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Analytical Developments for High-Precision Measurements of W Isotopes in Iron Meteorites

Liping Qin,*,†,‡ Nicolas Dauphas,†,‡ Philip E. Janney,‡,§ and Meenakshi Wadhwa‡,§

Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Avenue, Chicago, Illinois 60637, and Department of Geology, The Field Museum, 1400 South Lake Shore Drive, Chicago, Illinois 60605

A procedure was developed to accurately measure the W isotopic compositions of iron meteorites with a precision of better than ±0.1 ϵ on ϵ^{182}W and ϵ^{184}W (normalized to ^{186}W/^{183}W). Purification of W was achieved through a two-step, ion-exchange procedure. In most cases, the yield is better than 80%, and purified W solutions are clear of matrix elements and direct isobars of W. The final W solutions were analyzed using a Micromass Isoprobe multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). Tests performed on mixtures of terrestrial standards and meteorite samples demonstrate that the method is accurate and that ϵ^{182}W variations as small as ∼0.1 ϵ can be detected. Analyses of three different aliquots of the Gibeon (IVA) iron meteorite obtained over a period of 6 months show identical ϵ^{182}W values with a weighted mean of 3.38 ± 0.05, consistent with literature data for IVA iron meteorites, and indicating that the metal−silicate differentiation event in its parent body was either contemporaneous with or slightly post-dated (by up to ∼2.5 My) the formation of refractory inclusions. We demonstrate our ability to measure ϵ^{184}W accurately and precisely (within ±0.1 ϵ), which is useful for characterizing cosmogenic and nucleosynthetic effects that may be present in iron meteorites. We also report for the first time measurements of ϵ^{180}W, albeit with large error bars (<±4 ϵ, in most cases).

Tungsten ($Z = 74$) has five stable isotopes, 180, 182, 183, 184, and 186, with natural abundances of 0.1198, 26.4985, 14.3136, 30.6422, and 28.4259%, respectively.[1] Except for ^{182}W, which can be produced by β^- decay of ^{182}Hf with a half-life of 8.90 ± 0.09 My,[2] all other isotopes are nonradiogenic. Over the past several years, a great deal of effort has been devoted to analyzing accurately and precisely the W isotopic composition of iron

meteorites.[3−11] The primary motivation for measuring the W isotopic composition of such material is to establish the chronology of the early solar system. Indeed, several studies have demonstrated the former presence of the extinct radionuclide ^{182}Hf in meteorites, with an initial ^{182}Hf/^{180}Hf value of (1.07 ± 0.10) × 10^{-4} measured in refractory inclusions (which is similar within uncertainties to the initial value of (1.0 ± 0.08) × 10^{-4} given by the combined chondrite isochron).[6,8,12,13] With 50% condensation temperatures (at which half of the elements are condensed into solids for a slowly cooling gas of solar composition) of 1684 and 1789 K, Hf and W are classified as refractory elements.[14] The refractory nature of these elements is also demonstrated by the near-constant Hf/W ratio measured in bulk carbonaceous chondrites (^{180}Hf/^{183}W = 2.836), which is a good proxy for the solar ratio.[15]

Hafnium is lithophile while tungsten is moderately siderophile. If metal−silicate differentiation in asteroids and planets occurred while ^{182}Hf was still alive, the metallic cores would have evolved with subsolar ^{182}Hf/^{182}W ratios and would thus be expected to show deficits in ^{182}W relative to undifferentiated chondritic meteorites. Conversely, if metal−silicate differentiation occurred after complete decay of ^{182}Hf, then planetary cores should have chondritic ^{182}W isotopic compositions. It is thus possible to establish the timing of core formation in asteroids and planets based on W isotope measurements.[3−11] Iron meteorites have been extensively studied because some of them (the magmatic groups

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* To whom correspondences should be addressed. E-mail: qinlp@uchicago.edu.
† The University of Chicago.
‡ The Field Museum.
§ Current address: School of Earth and Space Exploration, Arizona State University, Box 871404, Tempe, AZ 85287.
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IIAB, IIIAB, IVA, and IVB) are thought to be derived from the cores of asteroids disrupted by collisions.[16]

Iron meteorites have been exposed in space to particle irradiation for long periods of time (up to 2.275 Gy, as for the Deep Springs ungrouped iron).[17,18] Thus, the tungsten isotopic composition of iron meteorites may have been altered by capture of secondary thermal neutrons generated by galactic cosmic rays (GCR).[3,11,19−21] This limits the potential of the ^{182}Hf−^{182}W system to establish early solar system chronology. Indeed, if cosmogenic effects are present, the variations measured in ^{182}W cannot be entirely ascribed to the decay of ^{182}Hf. A major challenge is to find a way to correct for these effects. Markowski et al. measured the W isotopic compositions along depth profiles in two iron meteorites, Grant (IIIAB) and Carbo (IID), and found correlations with the amount of cosmogenic helium.[21] They could thus estimate the W isotopic compositions prior to GCR exposure in space. A robust way of estimating cosmogenic effects on ^{182}W would be to identify correlated effects due to GCR irradiation in other W isotopes. In previous studies, no such correlated effects were observed.[21]

The application of the ^{182}Hf−^{182}W system may also be limited by W isotopic heterogeneity in the solar system. Although disputed by some workers,[22,23] iron meteorites contain correlated isotope anomalies for molybdenum and ruthenium, which are best explained by heterogeneous mixing in the protosolar nebula of material produced by the *s*-process of nucleosynthesis (where *s* stands for slow neutron capture).[24−26] Tentative evidence for the presence of W isotopic anomalies has also been found during leaching of the Murchison carbonaceous chondrite (CM).[27] So far no such effects have been identified in iron meteorites.

