak HCl–HF mixture from which often significant amounts of Ca,Mg,Al-fluorides precipitate, which can be accompanied by sequestration (and potentially isotopic fractionation) of certain trace elements.[40] However, this process cannot account for the analytical [183]W effect because tests have shown that only negligible amounts of W co-precipitate with these fluorides,[41] and because this artifact also occurs for sample matrices that do not form fluorides in general (*e.g.*, metals, solution standards) as well as for protocols that avoid fluoride precipitation.[15] The most plausible scenario is, therefore, that these spurious isotope anomalies are induced either during the chromatographic purification or during the subsequent dry-down procedure (*i.e.*, evaporation, oxidation, and re-dissolution) for the W cuts. Furthermore, as residual effects from an inadequate correction of (natural and chemistry-induced) mass-dependent fractionation can (for the same reasons as unaccounted instrumental mass bias; Section 4.1) be excluded, the [183]W effect most likely reflects a fractionation process that is mass-independent. This is, for example, supported by the fact that numerous studies report such mass-independent isotope fractionation in laboratory-scale chemical exchange reactions for various elements (see Fujii *et al.*[42] and references therein).

As the total W yield of the chemical separation procedure is typically <90%, analytical artifacts could potentially originate from anomalous fractionation effects during the ion exchange chromatography. For instance, Breton and Quitté[35] have shown that a non-quantitative recovery of W can result in significant mass-dependent isotope fractionation. While such mass-dependent fractionation itself cannot explain the observed W isotope variations, this process can potentially be accompanied by mass-independent isotope fractionation, as has, for example, been observed for Nd.[43] In this case, an inverse correlation between the spurious W isotope anomalies and the W yield of the chemical separation procedure would be expected. Indeed, the magnitude of the analytical [183]W effect increases with decreasing yield (Fig. 3c), meaning that samples with a high yield (>80%) are barely affected, whereas those with a low yield (50–60%) show the largest [183]W effect. Unexpectedly, however, the total procedural yield also scales with the amount of W that was processed through the chemical separation procedure, where samples with a large amount of W generally show a higher yield (Fig. 3d). We note that neither of these parameters is a function of the amount of sample matrix loaded onto the ion exchange columns; in fact,
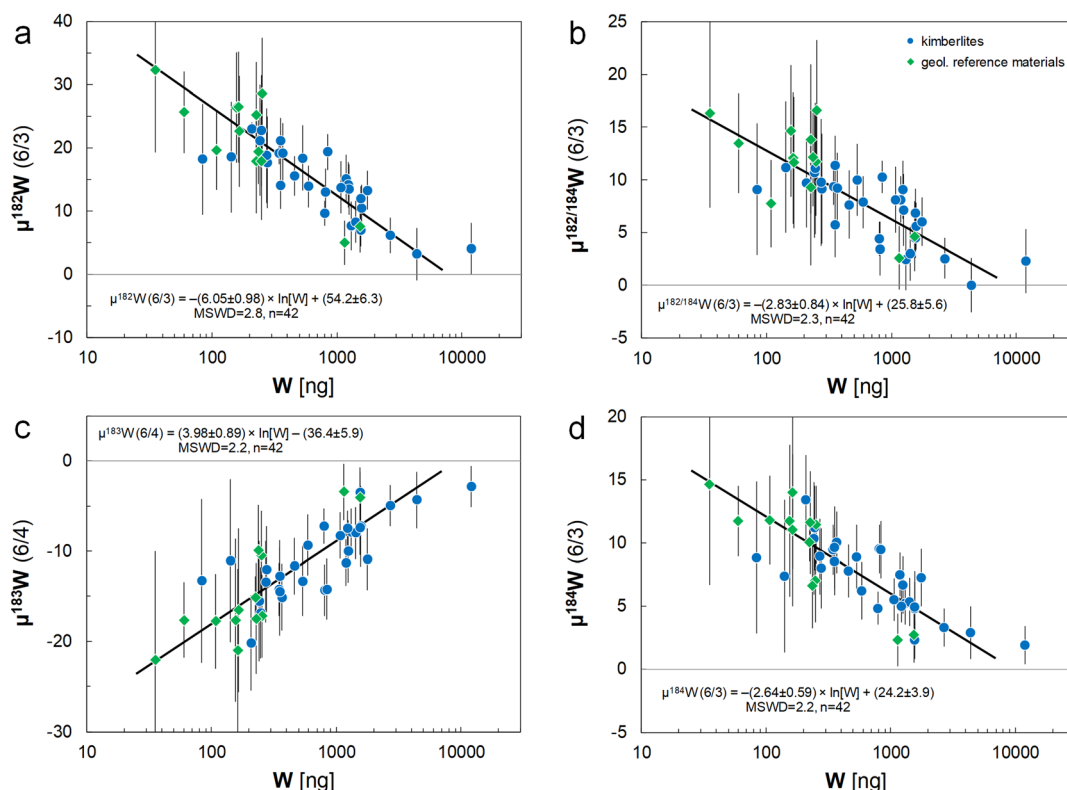

Fig. 4 W isotope anomalies as function of the amount of W that was processed through the chemical separation procedure (same samples as in Fig. 2). For most of the observed range, the samples define a linear correlation between the magnitude of the analytical [183]W effect and the W amount (on a logarithmic scale). Note that all data used here were obtained following the identical analytical protocol and by the same operator, in order to avoid any systematic variations potentially arising from differences in ion exchange chromatography, dry-down protocol, or mass spectrometric analyses. Kimberlite sample 'K18' (highest W amount) was excluded from regressions, which were calculated using the 'Model 1 fit' of *Isoplot* (v3.76); uncertainties represent 95% CI.

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samples with the same amount of material processed (~0.5 g) span virtually the entire range of W yields and amounts (as well as ^{183}W effect) observed here (Table S1†).

As a corollary of the above interrelations, our data set also reveals a clear correlation between the analytical ^{183}W effect and the amount of W processed. As demonstrated in Fig. 4, this relationship is for all W isotope ratios best described by a logarithmic function, where the magnitude of the ^{183}W effect decreases with increasing (initial) W amount. These empirical correlations are combined in Fig. 5, and show that this artifact is particularly relevant for samples containing several tens to hundreds of ng of W (as is the case for most MC-ICP-MS studies), but becomes barely resolvable when several μg of W are processed. Overall, the regressions obtained here display only little excess scatter (MSWD ≈ 2.3; Fig. 4), indicating that the magnitude of the ^{183}W effect is predominantly controlled by the amount of W that is processed, while other processes have only small, if any, effects. This conclusion is supported by the fact that replicate digestions processed under identical conditions (i.e., same analytical protocol and amount of W) yield very consistent results (e.g., reference materials in Budde et al.;[4,19] Kruijer et al.[22]). While this observation is based on data generated at the IfP, the broad correlation of the ^{183}W effect and W amount in a data subset from Tusch et al.[15] (Fig. S1†) demonstrates that it is not unique to the analytical protocol or sample set discussed here.

