Improved method for highly precise and accurate ^{182}W/^{184}W isotope measurements by multiple collector inductively coupled plasma mass spectrometry and application for terrestrial samples

Asako Takamasa,[1,2] Katsuhiko Suzuki,[1]* Yusuke Fukami,[1,3] Tsuyoshi Iizuka,[4] Maria Luisa G. Tejada,[5] Wataru Fujisaki,[1] Yuji Orihashi[6] and Takuya Matsumoto[7]

[1]Submarine Resources Research Center, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Natsushima, Yokosuka, Kanagawa 237-0061, Japan
[2]JAPAN NUS Co., Ltd, Nishi-Shinjuku Prime Square (Former Nishi-Shinjuku Kimuraya Building) 5F, 7-5-25 Nishi-Shinjuku, Shinjuku-ku, Tokyo 160-0023, Japan
[3]Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
[4]Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[5]Institute for Marine Geodynamics, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Natsushima, Yokosuka, Kanagawa 237-0061, Japan
[6]Department of Earth and Environmental Sciences, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan
[7]Isotope Hydrology Section, International Atomic Energy Agency (IAEA), Vienna International Centre, Vienna, 1400, Austria

The extinct, relatively short-lived nuclide ^{182}Hf produced ^{182}W as a decay product. Fractionation of Hf-W in the very early Earth led to variations in the ^{182}W/^{184}W ratios of terrestrial rocks; however, because these variations are very small, quantifying ^{182}W/^{184}W ratios requires an extremely precise method. Here, we propose an improved method for highly precise and accurate method for measuring the ^{182}W/^{184}W ratios of terrestrial rocks. Samples were extracted with 4-methyl-2-pentanone and purified by cation and anion exchange chromatography prior to determination of the W isotope ratio by multiple collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) system coupled with a desolvating nebulizer. Sample preparation removed matrix elements (e.g., Hf, Ta, Os, and dimers of Nb and Mo) with masses similar to those of W isotopes, resulting in these elements having a negligible influence on the measured ^{182}W/^{184}W ratios. A W standard solution processed by ion exchange chromatography and/or solvent extraction showed a ^{183}W deficiency, even after mass fractionation correction of the measured isotope data. As reported previously, mass-independent fractionation increases the ^{182}W/^{184}W ratio if the ^{183}W/^{184}W ratio is used to correct for mass fractionation to for better precision in natural samples. However, accurate ^{182}W/^{184}W ratios for a basalt reference material (JB-2) were obtained, even if ^{183}W was used for mass fractionation correction. Our results show that it is also possible to correct for the effects of mass-independent fractionation on the ^{183}W/^{184}W ratio by sample-standard bracketing using a W standard solution subjected to the same preparation procedure used for the samples. A major advantage of the newly developed method is that it requires a smaller amount of sample (0.2–0.3 g; 50–80 ng W for JB-2) compared with that needed for other reported methods (typically 0.7–15 g; 500–1000 ng W). This decrease in sample amount was possible by removing matrix elements from the sample solutions, and cleaning the membrane of the desolvating nebulizer between analyses also contribute to enhancing the W ion beam intensity and to high precision. Analysis of different basalts from the Loihi, Kilauea islands and Ontong Java Plateau with various W isotopic compositions consistent with the previous studies demonstrated the reliability of the method.

Keywords: ^{182}Hf-^{182}W isotope system, core-mantle interaction, early evolution of the Earth, multiple collector-ICP-mass spectrometry (MC-ICP-MS), mass fractionation correction

1. Introduction

Tungsten has five stable isotopes, which have masses of 180, 182, 183, 184, and 186. Tungsten-182 is produced by β-decay of the extinct nuclide ^{182}Hf, which has a relatively short half-life of 8.9 million years (Vockenhuber *et al.*, 2004). Because the abundance of ^{182}Hf was low at the time of the Earth's formation, the expected variation of ^{182}W in terrestrial samples is extremely small. The ^{182}W/^{184}W isotope ratio is, therefore, commonly shown as μ^{182}W in parts per million (ppm) relative to the value for a standard:

*Corresponding author (e-mail: katz@jamstec.go.jp)

$$\mu^{182}W \text{ (ppm)} = (^{182}W/^{184}W_{sample}/^{182}W/^{184}W_{standard} - 1) \times 10^6.$$

Hafnium is a lithophile and W is a siderophile; therefore, during segregation of the Earth's core, Hf remained in the silicate phase and W preferentially partitioned to the metal phase. It is expected that such Hf-W fractionation occurred prior to the extinction of ^{182}Hf on the early Earth and in lunar and meteorite parent bodies. Various investigators have reported positive and negative anomalies in μ^{182}W values relative to the present-day mantle value (μ^{182}W = 0) in extraterrestrial systems such as lunar basalt (+20 to +30; Kruijer $et~al.$, 2015; Touboul $et~al.$, 2015) and chondrites (−3,200 to +15,000; Hellmann $et~al.$, 2019). For terrestrial rocks, most ancient rocks older than 2.5 Ga generally show relatively uniform μ^{182}W values of +10 to +15 (Willbold $et~al.$, 2011, 2015; Touboul $et~al.$, 2012, 2014; Liu $et~al.$, 2016; Rizo $et~al.$, 2016; Dale $et~al.$, 2017; Mundl $et~al.$, 2018; Puchtel $et~al.$, 2018; Reimink $et~al.$, 2018; Tusch $et~al.$, 2019). In contrast, the komatiites from the Schapenburg and Komati Formation have a negative μ^{182}W value and a μ^{182}W value that is unresolved from the modern value, respectively (Touboul $et~al.$, 2012; Puchtel $et~al.$, 2018). Certain ocean island basalts also have negative μ^{182}W values (−25 to 0; e.g., Mundl $et~al.$, 2017; Mundl-Petermeier $et~al.$, 2019, 2020; Rizo $et~al.$, 2019). Rizo $et~al.$ (2016) reported the first significantly positive μ^{182}W anomalies for Phanerozoic rocks, but Kruijer and Kleine (2018) later pointed out a possible problem with their mass spectrometric analysis. Here, we discuss this analytical problem in detail and propose a method to address it.

To identify small variations in the μ^{182}W values of natural samples, an extremely precise and accurate method is required. Recent improvements in techniques for the analysis of W isotopes, including both chemical procedures for sample treatment and mass spectrometric methods, may facilitate the detection of small variations in W isotope ratios.