Increasing the precision of W isotope measurements in iron meteorites would potentially (i) improve the resolution of the ^{182}Hf−^{182}W chronometer for dating core segregation in asteroids, (ii) provide a means of correcting cosmogenic effects on ^{182}W from interaction with GCR in space, and (iii) constrain the degree of homogenization of the protosolar nebula. To improve the precision of W isotope analyses compared to earlier studies, we developed a method that allows us to separate W from large sample sizes while retaining high yields. The isotopic compositions were measured by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS), which offers high ion yield despite the high first ionization potential of tungsten (7.98 eV). We demonstrate that we can measure accurately isotopic ratios with precisions (2σ) of ±0.1 parts per 10 thousand for the major

isotopes of tungsten (^{182}W/^{183}W and ^{184}W/^{183}W ratios), after correction for instrumental mass fractionation by internal normalization (^{186}W/^{183}W = 1.985 94).[1] Although less precise, we also report the first measurements of the low-abundance isotope ^{180}W.

MATERIALS AND METHODS

Chemical Separation of Tungsten. Isobaric interference from ^{180}Hf, ^{184}Os, ^{186}Os, and molecular compounds can have unpredictable effects on W isotope measurements. This is an important issue with MC-ICPMS because ionization in a plasma torch is almost nondiscriminating for elements that have first ionization potentials lower than Ar (<15.759 eV). It is therefore crucial to separate W from direct isobars and matrix elements before analysis. Tungsten is present at trace levels in most natural samples, such as iron meteorites, where its concentrations range from 50 ppb to 9 ppm with a peak in the distribution at ~1 ppm.[28−33] Previous studies relied on anion-exchange columns to remove matrix and interfering elements and were limited to small sample sizes (typically <700 mg).[4−11] Samples with low concentrations had to be split between multiple columns in order to retrieve enough W for precise isotopic analysis. In this study, we developed an improved procedure for chemical separation of W by coupling a cation- and several anion-exchange columns, allowing us to obtain high-purity W with high yields (>85%) from large sample sizes (~2 g of iron meteorite).

(a) Sample Dissolution. All the chemistry was performed under clean laboratory conditions at the Isotope Geochemistry Lab of the Field Museum (Chicago). Iron meteorites weighing up to 3 g were first leached (3−4 cycles of alternating dissolution in 10 M HCL−1 M HF mixture at 30−40 °C and rinsing with water), until ~20% of the total mass was dissolved. The aim of this leaching procedure was to clean the samples from surface-sited terrestrial contamination. For several samples, the leachates were inspected for W concentrations. The amounts of W measured were roughly equal to the amounts expected from the dissolved masses of the meteorites. The remaining samples were then rinsed thoroughly with Millipore Milli-Q water (resistivity >18 MΩ·cm) and dissolved in a 12−18-mL mixture of concentrated HCl and HNO$_3$ (in 2:1 ratio by volume) in a Teflon beaker placed on a hot plate at ~70−80 °C overnight. The use of HNO$_3$ ensures that the metal is oxidized into ferric iron during dissolution. The solution was subsequently evaporated to dryness and taken back to solution with a minimum amount of concentrated HCl (~11 M) for loading on the column. For reference, 1.7 g of iron meteorite will typically dissolve in 5.5 mL of concentrated HCl. Chemical separation of W was achieved in a two-step, ion-exchange procedure.

(b) Cation Exchange. Strelow et al. documented partition coefficients for cation-exchange resin AG50W-X8 in HCl medium.[34] At low HCl molarity (<0.5 M), Fe, Ni, and Co partition strongly

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into the resin while W is not quantitatively retained. Because Fe, Ni, and Co make up the bulk of iron meteorites, cation-exchange resin provides a means of eliminating most of the matrix. Other trace metals such as molybdenum and platinum group elements have low partition coefficients for cation-exchange resins at low HCl molarity and follow W in the elution.[35] Since this column has the advantage of retaining the majority of the matrix elements in the column while leaving behind W in the elution, a quantitative yield is obtained for this step (usually, the presence of matrix reduces the retentivity of ion-exchange columns, which works for increasing the yield of the element of interest in this particular case).