The finding that the magnitude of the ^{183}W effect as well as the total W yield of the separation procedure depend on the amount of W processed (Fig. 3d and 4) is difficult to reconcile with this artifact originating from the chromatographic purification, because in this case a causal relationship would only be

expected between the yield and the ^{183}W effect. This conclusion is further supported by the fact that Willbold et al.[13] occasionally observed significant loss of W during their dry-down procedure for W cuts, which these authors attributed to the formation of insoluble oxide compounds. Moreover, Tusch et al.[15] report a significant increase of the ^{183}W effect, combined with much (~20%) lower total W yields, in case of an insufficient oxidation of the W cuts. While the latter points to organic compounds (rather than oxides) playing a major role, these observations combined indicate that significant W loss accompanied by a preferential sequestration of ^{183}W can occur during the treatment of W cuts from the ion exchange chromatography (see Section 5.2 for further discussion).

Consequently, a successful model for the origin of the analytical ^{183}W effect must be capable of explaining (i) that it is induced by mass-independent W isotope fractionation during the dry-down procedure, (ii) that the associated W loss dominates the total procedural yield, (iii) that its magnitude is strongly controlled by the amount of W processed, and (iv) that it occurs for very different sample matrices (silicates, metals, processed solution standards).

4.3. The case against a nuclear field shift effect

It has been demonstrated that most mass-independent isotope fractionation effects observed in laboratory-scale chemical exchange reactions can be explained by a nuclear field shift (NFS; e.g., ref. 42), which is an anomalous isotope effect resulting from differences in nuclear sizes and shapes.[44–46] To first order, this effect scales proportionally to $|\Psi(0)|^2 \ \delta\langle r^2\rangle$, where $|\Psi(0)|^2$ is the total electron density at the nucleus and $\delta\langle r^2\rangle$ is the difference in mean-square nuclear charge radii of the respective isotopes.[45,47] As such, a NFS is most significant for heavy elements (e.g., REEs, U) and, since odd isotopes typically have disproportionally small nuclear charge radii relative to the adjacent even isotopes,[42,46] it is often accompanied by a diagnostic odd-even isotope fractionation. Hence, this effect could potentially account for the observed deficits in ^{183}W relative to the other (even) W isotopes; in fact, a recent study has attributed the analytical ^{183}W effect to mass-independent fractionation by a NFS.[14] As we will demonstrate below, however, such NFS-driven isotope fractionation is inconsistent with revised nuclear parameters and other systematics observed in this study.

To explain the occurrence of the NFS effect during the dry-down procedure for W cuts (as discussed in Section 4.2), Cook and Schönbächler[14] proposed a redox reaction between insoluble oxide/organic compounds and the aqueous solution (i.e., the solution that will eventually be analyzed), where W has a higher oxidation state (most likely W^{6+}) in the insoluble compounds relative to the W species in solution (e.g., oxyanions, fluoride complexes). As the loss of 5d electrons during progressive oxidation beyond W^{2+} results in a higher electron density at the nucleus,[48] this would cause a preferential incorporation of light isotopes into the oxide/organic compounds.[44,45] Hence, if the odd isotope ^{183}W were to have an exceptionally small nuclear charge radius, relative to the
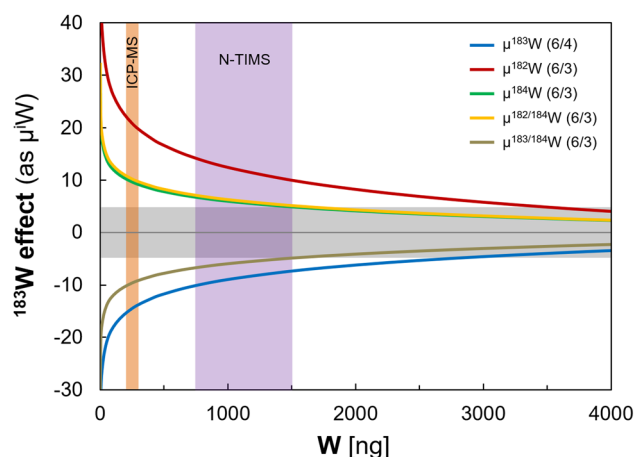

Fig. 5 Summary of empirically defined correlations from Fig. 4, demonstrating that the analytical ^{183}W effect (displayed as μ^iW variations) decreases logarithmically with increasing amount of W. Vertical bars represent W amounts typically processed for high-precision MC-ICP-MS (orange) and N-TIMS (purple) studies to achieve an uncertainty of about ±5 ppm (gray bar). We note that these trends are specific to a certain analytical protocol and not directly transferrable to other studies and data sets (Section 5.2). As such, the vertical bars are only shown for reference, indicating that a potential ^{183}W effect is generally expected to be less pronounced in typical N-TIMS analyses compared to most MC-ICP-MS data.

(mass-dependent) trend defined by the even W isotopes (see below), this incorporation would be disproportionally high for [183]W, as it would essentially behave as it had a lower atomic mass.[44] In this hypothetical scenario, a non-quantitative precipitation (or re-dissolution) of W could potentially result in the expected relative enrichment of [183]W in the insoluble compounds and a complementary deficit in the aqueous solution. However, it remains unclear whether W in the aqueous species actually has a lower oxidation state, and this process seems difficult to reconcile with the causal relationship between the magnitude of the [183]W deficit and the relative loss of W, as well as with the fact that both are inversely correlated with the amount of W processed (Fig. 3d and 4). This is because the NFS effect generally occurs in equilibrium systems and, therefore, its magnitude is not expected to scale with the fraction of W incorporated into the oxide/organic compounds. Moreover, a NFS would presumably be accompanied by significant correlated mass-dependent isotope fractionation, which is not observed here (Fig. 3a).