Chemical separation procedures used in methods for highly precise determination of W isotope ratios generally involve a combination of cation and anion exchange chromatography. For example, Touboul and Walker (2012) proposed a procedure consisting of four chromatography steps, and these investigators used their procedure to obtain W isotope data for rocks of various ages. Peters $et~al.$ (2019) modified Touboul and Walker's procedure and developed a low-blank, four-step separation method that uses cation and anion exchange chromatography with elution not only by HCl, HNO_3, and HF but also by citric acid; this method is also effective for separating Mo. These investigators then determined precise W isotope ratios by means of negative thermal ionization mass spectrometry (NTIMS). Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is an-

other method for high-precision determination of W isotope ratios. In a study involving this method, Kruijer $et~al.$ (2015) separated W from the sample matrix by means of a two-stage anion exchange chromatography procedure. More recently, Mei $et~al.$ (2018) employed cation exchange chromatography with AG50-X8 resin and subsequent extraction chromatography with TEVA Resin. These chromatographic procedures for the separation of W are complicated and time-consuming and result in a high blank level.

Rizo $et~al.$ (2016) reported excesses of ^{182}W in ~120 Ma Ontong Java Plateau (OJP) basalts (μ^{182}W = +24) and ~60 Ma Baffin Bay basalts (μ^{182}W = +8 to +48) measured by NTIMS. These are the first and, to date, the only positive μ^{182}W anomalies reported for Phanerozoic mantle-derived rocks. However, Kruijer and Kleine (2018) reported that they did not detect any μ^{182}W anomalies in the same OJP basalt samples that were measured by means of MC-ICP-MS. They claimed that a problem with the correction method using ^{183}W/^{184}W employed by Rizo $et~al.$ (2016) may have been responsible for the apparent positive μ^{182}W anomalies for the OJP basalts. Instead, Kruijer and Kleine reported W isotope data indicating a ^{183}W deficiency in chemically treated samples of reference material BVHO-2 and OJP basalts. They explained that this deficiency problem is due to a nuclear field shift effect, which they claimed resulted in the observed elevated ^{182}W/^{184}W ratios. ^{182}W/^{184}W ratios are elevated when mass fractionation was corrected for by double normalization with the ^{186}W/^{184}W and ^{183}W/^{184}W ratio. This ^{183}W deficiency has been reported previously. Cook and Schönbächler (2016) have reported that nuclear field shift effects on ^{183}W are induced during chemical purification of Tusch $et~al.$ (2019) recently claimed that high recoveries of W in the ion exchange chromatography and purification of W are effective for minimizing nuclear volume effects on ^{183}W and improve the analytical protocol. The method for precise determination of the ^{183}W/^{184}W ratio can also be applied to examine nucleosynthetic anomalous component of tungsten and component influenced by neutron capture in of the extra-terrestrial samples. Reliable analytical method to obtain precise ^{183}W/^{184}W is expected for this purpose.

In the present study, we used a combination of organic solvent extraction and cation and anion exchange chromatography to remove matrix and high-field-strength elements from the sample solutions prior to analysis by MC-ICP-MS. A ^{183}W deficiency was observed in the MC-ICP-MS data obtained for both a W standard solution and a reference material (JB-2) that had been similarly subjected to solvent extraction and ion exchange chromatography. To address this issue, we corrected our W isotope ratios by employing a bracketing method that used a standard solution subjected to the same procedure applied to the

samples. This approach allowed for accurate determination of $^{182}W/^{184}W$ ratios for the standard solution and reference material, even if ^{183}W was used for mass fractionation correction. The method reported herein allowed the acquisition of highly precise and accurate both $^{182}W/^{184}W$ and $^{183}W/^{184}W$ ratios for natural rock powders, using smaller amounts of sample needed than for those used in previous studies.

2. MATERIALS AND METHODS

2.1. Reagents and materials

All chemical reagents were obtained from commercial suppliers and used as received. Ultrapure-grade HCl, HF, $HClO_4$, and HNO_3 were obtained from Kanto Chemical Co., Japan. Electric Laboratory (EL)-grade HF, HNO_3, and HCl were obtained from Mitsubishi Chemical Corp., Japan. De-ionized water (18.2 MΩ cm^{-1}) was obtained with a Milli-Q Integral system (Merck Millipore Corp., Germany). Prior to use, 4-methyl-2-pentanone (atomic absorption spectrochemical analysis grade; Fujifilm Wako Chemicals Corp., Japan) was purified by extraction with a mixture of 7 M HCl + 2 M HF solution (Ultrapure-grade).

Throughout the study, sample decomposition and dilution were carried out in perfluoroalkoxy vials (Savillex Corp. USA) that had been cleaned sequentially in hot HF, HNO_3, and HCl (EL-grade) and then rinsed in a Milli-Q de-ionized water bath to keep the total chemical procedure blank low. The inside of each vial was further cleaned by putting a mixture of Ultrapur-grade HF and EL-grade HNO_3 in the vials, which were then heated at 100°C overnight, emptied, and then rinsed with Milli-Q de-ionized water to confirm cleanliness of the vials.

A W standard solution (SRM 3163) was obtained from the National Institute of Standards and Technology (NIST), USA, and used to examine the instrumental condition of the MC-ICP-MS. A reference material, JB-2 (basalt), supplied by the Geological Survey of Japan was used to validate the reliability of our procedure. In addition to the reference material, basaltic rocks from three locations (Kilauea, Loihi, and Ontong Java plateau) were also analyzed. The Kilauea basalt was collected in 2002 from the southern lava flows of the Puu Oo eruption in 2002–2004. The Loihi basalts were collected from the Loihi Seamount by a submersible vessel (Shinkai 6500) during the 2002 Japan Agency for Marine-Earth Science and Technology (JAMSTEC) Hawaii cruises (YK02-05 Leg 1B, 698-4B, 18–54.7°N, 155–12.6°W, 2815 m depth). The Ontong Java Plateau samples were obtained from Site 807C cores recovered during Ocean Drilling Program (ODP) Leg 130 (130-807C-79R-5W, 130-807C-77R-2W 130-807C-76R-1W) (http://www-odp.tamu.edu/publications/130_IR/130TOC.HTM).

2.2. Preparation of rock samples

Rock samples were cut, crushed to the size of a few centimeters, and then soaked in a warm water bath for at least 5 days to remove the salt derived from seawater. Subsequently, the samples were crushed to a particle size of approximately 5 mm and then pulverized. Tungsten carbide tools (WC) are commonly used to prepare rock powders because of their hardness. However, because of the possibility of contamination of the sample powder, WC mortar and pestle or mill were not used in this study; instead, samples were powdered using an alumina mill or a Multi-beads Shocker cell disruptor/pulverizer with polycarbonate container (Yasui Kikai Corp., Japan) installed at JAMSTEC. The pulverized samples were further ground into fine particles with an agate mortar and pestle to ensure complete dissolution of the sample.