Precleaned 150-mL Savillex Teflon columns (i.d. = 4 cm) were filled with 50 g (wet) of Bio-Rad AG50-X8 200−400 mesh hydrogen-form resin (∼60-mL resin volume). These were cleaned and conditioned with 500 mL of 0.2 M HCl−0.3% H_2O_2. The sample solutions in concentrated HCl (∼11 M) were diluted with Milli-Q water to a total volume of 110 mL and stabilized in 0.3% H_2O_2 (following ref 35). Whenever more than 1.7 g of material was dissolved, the samples were split into two columns. The resulting HCl molarity was less than 0.5 M in all cases. The elution sequence proceeded as follows. The sample solution was loaded on the column (in a sequence of 30, 40, and 40 mL), and the elution was collected in a 300-mL Savillex Teflon beaker. An additional 140 mL of 0.2 M HCl−0.3% H_2O_2 (in a sequence of 40, 50, and 50 mL) was run through the column and collected with the first elute. Using this technique, most of the matrix elements (Fe, Ni, Co) were retained on the column while W was quantitatively recovered. Approximately 0.5 mL of concentrated HF (28 M) was added to the eluate to prevent precipitation of W. The W cut was then evaporated to less than 1 mL and transferred to a 2-mL Savillex Teflon beaker, in which it was further evaporated to incipient dryness. A few drops of concentrated $HClO_4$ (12.1 M) were then added and evaporated at 200 °C to get rid of carbon compounds from both the sample and the resin. The residue was redissolved in 1 mL of 1 M HCl, and 18 μL of concentrated HF was subsequently added to stabilize W in solution. The resulting acid molarity of this solution was about 1 M HCl−0.5 M HF.

Tests were performed on two mixtures of ∼1.7 g of pure Fe and Ni powder (Fe/Ni in 9:1 ratio to make up a matrix similar to that of iron meteorites) to each of which ∼0.1 g of 1000 ppm NIST 3163 W standard solution was added. In both cases, the W yields were close to 100%. The total amount of material was reduced by more than 2 orders of magnitude (from a dissolved mass of ∼2 g to less than 20 mg).

(c) Anion Exchange. Further purification of W was achieved through a series of anion-exchange columns in HF−HCl medium (Figure 1). The procedure to clean the resin and remove matrix and isobaric elements was modified from refs 15 and 36. Precleaned Savillex Teflon microcolumns (i.d. = 0.64 cm) were filled with 2 mL of AG1-X8 200−400 mesh chloride-form resin. The resin was cleaned and conditioned with 10 mL of 6 M HNO_3−0.2 M HF−1% H_2O_2, 2 mL of Milli-Q water, 10 mL of 7 M HCl−1 M HF, and 10 mL of 0.5 M HCl−0.5 M HF. The sample solution in 1 mL of 1 M HCl−0.5 M HF was loaded on the anion-exchange column.
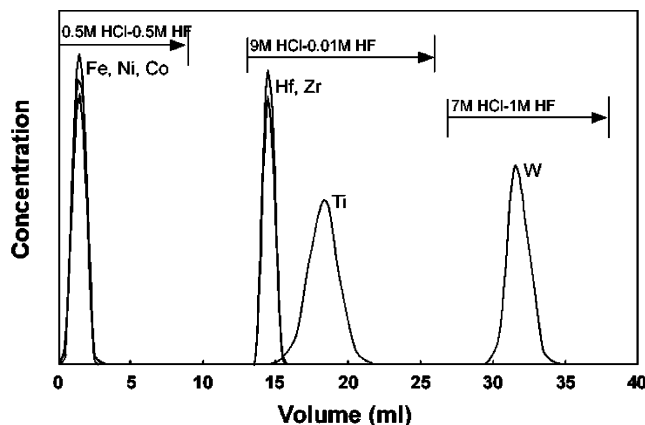

Figure 1. Measured elution sequence of matrix elements (Fe, Ni, Co), Hf, Zr, Ti, and W on AG1-X8 Cl-form 200−400 mesh anion-exchange resins. The concentration axis has an arbitrary scale.

Under these conditions, W partitions strongly onto the anion-exchange resin. Residual matrix elements (like Fe, Ni, and Co) not eliminated in the cation-exchange step were eluted in 8 mL of 0.5 M HCl−0.5 M HF. The resin was rinsed with 4 mL of 0.5 mM HCl−0.5 mM HF before introducing 13 mL of 9 M HCl−0.01 M HF to elute Ti, Zr, and Hf. In iron meteorites, the concentrations of lithophile elements such as Ti, Zr, and Hf are very low but silicate inclusions are sometimes present, and the procedure developed here may be easily extended to other kinds of sample matrixes. After rinsing the resin with 1 mL of 9 M HCl−1 M HF, W was collected with 11 mL of 7 M HCl−1 M HF. Under these conditions, molybdenum and possibly most platinum group elements stay fixed on the column while W is eluted.[37,38] One drop of $HClO_4$ was added before evaporation of the W eluate to prevent evaporation to complete dryness, promote loss of Os as a volatile tetraoxide, and break down any organic compounds that may be present. The anion-exchange chemistry sequence was repeated a total of three times, changing the resin in the column each time. A number of cycles (typically 3) of drying down the sample in $HClO_4$ to incipient dryness and taking it back to solution in a drop of the same acid were performed to destroy organic compounds and reduce the amount of Os remaining. The purified W was finally taken up in 10−12 mL of 0.5 M HNO_3−0.01 M HF for analysis by MC-ICPMS.