Most importantly, however, the interpretation from Cook and Schönbächler[14] was based on the nuclear charge radii compiled in Angeli,[49] which are inappropriate for assessing whether or not the spurious W isotope anomalies represent a NFS. Taken at face value, the Angeli[49] data set suggests that the $\delta\langle r^2 \rangle$ is essentially a linear function of the atomic mass for the even W isotopes, whereas the odd isotope [183]W ($\delta\langle r^2 \rangle \approx -0.4$ fm^2) is characterized by a substantial deviation from this trend (see Fig. 2 in Cook and Schönbächler[14]). If these data were correct, the NFS effect would manifest itself as a virtually pure [183]W deficit (or excess) in internally normalized isotope ratios (Table S2†), which would be consistent with the observed W isotope anomalies. A close inspection of this compilation, however, reveals major problems with the reported nuclear charge radius for [183]W: the magnitude of its deficit (∼0.03 fm compared to what would be expected from an [182]W–[184]W interpolation) seems physically implausible, and its uncertainty (±0.15 fm) is two orders of magnitude larger than those of the

other W isotopes (∼5 times larger than the proposed deviation itself). Of note, apparently due to a lack of alternative data, only the value for [183]W in Angeli,[49] which is a compilation that primarily focused on absolute nuclear charge radii, is based on nuclear parameters from De Wit et al.[50] The results of the latter study are compiled in Angeli,[51] which shows that the nuclear charge radii derived from the De Wit et al.[50] parameters are generally highly imprecise and characterized by considerable systematic deficits relative to other studies (including elements other than W).

It is important to recognize that this questionable value for [183]W from Angeli[49] has been abandoned in the most recent compilation of nuclear charge radii by Angeli and Marinova,[52] which, instead, provides a self-consistent data set that is in line with direct measurements of differences in mean-square nuclear charge radii for W isotopes using optical isotope shifts (OIS). Despite utilizing different techniques, such studies have obtained very consistent $\delta\langle r^2 \rangle$ values,[53–55] which is testament to the generally high accuracy and precision of data obtained by OIS. These $\delta\langle r^2 \rangle$ values show only subtle deviations from a mass-dependent trend (most pronounced for [180]W and [182]W) and, therefore, do not support a disproportionally small nuclear charge radius of [183]W (Fig. 6a). Based on these data, the internal normalization to [186]W/[183]W or [186]W/[184]W would result in roughly complementary anomalies in μ^{180}W and μ^{182}W that are significantly larger than those in μ^{183}W and μ^{184}W (Fig. 6b). Thus, the predicted W isotope variations resulting from the NFS effect are inconsistent with the observed [183]W deficits, as had already been noted by Shirai and Humayun.[30] In fact, in diagrams of μ^iW versus μ^jW, the predicted NFS-lines are roughly perpendicular to the regressions defined by the investigated samples (Fig. 2).

As the analytical [183]W effect cannot be attributed to a NFS, another mass-independent fractionation process is required to explain the spurious W isotope anomalies. One possibility is that this artifact reflects a magnetic isotope effect (MIE), which arises from chemical reactions that involve a spin-selective step,
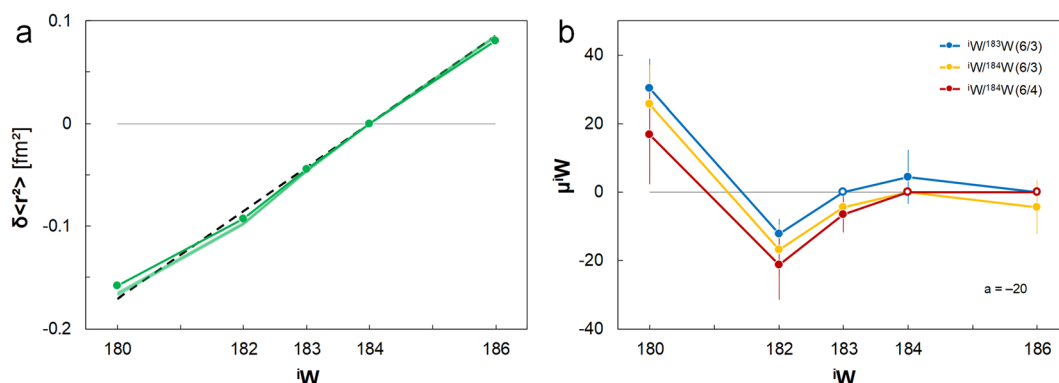

Fig. 6 Theoretical effect of a nuclear field shift (NFS) on internally normalized W isotope ratios. (a) Overall, the difference in mean-square nuclear charge radii ($\delta\langle r^2 \rangle$) is a linear function of the isotope mass (uncertainties are smaller than symbols); only [180]W and [182]W show subtle deviations from the mass-dependent trend (dashed line). Shown are data from Lee et al.,[55] which are consistent with previous (OIS) studies but of higher precision (see Section 4.3 for details). (b) Internal normalization to [186]W/[183]W ('6/3') or [186]W/[184]W ('6/4') results in roughly complementary anomalies for μ^{180}W and μ^{182}W that are significantly larger than those for μ^{183}W and μ^{184}W. Values were calculated using eqn (1) from Fujii et al.,[89] based on $\delta\langle r^2 \rangle$ from (a) and isotope masses from Wang et al.;[90] error bars represent propagated uncertainties of all $\delta\langle r^2 \rangle$ values involved.

resulting in the fractionation of isotopes according to their nuclear spin and corresponding magnetic moment (*e.g.*, ref. 56). This rather exotic effect is, for example, generally thought to be responsible for the substantial fractionation of odd Hg isotopes, which have a magnetic moment unlike the even isotopes, observed in natural and experimental systems.[57] Similarly, the nuclear spins of the even W isotopes are all zero, while the odd isotope [183]W is characterized by a spin of $-\frac{1}{2}$ and thus a magnetic moment and hyperfine structure.[55] A MIE, therefore, could selectively fractionate [183]W and potentially result in a significant [183]W deficit (or excess) that is unrelated to any potential mass-dependent fractionation, as is observed in this study (Fig. 3a). Moreover, this effect typically occurs during reactions involving organic components and is purely kinetic by nature (see Dauphas and Schauble[58] and references therein). As such, the MIE would be consistent with the hypothesis that W is lost by incorporation into insoluble oxide/organic compounds (Section 4.2) and with the fact that the [183]W deficit scales with the fraction of W that is sequestered (Fig. 3c), which points to disequilibrium fractionation of W isotopes between the aqueous species and oxide/organic compounds. In this scenario, a certain amount of W is incorporated into the insoluble compounds, which represents a larger fraction for samples with less W (Fig. 3d). Accordingly, the associated MIE-driven sequestration of [183]W is then also expected to be more pronounced for lower amounts of W, resulting in a larger [183]W deficit in the corresponding solution. Although this remains speculative, isotope fractionation by a magnetic isotope effect seems to represent a viable mechanism to produce the analytical [183]W effect and to account for its systematic variation with the total procedural yield and the amount of W processed.