2.3. Sample dissolution

To prevent contamination from the environment, the chemical procedures described in Subsections 2.3 and 2.4 were carried out in a class 1000 clean room. To prepare samples for precise determination of W isotope ratios, 200–300 mg of finely pulverized sample was weighed into a perfluoroalkoxy vial. Then 1 mL of 28.3 M Ultrapure-grade 28.3 M HF, 2 mL of 9 M Ultrapure-grade HCl, and 3 mL of 13.4 M Ultrapure-grade HNO_3 were added to the vial, which was tightly capped and heated on a hot plate at 140°C for 4 days. Then the vial was opened and the solution was evaporated by gradually increasing the temperature from 140 to 170°C. The residue was then dissolved by adding 1 mL of 9.45 M HCl and heating with the lid on at 150°C for 1 h and then completely evaporating at 170°C. Finally, 3 mL of a 7 M HCl + 2 M HF solution was added to the residue, and the solution was heated at 130°C for 4 h.

2.4. Chemical procedure

2.4.1. Solvent extraction
An aliquot (3.5 mL) of 4-methyl-2-pentanone, prepared as described in Subsection 2.1, was combined with 3 mL of sample solution in 7 M HCl + 2 M HF in a 10-mL centrifugation tube. The resulting mixture was shaken with a vibration mixer (Vortex-Genie 2; Scientific Industries, Inc., USA) for at least 1 min to extract W. Then the aqueous phase containing W was separated from the Ta-bearing organic phase into another vial and evaporated at 150°C. The residue was dissolved in 1 mL of 9.45 M HCl and the solution was heated at 150°C for 1 h and then evaporated at 170°C. The residue was collected in 2 mL of 6 M HCl, heated in an enclosed vial at 150°C for 3 h, cooled to room temperature, and diluted 10-fold with Milli-Q deionized water for the ion exchange chromatography procedure described in Subsection 2.4.2.

Table 1. Procedures for cation exchange chromatography

	Reagents	Volume (mL)	Eluted elements
AG50W-X8 #200–400	2 M HCl	5	
Cleaning	7 M HCl + 2 M HF	10	
Cleaning	Milli-Q water	25	
Cleaning	Milli-Q water	25	
Conditioning	0.6 M HCl	20	
Conditioning	0.6 M HCl	10	
Load sample	0.6 M HCl	20	W and other elements
Elute W	0.6 M HCl	30	W and other elements

Table 2. Procedures for anion exchange chromatography

	Reagents	Volume (mL)	Eluted elements
AG1X-8 #200–400	2 M HCl	1.6	
Cleaning	7 M HCl + 2 M HF	5	
Cleaning	Milli-Q water	12	
Cleaning	Milli-Q water	12	
Conditioning	0.1 M HF	5	
Conditioning	0.1 M HF	3	
Load sample	0.1 M HF	1	Matrix elements (Ca, Mg and others)
Wash	0.1 M HF + 2% H_2O_2	4	Fe, Ti
Wash	1 M HF + 0.2% H_2O_2	3	Ti, Fe, Hf, Zr
Wash	Milli-Q water	3	
Wash	6 M HCl	6	Hf, Zr, Fe
Wash	6 M HCl	2	Hf, Zr
Elute W	6 M HCl + 1 M HF	8	W

2.4.2. Ion exchange chromatography The two-step procedure used for ion exchange chromatography in this study was a modified version of that developed by Sahoo *et al.* (2006) and Takamasa *et al.* (2009) and is shown in Table 1. Cation exchange resin (AG50W-X8, analytical grade, 200–400 mesh, Bio-Rad Laboratories, Inc.) that had been sequentially precleaned with 3 M HNO_3 and 2 M HCl for at least 24 h at room temperature, and cleaned and then conditioned with dilute (0.6 M) HCl, was loaded into a commercially available empty Bio-Rad Poly-Prep Chromatography Column (bed volume, 2 mL; reservoir, 10 mL). In the first step, the major matrix elements (e.g., Ca and Mg) were removed as the sample solution passed through the resin. These matrix elements were adsorbed on the resin because they are positively charged in dilute HCl. Tungsten, which was not taken up by the resin, was collected with the sample solution into a vial and further eluted with the addition of 30 mL of 0.6 M HCl. The W recovery in this first step was 95–100%.

The W-rich solution obtained from the cation exchange column was evaporated to dryness, dissolved in 1 mL of 28.3 M HF, and the solution was heated at 120°C for 1 h. The solution was evaporated at 150°C, and the residue was collected in 1 mL of 0.1 M HF for further purification by anion exchange chromatography.

In the second chromatography step, W was further purified through an anion exchange resin (AG 1-X8, analytical grade, 200–400 mesh, Bio-Rad) according to the procedure described by Takamasa *et al.* (2009) and shown in Table 2. Briefly, after Fe, Ti, and other high-field-strength elements were eluted with HF + H_2O_2 and then with HCl, W was eluted with HCl + HF. The W recovery for this step was 90–100%, and the total blank was <150 pg.

Finally, the organic matter was decomposed by adding in a few drops of $HClO_4$ and HNO_3, and evaporation to dryness. The resulting purified W fraction was dissolved in 0.5 M HNO_3 + 0.01 M HF and analyzed by MC-ICP-MS.

2.5. Cleaning of the Aridus II desolvating nebulizer
The membrane of the desolvating nebulizer was cleaned and dried prior to each analysis. After a total analysis time of around 30 h, the intensity of the W ion beam, which are critical to obtain enough precision in the measurement of W isotopes, was reduced to 10–20%, even if the Ar and N_2 gases of the desolvating nebulizer to remove liquid through the membrane and ion lenses of the MC-ICP-MS spectrometer were re-tuned. Acid cleaning of the membrane recovered the intensity of the W ion

Neptune Plus Thermo Fisher Scienfitic Inc.	
RF power	1200 W
Guard electrode	On
Cooling gas	16 L/min (Ar)
Auxiliary gas	0.8 L/min (Ar)
Sample gas	0.8–1.0 L/min (Ar)
High vacuum	$<2 \times 10^{-7}$ mbar
Ion getter pressure	$<1 \times 10^{-8}$ mbar
Cup configuration	178(L4) 179(L3) 180(L2) 182(L1)
	183(C) 184(H1) 186(H2) 188(H3) 189(H4)
Mass resolution (M/ΔM)	400 (low-resolution mode)
Cycles/blocks	80/1
Integration	4 s
Sampler/skimmer cones	Ni Jet/Ni X
Nebulizer	PFA ESI-100
Ratio used for internal mass bias correction	$^{186}W/^{184}W = 0.92767$ (Rosman and Taylor, 1998) or
	$^{186}W/^{183}W = 1.98594$ (Harper and Jacobsen, 1996)
Aridus II CETAC Technologies	
Ar sweep gas	3–5 L/min
N_2 gas	1–3 mL/min
Spray chamber/desolvator temperatures	110°C/160°C

beam, suggesting the importance of reducing the amount of matrix materials in the sample solution to avoid gradual degradation of membrane function.

For cleaning, 10% HNO_3 was introduced into the sample line to soak the membrane, and left for at least 12 h. The membrane was then rinsed with Milli-Q water three times, followed by operation under typical measurement settings and temperature until no water was observed leaving the outlet lines. Then, 2-propanol was nebulized with a sample gas rate of 1 L/min overnight to completely dry the membrane.