(d) Isobaric Interferences. Scans of the mass spectra of a chemically processed iron meteorite sample (Gibeon, IVA) and a blank solution (0.5 M HNO_3−0.01 M HF) are compared in Figure 2. The final purified W sample solution is very clean. No peaks indicating the presence of molecular interferences are observed around the W mass region. Osmium, the major potential isobar on W isotopes, is present at a negligible level (the Os/W ratio after purification is estimated to be on the order of 10^{-5}, corresponding to a negligible correction of <0.01 ϵ on $\epsilon^{182}W$). The solutions contained trace amounts of Hf (after on-peak − zero blank subtraction). Although Hf peaks cannot be seen in Figure 2, the calculated correction on $\epsilon^{180}W$ due to ^{180}Hf interference is large (∼100 ϵ). The reason is that ^{180}Hf is the most abundant

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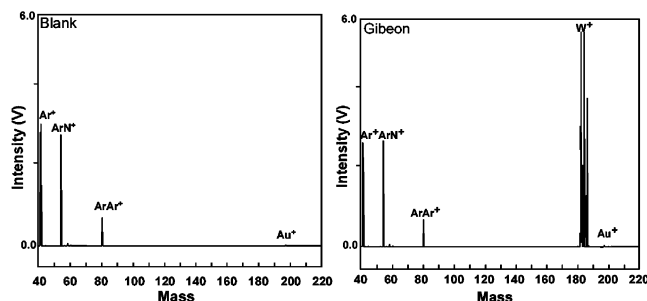
Figure 2. Peak scan spectra for a mass spectrometer blank (left panel) and W cut from Gibeon, IVA iron meteorite (right panel).

isotope of Hf (35.08%) while ^{180}W is the least abundant isotope of W (0.12%). It is likely that the Hf came from the concentrated reagents or containers used to process the samples. A similar level of Hf was also observed in pure W standards.

(e) Procedural Blank and Yield. As has already been reported by Kleine et al.,[15] Savillex Teflonware contains significant W, so all the Teflon vessels used in the chemistry were boiled twice in 50% trace metal grade HNO_3 and in Milli-Q water for 6 h each. Teflon vessels were further cleaned in aqua regia vapor at 120−140 °C for 6 h, followed by two cycles of 50% HCl−50% HF vapor at 160−180 °C for 8 h, and finally boiled in Milli-Q water for 6 h. We monitored the W blank for the whole chemistry each time that we processed samples. The procedural blank from sample dissolution to dilution for isotopic analysis ranges from 0.3 to 0.7 ng, which is negligibly small compared to the amount of W present in the dissolved samples (usually >500 ng).

Mass Spectrometry. The W isotopic composition was analyzed by Micromass Isoprobe MC-ICPMS at the Isotope Geochemistry Laboratory of the Field Museum. This instrument is equipped with nine Faraday collectors, allowing the simultaneous measurement of all W isotopes and monitoring of potential isobaric interferences. The majority of the measurements were acquired with the instrument operated in hard extraction mode (use of negative extraction voltage) with Ar in the hexapole collision cell at a flux of 1.8 L/min (the role of the hexapole collision cell is to thermalize the incoming ions to reduce the energy spread to <1 eV before mass/charge separation in the magnetic sector). Ion intensities of ^{179}Hf, ^{180}W + ^{180}Hf + ^{180}Ta, ^{181}Ta, ^{182}W, ^{183}W, ^{184}W + ^{184}Os, ^{186}W + ^{186}Os, and ^{188}Os were measured on Faraday collectors L3, L2, Axial, H1, H2, H3, H4, H6, respectively. Measuring ^{179}Hf, ^{181}Ta, and ^{188}Os allowed us to monitor the isobaric interferences from Hf, Ta, and Os. They were corrected for by using ^{180}Hf/^{179}Hf = 2.5754, ^{180}Ta/^{181}Ta = 0.0001, ^{184}Os/^{188}Os = 0.0015, and ^{186}Os/^{188}Os = 0.1198[39−41] and applying to these ratios the fractionation factor calculated based on the measured ^{186}W/^{183}W ratio. The samples were usually run at 30−80 ppb concentration. The measured intensities were in the range of $(3−8) \times 10^{-11}$ A on ^{184}W (measured as a 3−8 V signal with a 10^{11} Ω resistor). Care was taken to keep the signal under 9 V because of possible problems of nonlinearity in the response of the instrument when the measured signal is close to the saturation voltage of the

detector (10 V). The measurements were done in sequences of 20 cycles, with each cycle integrating the ion intensities for 15 s. Before sample acquisition, the blank solution (0.5 M HNO_3−0.01 M HF) was analyzed for 2 min and the measured intensities were subtracted from the sample measurement (on-peak-zero). Before introducing blank, the system was washed out in 0.5 M HNO_3− 0.01 M HF for 5 min after every sample or standard analysis. The NIST 3163 W standard was used as the reference material. Drift of instrumental mass fractionation was corrected for by bracketing sample analyses with standard measurements.