Further experimental and theoretical investigations, which are beyond the scope of this study, are needed to fully understand the analytical [183]W effect. Regardless of its exact origin, however, the results of our investigation reveal that the [183]W effect is an analytical artifact that can essentially be described as pure [183]W deficit and that its magnitude is (at least within a given analytical protocol) strongly controlled by the amount of W that is processed through the chemical separation procedure. These key observations have important implications for high-precision W isotope analyses in general, as they resolve apparent inconsistencies from previous studies, and because they allow the development of a method for the accurate correction of the analytical [183]W effect.

5. Implications for W isotope analyses

5.1. Comparison with N-TIMS studies

The methods for W isotope ratio measurements by N-TIMS utilized in early studies were only capable of obtaining high-precision [182]W/[184]W data, using [183]W/[184]W for a second-order mass fractionation correction.[12,59–61] Recent improvements of the measurement protocol,[10,62] however, now allow determining the full range of W isotope ratios with the same precision (*i.e.*, a few ppm) achieved by MC-ICP-MS, making it possible to identify nucleosynthetic isotope anomalies as well as a potential analytical [183]W effect. Surprisingly though, studies using this refined N-TIMS technique did not recognize such an artifact,[16,17,63–68] implying that the [183]W effect originates in the MC-ICP mass spectrometer, which in turn would be in conflict with our conclusion that it is induced during the chemical separation procedure.

A major difference between most MC-ICP-MS and N-TIMS studies is the amount of W that is processed, which exerts a strong control on the magnitude of the analytical [183]W effect (Section 4.2). Due to the lower ionization efficiency in the N-TIMS source, significantly more sample material is required, meaning that typically 0.75–1.5 μg W is processed through the chemical separation procedure (as opposed to several tens to few hundreds of ng for most samples measured by MC-ICP-MS at the IfP). Hence, even though the empirical correlations defined in this study (Fig. 4) cannot be transferred directly to other analytical protocols (Section 5.2), the general observation that the [183]W effect decreases with increasing amount of W implies that this artifact (if present) is likely less pronounced and thus difficult to resolve for typical N-TIMS analyses (Fig. 5). A detailed evaluation of the N-TIMS data is further complicated by the fact that details on the amount of W processed are often lacking, and that most studies do not report all relevant W isotope ratios and normalizations, particularly μ^{182}W (6/3) for which the [183]W effect would be most pronounced. Moreover, only very few processed terrestrial standards, for which natural (mass-independent) isotope anomalies can be ruled out, have been measured using the refined N-TIMS technique to date.

Nonetheless, some recent N-TIMS studies conducted at the Isotope Geochemistry Laboratory (IGL) at the University of Maryland[16,63,69–71] provide combined μ^{182}W (6/4), $\mu^{182/184}$W (6/3), and μ^{183}W (6/4) data, which allows a more quantitative assessment of the presence of the [183]W effect. Since most of the samples from these studies display radiogenic W isotope variations, as evident from the broadly correlated μ^{182}W (6/4) and $\mu^{182/184}$W (6/3) deficits, we here use the difference between the two normalizations $[\Delta\mu^{182}W = \mu^{182/184}W\ (6/3)_{meas} - \mu^{182}W\ (6/4)_{meas}]$, which cancels out any radiogenic contribution. The non-radiogenic W isotope variations for these samples are generally small (<15 ppm) and mostly unresolved, and (except for one sample) the data from Mundl *et al.*[16,63] scatter around zero within the expected range (Fig. 7). However, the other three data sets display a clear bias toward negative μ^{183}W (6/4) (−3 ppm on average) combined with excesses in $\Delta\mu^{182}$W. Of note, these anomalies are even more pronounced relative to the Alfa Aesar solution standard used at the IfP, which has a slightly different W isotope composition than the Alfa Aesar Specpure Plasma standard relative to which these N-TIMS data are reported (see Section 6). While nucleosynthetic anomalies would theoretically follow the same inverse correlation (Fig. 7), these $\Delta\mu^{182}$W–μ^{183}W systematics are most readily attributed to a small [183]W effect.

Recently, such an analytical origin was also proposed for W isotope anomalies measured in an earlier N-TIMS study,[61] which reported large μ^{182}W (corrected for second-order mass fractionation using [183]W/[184]W) excesses of 24 and 48 (±5) ppm for basalts/picrites from the Ontong Java Plateau (OJP) and Baffin Bay ('Pd-2'), respectively. These data are in disagreement with
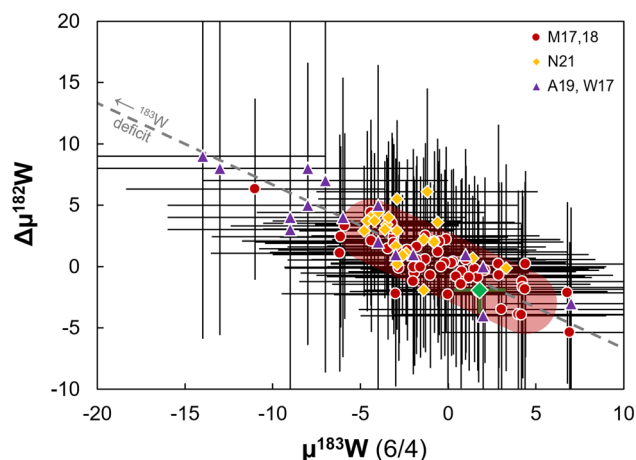
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Fig. 7 Diagram of $\Delta\mu^{182}W$ versus $\mu^{183}W$ (6/4) for samples analyzed by N-TIMS [Archer et al.[69] (A19); Mundl et al.[16,63] (M17,18); Nakanishi et al.[70] (N21); Worsham et al.[71] (W17)]. The $\Delta\mu^{182}W$ values represent the difference between measured $\mu^{182/184}W$ (6/3) and $\mu^{182}W$ (6/4) values (all uncertainties propagated); red area corresponds to the long-term reproducibility (±6 ppm for $\mu^{183}W$).[70] All data are reported relative to the Alfa Aesar Specpure Plasma standard used at the IGL in Maryland, which shows a small offset from the Alfa Aesar standard used at the IfP in Münster (green diamond; Section 6). In such a diagram, samples naturally follow the displayed slope of 0.667 (dashed gray line); nonetheless, some data sets are biased toward negative $\mu^{183}W$ coupled with excesses in $\Delta\mu^{182}W$, which is consistent with a small analytical ^{183}W effect (Section 5.1).

several MC-ICP-MS studies that found no resolvable $\mu^{182}W$ anomalies in other samples from these two locations,[11,13,72] and Kruijer and Kleine[11] argued that the apparent $\mu^{182}W$ excesses from Rizo et al.[61] most likely reflect a substantial ^{183}W effect. This interpretation is supported by the fact that these samples were subjected to an extensive chromatographic purification and dry-down procedure, and are characterized by low W yields (54 and 50%), consistent with our findings presented in Section 4.2.