2.6. MC-ICP-MS measurement

A Neptune Plus MC-ICP-MS spectrometer (Thermo Fisher Scientific Inc.) housed at JAMSTEC was used to measure W isotopes under the operating parameters listed in Table 3. A dry introduction system (Aridus II desolvating nebulizer, CETAC Technologies) equipped with a PFA ESI-100 nebulizer with a sample solution uptake rate of 100 μL/min was used. The spectrometer was equipped with a Ni Jet sampler cone and a Ni X skimmer cone. Measurements were conducted in low-resolution mode for an integration time of 4 s for 80 cycles. The baseline was measured for 80 cycles of 4 s integration using 0.5 M HNO_3 + 0.01 M HF, and the average of the integrated signal was subtracted from that for the sample. A single-element standard solution of W (NIST SRM 3163) was used as an isotope standard.

For W measurements with the Neptune Plus system, nine Faraday cups were used: L4 (^{178}Hf), L3 (^{179}Hf), L2

Table 4. Values of $\mu^{182}W$ for W solutions containing Mo or Mo and Nb, where $\mu^{182}W$ is the deviation of the $^{182}W/^{184}W$ value of the sample solution from the value of a terrestrial standard. SD = standard deviation

Sample solution	$\mu^{182}W$ (ppm)	2SD (ppm)
W 20 ppb	1.4	8.8
W 20 ppb + Mo 20 ppb	−2.9	8.2
W 20 ppb + Mo 100 ppb	0.5	6.8
W 20 ppb + Mo 500 ppb	3.1	6.2
W 20 ppb + Mo 100 ppb + Nb 2 ppb	−2.2	11.2

(^{180}W, ^{180}Ta, ^{180}Hf), L1 (^{182}W), C (^{183}W), H1 (^{184}W, ^{184}Os), H2 (^{186}W, ^{186}Os), H3 (^{188}Os), and H4 (^{189}Os). Although isobaric interferences of ^{186}Os on ^{186}W and ^{184}Os on ^{184}W can be estimated by monitoring ^{188}Os and ^{189}Os intensities, no Os was in fact detected; Os is volatile under oxidative conditions and it must have been lost during the evaporation processes in the HNO_3 or $HClO_4$. Hafnium or Ta signals were found to be negligible during analysis of the JB-2 reference material and the natural rock samples that had been subjected to the solvent extraction and ion chromatography. In addition, because interferences were negligible, no interference corrections were required in any of the measurements.

The W isotope ratios obtained for all the sample solutions (including the standard solution and the solutions derived from natural rocks) were corrected for mass bias using a $^{186}W/^{184}W$ ratio of 0.92767 (Rosman and Taylor,

Table 5. Result for standard solutions (a) dissolved in HClO₄ or H₂O₂ and then dried, (b) subjected to anion exchange chromatography alone or a combination of solvent extraction and anion or cation exchange chromatography, and (c) subjected to a combination of solvent extraction and anion and cation exchange chromatography

		N6/4		N6/3	
		$\mu^{182}W$	$\mu^{183}W$	$\mu^{182}W$	$\mu^{183}W$
Dissolution in HClO₄ and drying ($N = 9$)	Average	1.5	−1.1	2.5	2.6
	SD	6.9	7.5	3.7	7.6
Dissolution in H₂O₂ and drying ($N = 12$)	Average	−1.2	0.3	−0.4	0.0
	SD	4.9	10	5.5	6.7
Anion exchange, dissolution in HClO₄, and drying ($N = 4$)	Average	4.6	−12	−5.5	12
	SD	8.9	7.6	6.9	4.7
4-methyl-2-pentanone extraction, anion exchange, dissolution in HClO₄, and drying ($N = 4$)	Average	3.6	−18	6.5	13
	SD	5.7	10	7.9	7.3
4-methyl-2-pentanone extraction, cation exchange, dissolution in HClO₄, and drying ($N = 4$)	Average	3.9	−19	−7.4	17
	SD	5.0	10	13	7.0
4-methyl-2-pentanone extraction, cation and anion exchange, dissolution in HClO₄, and drying ($N = 13$)	Average	−1.0	−10	3.9	12
	SD	5.4	7.1	6.5	3.8

$\mu^{182}W$ and $\mu^{183}W$ are the deviations (ppm) of the $^{182}W/^{184}W$ and $^{183}W/^{184}W$ values from those of a terrestrial standard, respectively, for each solution. SD = standard deviation. Errors are shown in 1SD because variation is large after various chemical steps. N6/4 and N6/3 indicate W isotope ratios corrected using $^{186}W/^{184}W = 0.92767$ et and $^{186}W/^{183}W = 1.98594$ (Harper and Jacobsen, 1996), respectively, according to an exponential law.

1998) or a $^{186}W/^{183}W$ ratio of 1.98594 (Harper and Jacobsen, 1996) according to an exponential law. Then $^{182}W/^{184}W$ and $^{183}W/^{184}W$ corrected for mass bias were further normalized by sample-standard bracketing, as discussed in Subsection 3.2.

3. RESULTS AND DISCUSSION

3.1. Effects of Mo dimers on determination of W isotope ratios

Our chemical procedure effectively removed Hf and Ta from our samples, but a small amount of Mo (typically a few percent of the ion beam intensity of W for JB-2) remained in the purified fractions. Therefore, interferences of Mo dimers on ^{184}W and ^{186}W was checked by using a mixture of SRM 3163 and a series of single-element standard solutions of Mo: specifically, 20 ppb W solutions that contained Mo at concentrations ranging from 20 to 500 ppb were prepared. In addition, the isobaric interference of the ^{93}Nb dimer on ^{186}W was checked, because small amounts of Nb sometimes remained (less than one percent of the intensity of W for JB-2) in the final fraction. The results are shown in Table 4. Even when the Mo concentration was 1–25 times the W concentration, no significant shift was observed in the W isotope ratio; a 20 ppb W test solution containing 100 ppb Mo and 2 ppb Nb also showed no significant shift in the W

isotope ratio. Because none of the natural sample solutions contained Mo at a concentration that was 25 times the W concentration, these results indicate that the trace amount of Mo remaining after the chemical procedure had no effect on the precision of our method for measuring W isotope ratios.