(a) Correction of Instrumental and Natural Mass Fractionation. Tungsten isotope abundances can vary in a mass-dependent manner in meteorites due to natural processes such as evaporation and condensation. Mass fractionation can also be produced by chemical procedures conducted in the laboratory, such as chromatography if recovery of W is not 100%. Most importantly, the instrument itself causes large isotopic mass fractionation,[42,43] at the level of 1%/amu for W. The variability in instrumental mass fractionation limits the precision that can be obtained by simple standard bracketing. A widely accepted procedure for correcting natural and instrumental mass fractionation in the search of nucleosynthetic, cosmogenic, and radiogenic effects is to fix the ratio of a pair of reference isotopes to a given value, calculate the extent of the mass fractionation, and finally use this piece of information to correct other isotopic ratios (internal normalization). Maréchal et al.[43] showed that, in ICPMS, the exponential law provides an adequate description of the isotopic fractionation,

$$r = R(1 + \Delta M/M)^{\beta} \qquad (1)$$

where r is the measured (fractionated) ratio, R is the true (unfractionated) ratio, ΔM is the difference in mass of the two isotopes considered, M is the mass of the denominator isotope, and β is the mass bias factor for the exponential law.[43] To test the influence of mass fractionation laws on normalized W isotopic ratios, the raw ratios obtained for a Gibeon W solution were corrected for mass fractionation using linear and power mass fractionation laws, and the results are identical to the exponential law, albeit with slightly larger error bars (Table 1). In this study, we measured ^{180}W/^{183}W, ^{182}W/^{183}W, ^{184}W/^{183}W, and ^{186}W/^{183}W ratios. The latter value was used in eq 1 to calculate β by assuming

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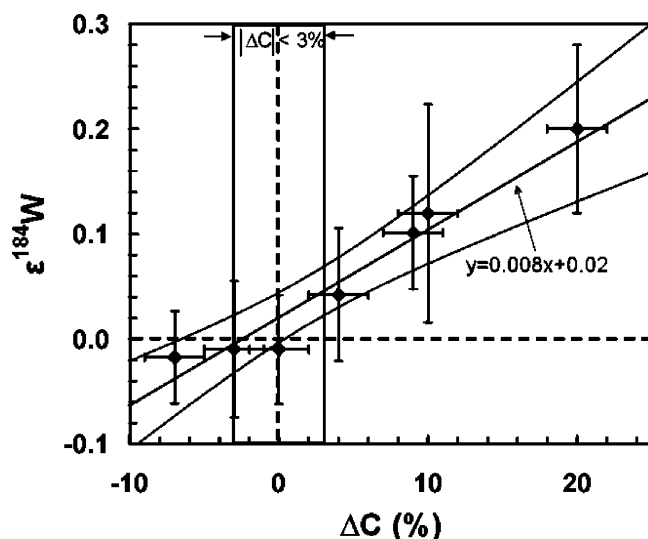(43) Maréchal, C. N.; Télouk, P.; Albarède, F. *Chem. Geol.* **1999**, *156*, 251− 273.

Figure 3. $\epsilon^{184}W$ vs relative difference in W concentration between standard and sample (ΔC). The samples are terrestrial W standards and mixtures of terrestrial W standard and Gibeon as listed in Table 3. Also plotted is the regression line and its 95% uncertainty envelope. The calculated MSWD (reduced χ^2) is 0.53, which is within the 95% confidence interval (0.17−2.57) given by statistics, showing that the dispersion of the data around the regression line is well explained by individual error bars.

an unfractionated $^{186}W/^{183}W$ ratio of 1.985 94.[1] Using this internal normalization method, the measured $^{182}W/^{183}W$ and $^{184}W/^{183}W$ ratios in the NIST 3163 W standard averaged over a period of 2 years are 1.851 74 ($\pm$43, 2 s) and 2.141 23 ($\pm$63, 2 s), respectively. These values agree within error with the ratios of 1.851 28 ($\pm$70) and 2.140 78 ($\pm$20) reported in ref 1. Because the expected isotopic variations in the samples are of limited magnitude, we used the ϵ notation, which is the deviation of sample relative to standard of internally normalized isotopic ratios in parts per 10 thousand. It is calculated using the following equation,

$$\epsilon_k = \left(\frac{R^k_{sample*}}{0.5R^k_{standard*} + 0.5R^{k+1}_{standard*}} - 1 \right) \times 10^4 \quad (2)$$

where k is the index of the kth sample measurement in the sequence, standard (1), sample (1), standard (2), ..., standard (k), sample (k), standard ($k + 1$), ..., standard (n), sample (n), standard ($n + 1$). The asterisk in the subscript (*) indicates that the ratios have been corrected for mass fractionation by internal normalization. The same sample solution was analyzed n times ($13 < n < 20$). The ϵ value is the average of the n replicate measurements, and it is calculated as follows (with the 95% confidence interval),

$$\epsilon = \frac{1}{n} \sum_{k=1}^{n} \epsilon_k \pm \sqrt{\frac{1}{n-1} \sum_{k=1}^{n} (\epsilon_k - \epsilon)^2} \frac{t_{0.95,n-1}}{\sqrt{n}}, \quad (3)$$

where $t_{0.95,n-1}$ is Student's t-value corresponding to a two-sided 95% confidence interval for $n - 1$ degrees of freedom.