Together, these observations strongly suggest that the analytical ^{183}W effect is also present in some N-TIMS data sets, which supports our conclusion that it is induced during the chemical separation procedure and not unique to MC-ICP-MS. Further systematic investigations are, however, necessary to better understand potential differences between these two mass spectrometer types; for instance, whether the specific sample introduction and ionization can influence the measured ^{183}W effect. Regardless, this highlights that also for N-TIMS measurements the ^{183}W effect, even though it is comparatively small or imperceptible in most studies, should be precisely quantified to ensure an accurate interpretation of W isotope data, especially when advances in analytical methods allow for smaller amounts of W to be measured with this technique.

5.2. Mitigating the analytical ^{183}W effect

While the size of the analytical ^{183}W effect is generally a function of the amount of W that is processed (Section 4.2), there are substantial variations in its overall magnitude between different studies that cannot be explained by this observation alone. Although the majority of high-precision MC-ICP-MS studies

report a significant ^{183}W effect, in some MC-ICP-MS[15,73–76] and many N-TIMS studies[16,17,63–67] this artifact was generally small or even absent. This was likely facilitated by the relatively large amounts of W processed in such studies (mostly 500–1000 ng); however, several observations indicate that these different outcomes primarily reflect differences in the analytical protocols, particularly in the dry-down procedures (i.e., evaporation, oxidation, and re-dissolution) for W cuts from the ion exchange chromatography.

For instance, Tusch et al.[15] demonstrated that a change in their dry-down procedure from a 'weak' [dilute HNO_3–HF + H_2O_2 (9 : 1); 1×] to a 'strong' oxidation [conc. HNO_3 + H_2O_2 (1 : 1); 3× at max. 60 °C] resulted in higher W yields (~80% instead of ~60%) and an imperceptible ^{183}W effect. While most N-TIMS studies (as well as Mei et al.[74]) also successfully applied an HNO_3–H_2O_2 oxidation step, others observed a significant ^{183}W effect with such a procedure[13,14] and found that an improvement was achieved instead by fluxing W cuts alternately with conc. HNO_3 and HF at 150 °C over night.[76] Similarly, a dry-down procedure [conc. HNO_3 + H_2O_2 (1 : 1), 2–3× at max. 80 °C] virtually identical to the 'strong' oxidation from Tusch et al.[15] had opposite effects when applied at the IfP.[77,78] It not only caused more frequent problems with organic interferences (on mass 183) during the MC-ICP-MS measurements, but also resulted in lower yields and a ^{183}W effect that was generally larger (up to about −60 ppm on $\mu^{183}W$) and, most importantly, more erratic in magnitude, compared to the high-temperature $HClO_4$ dry-down procedure (Section 2.2).

These contradictory observations are likely related to the specific matrix elements and organic materials present in the W cut, or even to the operator-specific execution of the dry-down procedure. For instance, HFSEs (Ti, Zr, Hf, Nb, Ta), which are usually eluted together with W during the initial chromatography stage, can form insoluble oxides during dry-downs with $HClO_4$ (ref. 40) that could potentially also sequester W. While large amounts of HFSEs (mainly Ti) might hamper an efficient oxidation, such a precipitation of oxide compounds itself (of W alone or in combination with HFSEs) cannot be the origin of the analytical ^{183}W effect, as it also occurs in the absence of HFSEs (metal samples, processed solution standards) and when no $HClO_4$ is used for the dry-down procedure. Based on the observation that the ^{183}W effect (and corresponding W loss) is not induced by simple evaporation/re-dissolution of W solutions (neither with $HClO_4$ nor with H_2O_2), but only if the solution has been subjected to ion exchange chromatography (even without dry-down steps, or when the solution was doped with W only after chromatography and dry-downs), it has recently been suggested that eluted organic material from the resin is responsible for this artifact.[31,79] Consequently, the particular type of ion exchange resin used for different chromatography stages and, therefore, the amount and physicochemical properties of resin-derived organic material in the W cut, may play a critical role in the generation of the ^{183}W effect. It is noteworthy that the IfP protocol (and some others[13,14]) uses only anion exchange resin (AG1-X8), whereas studies that better mitigated the ^{183}W effect by an HNO_3–H_2O_2 oxidation step utilized cation exchange resin (AG50W-X8) for the initial

separation of W (+HFSEs) from the sample matrix, and sometimes extraction chromatography resins (TEVA, DGA) for the subsequent purification.[12,15,39,74]

Although the exact processes involved remain enigmatic, it seems clear that not the details of the dry-down procedure alone (*e.g.*, reagents, temperature), but the specific combination of the chromatographic purification protocol (*i.e.*, the organic material, and possibly matrix elements, present in the W cut) and the dry-down procedure determines the overall magnitude of the ^{183}W effect. While some studies were generally successful in mitigating this artifact (see above), it should be noted that even for those protocols a noticeable ^{183}W effect may still occur occasionally. For instance, the vast majority of analyses from Mei *et al.*[73] and Tusch *et al.*[75] display no resolvable (*i.e.*, <3 ppm) μ^{183}W anomalies, but several samples show a significant ^{183}W effect (−6 to −11 ppm), in particular when smaller amounts (∼150 ng) of W were processed. This indicates that no analytical protocol should be relied on to fully prevent the ^{183}W effect, necessitating a close inspection of measured W isotope data for every individual sample. In some circumstances, it might even be more beneficial to apply a protocol that produces an elevated but very reproducible ^{183}W effect (as for the HClO$_4$ dry-down procedure preferred at the IfP; Section 4.2), which then can be corrected adequately (Section 5.3). This requires increased efforts and leads to slightly larger uncertainties, but it may yield more accurate and reliable results under certain conditions.

Taken together, the findings discussed above resolve the apparent inconsistencies between previous studies, as they demonstrate that the substantial variations in the overall magnitude of the analytical ^{183}W effect observed in different studies are primarily caused by differences in the analytical protocols, while there are systematic variations within a given protocol depending on the amount of W processed. As such, the combined observations from this study provide directions to better mitigate the effect in the first place as well as means to accurately correct it if necessary.