3.2. Mass independent fractionation effect

As mentioned previously, Kruijer and Kleine (2018) argued that a ^{183}W deficiency in a chemically treated sample was responsible for a false positive $\mu^{182}W$ anomaly in OJP basalts. Such mass-independent fractionation of ^{183}W was previously noted by Willbold *et al*. (2011) and further investigated by Cook and Schönbächler (2016) for Fe-Ni alloy and Tusch *et al*. (2019) for ancient rocks. In the present study, a W solution from the NIST SRM 3163 standard similarly processes through each step of the procedure described above was prepared and evaporated in HClO₄ or H₂O₂. The 10 ppm W solution was prepared from the original 10,000 ppm NIST SRM 3163 standard. A small amount, 0.1 g of this 10 ppm W solution, was taken in a PFA vessel, diluted with 1mL of 9.45 M HCl, heated, and evaporated completely. The residue was then processed as shown in Table 5. For measurement, aliquots containing 20 ppb W were prepared from chemically processed solution by adjusting their W ion beam intensities to that of the unprocessed 20 ppb W standard solution
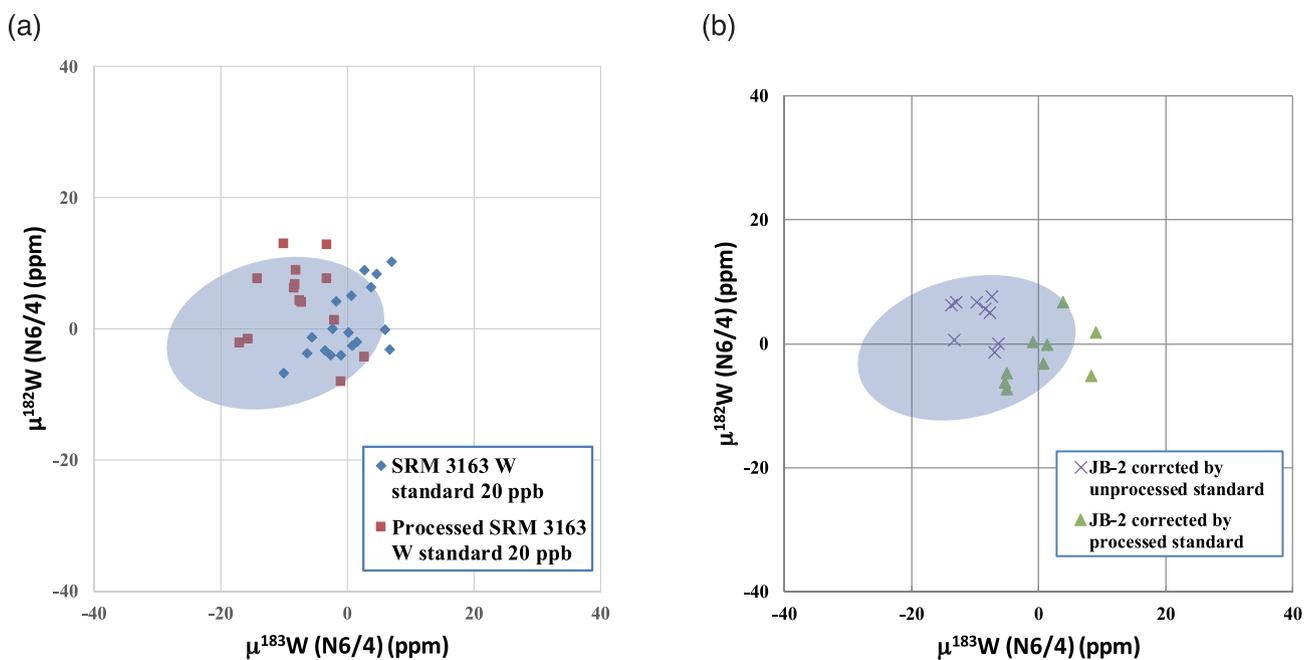
(a)

(b)

Fig. 1. (a) Relationship between $\mu^{182}W$ (N6/4) and $\mu^{183}W$ (N6/4) values (a) for processed and unprocessed NIST SRM 3163 W standard solutions and (b) for JB-2, with correction by data for the processed and unprocessed NIST SRM 3163 W standard solutions. The shaded area indicates values for two reference materials (BHVO-2 and BCR-2) and for natural samples of Ontong Java Plateau basalt obtained by Kruijer and Kleine (2018). N6/4 and N6/3 indicate W isotope ratios corrected using $^{186}W/^{184}W = 0.92767$ (Rosman and Taylor, 1998) and $^{186}W/^{183}W = 1.98594$ (Harper and Jacobsen, 1996), respectively, according to an exponential law.

prior to the measurement of the W isotopes.

The measurement results for these W solutions were compared with those of the unprocessed standard (Table 5). The analytical errors were relatively large, probably because the extent of mass fractionation varied for each step of the chemical procedure. The $\mu^{182}W$ and $\mu^{183}W$ values are deviations in ppm from the $^{182}W/^{184}W$ and $^{183}W/^{184}W$ values of the standard. No significant shifts in $\mu^{183}W$ were observed for the standard solution that was dried in $HClO_4$ or H_2O_2. In contrast, standard solutions subjected to anion exchange chromatography alone, extraction with 4-methyl-2-pentanone plus anion exchange chromatography, or extraction with 4-methyl-2-pentanone plus cation exchange chromatography showed negative shifts of approximately 10 in $\mu^{183}W$ (Table 5). The results of the analysis of a NIST SRM 3163 W standard solution subjected to the whole chemical procedure described in Subsection 2.4 were prepared. A mixture of HF, HCl and HNO_3 was added to 0.1 g of this 10 ppm W solution, heated, and evaporated completely. The residue was then processed in the same way as the natural samples as described in Subsection 2.4. aliquots containing 20 ppb W were prepared from chemically processed solution by comparison of the W ion beam intensities with that of the unprocessed 20 ppb W standard solution prior

to the measurement of the W isotopes. The analytical results of the processed W standard also compared with the results for an unprocessed standard solution (Fig. 1a); no shift in $\mu^{182}W$ was observed, but there was a shift of approximately –10 in $\mu^{183}W$. This result is consistent with the data obtained by Kruijer and Kleine (2018).

3.3. Application of our method to a geochemical reference material and terrestrial rock samples

We examined the reproducibility of the W isotopic data obtained from the geochemical reference material JB-2 (W = 0.26 ppm) (Table 6). When JB-2 was analyzed by means of the sample-standard bracketing method using the unprocessed standard solution, a negative $\mu^{183}W$ shift of approximately 10 ppm was observed. In contrast, when JB-2 was analyzed by means of the sample-standard bracketing method using the processed standard solution, no significant shift in $\mu^{182}W$ or $\mu^{183}W$ was observed. As a result, JB-2 was found to have present-day mantle values for $\mu^{182}W$ and $\mu^{183}W$: $\mu^{182}W$ (N6/4) = –2.1 ± 9.1 (2SD) and $\mu^{183}W$ (N6/4) = 0.7 ± 11 (2SD) (Table 6). Mundl-Petermeier (2020) reported $\mu^{182}W$ 2SD values of 3.3 and 9.7 ppm for Samoan and Hawaiian basalts, respectively, as determined by NTIMS. Kruijer and Kleine (2018) reported $\mu^{182}W$ 2SD values of 7.9–11 ppm for OJP basalts,