(b) Matching in Concentration between Standard and Sample. We found that mismatch of W concentrations between standards and samples can significantly affect the accuracy of the

$\epsilon^{184}W$ measurements, although $\epsilon^{182}W$ is not affected outside the error bars. For instance, a mismatch of 20% in concentration between two solutions of identical isotopic compositions can cause variations of 0.1 ± 0.1 and 0.2 ± 0.08 on $\epsilon^{182}W$ and $\epsilon^{184}W$, respectively. Figure 3 shows measured $\epsilon^{184}W$ values of terrestrial W (and mixtures of terrestrial W and small amounts of meteorite) as a function of the relative differences in W concentrations between samples and bracketing standards. There is a statistically significant correlation between the two (slope 0.008 ± 0.003, 95% confidence interval). Thus, it is crucial to match sample and standard concentrations to better than 3% difference (the intercept at $\Delta C = 0$ is $\epsilon^{184}W = 0.02 \pm 0.02\ \epsilon$). Accurate analyses with precisions better than $\pm\sim0.1\ \epsilon$ for $\epsilon^{182}W$ and $\epsilon^{184}W$ (typical 95% confidence interval for 13−20 replicates) can be obtained routinely with a total W amount in the sample of $\sim$500 ng of W.

RESULTS

Model simulations and laboratory measurements indicate that iron meteorites with extended histories of exposure to GCR have had their W isotopic compositions altered by nuclear reactions with secondary thermal neutrons.[19-21] To test the robustness of our methodology for high-precision W isotope measurements, we chose to analyze Gibeon, a IVA iron meteorite with a low exposure age of 21−32 My and a high shielding.[44-47] In this meteorite, any variations in the W isotope composition relative to the terrestrial standard can only be attributed to decay of ^{182}Hf in the early solar system, the presence of nucleosynthetic anomalies (cosmogenic effects can be ruled out), or both. Five specimens of Gibeon were analyzed over a period of 1 year (Table 2). The five $\epsilon^{182}W$ values range from −3.15 to −3.41. The two analyses done at an early stage of development of the method, and which had not been extensively leached before dissolution (only $\sim$5% weight loss), show $\epsilon^{182}W$ values slightly in excess of the more recent measurements treated by extensive leaching ($\sim$20% weight loss). This may be due to the presence of terrestrial contamination in the earlier measurements. Our best estimate of $\epsilon^{182}W$ for Gibeon is -3.38 ± 0.05 (weighted average, 95% confidence interval), based on the latest three analyses obtained over a period of 6 months. This is within the range of variations (−3.3 to −4.0) reported for IVA iron meteorites in earlier studies.[8,10,11] The value corresponds to a model age of metal−silicate segregation of 0.8 ± 1.7 My relative to the formation of refractory inclusions, using the following equation:

$$\Delta T_{A-B} = \frac{1}{\lambda} \ln\left(\frac{\epsilon^{182}W_A - \epsilon^{182}W_C}{\epsilon^{182}W_B - \epsilon^{182}W_C} \right) \quad (4)$$

where λ is the decay constant of ^{182}Hf (0.078 ± 0.002 My^{-1}),[2] $\epsilon^{182}W_C$ is the present day value of carbonaceous chondrites ($-1.9 \pm 0.1\ \epsilon$),[15] and $\epsilon^{182}W_A$ is the initial value of refractory inclusions ($-3.47 \pm 0.20\ \epsilon$).[8] The uncertainty in each parameter was

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Table 2. W Isotopic Compositions of Samples of the Gibeon Iron Meteorite[a]

sample	specimen no.	weight (g)[b]	ϵ^{180}W	ϵ^{182}W	ϵ^{184}W
Gibeon (IVA)	ME 569 1	1.7	-0.17 ± 3.57	-3.23 ± 0.06	0.05 ± 0.05
	ME 569 2	1.7	-1.03 ± 3.38	-3.13 ± 0.11	0.05 ± 0.07
	ME 569 3	1.8	-1.96 ± 8.97	-3.36 ± 0.09	0.04 ± 0.07
	ME 569 4	1.7	1.11 ± 3.31	-3.39 ± 0.06	0.07 ± 0.05
	USNM 1497	1.7	-16.74 ± 21.79	-3.41 ± 0.15	0.02 ± 0.06
	mean[c]		-0.39 ± 3.07	-3.38 ± 0.05	0.05 ± 0.04

[a] ϵ^nW $= \epsilon^n$W/^{183}W (normalized to ^{186}W/^{183}W) ($n = 180, 182, 184$). [b] The weight is that after leaching procedure. [c] The mean values for Gibeon are weighted averages of the last three measurements, since the first two may suffer from terrestrial contamination.