5.3. Quantification and correction

The observations that the analytical ^{183}W effect is inconsistent with a NFS origin but best described as pure ^{183}W deficit, and that its magnitude is (within a given analytical protocol) strongly controlled by the amount of W that is processed through the chemical separation procedure (Section 4.2), have important implications for the correction of this analytical artifact. Previous MC-ICP-MS studies have employed two different approaches, where the measured W isotope ratios are corrected either internally using empirically or theoretically determined μ^iW–μ^jW slopes,[11,25] or externally using processed geological reference materials as a proxy.[4,7]

The internal correction is generally applied to terrestrial rock samples and reference materials that are assumed to have no nucleosynthetic W isotope anomalies. In this simple scenario, all variations in the non-radiogenic ratios [μ^{183}W (6/4), μ^{184}W (6/3), $\mu^{183/184}$W (6/3)] can be attributed to the ^{183}W effect. Accordingly, these values can then, combined with the theoretical slopes for a pure ^{183}W deficit (Table S2†), be used to

correct the measured μ^{182}W of a given sample: μ^{182}W (6/3)$_{corr}$ = μ^{182}W (6/3)$_{meas}$ − 2 × μ^{184}W (6/3)$_{meas}$ and $\mu^{182/184}$W (6/3)$_{corr}$ = $\mu^{182/184}$W (6/3)$_{meas}$ − (−1) × $\mu^{183/184}$W (6/3)$_{meas}$. These corrected μ^{182}W values should then be indistinguishable from μ^{182}W (6/4), which is not modified by the ^{183}W effect and does thus not require any correction. For consistency, the non-radiogenic isotope ratios can be corrected using the measured μ^{182}W (6/3) and $\mu^{182/184}$W (6/3) of a given sample [the μ^{182}W (6/4) cannot be used as it does not scale with the ^{183}W effect], following the same approach as above: μ^{183}W (6/4)$_{corr}$ = μ^{183}W (6/4)$_{meas}$ − (−0.75) × μ^{182}W (6/3)$_{meas}$ and μ^{184}W (6/3)$_{corr}$ = μ^{184}W (6/3)$_{meas}$ − 0.5 × μ^{182}W (6/3)$_{meas}$ and $\mu^{183/184}$W (6/3)$_{corr}$ = $\mu^{183/184}$W (6/3)$_{meas}$ − (−1) × $\mu^{182/184}$W (6/3)$_{meas}$. For samples with no radiogenic ^{182}W variations, these corrected values should then be indistinguishable from the bracketing solution standard (compare Table S1†). We note that corrections using the slopes from Cook and Schönbächler[14] performed in some recent studies[11,15] are still accurate. Although these slopes were based on the assumption that the analytical ^{183}W effect represents a NFS (Section 4.3), the data used by Cook and Schönbächler[14] yielded μ^iW–μ^jW slopes that are virtually identical to those for a pure ^{183}W deficit (Table S2†).

Matters become, however, much more complicated for samples potentially having nucleosynthetic W isotope anomalies, which result in correlated μ^{182}W and μ^{183}W (or μ^{184}W) variations (Fig. 1). Several studies have demonstrated that significant nucleosynthetic (s- or r-process) W isotope variations [often >100 ppm on μ^{183}W (6/4)] exist in diverse Solar System materials such as calcium-aluminum-rich inclusions (CAIs),[5,7] chondritic components (chondrules, matrix, metal),[4,19] and acid leachates of primitive meteorites.[33,80,81] Of note, significant W isotope anomalies have recently been shown to also exist at the bulk meteorite scale. While most meteorites belonging to the '*non-carbonaceous*' suite show no or slightly negative (about −5 ppm) μ^{183}W anomalies relative to the terrestrial standard, '*carbonaceous*' (*i.e.*, carbonaceous chondrite-related) meteorites are characterized by resolved excesses in μ^{183}W, which are typically ∼10 ppm but can be as high as ∼50 ppm.[6,9,19] These observations demonstrate that for extraterrestrial (meteoritic) samples, and potentially even some exotic (*i.e.*, ancient or deep mantle-derived) terrestrial rocks (Section 5.3), it cannot be ruled out *a priori* that they have nucleosynthetic W isotope anomalies.

For such samples, the interpretation of the W isotope data is severely complicated by the complex interplay of the analytical ^{183}W effect as well as radiogenic and nucleosynthetic variations, which affects every isotope ratio in a different way (Fig. 1). For instance, the ^{186}W/^{183}W-normalized μ^{182}W values are most affected by the ^{183}W effect but show only a small, often negligible, effect of nucleosynthetic isotope anomalies. Conversely, the ^{186}W/^{184}W-normalized μ^{182}W values are not compromised by the ^{183}W effect, but are strongly affected by nucleosynthetic isotope anomalies. Correction of the latter (in order to unveil radiogenic contributions), however, requires knowledge of the true μ^{183}W (6/4) of a given sample,[4,7,33] but this ratio again is modified by the ^{183}W effect. Hence, for samples with nucleosynthetic anomalies the chronological interpretation not only of the μ^{182}W (6/3), but indirectly also of the μ^{182}W (6/4) values,

critically depends on the accurate correction of the [183]W effect. However, in this case none of the original (*i.e.*, pre-[183]W effect) isotope ratios are known, meaning that the internal correction procedure described above cannot be applied and, instead, an independent quantification of the [183]W effect is required.

For this, studies typically utilize geological reference materials that are assumed to have no radiogenic or nucleosynthetic W isotope anomalies (*e.g.*, BHVO-2, BCR-2, JB-2, SRM 129c), which are processed through the entire analytical protocol and analyzed together with the actual samples. The W isotope ratios of the samples are then corrected by simply subtracting the average μ^iW values measured for the reference material from those of the samples.[4,7,31] While this external correction is a reasonable approach that has generally proven capable of correcting the [183]W effect, it relies on the assumption that the effect observed for the reference materials is representative for the investigated samples. Our results demonstrate, however, that this may not always be justified because the magnitude of the [183]W effect strongly depends on the amount of W processed (Fig. 4 and 5).

Hence, it is crucial that the amount of W processed through the analytical protocol for all samples is well known and closely matches that of the corresponding reference material that is used to quantify the analytical [183]W effect. A more reliable correction, particularly if the investigated samples show a large range in W contents, can probably be achieved by analyzing a suite of reference materials with varying W amounts. This will yield an empirical correlation between the magnitude of the [183]W effect and the amount of W processed, which can then be used to individually correct the measured W isotope ratios of each sample: $\mu^i W_{corr} = \mu^i W_{meas} - (m \times \ln[W] + b)$, where m and b are the slope and intercept, respectively, of the corresponding μ^iW–ln[W] regression defined by the reference materials. We emphasize again that such correlations are specific to a certain analytical protocol (and maybe even operator) and not applicable to other data sets (Section 5.2). Thus, the correction parameters must be determined separately for each chemical separation procedure employed for high-precision W isotope analyses.