Table 6. Tungsten isotope ratios of reference material JB-2.

| | JB-2 data corrected by data for an unprocessed W standard | | | |
| | N6/4 | | N6/3 | |
	$\mu^{182}W$	$\mu^{183}W$	$\mu^{182}W$	$\mu^{184}W$
JB-2-#1	5.5	−8.5	3.8	10.3
JB-2-#2	7.6	−7.4	−0.8	−2
JB-2-#3	6.6	−13	2	1.7
JB-2-#4	0	−6.4	−1.8	8.9
JB-2-#5	5	−7.8	1.3	−1.8
JB-2-#6	6.6	−9.8	10.2	7.8
JB-2-#7	6.1	−13.8	1	10.5
JB-2-#8	0.6	−13.4	2.8	10.2
JB-2-#9	−1.4	−7	−3.4	6
Average	4.1	−9.7	1.7	5.7
2SD	6.7	5.9	7.8	10.3

| | JB-2 data corrected by data for a processed W standard | | | |
	$\mu^{182}W$	$\mu^{183}W$	$\mu^{182}W$	$\mu^{184}W$
JB-2-#1	−6.3	−5.4	2.2	3.6
JB-2-#2	−5.2	8.2	−10.7	−5.4
JB-2-#3	−0.3	1.2	−2.8	−2.7
JB-2-#4	6.6	3.8	−4.6	−6.7
JB-2-#5	−4.8	−5.1	−3.6	0.9
JB-2-#6	−7.4	−5.1	−6.3	−0.1
JB-2-#7	0.3	−0.9	0.3	−4.1
JB-2-#8	1.8	9	−6.9	−7.1
JB-2-#9	−3.3	0.7	−1.8	−2.4
Average	−2.1	0.7	−3.8	−2.7
2SD	9.1	11.0	7.8	7.2

$\mu^{182}W$, $\mu^{183}W$ and $\mu^{184}W$ are the deviations (ppm) of $^{182}W/^{184}W$, $^{183}W/^{184}W$ and $^{184}W/^{182}W$ of the sample solutions, respectively, from those of a terrestrial standard. SD = standard deviation. N6/4 and N6/3 indicate W isotope ratios corrected using $^{186}W/^{184}W = 0.92767$ (Rosman and Taylor, 1998) and $^{186}W/^{183}W = 1.98594$ (Harper and Jacobsen, 1996), respectively, according to an exponential law.

Table 7. Tungsten isotope ratios of terrestrial samples

			$\mu^{182}W$	W conc. (ppm)
Loihi		Average	−14	
698-4B-1	$N = 4$	2SD	5.9	0.6
Loihi		Average	−13	
698-4B-2	$N = 4$	2SD	14	0.38
Kilauea		Average	0.5	
	$N = 4$	2SD	8.0	0.41
Ontong Java Plateau		Average	−4.8	
76R-01W	$N = 4$	2SD	12	0.39
Ontong Java Plateau		Average	−3	
79R-5W	$N = 2$	2SD	0.7	0.42
Ontong Java Plateau		Average	0.4	
77R-2W	$N = 2$	2SD	3.8	0.42

$\mu^{182}W$ and $\mu^{183}W$ are the deviations (ppm) of $^{182}W/^{184}W$ and $^{183}W/^{184}W$, respectively, of the sample solutions from those of a terrestrial standard. SD = standard deviation.

as determined by MC-ICP-MS. Thus, the standard deviations for the data obtained from natural samples determined so far by MC-ICP-MS, both in the present study and in the study by Kruijer and Kleine (2018), were slightly larger than or comparable with those obtained by NTIMS. As discussed above, ^{183}W deficiency due to mass-independent fractionation could be corrected for by sample-standard bracketing MC-ICP-MS measurements using a W standard solution subjected to the same procedure used for the samples. An accurate $\mu^{182}W$ value was obtained for the reference material (JB-2), even if ^{183}W was used for mass fractionation correction. However, we did not use ^{183}W for mass fractionation correction of a $\mu^{182}W$ value.

An important advantage of the present method is that a small amount of sample (0.2–0.3 g; equivalent to 50–80 ng W for JB-2, which contained 260 ppb W; Imai et

al., 1995) was required for the precise and accurate $^{182}W/^{184}W$ measurement compared to that of previous works. Mundl-Petermeier et al. (2020) analyzed several OIB samples and needed to digest 0.7–15 g of sample to recover at least 1000 ng W for precise isotope analysis by NTIMS. Precise measurement of W isotopes by NTIMS generally requires higher amounts of W than necessary for MC-ICP-MS. For example, Mei et al. (2018) reported that only 1–5 g of sample powder needed to be digested to obtain 500 ng W for MC-ICP-MS measurement without a desolvating nebulizer. Our reduction of the amount of sample needed (0.2–0.3 g) was possible probably because the combination of solvent extraction and cation and anion exchange chromatography markedly reduced the amount of matrix elements present in the purified solutions. In addition to this separation methodology, the desolvating nebulizer was thoroughly cleaned prior to every measurement. Matrix elements were found to markedly degrade the W ion beam intensity, and removal of those matrix elements from the sample solutions likely contributed to enhancing and stabilizing the W ion beam intensity during analysis.

We also used our method to analyze terrestrial rock samples collected from Hawaii and the OJP. The noble gas isotopic compositions in the Loihi basalts have already been reported by Matsumoto et al. (2008). They analyzed the noble gas isotopic composition of a by a high-resolution stepwise crushing of basaltic glass and olivine separates. In our study, we separated the Loihi sample into two parts, one part comprising the glass phase (698-4B1) and one part excluding the glass phase (698-4B2). The basaltic glass (698-4B1) had a $^{3}He/^{4}He$ ratio
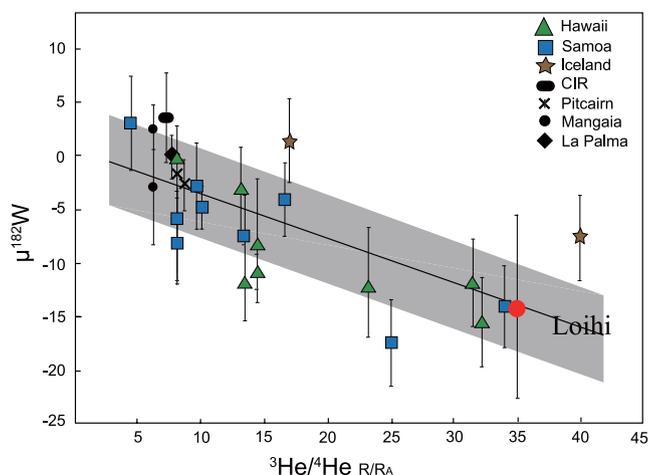
Fig. 2. The plot of the obtained data for the Loihi basalt (698-4B1) on the correlation diagram between $\mu^{182}W$ of and $^3He/^4He$ (Ra) reported by Mundl et al. (2017). The diagram is reproduced with permission from American Association for the Advancement of Science.

as high as 35 Ra. The average $\mu^{182}W$ values for samples 698-4B1 and 698-4B2 were –14 ± 5.9 (2SD, N = 4) and –13 ± 14 (2SD, N = 4), respectively (Table 7). The 698-4B-1 data is plotted on the He-W isotope correction line showing the correlation between the He and W isotope data for Hawaiian-Samoan basalts analyzed by Mundl *et al.* (2017) (Fig. 2), confirming that their results could be reproduced with our method. The $\mu^{182}W$ value of 0.5 ± 8.0 was obtained for the Kilauea basalt (2SD, N = 4).