Table 3. W Isotope Compositions of NIST W Standard and Mixtures of Gibeon and NIST W Standard

sample	ϵ^{180}W	ϵ^{182}W	ϵ^{184}W	ϵ^{182}W$_{expected}$
NIST W	-1.47 ± 3.22	-0.03 ± 0.07	-0.01 ± 0.05	0.00 ± 0.00
2% Gibeon[a]	-3.24 ± 3.19	-0.05 ± 0.06	-0.02 ± 0.04	-0.08 ± 0.01
8% Gibeon[a]	-3.92 ± 3.24	-0.13 ± 0.05	0.04 ± 0.06	-0.25 ± 0.03
15% Gibeon[a]	-0.16 ± 3.35	-0.37 ± 0.10	0.12 ± 0.10	-0.47 ± 0.07

[a] Analyses where the relative difference in W concentration between sample and standard $|\Delta C|$ was >3%.

propagated to the model age. The main source of uncertainty is from ϵ^{182}W$_A$. This model age shows that core−mantle differentiation in the parent body of Gibeon was contemporaneous or slightly postdated (by at most ∼2.5 My) the condensation of the first solids in the protosolar nebula. Four out of five analyses have ϵ^{184}W values equal to 0 within error. The slightly positive weighted average of 0.05 ± 0.04 (based on the three most recent measurements) may reflect the presence of small nucleosynthetic anomalies, although this is barely resolvable with the present level of precision.

To test the method, we have also analyzed the W isotopic compositions of mixtures of terrestrial NIST W standard with variable amounts of Gibeon (2, 8, and 15% contributions to the total amount of W) (Table 3). Pure Fe, Ni powder (∼1.6 g, Fe/Ni in 9:1 ratio) was added to the mixtures to make a matrix similar to that of iron meteorites. The motivation for preparing such mixtures with variable ϵ^{182}W values and matrixes similar to iron meteorites was to test the accuracy of our method without introducing isotopic spikes in the clean laboratory. The expected compositions of the mixtures are given by

$$\epsilon^{182}W_{mixture} = f\epsilon^{182}W_{Gibeon} \qquad (5)$$

where f is fraction of the total W derived from Gibeon. Interestingly, if the W concentrations and masses are perfectly known, the calculated uncertainty for the mixture is also scaled by f. A pure terrestrial NIST W standard was also processed and analyzed. The measured ϵ^{182}W values in the mixtures are plotted against the expected values in Figure 4. Except for one measurement, all measured values are equal to calculated values within 95% confidence intervals. This result indicates that we can accurately detect variations in ϵ^{182}W as low as ∼0.1 ϵ. Terrestrial contamination from the Fe/Ni powder used to make a matrix similar to that of iron meteorites might be the cause for the departure of the 8%
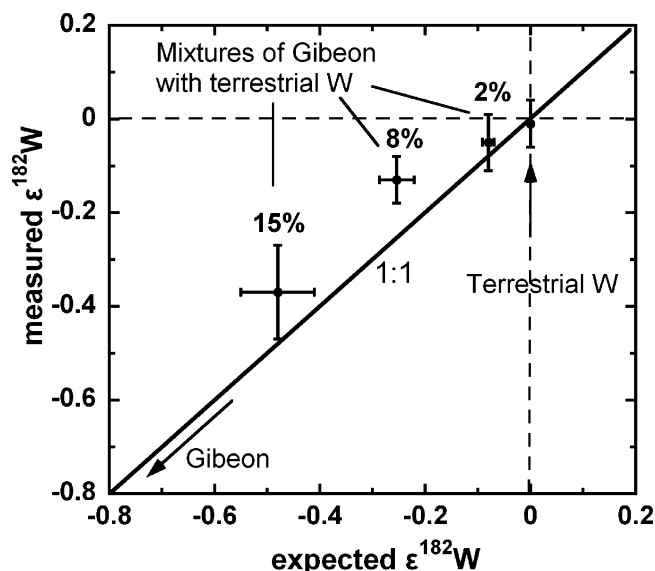

Figure 4. ϵ^{182}W values in mixtures of terrestrial NIST W standard and varying amounts (2, 8, and 15%) of the Gibeon iron meteorite (ϵ^{182}W $= -3.38 \pm 0.05$). There may be variations in the W concentration of Gibeon from one sample to another (John Wasson, personal communication). For this reason, the W concentration in the Gibeon specimen ME 569 was quantified by measuring the W abundance in the eluate from the cation-exchange column of pure Gibeon solution (the yield of this column is close to 100% based on our tests). The W concentration in this specimen is estimated to be 530 ppb (with a 2σ error of $\pm 10\%$), which is somewhat lower than the values (630 and 670 ppb) reported in ref 32. The uncertainty in the W concentration was propagated to the expected ϵ^{182}W.

dilution from the 1:1 line. As discussed previously, all isotope ratios were corrected for natural, chemical, and instrumental mass fractionation by internal normalization. Therefore, all terrestrial samples should have ϵ values equal to 0 within uncertainties for all W isotopes. This is exactly what is measured in the pure terrestrial W standard (ϵ^{182}W $= -0.03 \pm 0.07$ and ϵ^{184}W $= -0.01 \pm 0.06$, Table 3 and Figure 4). The accuracy and precision we obtained on ϵ^{184}W for terrestrial W, along with those for Gibeon specimens, show that ϵ^{184}W may be useful for characterizing cosmogenic and nucleosynthesic effects that may be present in iron meteorites.