5.4. Significance of the analytical [183]W effect

Although the analytical [183]W effect is typically <20 ppm and often smaller than the analytical uncertainty, it can have a significant impact on the evaluation of measured W isotope data. For instance, μ^{182}W values of iron meteorites are used to date core formation in their parent bodies by calculating [182]Hf–[182]W model ages (see Kleine and Walker[1]). The precision and accuracy of these ages, however, critically depend on those of the used μ^{182}W and are thus very sensitive to the [183]W effect, regardless of which isotope ratio is used. For example, the μ^{182}W (6/3) are directly affected by this analytical artifact, meaning that an unrecognized [183]W effect shifting this ratio by +10 ppm (a typical value for MC-ICP-MS analyses) would result in an apparent model age that is ~0.9 Ma too young. In contrast, the μ^{182}W (6/4) are not directly compromised by the [183]W effect and thus commonly used for Hf–W chronology. However, the

μ^{182}W (6/4) can be strongly affected by nucleosynthetic isotope anomalies that need to be quantified using the corresponding μ^{183}W (6/4), which are in turn modified by this artifact (Fig. 1, Section 5.3). For example, a [183]W effect of only −7 ppm on μ^{183}W (6/4), which is misinterpreted (and corrected for) as nucleosynthetic anomaly, would cause a shift of +10 ppm in μ^{182}W (6/4), again resulting in a model age that is ~0.9 Ma too young. Hence, directly or indirectly, even a moderate unaccounted [183]W effect can result in inaccurate Hf–W model ages, exceeding the typical uncertainties (~0.5–0.7 Ma) obtained in recent high-precision studies.[6,24] Of note, the slightly negative, albeit unresolved, μ^{183}W (6/4) values of many '*non-carbonaceous*' iron meteorites (Section 5.3) are commonly attributed to an insufficient correction of the analytical [183]W effect. However, it is also possible that these small μ^{183}W deficits are real, and would then reflect small nucleosynthetic W isotope anomalies. In this case, the reported Hf–W model ages based on the measured μ^{182}W (6/4), which have not been corrected for nucleosynthetic anomalies, may be too old by up to several hundred thousand years.

Over the past decade, W isotope variations in terrestrial samples have become the focus of sustained attention, as they provide critical insights into past and present workings of the silicate Earth. Several MC-ICP-MS and N-TIMS studies report small (mostly <15 ppm) μ^{182}W anomalies for some ancient (*i.e.*, Hadean to Archean) komatiites and supracrustal rocks as well as for modern plume-related basalts (see Zhang and Liu[82] for references and a recent data compilation), which provide evidence for the existence and preservation of isotopically anomalous portions of the mantle.[1] Generally, these variations are interpreted to solely reflect radiogenic anomalies; however, a full assessment of the origin of these variations is often not possible, for example, because some studies report only $\mu^{182/184}$W (6/3) or μ^{182}W (6/3) values that may potentially be affected by the [183]W effect. Of note, the observation that bulk meteorites (and thus the assumed building blocks of Earth) show significant nucleosynthetic W isotope anomalies (Section 5.3), combined with the recent discovery of nucleosynthetic Ru isotope anomalies in some ancient terrestrial rocks,[83] implies that nucleosynthetic W isotope variations might not only have existed during Earth's early formative period but could even have been preserved until today, either in primordial mantle domains or in rocks that formed very early in Earth's history. Hence, it cannot be ruled out *a priori* that such exotic (*i.e.*, ancient or deep mantle-derived) terrestrial rocks have small nucleosynthetic W isotope anomalies. This in turn means that for some of these samples the observed μ^{182}W variations may, at least in part, reflect unrecognized nucleosynthetic contributions, which is particularly relevant for the μ^{182}W (6/4) values.

These examples highlight that even a small analytical [183]W effect can severely compromise the chronological interpretation of μ^{182}W variations and hamper the identification of nucleosynthetic W isotope anomalies in meteoritic and terrestrial samples. Resolving the above issues, therefore, requires a very precise quantification of the [183]W effect in the analyses of such samples, which will become even more important as the analytical precision improves and sample sizes decrease in the

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future. As such, increased efforts to accurately correct the ^{183}W effect will be pivotal for establishing a fine-scale Hf–W chronology of the early Solar System as well as for improving our understanding of Earth's accretion and differentiation history.

6. Tungsten isotope composition of bulk silicate Earth

With respect to mass-independent (*i.e.*, internally normalized) isotope variations, it is generally assumed that high-purity elemental standards, relative to which the measured data are reported, are representative of the isotopic composition of bulk silicate Earth (BSE). However, several studies have demonstrated that this assumption may not always be valid because solution standards can display anomalous (*i.e.*, mass-independent or non-exponential mass-dependent) isotope fractionation effects, potentially induced during the elemental purification/enrichment in the production process or during the genesis of the ores from which these standards were made (*e.g.*, Akram and Schönbächler,[84] Zr; Budde *et al.*,[85] Mo; Steele *et al.*,[86] Ni; Zhang *et al.*,[87] Ti).

In the case of W isotopes, this issue is emphasized by the fact that different solution standards have slightly different isotopic compositions (Fig. 8). For this study, we have repeatedly measured the two most commonly used W isotope standards against each other (by MC-ICP-MS) and found that the Alfa Aesar Specpure Plasma standard, which is used for N-TIMS analyses in the IGL at the University of Maryland (Section 5.1), is characterized by a small offset from the Alfa Aesar standard used in the IfP at the University of Münster (Table S1;† Fig. 2). Although these μ^iW deviations are only on the order of 1–2 ppm and barely resolvable, they are internally consistent and, given

Fig. 8 Diagram of μ^{183}W (6/4) *versus* μ^{182}W (6/3) showing different W isotope solution standards and constraints on the composition of bulk silicate Earth (BSE). All data are reported relative to the Alfa Aesar standard used in the IfP at the University of Münster (μ^iW ≡ 0). The '100%-intercepts' are theoretical values that presumably represent an upper limit for BSE's W isotope signature; a conservative estimate of the BSE composition is highlighted in blue (see Section 6). Data for NIST SRM 3163 is from Kruijer *et al.*;[25] regression line and processed rock samples (gray symbols) are the same as shown in Fig. 2c.

the small magnitude of natural variations, of significance for the adequate comparison and interpretation of W isotope data. We note that Mundl *et al.*[16] did not find a difference between the two standards during a cross-calibration by N-TIMS; however, their uncertainties (∼5–9 ppm; $n = 4$) were much larger than the differences identified here. Regardless, the above observations combined raise the question of how accurately these solution standards reflect the W isotope composition of BSE in general. Note that an anomalous isotopic composition of a solution standard could only lead to a constant offset from terrestrial rock samples and, therefore, cannot account for the large range of W isotope variations observed here and in previous studies for processed samples and solution standards.