The W isotope ratios were also determined for OJP basalt samples collected during Ocean Drilling Program Leg 130. Among the samples, three OJP basalt types were recognized: Singgalo, Kwaimbaita, and Kroenke (Tejada *et al.*, 2002; Fitton and Godard, 2004). These basalts can be divided into two isotopically distinct groups. Singgalo-type basalts have $\varepsilon Nd(t)$ = +3.8 to +3.9, ($^{206}Pb/^{204}Pb$)t = 17.71–17.85, and ($^{87}Sr/^{86}Sr$)t = 0.7040–0.7042, and higher abundances of highly incompatible elements relative to Kwaimbaita-type basalts. Kroenke-type basalts are parental to Kwaimbaita-type basalts and both have $\varepsilon Nd(t)$ = +5.4 to +5.6, ($^{206}Pb/^{204}Pb$)t = 18.12–18.40, and ($^{87}Sr/^{86}Sr$)t = 0.7037–0.7039, and lower abundances of highly incompatible elements relative to the Singgalo-type (Tejada *et al.*, 2004). Rizo *et al.* (2016) reported that a Kroenke-type OJP basalt sample (192-1187A-9R-4) showed an extremely positive anomaly ($\mu^{182}W$ = +24). However, as mentioned above, Kruijer and Kleine (2018) pointed out that mass fractionation correction of the data of Rizo *et al.* (2016) was the most likely cause of this apparent positive anomaly and reported that their analysis showed no $\mu^{182}W$ anomalies for the same Kroenke-type basalt. The samples analyzed in the present study also yielded a non-

anomalous $\mu^{182}W$ of 0.4 to –4.8 like that of the present-day mantle and so were considered to be Singgalo-type basalts. These results indicate that the OJP mantle source is quite homogeneous with respect to W isotope composition.

4. CONCLUSIONS

Here, we report a improved method for the precise and accurate determination of W isotope ratios that involves a combination of solvent extraction, cation and anion exchange chromatography, and MC-ICP-MS system equipped with a desolvating nebulizer, a Ni Jet sampler cone, and a Ni X skimmer cone. The reproducibility of the $\mu^{182}W$ values was 6–9 ppm (2SD) for 0.2–0.4 g powder of geological reference material JB-2. The chemical procedure developed here effectively removes the matrix elements that interfere with the measurement of W isotopes and allowed precise $\mu^{182}W$ data to be obtained. ^{183}W deficiency was observed in the measurements of both W standard solution and JB-2 rock standard subjected to chemical separation (solvent extraction and ion exchange chromatography). However, it was found that even the mass-independent fractionation of ^{183}W could be properly corrected, and that accurate $\mu^{182}W$ values could be obtained by means of a sample-standard bracketing method, provided that the standard was processed in the same way as the samples.

Our newly developed method gave reproducible data for JB-2 that are consistent with the present-day mantle value. The Loihi basalt sample that was analyzed showed a negative anomaly in $\mu^{182}W$ (–14 ppm), which is in agreement with that reported by Mundl *et al.* (2017). Also analyzed were Singgalo-type OJP basalts, which are isotopically different from the Kroenke-type basalts demonstrated by previous work to have no ^{182}W anomaly (Kruijer and Kleine, 2018), also produced no resolvable ^{182}W anomaly, indicating that the OJP mantle source is quite homogeneous with respect to its W isotope composition.

Taken together, our results indicate that our method gives reliable results for natural samples. Moreover, a major advantage of the present method is that the amount of sample (0.2–0.3 g, equivalent to 50–80 ng W for JB-2) used was smaller than that required in previous studies by other investigators (0.7–15 g sample powder, equivalent to 500–1000 ng W). This reduction was possible probably by intensive removal of matrix elements from the purified samples and was also contributed by cleaning of the membrane of the desolvating nebulizer.

The method described here can yield not only the precise $^{182}W/^{184}W$ but also $^{183}W/^{184}W$ ratios, which will be useful for the analysis of extra-terrestrial samples that could contain nucleosynthetic tungsten anomalies or any components influenced by neutron capture.

REFERENCES

Cook, D. L. and Schönbächler, M. (2016) High-precision measurement of W isotopes in Fe-Ni alloy and the effects from the nuclear field shift. *J. Anal. Atom. Spectrom.* **31**, 1400–1405.

Dale, C. W., Kruijer, T. S. and Burton, K. W. (2017) Highly siderophile element and ^{182}W evidence for a partial late veneer in the source of 3.8 Ga rocks from Isua, Greenland. *Earth Planet. Sci. Lett.* **458**, 394–404.

Fitton, J. G. and Godard, M. (2004) Origin and evolution of magmas on the Ontong Java Plateau. *Origin and Evolution of the Ontong Java Plateau* (Fitton, J. G., Mahoney, J. J., Wallace, P. J. and Saunders, A. D., eds.), *Geological Society (London) Special Publication* **229**, 151–178.

Harper, C. L. and Jacobsen, S. B. (1996) Evidence for ^{182}Hf in the early Solar System and constraints on the timescale of terrestrial accretion and core formation. *Geochim. Cosmochim. Acta* **60**, 1131–1153.

Hellmann, J. L., Kruijer, T. S., Van Orman, J. A., Metzler, K. and Kleine, T. (2019) Hf-W chronology of ordinary chondrites. *Geochim. Cosmochim. Acta* **258**, 290–309.

Imai, N., Terashima, S., Itoh, S. and Ando, A. (1995) 1994 Compilation of analytical data for minor and trace elements in seventeen GJS geochemical reference samples, "Igneous Rock Series", *Geost. Newslett.* **19**, 135–213.

Kruijer, T. S. and Kleine, T. (2018) No ^{182}W excess in the Ontong Java Plateau source. *Chem. Geol.* **485**, 24–31.

Kruijer, T. S., Kleine, T., Fischer-Gödde, M. and Sprung, P. (2015) Lunar tungsten isotopic evidence for the late veneer. *Nature* **520**, 534–537.

Liu, J., Touboul, M., Ishikawa, A., Walker, R. J. and Graham Pearson, D. (2016) Widespread tungsten isotope anomalies and W mobility in crustal and mantle rocks of the Eoarchean Saglek Block, northern Labrador, Canada: Implications for early Earth processes and W recycling. *Earth Planet. Sci. Lett.* **448**, 13–23.