All the samples matched within 3% in concentration with bracketing standards, including the terrestrial W analysis, have ϵ^{180}W values equal to 0, albeit with large error bars (<±4 ϵ, in most cases). Figure 5 shows the 95% confidence ellipse for ϵ^{184}W and ϵ^{180}W. Point (0, 0) is within the ellipse, demonstrating that the measurements are free of analytical artifacts. Two analyses

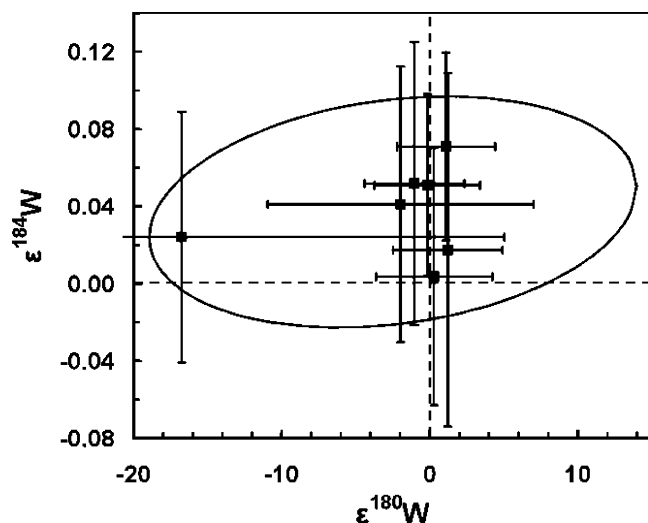**Figure 5.** $\epsilon^{184}W$ vs $\epsilon^{180}W$ for the measurements where the W concentration difference between sample and standard is <3%. Also shown is the 95% error ellipse for the mean.

where the mismatch in W concentration between samples and standards was >3% show $\epsilon^{180}W$ values slightly outside the error bars. This is the first time that the abundance of the low-abundance isotope ^{180}W is reported in a natural sample (Gibeon). Tungsten-180 is potentially interesting because model simulations (Jozef Masarik, personal communication) indicate that the cosmogenic effect on $\epsilon^{180}W$ may be large and could be used to monitor $\epsilon^{182}W$ variations due to irradiation by GCR. The results for $\epsilon^{180}W$ as well as for $\epsilon^{184}W$ demonstrate that we can measure accurately the nonradiogenic W isotopes including ^{180}W, which opens the possibility of documenting and correcting cosmogenic/nucleosynthetic effects on $\epsilon^{182}W$ in iron meteorites.

CONCLUSIONS

New chemical and mass spectrometric procedures have been developed to analyze the W isotopic compositions of iron meteorites accurately and precisely. The $\epsilon^{184}W$ corrected for mass fractionation by internal normalization is sensitive to concentration matching between samples and standards. As long as W concentrations are matched within 3%, no artifacts on $\epsilon^{184}W$ are present within error. Precisions of better than $\pm 0.1\ \epsilon$ on $\epsilon^{182}W$ and $\epsilon^{184}W$ can be achieved routinely. Tests performed on mixtures of meteorite samples with terrestrial standards demonstrate that the method is accurate and that we can detect $\epsilon^{182}W$ variations as small as $\pm 0.1\ \epsilon$.

Gibeon, a IVA iron meteorite with low GCR exposure and high shielding, has $\epsilon^{182}W$ (3.38 $\pm$ 0.05) similar to or slightly in excess of the initial value of refractory inclusions found in primitive meteorites. This indicates that metal−silicate differentiation in the parent body of Gibeon was contemporaneous with or slightly postdated the formation of the solar system. This result is in agreement with conclusions from earlier studies.

All measurements of terrestrial standards and Gibeon specimens show close to normal (terrestrial) compositions for nonradiogenic W isotopes ($\epsilon^{184}W = 0$ and $\epsilon^{180}W = 0$ within error bars). This shows that we can measure accurately the abundances of these isotopes, which may be useful for documenting cosmogenic and nucleosynthetic effects in iron meteorites. This is the first time that measurements of the low-abundance isotope ^{180}W are reported. At this stage, the precision on $\epsilon^{180}W$ is limited and much development remains to be done before this isotope can be used to monitor ^{182}W burnout by neutron capture during exposure in space, which would require an order of magnitude improvement in terms of precision.