Generally, the validity of using a given solution standard as proxy for the BSE can be assessed by the analyses of a comprehensive suite of terrestrials rocks. In the case of W, however, this is hampered by the widespread analytical ^{183}W effect that is induced during the chemical separation of W, because any measured difference between terrestrial samples and the solution standard could partly or wholly reflect this artifact. Nevertheless, the data for processed rock samples compiled in this study allow placing important constraints on BSE's W isotope signature. In particular, these samples yield well-defined correlation lines in the W isotope diagrams (Fig. 2), which represent the direction of the ^{183}W effect-induced shift. A corollary of this is that the original composition of the samples and, therefore, the true signature of BSE lies on these μ^iW–μ^jW regressions. This assumption is justified by the lack of μ^{182}W (6/4) anomalies in the investigated samples, which indicates that the ^{183}W effect is the sole origin of the measured anomalies and that there is no systematic (geological) bias in this data set (Section 3).

One way to constrain the BSE position on the μ^iW–μ^jW regression lines is based on the correlation between the magnitude of the ^{183}W effect and the W yield of the chemical separation procedure (as exemplified for μ^{182}W (6/3) in Fig. 3c). Extrapolating these linear regression lines to a yield of 100%, provides μ^iW values which represent a theoretical composition [*e.g.*, μ^{183}W (6/4) ≈ 4] that is presumably free of the ^{183}W effect. These '100%-intercepts' deviate systematically in the opposite direction than processed rock samples and plot on the μ^iW–μ^jW regressions defined by these samples (Fig. 8), indicating that the deviation from the IfP standard is significant, albeit not resolved [except for μ^{182}W (6/3)] (Table S1†). One problem with this approach is, however, that the ^{183}W effect might not further decrease linearly in the interval between ∼90% and 100% yield (*i.e.*, there might be a disproportionately large effect at very high yields). As such, the 100%-intercepts rather represent only an upper limit, meaning that the true BSE composition is likely closer to that of the solutions standards. In contrast, a lower limit for the μ^iW values of BSE can be inferred directly from the processed rock samples with the smallest ^{183}W effect. Considering the associated uncertainties, the data obtained by MC-ICP-MS allow, for example, for a small deficit in μ^{183}W (6/4) of about −3 ppm (Fig. 8), which would also still be within uncertainty of some samples with slightly positive μ^{183}W analyzed by N-TIMS (Fig. 7). Taken together, these constraints provide

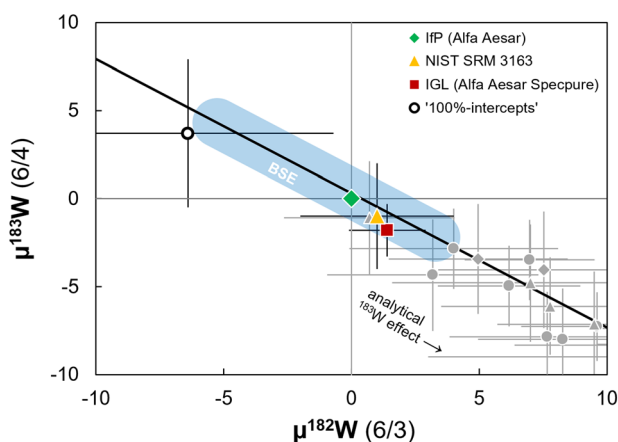a conservative estimate of BSE's W isotope signature, where the μ^{183}W (6/4) of BSE is between about -3 and $+4$ ppm relative to the IfP standard.

It is noteworthy that the μ^iW–μ^jW correlation lines pass exactly (*i.e.*, within ~1 ppm) through the IfP as well as IGL solution standards (Fig. 2), which implies that both are probably very close to the true composition of the BSE. This is because any significant anomalous (*i.e.*, non-exponential) isotope fractionation would likely have resulted in distinct W isotope systematics and caused a deviation from those regressions. Furthermore, the IfP standard represents an endmember composition, meaning that all analyzed rock samples, for which effects of nucleosynthetic isotope anomalies can be excluded, as well as other solution standards (IGL standard, NIST SRM 3163) deviate in the direction of the analytical ^{183}W effect (*i.e.*, ^{183}W deficit) (Fig. 8). It remains unclear, however, whether this indicates that the IfP standard is the most appropriate proxy for the BSE composition. In any case, further work is necessary to more precisely define the W isotope signature of bulk silicate Earth as well as to assess the extent of potential heterogeneities in the mantle. This will, for instance, be important for obtaining a better understanding of BSE's position relative to the dichotomous nucleosynthetic W isotope anomalies in '*carbonaceous*' and '*non-carbonaceous*' meteorites (*e.g.*, ref. 6 and 9 Section 5.3), and for investigating geological processes that may generate W isotope anomalies in the silicate Earth.[88]

7. Conclusions

Our evaluation of high-precision W isotope data for diverse terrestrial samples from numerous recent studies demonstrates that W isotope analyses are often compromised by an analytical artifact that manifests itself as an apparent deficit in ^{183}W. This analytical ^{183}W effect can be present in MC-ICP-MS as well as TIMS data, and can be attributed to a mass-independent fractionation of ^{183}W that is inconsistent with a nuclear field shift, but may instead reflect a magnetic isotope effect. Regardless of its exact origin, our investigation reveals that this widespread artifact is induced during the chemical separation of W and that the specific combination of chromatographic purification and dry-down procedure determines its overall magnitude. Within a given analytical protocol, however, its size is strongly controlled by the amount of W that is processed, where the ^{183}W effect increases with decreasing amount of W. This work, therefore, provides directions for mitigating the ^{183}W effect and resolves apparent inconsistencies between previous studies regarding its occurrence and magnitude. Further, our observations make it possible to precisely quantify and correct the analytical ^{183}W effect using an empirical correlation between its magnitude and the W amount processed, which can be obtained by analyzing a suite of geological reference materials. This approach will result in an overall improved precision and accuracy of W isotope ratios involving ^{183}W, which is essential for identifying and disentangling radiogenic and nucleosynthetic anomalies and, therefore, a prerequisite for the adequate interpretation of isotopic data for terrestrial and meteoritic materials.

Conflicts of interest

There are no conflicts to declare.

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