Matsumoto, T., Orihashi, Y., Matsuda, J. I. and Yamamoto, K. (2008) Argon isotope ratio of the plume-source deduced from high-resolution stepwise crushing extraction. *Geochem. J.* **42**, 39–49.

Mei, Q.-F., Yang, J.-H. and Yang, Y.-H. (2018) An improved extraction chromatographic purification of tungsten from a silicate matrix for high precision isotopic measurements using MC-ICPMS. *J. Anal. Atom. Spectrom.* **33**, 569–577.

Mundl-Petermeier, A., Walker, R. J., Jackson, M. G., Blichert-Toft, J., Kurz, M. D. and Halldórsson, S. A. (2019) Temporal evolution of primordial tungsten-182 and ^{3}He/^{4}He signatures in the Iceland mantle plume. *Chem. Geol.* **525**, 245–259.

Mundl-Petermeier, A., Walker, R. J., Fischer, R. A., Lekic, V., Jackson, M. G. and Kurz, M. D. (2020) Anomalous ^{182}W in high ^{3}He/^{4}He ocean island basalts: Fingerprints of Earth's core? *Geochim. Cosmochim. Acta* **271**, 194–211.

Mundl, A., Touboul, M., Jackson, M. G., Day, J. M. D., Kurz, M. D., Lekic, V., Helz, R. T. and Walker, R. J. (2017) Tungsten-182 heterogeneity in modern ocean island basalts. *Science* **356**, 66.

Mundl, A., Walker, R. J., Reimink, J. R., Rudnick, R. L. and Gaschnig, R. M. (2018) Tungsten-182 in the upper continental crust: Evidence from glacial diamictites. *Chem. Geol.* **494**, 144–152.

Peters, B. J., Mundl-Petermeier, A., Horan, M. F., Carlson, R. W. and Walker, R. J. (2019) Chemical separation of tungsten and other trace elements for TIMS isotope ratio measurements using organic acids. *Geostand. Geoanal. Res.* **43**, 245–259.

Puchtel, I. S., Blichert-Toft, J., Touboul, M. and Walker, R. J. (2018) ^{182}W and HSE constraints from 2.7 Ga komatiites on the heterogeneous nature of the Archean mantle. *Geochim. Cosmochim. Acta* **228**, 1–26.

Reimink, J. R., Chacko, T., Carlson, R. W., Shirey, S. B., Liu, J., Stern, R. A., Bauer, A. M., Pearson, D. G. and Heaman, L. M. (2018) Petrogenesis and tectonics of the Acasta Gneiss Complex derived from integrated petrology and ^{142}Nd and ^{182}W extinct nuclide-geochemistry. *Earth Planet. Sci. Lett.* **494**, 12–22.

Rizo, H., Walker, R. J., Carlson, R. W., Horan, M. F., Mukhopadhyay, S., Manthos, V., Francis, D. and Jackson, M. G. (2016) Preservation of Earth-forming events in the tungsten isotopic composition of modern flood basalts. *Science* **352**, 809.

Rizo, H., Andrault, D., Bennett, N. R., Humayun, M., Brandon, A., Vlastelic, I., Moine, B., Poirier, A., Bouhifd, M. A. and Murphy, D. T. (2019) ^{182}W evidence for core-mantle interaction in the source of mantle plumes. *Geochem. Perspect. Lett.* **11**, 6–11.

Rosman, K. J. R. and Taylor, P. D. P. (1998) Isotopic compositions of the elements 1997 (Technical Report). *Pure Appl. Chem.* **70**, 217.

Sahoo, Y. V., Nakai, S. i. and Ali, A. (2006) Modified ion exchange separation for tungsten isotopic measurements from kimberlite samples using multi-collector inductively coupled plasma mass spectrometry. *Analyst* **131**, 434–439.

Takamasa, A., Nakai, S. i., Sahoo, Y., Hanyu, T. and Tatsumi, Y. (2009) W isotope compositions of oceanic islands basalts from French Polynesia and their meaning for core-mantle interaction. *Chem. Geol.* **260**, 37–46.

Tejada, M. L. G., Mahoney, J. J., Neal, C. R., Duncan, R. A. and Petterson, M. G. (2002) Basement geochemistry and geochronology of Central Malaita, Solomon Islands, with implications for the origin and evolution of the Ontong Java Plateau. *J. Petrol.* **43**, 449–484.

Tejada, M. L. G., Mahoney, J. J., Castillo, P. R., Ingle, S. P., Sheth, H. C. and Weis, D. (2004) Pin-pricking the elephant:

evidence on the origin of the Ontong Java Plateau from Pb-Sr-Hf-Nd isotopic characteristics of ODP Leg 192 basalts. *Geol. Soc., London, Spec. Publ.* **229**, 133.

Touboul, M. and Walker, R. J. (2012) High precision tungsten isotope measurement by thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **309**, 109–117.

Touboul, M., Puchtel, I. S. and Walker, R. J. (2012) ^{182}W evidence for long-term preservation of early mantle differentiation products. *Science* **335**, 1065.

Touboul, M., Liu, J., O'Neil, J., Puchtel, I. S. and Walker, R. J. (2014) New insights into the Hadean mantle revealed by ^{182}W and highly siderophile element abundances of supracrustal rocks from the Nuvvuagittuq Greenstone Belt, Quebec, Canada. *Chem. Geol.* **383**, 63–75.

Touboul, M., Puchtel, I. S. and Walker, R. J. (2015) Tungsten isotopic evidence for disproportional late accretion to the Earth and Moon. *Nature* **520**, 530–533.

Tusch, J., Sprung, P., van de Löcht, J., Hoffmann, J. E., Boyd, A. J., Rosing, M. T. and Münker, C. (2019) Uniform ^{182}W isotope compositions in Eoarchean rocks from the Isua region, SW Greenland: The role of early silicate differentiation and missing late veneer. *Geochim. Cosmochim. Acta* **257**, 284–310.

Vockenhuber, C., Oberli, F., Bichler, M., Ahmad, I., Quitté, G., Meier, M., Halliday, A. N., Lee, D. C., Kutschera, W., Steier, P., Gehrke, R. J. and Helmer, R. G. (2004) New half-life measurement of ^{182}Hf: Improved chronometer for the early solar system. *Phys. Rev. Lett.* **93**, 172501.

Willbold, M., Elliott, T. and Moorbath, S. (2011) The tungsten isotopic composition of the Earth's mantle before the terminal bombardment. *Nature* **477**, 195–198.

Willbold, M., Mojzsis, S. J., Chen, H. W. and Elliott, T. (2015) Tungsten isotope composition of the Acasta Gneiss Complex. *Earth Planet. Sci. Lett.* **419**, 168–177.